Metal–Acetylide Bonding in (η^5-C₅H₅)Fe(CO)₂C≡CR Compounds. Measures of Metal-dπ–Acetylide-π Interactions from Photoelectron Spectroscopy

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Abstract: Gas-phase He I and He II photoelectron spectroscopy is used to experimentally determine the bonding interactions of η^1-acetylide ligands in (η^5-C₅H₅)Fe(CO)₂C≡CR compounds (R = H, ‘Bu, or phenyl). The spectra show a large amount of interaction between the metal dπ orbitals and the acetylide π orbitals. Evidence for this is obtained from the splitting of metal-based ionization bands, from the shifts in Cp-based and acetylide-based ionizations, from the changes in ionization cross sections between the He I and He II spectra, and from vibrational fine structure in the metal-based ionizations. The data indicate that the predominant π interactions between the acetylide ligands and the metal are filled/filled interactions between the occupied acetylide π bonds and the occupied metal dπ orbitals. The electronic interactions of the C≡CR ligands with the metal are compared with those of CH₃ (a primarily σ donor ligand), halides (π donor ligands), and C≡N (a weak π^* acceptor ligand), and are very similar to the interactions of the chloro ligand. Metal-to-acetylide-π^* back-bonding is extremely small in the acetylide compounds. Varying the acetylide substituent causes significant changes in the σ and π donor properties of the C≡CR ligand. Compared to C≡CH, the C≡C'Bu ligand is a stronger σ donor ligand and also has a stronger filled/filled interaction between the metal dπ and acetylide π orbitals. The electronic mixing with the C≡CPh ligand is even more extensive, since the metal dπ orbitals and the C≡C π bonds are further mixed with the phenyl ring π orbitals. The nature of these π interactions helps to explain the observed reactivity of electrophiles with ML$_n$C≡CR compounds and the observed electronic communication along the metal–carbon–carbon atom chain in transition metal–acetylide compounds.

I. Introduction

Organometallic compounds with η^1-acetylide ligands were first reported in 1968, and many studies of their structure and chemical properties have followed.[1–4] Current interests in transition metal–acetylide compounds range from studies of basic chemical transformations with functionalized alkynes[5–7] to investigations of nonlinear optical and other special material properties.[8] Questions remain about the bonding interactions of η^1-acetylide ligands (C≡CR) that are important to the understanding of these properties. For example, electronic communication between the metal and the coordinated acetylide is suspected to be important

in metallapoly-ynes,[9] transition metal nonlinear optical materials,[8] and bridging buta-1,4-diyne compounds,[10] but the specific electronic interactions that would allow communication have not been evaluated directly. Although the C≡CR⁻ ligand is isoelectronic with CO (a strong π acceptor) and CN⁻ (a weak π^* acceptor), the extent of metal-to-acetylide-π^* back-bonding is still not clear. As discussed below, the present bonding evidence, which consists of information from reactivity studies, crystal structures, C≡C stretching frequencies, and calculations, is often conflicting or unconvincing.

The reactivity of metal acetylides with electrophiles gives some indirect indications about the metal/acetylide bonding interactions.[11,12] Electrophiles generally attack the acetylide β carbon atom, as shown below, to give vinylidenes. This reactivity can
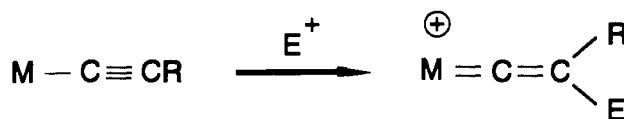
also occur with coordinated CO and CN⁻, where the oxygen or nitrogen (β atom) is susceptible to attack by electrophiles (or Lewis acids).[13] For these ligands, the concentration of negative charge on the β atom is attributed to metal-to-ligand-π^* back-

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Bonding in (η⁵-C₅H₅)Fe(CO)₂C≡CR

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Table I. Comparison of C≡C Stretching Frequencies for HC≡CR, CH₃C≡CR, and CpFe(CO)₂C≡CR

	C≡C stretching frequencies (cm⁻¹)					
R	CpFe(CO)₂C≡CR	ref	HC≡CR	ref	CH₃C≡CR	ref
H	1961[d]	this work	1974[e]	21	2123[h]	21
CH₃	2140	1a	2123[h]	21	2233[e]	19
ᵗBu	2116[c]	this work	2108[h]	21	2200[c]	20
Ph	2105[d]	this work	2115[h]	21	2250[c]	20

[a] Raman. [b] CCl₄ solvent. [c] THF solvent. [d] Nujol mull. [e] Neat.

bonding. Metal-to-acetylide-π* back-bonding has also been proposed to explain the reactivity of acetylide compounds. However, other bonding interactions could also explain the reactivity, as we will show later.

The Fe–C and C–C bond lengths in MLₙC≡CR compounds are often examined to detect the presence of back-bonding. From the crystal structure of CpFe(CO)₂C≡CPh (Cp = η⁵-C₅H₅), the Fe–C_α bond length is 1.920(6) Å.[14] Similar Fe–C bond lengths are observed in Cp*Fe(CO)₂C≡CH (1.921(3) Å) and Cp*Fe-(CO)₂C≡CPh (1.924(7) Å) (Cp* = η⁵-C₅Me₅).[15] The Fe–C_sp¹ single bond length in CpFe(CO)₂(η¹-C₅H₅) is 2.146(10) Å,[16] and for [Cp(CO)₂Fe–(CH₂)₃–FeCp(CO)₂] is 2.08 Å.[17] If one assumes that the Fe–C_α bond is contracted by approximately 0.06 Å due to sp versus sp³ hybridization (from covalent radii), then the Fe–C_α bonds in the acetylide compounds are about 0.1 Å shorter than expected for an Fe–C_sp single bond. Similarly, in the W₂-(PMe₃)₄(Cl)₂(C≡CR)₂ compounds, the metal–carbon bond is 0.11 Å shorter than the W–C_sp single bond.[9] The cause of this contraction could be due to back-bonding from the metal to the acetylide π* orbitals. If this occurs it is reasonable to expect a concomitant lengthening of the acetylide C≡C bond. The acetylide C–C bond distance in CpFe(CO)₂C≡CR compounds is 1.20 ± 0.02 Å,[14,15] which is identical with the length of the C–C bond in acetylene (1.20 Å). However, the length of the triple bond is an unreliable measure of bond order or back-bonding ability. Even for coordinated CO, the C–O bond lengthens by only 0.02 Å compared to the C–O bond distance in free CO.[18]

Like a CO stretching frequency, the C≡C stretching frequency (ν(C≡C)) should also be sensitive to electronic interactions with the metal center. The ν(C≡C) for the CpFe(CO)₂C≡CR compounds are within 10 cm⁻¹ of the ν(C≡C) for the corresponding HC≡CR molecules (see Table I).[19–21] The similar ν(C≡C) frequencies suggest that little metal-to-acetylide-π* back-bonding is occurring. However, comparisons of the ν(C≡C) for HC≡CR and MLₙC≡CR are not straightforward, because C≡C stretching frequencies are significantly different for mono- and disubstituted acetylenes. The ν(C≡C) for disubstituted R'C≡CR acetylenes, where R' and R are organic substituents, are approximately 100 cm⁻¹ higher than ν(C≡C) for monosubstituted HC≡CR acetylenes. This effect is not caused by mass or force constant effects, but rather from coupling of the C≡C and C–H stretching vibrations in the HC≡CR acetylenes.[19] The absence of this coupling in disubstituted acetylenes causes the vibration assigned to ν(C≡C) to be higher in frequency. A similar trend is observed for organometallic acetylides. The ν(C≡C)'s

for MLₙC≡CR compounds are approximately 100 cm⁻¹ higher than the ν(C≡C)'s for MLₙC≡CH compounds. If the same trend holds for CpFe(CO)₂C≡CR and HC≡CR, then one might expect the ν(C≡C) for CpFe(CO)₂C≡CR to be about 100 cm⁻¹ higher than for HC≡CR in the absence of other electronic effects. It follows that the similar ν(C≡C)'s of CpFe(CO)₂C≡CR and HC≡CR could be due to a cancellation of two effects: an increase in ν(C≡C) that occurs because of H atom substitution and a decrease in ν(C≡C) that occurs with back-bonding from the metal into the C≡C π* orbital. These effects are not easily separated.

