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Experimental Investigation of the Electronic Structures of Enneacarbonylbis(μ_3-X-methylidyne)triiron Complexes (X = H, F, Cl, Br) by Means of He I/He II Gas-Phase UV Photoelectron Spectroscopy

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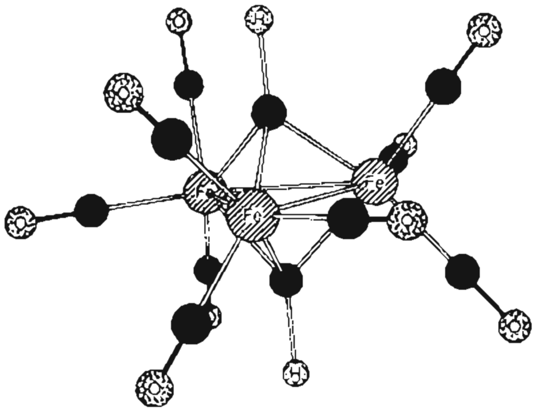
The electronic structures of three novel trinuclear clusters of iron {$[Fe_3(CO)_9(CX)_2]$, X = H, Cl, Br} have been investigated by means of He I/He II gas-phase UV photoelectron spectroscopy. A detailed assignment of the photoelectron spectra of the title molecules has been achieved by making use of the *first principle* theoretical calculations recently published for the isoelectronic and isostructural $[Fe_3(CO)_9(CF)_2]$. The experimental data confirmed that both the e_g-like and the t_{2g}-like levels of the $Fe_3(CO)_9$ fragment actively participate in the interaction between the $Fe_3(CO)_9$ and the $(CX)_2$ moieties. Furthermore, the analysis of the relative intensity variations on passing from the He I to the He II ionizing source allowed us to discriminate among the different extents of bonding between the two fragments along the series, confirming, at the same time, the leading role played by the $[Fe_3(CO)_9]$–C_{apical} interaction in stabilizing the whole cluster. Interestingly, in the $[Fe_3(CO)_9(CH)_2]$ and $[Fe_3(CO)_9(CBr)_2]$ derivatives at least one component of the two C_{apical} lone pairs has been experimentally detected. Additionally, in the He II spectrum of the former compound it has been identified as the band due to the ionization from the molecular orbital responsible for the direct Fe–Fe σ bond. The presence of a common bonding scheme for the investigated molecules agrees fairly well with electrochemical measurements.

Introduction

The electronic structures of polynuclear organometallic molecules have been the object of several investigations involving both theoretical and experimental approaches.[2] The main goal of these investigations is the explanation of the nature of the multicentered metal–metal (hereafter M–M) and metal–ligand (M–L) interactions, which are peculiar to this class of molecules. An even more appealing issue, associated with an intimate comprehension of the M–L multicentered interactions, is the well-known assumption that metal clusters may serve as models for miniature metal surfaces or highly dispersed supported catalysts.[3]

Some of the authors have already focused their attention on the electronic structures of enneacarbonyl mono- and bis-substituted (methylidyne) trimetallic clusters {$[Co_3(CO)_9](\mu_3$-CY), Y = H, CH_3, CF_3, $COOCH_3$, F, Cl, Br, I; $[Fe_3(CO)_9](\mu_3$-$CF)_2]$}[2,4,5] looking into the main differences in the bonding schemes on passing from the mono- to the bis-substituted compounds.

In the present contribution, which is part of a comprehensive study of the electronic structure of polynuclear organometallic molecules,[2,4–6] we report the results of an experimental investigation of the bonding schemes of three novel trinuclear clusters $[Fe_3(CO)_9](\mu_3$-$CX)_2$, X = H (I), Cl (II), Br (III), by using He I/He II gas-phase UV photoelectron (PE) spectroscopy. The assignment of the PE spectra of I–III was accomplished by taking advantage of *first principle* discrete variational- (DV-) Xα results recently published by some of us concerning the electronic structure of the isoelectronic and isostructural $[Fe_3(CO)_9](\mu_3$-$CF)_2$ (IV)[5] (see the following figure where the main features of the molecular structure of the H derivative are reported),[7] as well as of relative intensity variations on passing from the He I to the He II ionizing source.



Incidentally, we should also mention the lack of crystallographic data for I–III which prevented the possibility of carrying out a theoretical investigation of their electronic structures.