Results from a Fenske–Hall molecular orbital calculation on CpFe(CO)₂(C≡CH) predict very little metal-to-acetylide-π* back-bonding.[22] The calculation suggests that the primary π interactions are four-electron–two-orbital interactions (filled/filled interactions) between the metal dπ and acetylide π bond orbitals. Previous photoelectron spectroscopy studies are limited to trans-(PEt₃)₂M(C≡CR)₂ compounds (M = Pt, Pd; R = H, CH₃), in which a filled/filled interaction and no metal-to-acetylide-π* back-bonding was observed.[23]

Photoelectron spectroscopy (PES) is uniquely qualified to observe the electronic interactions of η¹-acetylides with metals.[24] One advantage of the technique over most other methods is the capability to separate, by symmetry, the σ and π bonding influences. Since the bonding interactions of the [CpFe(CO)₂] fragment (Fp) with many ligands, including CN, CH₃, SiR₃, and halogens, are well understood,[25–27] the bonding of the acetylide ligands can be compared directly. In this paper, the photoelectron spectra of a series of CpFe(CO)₂C≡CR compounds are reported, where R is H, C(CH₃)₃ (ᵗBu), or C₆H₅ (Ph). The data show that the primary π electronic interaction involves mixing between the filled metal dπ orbitals and the filled acetylide π bond orbitals, which results in electronic communication along the metal and acetylide chain. The metal-to-acetylide-π* back-bonding has little influence on the valence ionizations.

II. Experimental Section

Data Collection. Photoelectron spectra were recorded using an McPherson ESCA36 instrument that features a 36-cm hemispherical analyzer (10-cm gap) and custom-designed sample cells and detection and control electronics.[28,29] The excitation source is a quartz capillary lamp that produces both He I and He II radiation, depending on the operating conditions.[29b,c] Data were referenced internally to the argon ²P₃/₂ ionization at 15.759 eV. The kinetic energy scale was calibrated by using the position of CH₃I iodine lone-pair ionization at 9.538 eV relative to the Ar ²P₃/₂ ionization. During collection, the instrument resolution (measured using fwhm of the Ar ²P₃/₂ peak) was always better than 0.030 eV and was usually better than 0.025 eV. The He II spectra were referenced internally to the Ar ²P₃/₂ peak (located at 35.355 eV) as described before.[29] All data were intensity corrected according to the experimentally determined sensitivity of the instrument analyzer with electron kinetic energy. The He II data were also corrected for the He II β line spectrum, which occurs because of the presence of this additional

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source line energy.[30] The sublimation temperatures were: CpFe-(CO)₂C≡CH, 41 °C; CpFe(CO)₂C≡C'Bu, 29 °C; CpFe(CO)₂C≡CPh, 95 °C; and Cp*Fe(CO)₂C≡C'Bu, 50 °C (monitored using a "K"-type thermocouple). All samples vaporized cleanly with no detectable evidence of decomposition products in the gas phase or as a solid residue. Samples were tested independently for purity with ¹H NMR or IR spectroscopy, using recrystallized or freshly sublimed product.

In close-up spectra, the valence ionization bands are represented analytically with the best fit (Program IFIT5)[31] of asymmetric Gaussian peaks. The bands are defined with the position, amplitude, half-width for the high binding energy side of the peak, and the half-width for the low binding energy side of the peak. The peak positions and half-widths are reproducible to about ±0.02 eV (≈3σ level). A minimum number of peaks, based solely on the features of a given band profile, were used. The parameters describing an individual ionization peak are less certain when two or more peaks are close in energy and overlapping. The confidence limits for the relative integrated peak areas are about 5%, with the primary source of uncertainty being the determination of the base line subtracted from the peak. For all spectra in this study, the area of the M3 band is set to 1.00, and areas of the other bands are reported relative to M3. More detailed discussion of modeling criteria are described in the literature.[31] For representation of the He II data, the position and width values of the asymmetric Gaussians were all constrained to He I values, which were more accurately determined from the He I spectra. The amplitudes were then allowed to vary to account for the different cross sections for the He II ionizations.

Preparation of Compounds. CpFe(CO)₂C≡CH was prepared from CpFe(CO)₂I and LiC≡CH(eda) (Aldrich) using the method analogous to that reported for Cp*Fe(CO)₂(C≡CH).[32] Purification by sublimation (0.1 mTorr, 50 °C) gave a very air-sensitive yellow gum: IR (cm⁻¹, Nujol) 3228(m), ν(≡C–H); 2039(s), 1988(s), ν(CO); and 1961(s), ν-(C≡C). CpFe(CO)₂C≡CPh and CpFe(CO)₂(C≡C'Bu) were prepared using the method reported by Bruce, et al.[33] CpFe(CO)₂C≡CPh was obtained as a gold powder: IR (CH₂Cl₂) 2108(m), ν(C≡C); 2041(s), 1990(s), ν(C≡O). ¹H NMR: 5.073 (s, C₅H₅); 7.1–7.3 (multiplet). For CpFe(CO)₂C≡C'Bu: IR (cm⁻¹, THF) 2116 (w), ν(C≡C); 2034 (s), 1984 (s), ν(CO). ¹H NMR (C₆D₆): δ 4.07 (s, 5 H, Cp), δ 1.44 (s, 9 H, 'Bu). Cp*Fe(CO)₂C≡C'Bu was prepared from Cp*Fe(CO)₂I (prepared from [Cp*Fe(CO)₂]₂[34]) using the previously established method.[33] Sublimation at 0.1 mTorr at 50 °C gave a yellow, air-sensitive wax in about 25% yield. IR (cm⁻¹, hexane) 2192, ν(C≡C); 2021, 1970, ν(CO). ¹H NMR (CDCl₃): 1.17 (s, 9 H, C(CH₃)₃); 4.93 (d, 5 H, C₅(CH₃)₅).

III. Photoelectron Spectra and Ionization Band Assignments

The full valence spectra (6 to 16 eV) of the CpFe(CO)₂C≡CR compounds are shown in Figure 1. The region from approximately 13 to 16 eV consists of many overlapping ionization bands (ionizations) which originate from C–H and C–C bonds, and the CO 5σ and 1π orbitals. There is little useful information here. In the region from 6 to 12.5 eV, there are many well-resolved ionizations that contain much information about the bonding of the acetylide ligand to the [CpFe(CO)₂] fragment (Fp). All of the FpC≡CR spectra of this region show three metal-based ionizations corresponding to the formally d⁶ metal configuration. The valence region also contains ionizations that originate from the cyclopentadienyl ring (Cp) π e₁″ orbitals and acetylide π orbitals. In addition, the metal–carbon (acetylide) σ bond ionization is observed in the spectrum of FpC≡CH. The ionizations of FpC≡CR are assigned by comparing He I and He II spectra and by comparing He I spectra to those of FpR compounds (R = H, CH₃, Cl, CN).[26,27] These comparisons also give more detailed information on the extent of metal and ligand mixing that is associated with each individual ionization.

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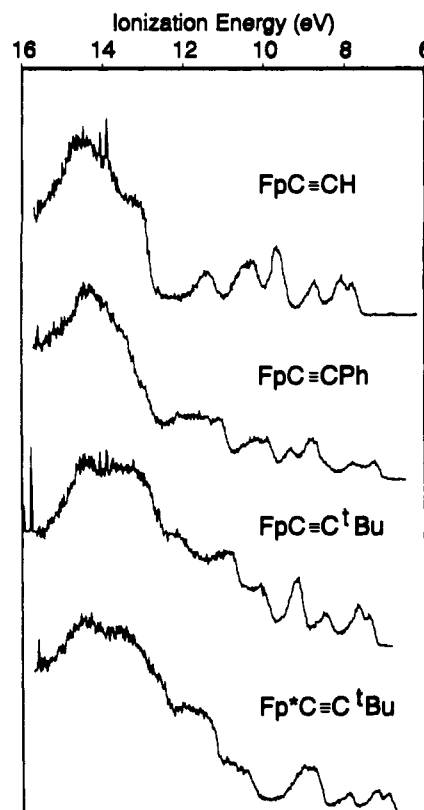

Figure 1. Full spectra (6 to 16 eV) of CpFe(CO)₂C≡CH, CpFe(CO)₂-C≡CPh, CpFe(CO)₂C≡C'Bu, and Cp*Fe(CO)₂C≡C'Bu (Fp = CpFe(CO)₂, Fp* = Cp*Fe(CO)₂).
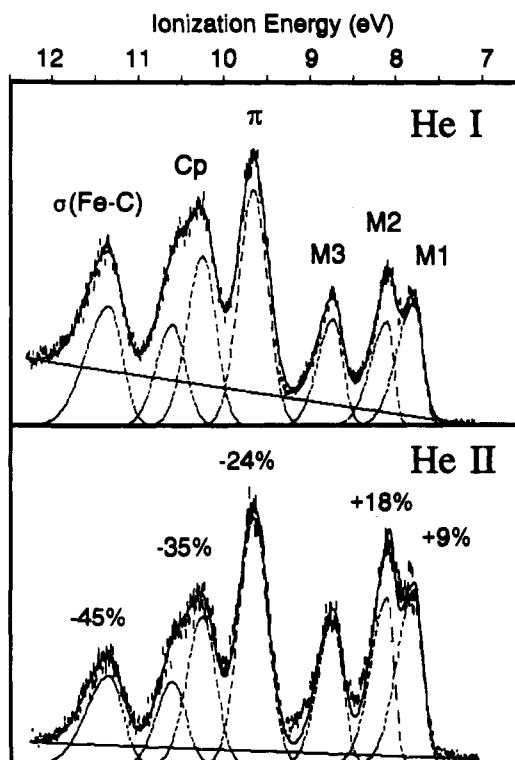

Figure 2. He I and He II spectra of the valence region of CpFe(CO)₂-C≡CH. The labels in the He II spectrum indicate % change in area (from He I to He II) for a given band, relative to M3.