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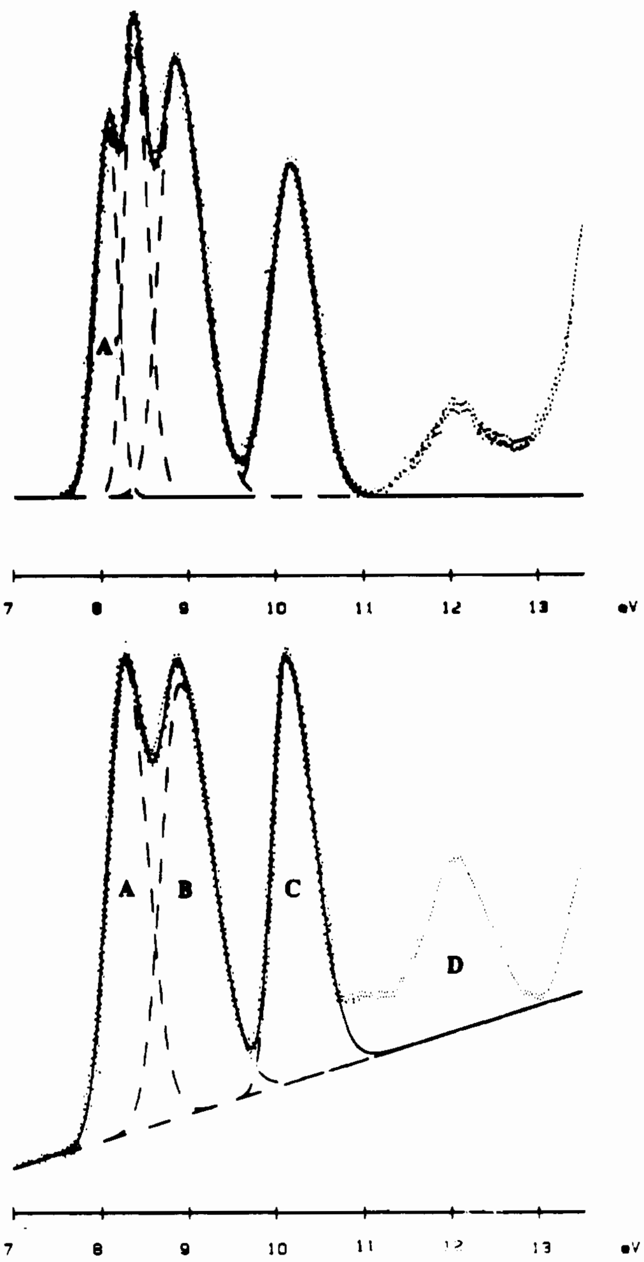

Figure 1. He I (bottom)/He II (top) PE spectra of $[Fe_3(CO)_9](\mu_3\text{-}CH)_2$.

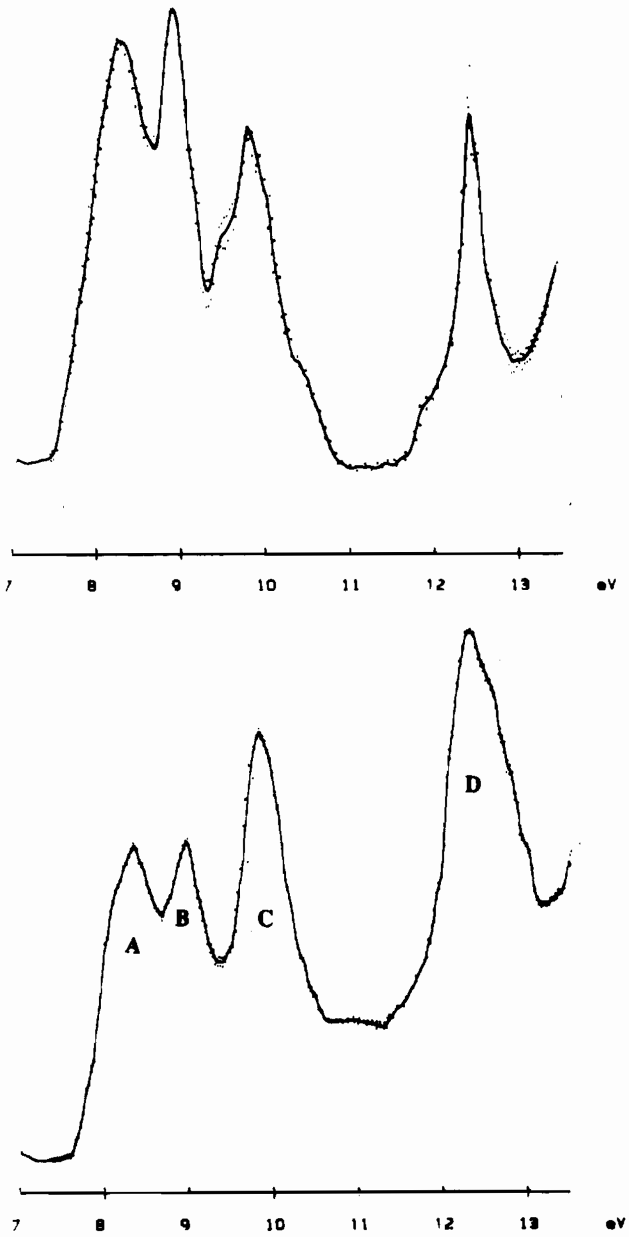

Figure 2. He I (bottom)/He II (top) PE spectra of $[[Fe_3(CO)_9](\mu_3\text{-}CCl)_2$.