CpFe(CO)₂C≡CH. The He I spectrum of the valence region of CpFe(CO)₂C≡CH is shown in Figure 2. The ionization bands are modeled with asymmetric Gaussian peaks, which define the position, relative area, and width of the ionization bands. This information as well as labels for the ionizations are given in Table

Table II. Fit Parameters for He I and He II Spectra of $ML_nC\equiv CR$ Compounds

compound[a]	position (eV)	half-widths		area (relative to M3)			label	orbital origin
		high	low	He I	He II	He II/He I		
FpC≡CH	7.79	0.49	0.22	1.16	1.26	1.09	M1	d_{xz}
	8.10	0.47	0.17	0.89	1.05	1.18	M2	d_{yz}
	8.73	0.43	0.26	1.00	1.00	1.00	M3	$d_{x^2-y^2}$
	9.66	0.41	0.38	2.52	1.94	0.76	π	C≡CH π e set
	10.25	0.44	0.36	1.84	1.19	0.65	Cp	Cp e set
	10.60	0.44	0.36	1.10	0.67	0.61	Cp	
	11.34	0.64	0.36	1.63	0.90	0.55	σ(Fe–C)	σ bond
FpC≡C'Bu	7.42	0.50	0.31	1.32	1.18	0.89	M1	d_{xz}
	7.69	0.55	0.16	1.13	1.16	1.02	M2	d_{yz}
	8.49	0.48	0.27	1.00	1.00	1.00	M3	$d_{x^2-y^2}$
	9.19	0.48	0.20	2.56	1.90	0.74	π	C≡CH π e set
	10.06	0.48	0.36	2.20	1.31	0.59	Cp	Cp e set
	10.48	0.58	0.36	1.28	0.46	0.61	Cp	
Fp*C≡C'Bu	6.97	0.47	0.23	1.16			M1	d_{xz}
	7.27	0.51	0.17	1.04			M2	d_{yz}
	7.93	0.47	0.22	1.00			M3	$d_{x^2-y^2}$
	8.75	0.43	0.29	2.62			π	C≡CH π e set
	9.08	0.71	0.29	3.07			Cp	Cp e set
FpC≡CPh	7.26	0.50	0.31	1.24	1.31	1.06	M1	d_{xz}
	7.78	0.50	0.31	1.01	1.20	1.19	M2	d_{yz}
	8.52	0.50	0.31	1.00	1.00	1.00	M3	$d_{x^2-y^2}$
	8.76	0.26	0.25	1.34	1.05	0.78	b_1	phenyl b_1
	8.98	0.41	0.25	1.38	1.05	0.76	a_2	phenyl a_2
	9.36	0.47	0.29	1.60	1.10	0.69	$\pi_\parallel$	C≡CPh $\pi_\parallel$
	9.89	0.30	0.25	1.51	0.91	0.60	$\pi_\perp$	C≡CPh $\pi_\perp$
	10.19	0.35	0.34	1.99	1.10	0.55	Cp	Cp e set
	10.51	0.35	0.34	1.40	0.52	0.37		
HC≡CPh	8.82						b_1	phenyl b_1
	9.49						a_2	phenyl a_2
	10.33						$\pi_\parallel$	C≡C $\pi_\parallel$
	11.03						$\pi_\perp$	C≡C $\pi_\perp$

[a] Fp = CpFe(CO)₂ and Fp* = Cp*Fe(CO)₂.

II. The first three ionization bands (from 7 to 8.5 eV) correspond to the three occupied iron-based d orbitals from the formally d⁶ compound. These are labeled M1, M2, and M3 in Figure 2. The fourth band in the spectrum, labeled π, is assigned to the acetylide π ionizations and corresponds to two nearly degenerate acetylide π orbitals. The overlapping fifth and sixth bands at about 10.5 eV are assigned to the Cp e_1'' set ionizations. The Cp ionizations show the same splitting and intensity pattern observed in the spectra of three-legged piano stool compounds.[24] The seventh band, located at 11.34 eV, originates from the iron–carbon σ bond and is labeled σ(Fe–C). The labels given to the ionization bands correspond to the primary origins of the ionizations in a molecular fragment approach. These labels are retained throughout the discussion for convenience, but it should be remembered that the important point for understanding the electronic interactions is to evaluate the extent of mixing that takes place between the fragment ionization states.

The changes that occur in the spectrum obtained with He II excitation support these formal assignments and give additional information on the mixing of the fragment orbitals in the ionizations. The relative band intensities change with He II excitation in comparison to He I excitation because of inherent differences in the characteristic photoionization cross sections of atoms. According to calculations, the photoionization cross section for carbon 2p electrons decreases by about a factor of 3 from He I radiation to He II radiation.[36] For iron 3d electrons, the photoionization cross section increases by almost a factor of 2 from He I to He II excitation. This relative change in cross section is observed experimentally in the He II spectra, where the relative areas of iron-based ionizations increase relative to carbon-based ionizations. Inspection of the He II spectrum of FpC≡CH (Figure 2) shows that the first three bands, labeled M1, M2, and M3, increase in intensity in He II mode relative to the other ionizations. Therefore, they are primarily metal-based ionizations.

The area of the Cp band decreases by 35% in going from He I to He II excitation (relative to the area of the M3 band, which is set to 1.00). This change in area is comparable to other Cp compounds we have studied.[24,29c] Ionization bands that originate from pure carbon 2p orbitals would decrease by about 70%. The 35% decrease shows that the Cp ionizations have a significant amount of metal character. The most interesting information in the He II spectrum is the acetylide π ionization, which decreases by only 24%. This is evidence for a substantial amount of iron character in the acetylide π ionization. Finally the seventh band, assigned to the Fe–C bond, decreases by 45%. This ionization appears to have the most pure carbon character, even though it is the Fe–C bond. This points out the dative nature of this bond and the weak σ donor ability of the acetylide ligand which is discussed later. The information from the He II spectrum confirms the general assignments, and also shows that the acetylide π system is mixing significantly with the metal dπ orbitals.

CpFe(CO)₂C≡C'Bu and Cp*Fe(CO)₂C≡C'Bu. Substitution of the hydrogen in CpFe(CO)₂C≡CH with a *tert*-butyl ('Bu) group causes the photoelectron spectrum to change significantly, and these perturbations provide a more complete understanding of the electronic interactions. The full spectrum (6 to 16 eV) of CpFe(CO)₂C≡C'Bu (Figure 1) shows many unresolved 'Bu C–C bond ionizations in the region from 11 to 12 eV. These ionizations obscure the metal–carbon σ bond ionization and the high binding energy side of the Cp ionization, but the remaining ionizations are clearly observed. A close-up spectrum in Figure 3 shows the ionization bands modeled with asymmetric Gaussian peaks, and the parameters for the peaks are given in Table II. The FpC≡C'Bu spectrum is assigned analogously to the FpC≡CH spectrum. The two leading ionizations are assigned to M1 (7.42 eV) and M2 (7.69 eV), and the third ionization band is assigned to M3 (8.49 eV). A quite intense and narrow band at 9.19 eV is similar to the acetylide π band observed in FpC≡CH spectrum. The ionizations at 10.06 eV and 10.48 eV are the cyclopentadienyl π e_1'' set ionizations.

(35) Reference deleted in proof.
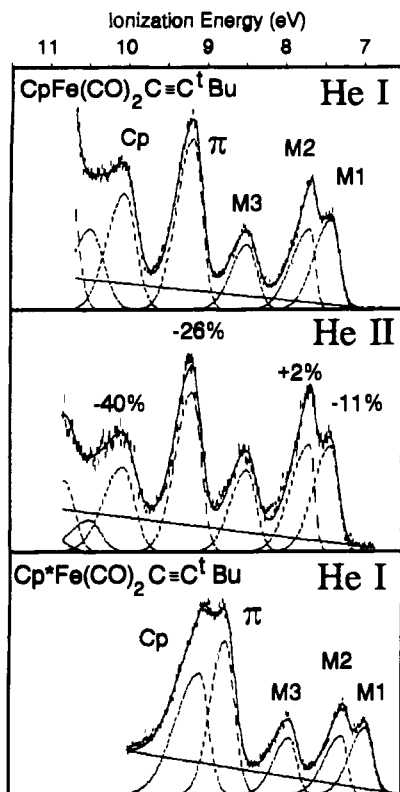(36) Yeh, J. J.; Lindau, I. *At. Data Nucl. Data. Tables* **1985**, *32* (*1*), 7.

Figure 3. He I and He II spectra of CpFe(CO)₂C≡C'Bu and the He I spectrum of Cp*Fe(CO)₂C≡C'Bu. Numbers indicate % change in area (from He I to He II) relative to M3.

These assignments are supported by the He II spectrum of FpC≡C'Bu. As discussed above, the ionization bands with iron character will increase in relative intensity in He II spectra. Comparing the He I and He II spectra in Figure 3 shows that the M1, M2, and M3 ionization bands increase in intensity in the He II mode, relative to the Cp and π ionizations. Therefore M1, M2, and M3 are predominantly iron-based ionizations. The acetylide π band, labeled π, decreases by 26% relative to M3, which indicates considerable iron character in the acetylide π ionization and the corresponding orbital. The Cp ionizations shrink by 40%, which again indicates a significant amount of metal character and is comparable to other Cp compounds observed.[24,29c]

Further evidence for the assignments of the ionizations of FpC≡C'Bu is provided by the spectrum of (η⁵-C₅Me₅)Fe-(CO)₂C≡C'Bu (Fp*C≡C'Bu). Permethylation of the cyclopentadienyl ring has predictable effects on the ionizations that have been documented by this group and others.[28b] Typically, when a Cp is replaced by a Cp*, the cyclopentadienyl e₁″ π ionizations are destabilized by approximately 1.1 eV. This is caused by a filled–filled interaction between the Cp e₁″ orbital and the e symmetry combination of the methyl C–H bonds. The metal ionizations are also destabilized, but to a lesser extent (≈0.5 eV), which is caused by the better donor ability Cp* compared to Cp. The full spectrum of Fp*C≡C'Bu (Figure 1) shows the general destabilization of these valence ionizations. The close-up spectrum of the region from 7 to 11 eV is shown in Figure 3. The M1, M2, and M3 bands are assigned analogously to their counterparts in FpC≡C'Bu and are destabilized by 0.45 (M1), 0.42 (M2), and 0.56 eV (M3). The broad band between 8.5 and 10 eV includes the Cp* e set and the acetylide π ionizations and is modeled with two asymmetric Gaussians. The broad band at 9.08 eV is assigned to the Cp* e set ionizations, which corresponds to a 1.0 eV destabilization from the positions in FpC≡C'Bu. These shifts are completely consistent with the known perme-

(37) Reference deleted in proof.

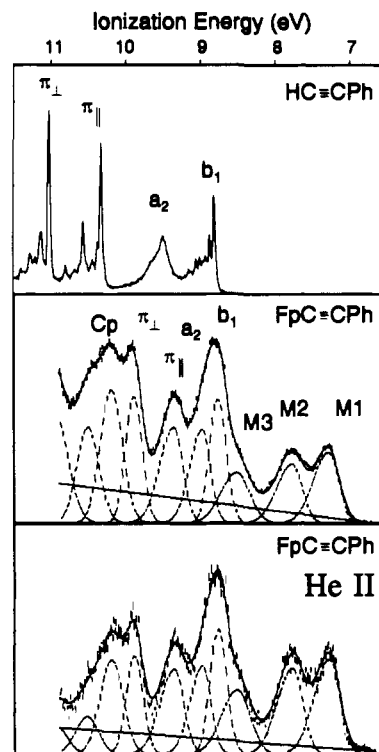**Figure 4.** He I spectrum of HC≡CPh and He I and He II spectra of the valence region for CpFe(CO)₂C≡CPh, shown fitted with Gaussian bands.

thylation effect. The sharp band at 8.75 eV is assigned to the acetylide π ionization and has been destabilized by 0.44 eV upon permethylation. This shows that donation of more electron density onto the metal center (with ring permethylation) affects the ionization labeled π (acetylide) to the same degree as the ionizations labeled M1 and M2. This is further evidence for mixing between the acetylide π and the metal orbitals.

CpFe(CO)₂C≡CC₆H₅ and HC≡CPh. The introduction of the phenyl group on the acetylide complicates the spectrum of CpFe-(CO)₂C≡CPh. The close-up He I and He II spectra are shown in Figure 4. The spectra are shown modeled with asymmetric Gaussian peaks, and the parameters are given in Table II. The ionization bands are assigned analogously to the other FpC≡CR spectra, except that now there are four ionizations from the phenylacetylide (C≡CPh) ligand. The first two bands of the compound are the M1 (7.27 eV) and M2 (7.70 eV) metal-based ionizations. The third band (modeled at 8.52 eV) is partially obscured. This shoulder is assigned to the M3 ionization. The ionizations at 10.19 eV and 10.51 eV have the characteristic splitting for the Cp e₁″ set ionizations and are assigned as such. The remaining ionizations originate from orbitals of the phenylacetylide ligand π system.

Since the C≡CPh ionizations originate from orbitals that are similar to those of phenylacetylene (HC≡CPh), the valence PES of phenylacetylene was obtained. Figure 4 shows the four valence ionizations of HC≡CPh, which represent the π orbitals of phenylacetylene. The assignments are as follows: the ionization at 8.82 eV originates from the phenyl b₁ orbital, the ionization at 9.50 eV is from the phenyl a₂ orbital, the ionization at 10.33 eV is from the π∥ orbital, and the ionization at 11.03 eV is from the π⊥ orbital. The π system of phenylacetylene will be addressed in detail in the Discussion. In the spectrum of FpC≡CPh, the C≡CPh ligand ionizations correspond to these four HC≡CPh ionizations. The phenylacetylide π⊥ ionization is assigned to the sharp band at 9.89 eV, on the low binding energy side of the Cp ionizations. The π∥ is assigned to the sixth band (9.36 eV). The shape and intensity of the band at approximately 9 eV are indicative of two ionizations, so this band must include both the
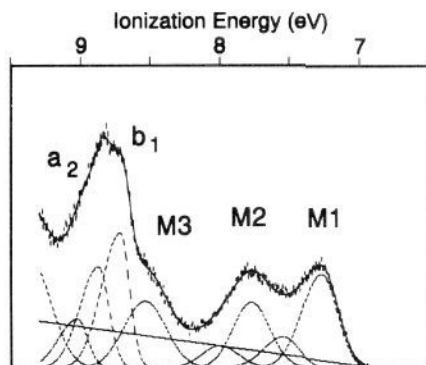
Bonding in (η^5-C_5H_5)$Fe(CO)_2C{\equiv}CR$

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Ionization Energy (eV)

Figure 5. Close-up spectrum of CpFe(CO)$_2$C$\equiv$CPh in the region from 7 to 9 eV.

a$_2$ and b$_1$ ionizations. A close-up spectrum (7 to 9.5 eV) of FpC$\equiv$CPh, shown in Figure 5, has better resolution and shows more detailed fine structure. This spectrum has three important features. First, the fine structure shows that there are two ionizations under the band between 8.5 and 9.0 eV. The phenyl b$_1$ is assigned to the band at 8.76 eV, and the phenyl a$_2$ is assigned to the narrow shoulder at 8.98 eV. The consistency of these assignments will become clear in the discussion section. Second, the finer detail in the band from 8.4 to 9.4 eV shows M3 as a shoulder on the low binding energy side. Third, the ionization envelope of the M1 and M2 ionizations has changed considerably compared to the shape of the M1 and M2 ionizations in the other acetylide spectra.

The He II spectrum, also shown in Figure 4, confirms that the M1, M2, and M3 ionizations are metal-based, since they gain intensity relative to the other ionizations. The Cp ionizations decrease in intensity by 45%, which is comparable to the Cp ionizations in the other FpC$\equiv$CR compounds. The He II spectrum of CpFe(CO)$_2$C$\equiv$CPh also shows several unusual features for the phenylacetylide-based ionizations. The b$_1$ and a$_2$ bands decrease by 22% and 24%, respectively, which indicates a large amount of metal character in both ionizations. The $\pi_\perp$ ionization decreases by 40%, which shows much less metal character than observed in the other acetylide π ionizations in this study. Also, the $\pi_\parallel$ band decreases by 31%, which indicates a significant amount of metal character in the corresponding orbital.