Experimental Section

Preparation. The title compounds were synthesized as described in detail in refs 8e,f. After crystallization, their purity was checked by IR, MS, and NMR spectroscopies.

Spectra. He I and He II gas-phase PE spectra of I–III are shown in Figures 1–3, respectively, where bands have been alphabetically labeled. The PE spectra were recorded by directly interfacing an IBM AT computer to a Perkin-Elmer PS-18 spectrometer modified for He II measurements by inclusion of a hollow-cathode discharge lamp giving high output of He II photons (Helectros Developments). Resolution measured on the He $1s^{-1}$ line was always around 22 meV. The He II spectra were corrected only for the He IIβ "satellite" contributions (8% based on the reference N_2 spectrum). The spectra were obtained in the 60–80 °C temperature range, and they were calibrated by reference to admitted inert gases (Xe–Ar) and to the He $1s^{-1}$ self-ionization. Depending on temperature, different amounts of free CO were detected. However, the identical patterns of the spectra, with regard to both relative intensities and positions of the peaks, led us to exclude the presence of different volatile species other than the title compounds. To provide a comparison with the already published experimental data for IV,[5] the relative He I/He II PE spectra have been once more recorded and are shown in Figure 4.

The deconvolution of the He I/He II spectra of I was carried out by fitting the experimental profiles up to 10.5 eV with a series of asymmetrical Gaussian curves after subtraction of background. The agreement factors, $R = [\Sigma(F_o - F_c)^2/\Sigma(F_o)^2]^{1/2}$, after the minimization of the function $\Sigma(F_o$

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(7) The molecular structures of the bis(alkylidyne) clusters $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COCH_3)$,[8a] $Fe_3(CO)_9(\mu_3\text{-}CF)_2$,[8b] $Fe_3(CO)_9(\mu_3\text{-}CH_3)[\mu_3\text{-}CN(CH_3)_2]$,[8c] $Fe_3(CO)_9(\mu_3\text{-}COCH_3)_2$,[8d] $Fe_3(CO)_6(\eta^6\text{-}C_6H_6)(\mu_3\text{-}CCl)(\mu_3\text{-}CCOOC_2H_5)$,[8e] and $Fe_3(CO)_9(\mu_3\text{-}CH)(\mu_3\text{-}CCOOCH_3)$[8f] have been experimentally determined. All of them possess the trigonal bipyramidal cluster framework (see the figure in the Introduction) which has significant differences in bond lengths only for $Fe_3(CO)_9(\mu_3\text{-}CH_3)[\mu_3\text{-}CN(CH_3)_2]$[8c] [Fe(1)–CN = 2.215(4) Å, Fe(2)–CN = 1.941(3) Å]. The title molecules exhibit very similar IR spectra in the CO stretching frequency region[8e,f] compared to $Fe_3(CO)_9(\mu_3\text{-}CF)_2$,[8b] demonstrating that these compounds have similar symmetries (the symmetry of IV in the solid state is close to $3/m$, C_{3h}).[8b] In addition, the ^{13}C NMR spectra show low-field resonances at δ 321.2 (I), 336.4 (II), 326.1 (III), and 365.8 (IV) for the C_{apical} atoms which are typical for these bis(alkylidyne) clusters.

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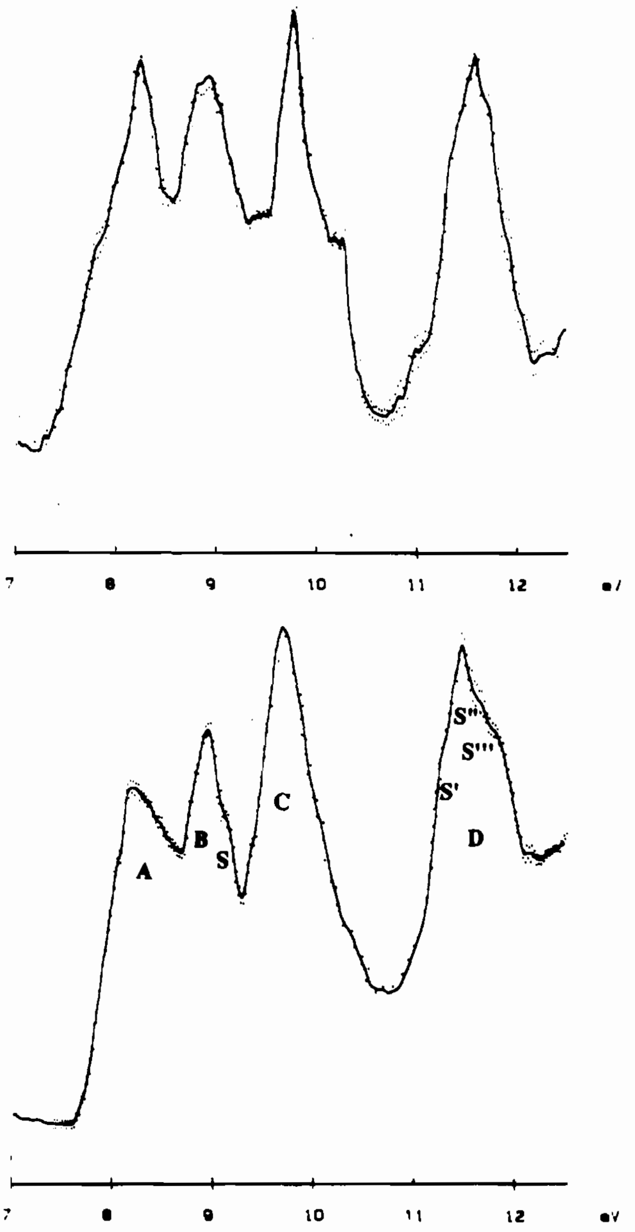