IV. Discussion

Electronic Interactions in CpFe(CO)$_2$C$\equiv$CH. Before discussing the information provided by the photoelectron spectra, it is helpful to describe the qualitative bonding picture for CpFe(CO)$_2$C$\equiv$CH. Figure 6 shows the valence orbitals of the [CpFe(CO)$_2$]$^+$ and [C$\equiv$CH]$^-$ fragments and the interactions between them. The electronic structure of the [CpFe(CO)$_2$]$^+$ fragment, which has been well characterized, is a pseudo-octahedral fragment with one ligand removed.[38] The [CpFe(CO)$_2$]$^+$ fragment is placed in a coordinate system with the empty coordination site on the z axis and the carbonyls bisecting the x and y axes. The three filled metal levels are then primarily the d$_{xz}$, d$_{yz}$, and d$_{x^2-y^2}$ orbitals. All three metal-based orbitals are affected by charge potential effects of the ligand R. The d$_{xz}$ and d$_{yz}$ orbitals each back-bond with one carbonyl and can potentially interact with orbitals on R that have π symmetry. The d$_{x^2-y^2}$ orbital back-bonds extensively into both carbonyl π^* orbitals, but has δ symmetry with respect to R and is therefore not affected by π interactions of R. These different interactions of the metal-based orbitals allow comparison of the π acceptor and π donor ability of the R ligand.[25] The LUMO of the [CpFe(CO)$_2$]$^+$ fragment is primarily the d$_{z^2}$ orbital, which forms the σ bond with the R
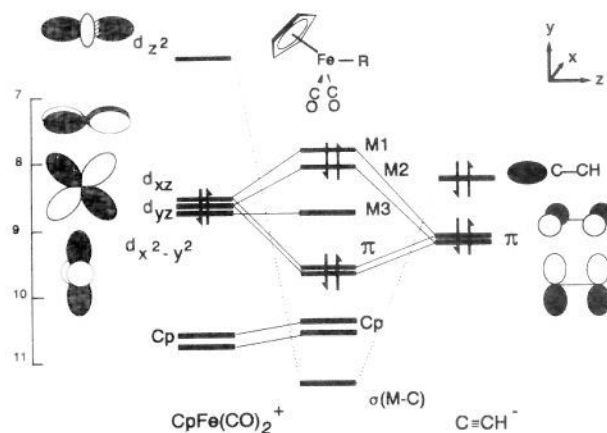
(38) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

Figure 6. Interaction diagram for [CpFe(CO)$_2$]$^+$ and C$\equiv$CH$^-$ fragments, showing filled/filled interaction between metal dπ and acetylide π orbitals.

ligand. Also present are the cyclopentadienyl ring (Cp) e$_1''$ set orbitals, which donate into the empty metal levels to form the key Cp—Fe bond. The Cp e$_1''$ levels are also affected by charge potential effects at the metal center, and can sense ligand overlap effects as will be shown later. For the acetylide fragment, the valence orbitals are a degenerate e set of π bond orbitals, π_x and π_y. The acetylide ligand also has a σ_{sp} orbital (doubly occupied for the formal anion) that is directed toward the metal.

Figure 6 shows the interaction of the [CpFe(CO)$_2$]$^+$ fragment with the acetylide CCH$^-$ fragment. The levels of the CpFe(CO)$_2$C$\equiv$CH molecule are placed at the experimental ionization potentials. The relative energies of the [CpFe(CO)$_2$]$^+$ levels are based on a Fenske–Hall calculation. The calculated [CpFe(CO)$_2$]$^+$ orbital energies are placed so that the d$_{x^2-y^2}$ orbital energy and the M3 ionization of CpFe(CO)$_2$C$\equiv$CH are aligned. This accounts for shifts due to the charge potential of the fragment, electron relaxation energies, and other effects associated with the approximate method. The energies of the [C$\equiv$CH] fragment are estimates based on the characters of the ionizations of FpC$\equiv$CH. There are two main orbital overlap interactions between the acetylide orbitals and the [CpFe(CO)$_2$]$^+$ fragment. The acetylide σ_{sp} orbital donates into the empty d$_{z^2}$ orbital and forms the metal–carbon σ bond. Secondly, the d$_{xz}$ and d$_{yz}$ orbitals have the correct symmetry to interact with the acetylide π and π^* orbitals. This forms three-center–four-electron π combinations. The totally symmetric π combination is labeled here (and in the spectrum) as the π ionization. The next occupied π combinations are labeled M1 and M2 because their primary character is from the d$_{xz}$ and d$_{yz}$ metal-based orbitals. This combination has one node in the Fe–C–C atom chain. The location of the node depends on how much the π and π^* orbitals of the acetylide contribute. The evidence from the photoelectron spectra and other Fenske–Hall calculations[22] indicate that the Fe dπ orbitals interact primarily with acetylide π orbitals, making the node between the metal and acetylide α carbon atom. A qualitative picture of the π combinations is shown in Figure 7. An extended Hückel calculation[39] also predicts that the π system is much like a three-centered poly-yne, with a very small coefficient on the α carbon.

The photoelectron spectra give direct evidence that the dominant π interactions are filled/filled interactions between iron dπ and acetylide π orbitals. For one point, the acetylide π ionizations have a large amount of metal character in the acetylide π ionization, which shows mixing of metal dπ and acetylide π levels. Further evidence is observed in the splitting of the M1 and M2 metal bands away from the M3 metal band. In FpR compounds, all three metal bands are affected by the charge potential effects of R. In addition, the M1 and M2 bands

(39) Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 3399.
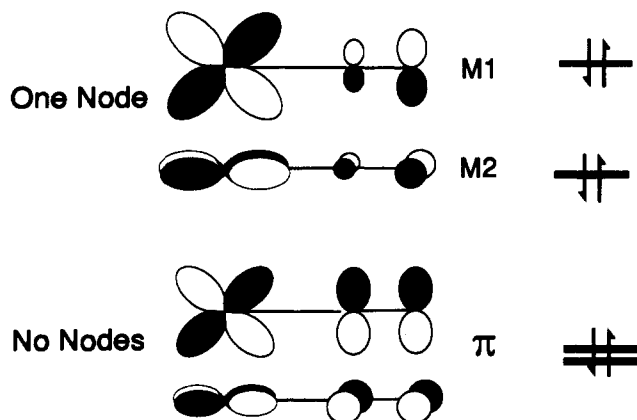
Figure 7. Qualitative nodal characters of CpFe(CO)₂C≡CR valence orbitals, showing the mixing that results from a filled/filled interaction between metal dπ and acetylide π orbitals.

correspond to dπ orbitals which can be destabilized by the π donor orbitals on R or stabilized by the π* acceptor orbitals on R. The value of the splitting shown in eq 1 is a measure of the

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

amount of π acceptor or donor ability. When R is a pure σ donor such as hydride (H), this value is 0.67 eV.[27] For FpC≡CH, the metal band splitting (eq 1) increases to 0.79 eV, which shows that the M1 and M2 orbitals are being destabilized by a filled/filled interaction with the acetylide π orbitals. It must be noted that the metal band splitting reflects the net π donor and π acceptor ability of the R ligand. The magnitude of the metal band splitting for C≡CH means that C≡CH is a net π donor ligand, but does not rule out the possibility for some π* acceptor ability as well.

Electronic Interactions of C≡CH Compared to CH₃, Cl, and C≡N Ligands. The electronic interactions of the C≡CH ligand compared to the more widely studied interactions of CH₃, Cl, and C≡N ligands are especially revealing. A correlation diagram in Figure 8 shows the shifts in ionization energies for the CpFe(CO)₂R compounds (FpR) as R is varied from CH₃ to C≡CH, Cl, and C≡N.

In the FpC≡CH spectrum, the separation of the M1 and M2 ionizations from the M3 is greater than in the FpCH₃ spectrum. The larger separation for FpC≡CH is reflected in the metal band splitting (eq 1) value. In FpCH₃ the metal band splitting is 0.70 eV, which is very close to that of the FpH (0.67 eV).[27,29c] The methyl ligand therefore has minimal π donation in FpR compounds. The metal band splitting for FpC≡CH increases to 0.79 eV, showing that the overall π bonding interactions for an acetylide is that of a π donor.