Figure 3. He I (bottom)/He II (top) PE spectra of $[Fe_3(CO)_9](\mu_3\text{-}CBr)_2$.

$- F_c)^2$ converged to values ≤0.037. The areas of bands thus evaluated were corrected for the analyzer transmission function. The described procedure was limited to I because it is evident (see Figures 1–4) that the He I relative intensity A:B ratio changes on passing from I to the other compounds. Moreover, an extra band is present on the lower ionization energy (IE) side of band A in the He II spectrum of the H derivative (see Figure 1). Relevant PE data (experimental IEs and relative intensities) are compiled in Table I.

Results and Discussion

For discussion purposes, the PE spectra of I–IV (see Figures 1–4) can be conveniently divided in two distinct IE regions (I, 7.5–10.8 eV; II, 10.8–13 eV). A further IE region, that beyond 13 eV, mainly due to the ionizations from metal–CO σ-bonding molecular orbitals (MOs), to 1π and 4σ CO-localized levels, and to fluorine π MOs,[4,5] is not shown in the figures because a detailed assignment of this zone is beyond the scope of the present contribution.

As anticipated, a thorough description of the electronic structures of the investigated molecules can be achieved by taking advantage of literature theoretical data.[5] In order to facilitate comprehension of the following discussion, let us briefly summarize the main features of the DV–Xα results relative to IV.[5]

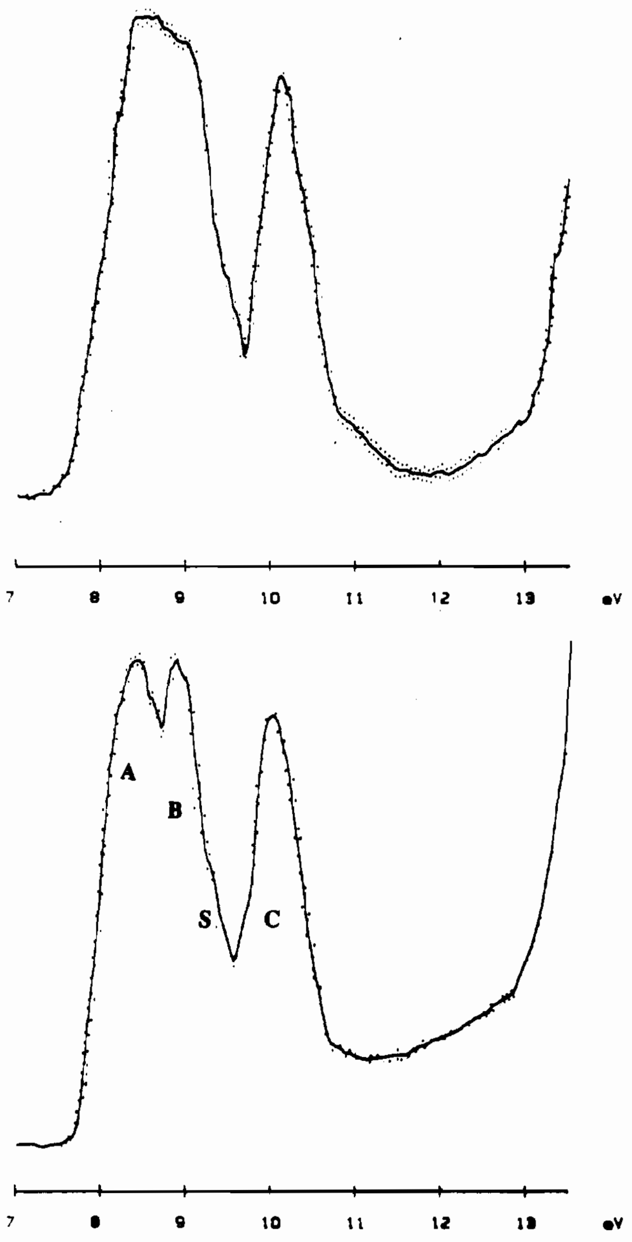

Figure 4. He I (bottom)/He II (top) PE spectra of $[Fe_3(CO)_9](\mu_3\text{-}CF)_2$.