The ionization energy of the iron–carbon σ bond in FpC≡CH and FpCH₃ shows that the C≡CH ligand is a poorer σ donor than CH₃. The σ(Fe–C) ionization in FpC≡CH is 2.14 eV more stable than in FpCH₃. The σ lone pair orbital in C≡CH is comprised of a sp hybrid, while the σ lone pair of CH₃ is comprised of a sp³ hybrid. The overlap of the sp hybrid with the metal center is not as good as that of the sp³ orbital. Also, Fenske–Hall calculations of C≡CH⁻ and CH₃⁻ place the σ donor orbital of C≡CH⁻ approximately 3 eV more stable than the analogous orbital in CH₃⁻. This makes the σ donor ability of the C≡CH ligand much poorer than that of the CH₃ ligand. The shifts of the Cp and M3 ionizations also show the poorer σ donor ability of C≡CH. As mentioned above, in FpR compounds the M3 and Cp ionizations primarily reflect the charge potential effects of R on the metal center. In FpC≡CH, the M3 and Cp ionization bands are stabilized compared to their positions in FpCH₃. This reflects the poorer σ donor ability for C≡CH compared to CH₃. Interestingly, the Cp ionization shows a 0.23-eV greater stabilization than the M3 ionization, which must be due to an
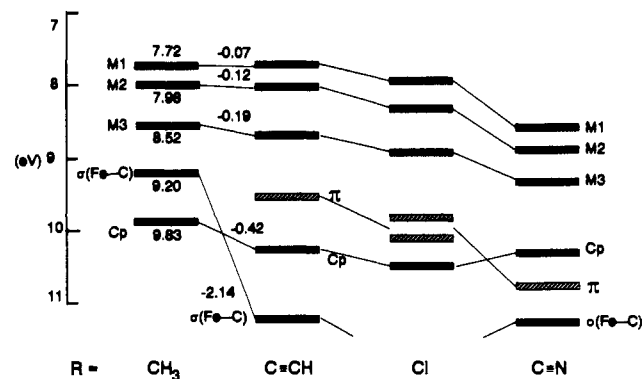

Figure 8. Correlation diagram for CpFe(CO)₂R compounds, where R is CH₃, C≡CH, and C≡N, showing ionization energies of valence ionization bands.

additional, stabilizing interaction for the Cp orbitals. We have observed filled/filled interactions between Cp π and halogen lone pair orbitals in CpRe(NO)(CO)(X) (X = halide) compounds when the ionizations are close in energy.[40] A similar interaction must be occurring here, where the Cp and acetylide π orbitals are involved in a filled/filled interaction that stabilizes the Cp and destabilizes the acetylide π. This provides further emphasis for the significance of the acetylide π orbitals in interactions with the metal fragment.

Comparison of the spectra of FpCl and FpC≡CH shows that the C≡CH ligand has similar interactions as a Cl ligand, which is a known π donor. In the CpFe(CO)₂Cl spectrum,[26,41] the splitting in the metal-based ionizations from eq 1 is 0.79 eV. This is identical with that observed for the acetylide compound. Figure 8 shows a strong similarity in the ionization patterns between the chloride and acetylide compounds, with the ionizations of the chloride compound at slightly higher ionization energy (≈0.2 eV). This indicates that the chloride ion is a slightly poorer σ donor than the acetylide, or, stating it alternatively, the chloride is slightly more electronegative than the acetylide. The corresponding ionizations of the bromide compound are generally only about 0.1 eV greater than those of the acetylide compound. This agrees very well with the group electronegativity of the acetylide, which on the Pauling scale is 2.90 for acetylide[42] in comparison to 2.96 for bromide and 3.16 for chloride.[43] All in all, the electronic interactions of the halides and the C≡CH ligand are extremely similar, with evidence of substantial mixing between the occupied π levels, and negligible back-bonding from the metal to π* orbitals. There is one notable difference between the Cl and C≡CH compounds. In the FpC≡CH spectrum, the two π bond ionizations of the C≡CH ligand are nearly degenerate, but in FpCl, the Cl pπ lone pair ionizations are split by 0.27 eV. The origin of this splitting is not due to spin–orbit coupling of Cl, which has magnitude of 0.07 eV. However, the PES of FpCN and FpCS show degenerate π levels for the CS and CN two π bond orbitals. It is possible that the π system of a diatomic ligand can accommodate an electronic change that the Cl ligand pπ orbitals cannot.

Comparison of the spectra of FpC≡N[41] and FpC≡CH shows that the C≡CH ligand has interactions very different from those of a cyanide ligand, which is known to be a weak π acceptor ligand. The trends in the ionization potentials of FpC≡CH and FpCN are shown in Figure 8. The similar energy of the iron–carbon σ bond, σ(Fe–C), suggests that C≡CH and CN ligands have similar σ donor abilities. However, the M3 and Cp ionization bands, which usually shift together, shift by different amounts

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(41) Hubbard, J. H. *Diss. Abstr. Int. B* **1983**, *43* (7), 2203.
(42) Huheey, J. E. *J. Phys. Chem.* **1966**, *70*, 2086.
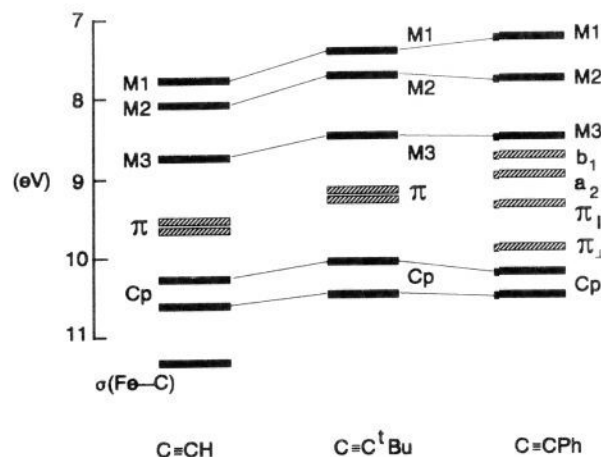(43) Huheey, J. E. *Inorganic Chemistry,* 3rd ed.; Harper and Row: New York, 1983.

Figure 9. Correlation diagram for the valence ionization bands of $CpFe(CO)_2C\equiv CH$, $CpFe(CO)_2C\equiv C^tBu$, and $CpFe(CO)_2C\equiv CPh$ compounds.

Figure 10. Interaction diagram of $[C\equiv CH]^+$ and $[C_6H_5]^-$ π levels and the resulting π levels of phenylacetylene ($HC\equiv CPh$). The levels of phenylacetylene are placed at the experimental ionization energies.

from FpCN to FpC≡CH. In FpCN, the CN π levels are slightly more stable than the Cp ring π levels. This is the result of a filled/filled interaction between the CN π and the Cp orbitals that stabilizes the CN π and destabilizes the Cp ring π. This is the opposite effect from what occurs in FpC≡CH, where a filled/filled interaction has destabilized the acetylide π and stabilized the Cp ring π.

The π interactions of C≡CH and CN with the metal center are very different. The metal band splitting for FpCN is 0.56 eV, which is much smaller than in FpH. The smaller value reflects the stabilization of the M1 and M2 bands toward M3, due to dπ-to-cyanide-π* back-bonding. More evidence for back-bonding is seen in the overall energy of the metal bands in FpC≡N, which are much more stable than the metal bands in FpC≡CH (see Figure 8). This reflects a transfer of electron density away from the metal in FpC≡N, caused by metal-to-cyanide-π* back-bonding. Since the metal bands in the acetylide compound do not benefit from this type of stabilization, and since the σ donor ability of C≡CH are C≡N are comparable, metal dπ to acetylide-π* back-bonding must be very small in FpC≡CH.

Effect of Substitution on Electronic Interactions. Figure 9 compares the ionization energies for the series of CpFe-(CO)$_2$C≡CR acetylide compounds. One important observation is that the σ donor ability of the C≡CR ligand is altered by varying R. As discussed above, shifts in the M3 and Cp ring ionizations primarily reflect the σ donor ability (inductive effects) of the acetylide. In FpC≡C^{t}Bu, the M3 and Cp levels are destabilized by about 0.25 eV from their positions in FpC≡CH, showing the superior σ donor ability of the C≡C^{t}Bu ligand. This implies that the overall energy of the organometallic compound can be tuned by varying the acetylide substituent.

Another important observation is that the dπ-acetylide-π interactions have increased in FpC≡C^{t}Bu. Figure 9 shows that the M1 and M2 (the dπ ionizations) in FpC≡C^{t}Bu are split away from the M3 ionization, a phenomenon that is reflected in the value of the metal band splitting of 0.93 ± 0.02 eV. This shows that C≡C^{t}Bu has a much stronger filled/filled interaction with the metal dπ orbitals and C≡CH. Supporting evidence for this is seen in the He II spectra of FpC≡CH and FpC≡C^{t}Bu. In the FpC≡CH spectrum, the M1 and M2 ionizations both increase in He II spectrum, but the M1 and M2 ionizations in FpC≡C^{t}Bu do not. The difference is significant beyond the 3σ level and indicates slightly less metal character (more carbon character) in the M1 and M2 ionizations in FpC≡C^{t}Bu compared to FpC≡CH. Overall, the evidence shows more acetylide-π-metal-dπ mixing in the FpC≡C^{t}Bu compound.