Table I. Experimental Ionization Energies (eV)

compd	band	IE (eV)	rel intens^a He I	rel intens^a He II
I	A′	8.13		2.08
	A	8.28	3.99	2.23
	B (S)	8.80 (9.0)	5.01	4.70
	C	10.15	4.25	3.94
	D	12.05		
II	A	8.31		
	B	8.92		
	C	9.79		
	D	12.32		
III	A	8.24		
	B (S)	8.92 (9.1)		
	C	9.71		
	(S′) D (S″, S‴)	(11.3) 11.49 (11.7, 11.8)		
IV	A	8.40		
	B (S)	8.89 (9.20)		
	C	9.96		

^{a} See Figure 1.

The outermost occupied thirteen MOs of the fluorine derivative were computed to be all strongly localized on the metal centers. These orbitals can be usefully separated into two sets: one consists of the nine t_{2g}-like orbitals (2a′ + a″ + 2e′ + e″) deriving from the interaction of the three occupied $Fe(CO)_3$ t_{2g}-like levels;[9] the other one, deriving from the half-occupied e_g-like orbitals of the same fragment, consists of two MOs (e′ + e″) accounting for the Fe–Fe (e′ MO) and the Fe–C_{apical} (e″ MO) bonding interaction. Furthermore, it is important to note that the latter e_g-like orbital is also C–F and Fe–Fe antibonding in character, so that only two MOs (degenerate e′, e_g-like level) contribute to the bonding within the metallic triangle at variance with the isoelectronic cobalt clusters ($[Co_3(CO)_9](\mu_3\text{-}CX)$), where three Co–Co bonding levels are present.[2,4] An important consequence of such a result is that the $[Fe_3(CO)_9]$–C_{apical} bond plays a leading role in ensuring the overall cluster stability.

As far as the assignment of PE data relative to IV is concerned, we showed, according to theoretical results,[5] that all the ionizations lying below 11 eV are due to MOs significantly localized on the metal atoms. In particular, band A (see Figure 4) was assigned to the ionization from the e_g-like orbitals responsible of the Fe–C_{apical} (9e″ MO) and Fe–Fe (13e′ MO) bonding interactions (see Figure 3 of ref 5), as well as to a t_{2g}-like level (10a″ MO).[5] Band B and the shoulder S on its higher IE side were associated with the ionization from four purely nonbonding t_{2g}-like orbitals (12e′ + 14a′ + 13a′ MOs), while band C was related to the ionization from four t_{2g}-like levels (11e′ and 8e″ MOs) significantly stabilized (more than 1 eV) with respect to the remaining ones by the interaction with the e′ and e″ orbitals of the two methylidyne groups.

The obtained results[5] are clear experimental evidence that the interaction between the $[Fe_3(CO)_9]$ and the apical $(CX)_2$ fragments is not limited to the e_g-like levels of the former but extends to its t_{2g}-like orbitals too, with the net effect of further strengthening the bonding between the metallic triangle and C_{apical}. The contribution of the inner t_{2g}-like levels, normally considered as π-bonding to the M–CO groups only, to the M–L interaction is not particularly surprising. Actually, our group has demonstrated for other polynuclear organometallic complexes the contribution of these orbitals to the multicentered M–L interactions.[2,11] For instance, the bonding scheme of all the members of the series $[Co_3(CO)_9](\mu_3\text{-}CX)$ (X = H, F, Cl, Br), isoelectronic with I–IV, is characterized by a strong interaction between the highest occupied π orbital (carrying a single electron) of the C–X fragment and two t_{2g}-like levels, e in symmetry, resulting in significant stability with respect to the remaining ones.[2,4a] Furthermore, it should be mentioned that the involvement of the t_{2g}-like orbitals in the M–L interaction is counter to the usual view of $Fe(CO)_3$ as isolobal with BH (as a whole, if the t_{2g}-like levels were purely nonbonding in character, $[Fe_3(CO)_9](\mu_3\text{-}CH)_2$ would be isolobal with the closo $C_2B_3H_5$ molecule).[12,13]

Now, with the assumption that the bonding scheme of IV holds along the whole series, we can use the energy positions of PE bands as well as their variations in relative intensity on passing from the He I to the He II ionizing source[14] to monitor, along the series, the different extents of the $[Fe_3(CO)_9]$–C_{apical} bonding interactions.

Band D. Comparison of Figures 1–3 with Figure 4 indicates in I–III the presence of an extra band (band D) in the IE region II. The assignment of this band along the series is straightforward if we remember the nature of the outermost MOs mainly localized on each C–X fragment. In a simple hybrid picture, a single C–H group (taken as a model) has three hybrids with one electron each. In the delocalized picture these hybrids combine to form a C_{apical} lone pair pointing away from the hydrogen[16] and a degenerate pair of perpendicular π orbitals. Symmetric and antisymmetric combinations of these levels will be present in the whole cluster. Furthermore, when X is a halogen, each CX unit contributes with two further MOs, strongly polarized toward the X atom, accounting for the C–X π bond. The antibonding partners of such an interaction are the C_{apical}-based π orbitals indicated above.

In I, where the H atoms have no occupied π orbitals, we can with confidence assign band D to the ionization from the n^- combination of the C_{apical} lone pairs. The dramatic decrease in relative intensity of band D on passing from the He I to the He II ionizing source is perfectly in agreement with such an assignment.[14] As far as band D in II and III is concerned, we propose to assign it to the ionization from the π C–X bonding orbitals primarily X in character. The actual IE values of band D in II and III (see Table I) lie in proximity to the higher IE boundary of the IE ranges typical of each halogen atom,[15b] indicating an electron deficiency on X, which in turn can be related to X→C_{apical} π-bonding donation. This is in agreement with the He I PE data for $[Co_3(CO)_9]CCl$ and $[Co_3(CO)_9]CBr$,[4] as well as with ^{35}Cl NQR[17] and IR[18] results which predicted for $[Co_3(CO)_9]CCl$ a significant amount of π character in the Cl–C_{apical} bond. The decrease in relative intensity of band D in II and III (particularly evident in II) on switching from the He I to the He II lamp agrees well with such an assignment. The rather complex nature of band D in III (at least three very evident shoulders, one on the lower IE side and two on the higher IE side), as well as the less pronounced decrease in relative intensity under the He II radiation,[19] could be tentatively explained by assuming that at least one component of the C_{apical} lone pairs (the n^- one) is hidden under the higher IE side of band D. Quite reasonably, the higher electronegativity of Cl[21] shifts this ionization in the IE region III, not shown in the figures.

Band C. As already pointed out, band C in IV was assigned to the ionization of four t_{2g}-like orbitals (11e′, 8e″ MOs)[5] stabilized by the interaction with the e′ and e″ levels of the methylidyne fragments (the C_{apical}-based π orbitals). The energy position of this band along the whole I–IV series (see Table I) seems to be counterintuitive. Actually, one would expect the smallest stabilization in IV, where the energy matching between the t_{2g}-like levels of the $Fe_3(CO)_9$ fragment and the C_{apical}-based π orbitals should be the worst.[22] This apparent controversy can be easily resolved by taking into account the fact that the actual energy

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[9] The outermost MOs of the $Fe(CO)_3$ fragment can be obtained from those of a hypothetical $Fe(CO)_3L_3$ complex by taking away the three L ligands (assuming they are on one face, the C–Fe–C angles are 90°). To a certain extent, $Fe(CO)_3$ "remembers" its octahedral parentage[10] and the three inner-lying orbitals are related to the t_{2g} set (e + a_1 in the local C_{3v} symmetry), while the two higher-lying levels (e in the local C_{3v} symmetry) are reminiscent of the e_g ones. In a d^8 system, such as the $Fe(CO)_3$ fragment, the t_{2g}-like orbitals are completely occupied, while the e_g-like levels carry only two electrons.

[10] (a) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39. (b) Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126.

[11] Casarin, M.; Rizzi, G. A.; Gulino, A.; Kraakman, M. J. A.; Vittadini, A.; Vrieze, K. *Inorg. Çhem.* **1991**, *30*, 1906.

[12] Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

[13] Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

[14] In fact, on the basis of the Gelius model,[15a] we expect a marked decrease in the following cross-section ratios on passing from the He I to the He II excitation source:[15b] σ(X *n*p)/σ(Fe 3d) (X = halogen), σ(C 2p)/σ(Fe 3d), σ(H 1s)/σ(Fe 3d).

[15] (a) Gelius, U. In *Electron Spectroscopy*; Shirley, D. A., Ed.; North Holland: Amsterdam, 1972; p 311. (b) Rabalais, J. W. In *Principles of UV Photoelectron Spectroscopy*; Wiley Interscience: New York, 1977.

[16] This orbital is very similar in nature to the 5σ MO of CO. In other words, it may thought as a lone pair on the C_{apical} atom which donates electron density into the acceptor orbitals of the $Fe_3(CO)_9$ fragment. Obviously, the presence of two CH units will originate a symmetric (n^+) and antisymmetric (n^-) lone pair combination.

[17] Miller, D. C.; Brill, T. B. *Inorg. Chem.* **1978**, *17*, 240.

[18] (a) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97. (b) Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* **1973**, *6*, 73. (c) Palyi, G.; Piacenti, F.; Markò, L. *Inorg. Chim. Acta Rev.* **1970**, *4*, 109. (d) Borg, G. *Proc. Symp. Coord. Chem.* **1965**, *1964*, 361.