There is also evidence that changing the organometallic fragment changes the degree of dπ-acetylide-π mixing. The value
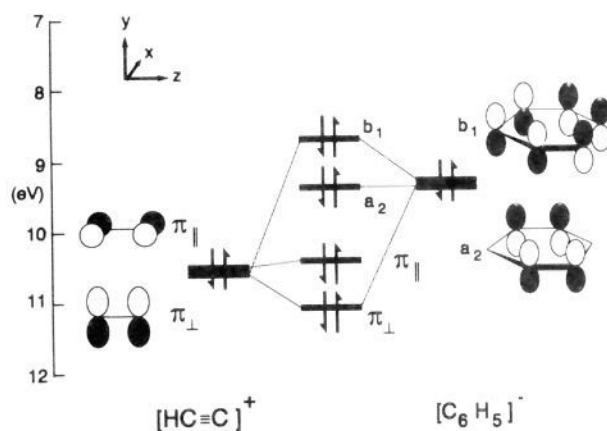
of the metal band splitting for Fp*C≡C^{t}Bu is 0.81 eV, which is significantly smaller than for FpC≡C^{t}Bu (0.93 eV). This indicates that the filled-dπ–filled-acetylide-π interaction is smaller in Fp*C≡C^{t}Bu than in FpC≡C^{t}Bu. Permethylation of the Cp ring raises the energy of the metal dπ levels away from the acetylide π orbitals, which results in poorer energy matching and less efficient dπ–acetylide-π mixing.

The explanation for the difference in metal band splitting for FpC≡CH, FpC≡C^{t}Bu, and Fp*C≡C^{t}Bu is that the degree of filled/filled interaction is directly related to the energy of the filled π orbitals. Changing the acetylide substituent to a more electron-rich group raises the energy of the acetylide π levels closer in energy to the dπ orbitals in Fp. This allows better energy matching and therefore more efficient dπ-acetylide-π mixing.

Electronic Interactions in $CpFe(CO)_2C\equiv CPh$. Since the orbitals of the phenylacetylide (C≡CPh) ligand are derived from those of phenylacetylene (HC≡CPh), the π orbitals of HC≡CPh will be discussed first. The valence orbitals of HC≡CPh can be constructed by considering an interaction of a phenyl ring and C≡CH fragments. The valence orbitals of a phenyl ring π system consist of two orbitals, labeled a_2 and b_1 according to the C_{2v} symmetry of the phenylacetylene. The phenyl a_2 and b_1 orbitals each have one node that is normal to the plane of the ring. The π system of $[C\equiv CH]^+$ fragment has an e set of π orbitals, labeled $\pi_{\parallel}$ and $\pi_{\perp}$. These fragment orbitals and their interactions are shown in Figure 10. The acetylide $\pi_{\parallel}$ (parallel to the plane of the phenyl ring) is nonbonding with respect to the phenyl π system. The phenyl a_2 is also nonbonding with respect to the $[C\equiv CH]^+$ fragment, because it has a node at the carbon atom bound to the C≡CH substituent (C_1). The phenyl b_1 orbital has a major coefficient on the C_1 carbon and interacts with the $[C\equiv CH]\pi_{\perp}$ orbital (perpendicular to the plane of the phenyl ring). The result is a filled/filled interaction that destabilizes the phenyl b_1 orbital and stabilizes the acetylene $\pi_{\perp}$ and causes extensive mixing between them. (The phenyl b_1 and acetylene $\pi_{\perp}$ labels are retained for the discussion of the phenylacetylene molecule, even though the two are mixed extensively). The four valence orbitals of HC≡CPh have corresponding ionization bands in the spectrum of phenylacetylene (see Figure 4). The b_1 and $\pi_{\perp}$ ionizations have similar vibrational progressions of 0.24 eV, corresponding to the C–C stretching vibration in HC≡CPh, which is evidence for extensive mixing between the phenyl b_1 and the acetylene $\pi_{\perp}$ orbitals. The large splitting between the a_2 and b_1 ionizations shows the destabilization of b_1 away from a_2, which is also due to the filled/filled interaction between the phenyl π b_1 and acetylide $\pi_{\perp}$.

As mentioned, the four valence orbitals of HC≡CPh are analogous to those of the phenylacetylide ligand in FpC≡CPh. Unlike the other acetylide ligands, the C≡CPh ligand has three

orbitals that can interact in a π fashion with the dπ orbitals: the b_1, $\pi_\|$, and $\pi_\perp$. (Because the C≡CPh ionizations originate from orbitals similar to the phenylacetylene orbitals, the phenylacetylene labels are retained for the C≡CPh orbitals.) There are several unique features in the CpFe(CO)$_2$C≡CPh spectrum that syhow how these orbitals interact. Most obvious is the shape of the M1 and M2 ionizations, shown in Figure 5 and Figure 11. The M2 ionization is best modeled with two bands split by 0.21 ± 0.02 eV, which represents a vibrational progression. This is more similar to a ring vibration than a C≡C or C≡O stretching frequency. The d$_{yz}$ (M2) must therefore be interacting in a filled/ filled fashion with a phenylacetylide orbital that has ring character. Both the b_1 and $\pi_\perp$ have the correct symmetry to interact with the d$_{yz}$, but the interaction of b_1 predominates, since b_1 is closer in energy to the metal orbitals. The He II data support this, since we observe more metal character in the b_1 ionization than in the $\pi_\perp$ ionization. The other phenylacetylide π ionization ($\pi_\|$) decreases by only 31% in the He II spectrum, showing significant metal character. This suggests that the corresponding $\pi_\|$ orbital is interacting with a metal-based orbital, probably the d$_{xz}$ orbital, in a filled/filled interaction.

The energies of the FpC≡CPh ionizations show an unequal interaction for the two dπ orbitals. Comparison of the FpC≡C^{t}Bu and FpC≡CPh ionizations in Figure 9 shows that the M3 ionization does not shift in going from FpC≡C^{t}Bu to FpC≡CPh. This implis that the σ donor abilities of C≡C^{t}Bu and C≡CPh are similar. However, the M1 is destabilized more than M2, which implies that the d$_{xz}$ (M1) orbital is involved in a stronger filled/filled interaction than the d$_{yz}$ (M2). In other words, the interaction between the phenylacetylide $\pi_\|$ and d$_{xz}$ orbitals is greater than the interaction between phenylacetylide b_1 and d$_{yz}$. This is reasonable because the b_1 orbital is also delocalized onto the phenyl ring.

The trends in Figure 9 also show that the Cp levels are stabilized by 0.16 eV in the FpC≡CPh compound compared to the FpC≡C^{t}Bu compound. The Cp levels in the other FpC≡CR compounds also show this stabilization, although to a lesser extent. As in the other acetylide compounds, we believe this is due to a filled/filled interaction between the Cp π levels and the acetylide π orbitals. This interaction would cause the Cp π levels to be stabilized and the acetylide π to be destabilized. The stabilization of the Cp ionization is more pronounced in the C≡CPh case than in the other acetylide ligands, probably because the C≡CPh levels are closer in energy to the Cp e_1'' levels. It is obvious that, in these acetylide compounds, the Cp levels are not simply "spectator orbitals" and can be affected by filled orbitals on C≡CR or other ligands.[44]

Evidence for dπ-Acetylide-π Mixing from Vibrational Fine Structure. Supporting evidence for a filled/filled interaction can be seen in close-up spectra of the metal band region (Figure 11). In the FpC≡CH spectrum, the M2 and M3 ionizations have shoulders on the high binding energy sides, which correspond to a vibrational progression of 0.28 eV. The extra intensity of the M2 ionization compared to the M1 ionization implies that M1 also has a similar vibrational progression of 0.28 eV that is near the same energy as the M2 vertical ionization. This vibrational fine structure is similar to the vibrational fine structure observed on metal-based ionization bands of Mo(CO)$_6$ and W(CO)$_6$ molecules,[45] which corresponds to CO stretching vibrations activated by back-bonding into the carbonyls. This structure is normally seen only in the metal-based ionizations of symmetrical metal–carbonyl molecules. The spectra of FpH and FpCH$_3$ do not show clear vibrational progressions on the metal-based ionizations, presumably because of the lower vibrational and electronic symmetry of these molecules.[27,29c] In the case of the
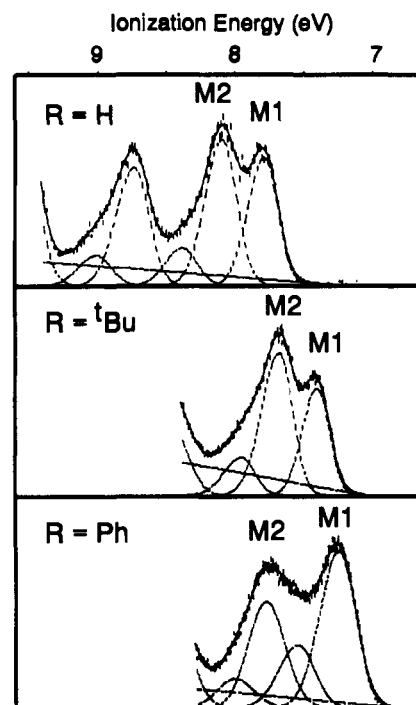
(44) Similar mixing of Cp orbitals seen in: Knight, M. T.; Myers, L. K.; Thompson, M. E. *Organometallics* **1992**, *11*, 3691.