[19] Both Cl 3p and Br 4p subshell photoionization cross sections significantly decrease on passing from the He I to the He II source, even though such a decrease is more intense in the former. Actually, $\sigma(Cl_{3p})_{He\,II}/\sigma(Cl_{3p})_{He\,I} = 4.67 \times 10^{-2}$ while $\sigma(Br_{4p})_{He\,II}/\sigma(Br_{4p})_{He\,I} = 6.20 \times 10^{-2}$.[20]

[20] Yeh, J. J.; Lindau, I. Atomic Subhsell Photoionization Cross Section and Asymmetry Parameters: $1 \leq Z \leq 103$. *At. Data Nucl. Data Tables* **1985**, *32*, 1.

[21] Allread, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.

position of band C is due to a delicate balance of two different and opposite effects: on one side, the stabilizing interaction with the C_{apical}-based π orbitals; on the other side, the destabilizing interaction with the π C–X bonding orbitals primarily X in character.[23] In I, where the latter is absent, only the stabilizing effect is active and band C lies at the highest IE (see Table I). The IE position of band C in II and III is determined by the balance of both effects, while in IV the active mechanism is once more the only stabilizing one, reasonably because the F-based π orbitals lie too deep in energy to significantly interact with the $Fe_3(CO)_9$ t_{2g}-like levels. The decrease in relative intensity of band C, particularly evident in II and III and less pronounced in I and IV,[19,24] on passing from the He I to the He II excitation source demonstrates the significant participation of methylidyne levels in the MOs from which band C is originated.

Bands B and A. We decided to treat bands B and A together for several reasons: (i) they are rather close in energy; (ii) they are mainly due to the ionization from MOs strongly localized on the metallic $Fe_3(CO)_9$ fragment; (iii) only slight variations in their IE positions are observed (see Table I). As far as band B is concerned, a relative intensity increase with respect to band C is very evident in II and III on passing from the He I to the more energetic radiation. This agrees fairly well with the assignment we already proposed for IV; i.e., band B arises from the ionization from four t_{2g}-like MOs mainly nonbonding in character. Furthermore, the ionization from the fifth t_{2g}-like level is assumed to be hidden under band A. On moving to I, we have already pointed out that the He I A:B relative intensities fit the ratio 4:5 (see Table I). Furthermore, band B slightly decreases in relative intensity on passing from He I to He II ionizing source (see Table I). The only assignment consistent with these data is the association of band B with the ionization from five MOs, namely three nonbonding t_{2g}-like levels plus the e_g-like e″ MO, which accounts for the Fe–C_{apical} interaction. The 0.1-eV shift of band B toward lower IEs in I can be traced back both to the presence of the ionization from the e″ MO on the lower IE side of band B and to the lower electronegativity of H compared to that of the halogen atoms.[21] It is worthy of note that in I the e_g-like e″ MO is stabilized by about 0.3–0.4 eV with respect to the same orbital in the other derivatives, indicating a very strong bonding interaction between the e″ e_g-like orbitals of the $Fe_3(CO)_9$ fragment and the C_{apical}-based e″ levels.[25] Such a fact is indicative of a very good energy matching between the e″ frontier MOs of the two fragments, and it can only be due to the nature of the e″ level of the $(CH)_2$ moiety which, as already pointed out, is not antibonding in character with respect to the C–H interaction.

On passing to the analysis of band A, it has to be noted that the IE trend (see Table I) for the halogen derivatives correlates with the different electronegativities of the X substituents. Moreover, it is rather evident in II and III that there is a slight increase of the higher IE side of band A under the He II lamp, which consistently is assigned to the ionization from the fifth t_{2g}-like MO mentioned above and to the ionization from the e′ MO responsible for the Fe–Fe direct interaction. As far as the lower IE side of band A in II and III is concerned, this is associated with the ionization from the e″ e_g-like MO, Fe–C_{apical} bonding but Fe–Fe and C–X antibonding in character. Such an assignment agrees with the literature transition-state calculations[5] for IV.

In contrast to experimental findings pertaining to II–IV, the whole band A of the H derivative shows, with respect to band B, an increase in relative intensity on passing from the He I to the He II ionizing source. Moreover, a further well resolved band (A′) is present at 8.13 eV in the He II spectrum of I. The two bands can be tentatively assigned by remembering the following points: (i) band A as a whole is due in I to the ionizations from four MOs; (ii) band A increases in relative intensity with respect to band B under the He II radiation; (iii) bands A and A′ have the same relative intensity in the He II spectrum (see Table I). On this basis, we propose to assign bands A′ and A to the ionizations from the e′ MO responsible for the direct Fe–Fe interaction and to two "nonbonding" (a″ + a′) t_{2g}-like levels, respectively. The presence, at low IE values, of two ionization events rather than a single one involving the t_{2g}-like levels further confirms the involvement of these orbitals in the M–L interaction. Actually, keeping in mind the lower IE position of the C_{apical} lone pairs in I with respect to II–IV, as a consequence of the lower electronegativity of the substituent,[21] it is reasonable to expect in the H derivative a better energy matching between the a′ and a″ combinations of the C_{apical} lone pairs and suitable t_{2g}-like levels.[26]

Alternatively, it could be proposed to reverse the assignments of bands A and A′ of the He II spectrum of I, associating the former with the ionization from two t_{2g}-like orbitals and the latter with the e′ e_g-like level. However, such an assignment would seem to contradict the electrochemical measurements[27] (see below) carried out by some of us on the title compounds.