(45) Hubbard, J. L.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 2132.

Ionization Energy (eV)

Figure 11. Close-up spectra of the metal band region for CpFe-(CO)$_2$C≡CR compounds (R = H, ^{t}Bu, Ph). Vibrational progression is most noticeable as a shoulder on the high binding energy side of the M2 ionization in the R = ^{t}Bu compound.

acetylide compounds, the M1 and M2 ionizations correspond to orbitals that each back-bond to the π^* of one CO and mix with the π bond of the acetylide. It appears that there is sufficient electronic and vibrational symmetry in the metal-based ionizations of FpC≡CH to allow observation of the vibrational progression, which may be due to the coupling of C≡C, CO, or both.

In CpFe(CO)C≡C^{t}Bu, the vibrational fine structure on the metal ionizations also gives evidence for dπ-acetylide-π mixing. As seen in Figure 11, a shoulder on the high binding energy side of M2 is very pronounced and corresponds to a vibrational progression of 0.28 eV. The larger intensity of the M2 ionization compared to the M1 ionization implies that the M1 has a similar vibrational progression, which coincides with the vertical ionization of M2. Interestingly, the PES of HC≡C^{t}Bu shows an identical C≡C stretching vibrational progression of 0.28 eV on the HC≡C^{t}Bu π ionization.[29c]

π Ionization Energy Shifts from Alkynes to Coordinated Acetylides. By observing the trends in energies for the alkyne π bond ionizations and acetylide π bond ionizations, it becomes clear that the extent of mixing between the acetylide π bond orbitals and the metal dπ orbitals depends on the energy separation between them. The π ionization in FpC≡CH is shifted 1.74 eV to lower ionization energy from the π bond ionization of free acetylene at 11.40 eV.[46] The shift to lower ionization energy is primarily due to the formal negative charge of the acetylide compared to the neutral free acetylene. In FpC≡C^{t}Bu, the π ionization is shifted by only 0.75 eV to lower ionization energy compared to the corresponding ionization of free HC≡C^{t}Bu at 9.94 eV (this work). Figure 12 shows this shift for all the FpC≡CR compounds correlated to the π bond ionization energy in HC≡CR. Of the alkynes in this study, acetylene has the highest π bond ionization energy and shows the largest shift (to lower ionization energy) to the corresponding FpC≡CH acetylide π ionization. The *tert*-butylacetylene molecule has a much lower π bond ionization energy and shows a much lower shift to the corresponding π ionization of the metal acetylide. The smaller

(46) Turner, D. W. *Molecular Photoelectron Spectroscopy*; Wiley: New York, 1970.

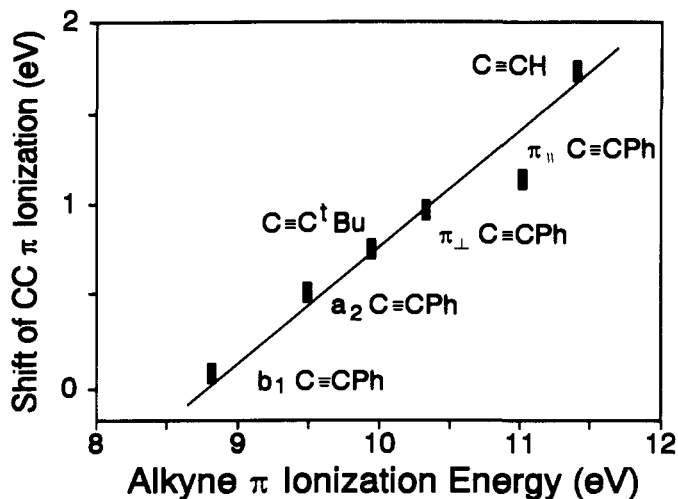**Figure 12.** The alkyne π ionization energy versus the shift of the CC π to lower ionization energy from free alkynes to CpFe(CO)₂C≡CR acetylides.

shift occurs because the destabilization of the levels due to the formal negative charge is countered by a stabilization due to increased filled/filled interactions with the occupied dπ levels. The same is true for all of the valence levels of the FpC≡CPh. The closer the initial acetylene π valence levels are to the metal levels, the smaller the shift of the π ionizations and the greater the dπ-acetylide-π mixing. The net shift of the b₁ level is near zero. The $\pi_\parallel$ level appears to be getting some exceptional stabilization from mixing with the metal, because it is the only level that does not fall on the line. As mentioned in the previous section, the comparison of He I/He II data indicates that the $\pi_\parallel$ level is mixing strongly with the metal. It is surprising to us that the phenylacetylene a₂ level also follows this correlation, because we do not expect it to have much overlap interaction with the metal. The correlation shows that the energy matching between the acetylide levels and the metal levels is extremely important in determining the extent of mixing.

Frontier Orbitals and Reactivity. As pointed out in the Introduction, the reactivity of electrophiles implies that the HOMO of the CpFe(CO)₂C≡CR compound is partially localized on the acetylide β carbon, which has indicated to some that the metal is back-bonding into the π^* of the acetylide. The photoelectron data suggest that the β carbon in CpFe(CO)₂C≡CR is nucleophilic because of a filled acetylide-π-filled-dπ interaction, which also causes the HOMO to have significant electron density on the β carbon. As seen in Figure 7, the HOMO contains a node near the α carbon, which therefore has a smaller coefficient (i.e., is less electron rich) than the β carbon. This would make the β carbon nucleophilic and susceptible to electrophilic attack. No metal-to-acetylide-π^* back-bonding need to be present for this to occur. This reactivity is directly analogous to that of the thiol CpFe(CO)₂SR compound, in which electrophilic attack also occurs at the nondonor (R) atom. In this case, the R atom is thought to be nucleophilic as a result of metal dπ/sulfur pπ overlap.[47]

V. Conclusions

The photoelectron spectra of the CpFe(CO)₂C≡CR compounds show that the π orbitals of the acetylide ligands dominate the π-type interactions with the metal fragment. In this system, there are filled metal dπ orbitals that have the proper energy to mix extensively with the filled acetylide π orbitals. The dπ electrons of the CpFe(CO)₂ fragment have essentially become conjugated with the acetylide π system through this filled/filled interaction. The interactions of the acetylide π orbitals with the fragment are also evidenced in the Cp ionizations. We cannot rule out back-bonding completely, but the body of evidence suggests that back-bonding is negligible compared to the metal-dπ-acetylide-π mixing. The CpFe(CO)₂C≡CH and CpFe-(CO)₂C≡C'Bu compounds can be thought of as a three-centered poly-yne.

We also find that substitution on the acetylide significantly influences the extent of electronic mixing with the metal fragment. The filled/filled interaction is more extensive in the C≡C'Bu and C≡CPh compounds than in CpFe(CO)₂C≡CH. This is a direct result of raising the energy of the acetylide π orbitals closer to the dπ orbitals, which facilitates better dπ-acetylide-π interaction. Changing the organometallic fragment from [Cp-Fe(CO)₂] to [Cp*Fe(CO)₂] also appears to influence the extent of dπ-acetylide-π mixing. Permethylating the Cp ring raises the energy of the dπ orbitals further away from the acetylide π orbitals, which results in less efficient dπ-acetylide-π mixing.

The observed dπ-acetylide-π overlap also explains the observed electronic communication along the metal–carbon–carbon chain in acetylide compounds, since the metal π and acetylide π electrons are essentially coupled. The same type of metal/acetylide coupling should also be present in other MLₙ(C≡CR) compounds that have filled metal orbitals with the proper symmetry and energy. By changing the substituents on the acetylide, it should be possible to vary the metal/acetylide conjugation and tune the overall electron distribution in the highest occupied orbitals. Changing the metal fragment should also affect the filled/filled interactions, and a sufficiently electron-rich metal center may also facilitate extensive back-bonding to the acetylide π^* orbitals. Compounds of the type CpRu(PMe₃)₂(C≡CR), where the metal center is expected to be more electron rich, are currently being investigated using PES.[48]

(47) Ashby, M. T.; Enemark, J. E.; Lichtenberger, D. L. *Inorg. Chem.* **1988**, *27*, 191.

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