Conclusions

The use of literature theoretical data for IV coupled with the deconvolution of the He I/He II PE spectra of I allowed us to assign all the PE spectral features of compounds I–III, proving that the bonding scheme proposed for the fluorine derivative holds along the whole investigated series. In particular, we have confirmed the presence of only two, rather than three, σ M–M bonds and the leading role played by the Fe_3–C_{apical} interaction to ensure the overall cluster stability. In this regard, we experimentally confirmed that such an interaction is not limited to the e_g-like orbitals but extends to the t_{2g}-like orbitals also. This result is not at all surprising,[2,11] but it deserves to be stressed because of the significant stabilization (about 1 eV) undergone by the four e′ + e″ t_{2g}-like levels.

The herein reported data can be useful to interpret the electrochemical results obtained by some of us for the title compounds.[27] Actually, it is known[27] that, in general, the triiron clusters all undergo a chemically reversible one-electron reduction step. Further electrode processes, i.e. a second reduction or an oxidation step, usually result in disintegration or reorientation[28] of the clusters. The cyclic voltammogram of IV is characterized by the presence of a well-defined reduction wave at $E_{1/2} = -0.88$ V,[27,29] indicating that in $[Fe_3(CO)_9(CF)_2]$ no structural change follows the formation of the radical ion $[Fe_3(CO)_9(CF)_2]^-$. This is rather interesting because it allows us to gain new insights into the nature of the lowest unoccupied MO (LUMO) of IV.

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(22) When X is a halogen, the C_{apical}-based π orbitals are the antibonding partners of the C–X π bond. It is experimentally confirmed that the π-bonding levels in IV lie deeper in energy than those in II and III. Accordingly, it is reasonable to assume that the antibonding counterpart in IV will lie higher in energy than those in the chlorine and bromine derivatives with a consequent poorer energy matching between the C_{apical}-based π orbitals and the t_{2g}-like levels of $Fe_3(CO)_9$ fragment.

(23) Chesky, P. T.; Hall, M. B. *Inorg. Chem.* **1981**, *20*, 109.

(24) $\sigma(H_{1s})_{He\,II}/\sigma(H_{1s})_{He\,I} = 1.53 \times 10^{-1}$; $\sigma(F_{2p})_{He\,II}/\sigma(F_{2p})_{He\,I} = 9.05 \times 10^{-1}$.[20]

(25) The actual IE position of this e″ MO is once more the balance of two opposite effects, namely the stabilizing (destabilizing) interactions between the e″ e_g-like (t_{2g}-like) orbitals of the metallic triangle and the e″ levels of the $(CX)_2$ moiety.

(26) The interaction between the occupied a′ and a″ t_{2g}-like orbitals and the n^+ and n linear combinations of the C_{apical} lone pairs cannot contribute to the overall covalent bond between the metallic bed and the $(CX)_2$ fragment. In any case, the a′ and a″ MOs mainly t_{2g}-like in character represent the antibonding components of such an interaction.

(27) Lentz, D.; Michael-Schultz, H.; Moock, K. Manuscript in preparation.

(28) Osella, D.; Gobetto, R.; Montanegro, P. *Organometallics* **1986**, *5*, 1247.

(29) A second poorly defined reduction wave is revealed at $E_{1/2} = -1.96$ V.[27] An irreversible oxidation occurs within the range of solvent stability at +1.58 V. Electrochemical experiments carried out under CO atmosphere improve the reversibility of the second reduction and the oxidation step. Substitution of the (μ_3-CX) (X = F, Cl, Br, H) moiety in the cluster results in the shift of the $E_{1/2}$ values to higher potentials, in agreement with the different X electronegativities. I–III do not show a second reduction step within the range of solvent stability.

Actually, according to the qualitative extended Hückel type interaction diagram for $[Fe_3(CO)_9(CF)_2]$ we reported in ref 5, as well as to the orbital scheme proposed by Schilling and Hoffmann[30] for the $Fe_3(CO)_9$ fragment,[31] the LUMO of IV should account for an overall antibonding interaction between C_{apical} and the $Fe_3(CO)_9$ moiety, as well as between the Fe atoms within the metallic bed. The single, reversible reduction step undergone by the whole cluster series, coupled with the irreversible (with decomposition) oxidation process,[32] indicates that the interaction between the empty orbitals of the metallic bed and the π levels of the $(CX)_2$ fragment is at least as important as the direct metal–metal bond in ensuring the overall cluster stability.

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(30) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

(31) In ref 30 the authors reported the orbital scheme for $Fe_3(CO)_9$ assuming a C_{3v} symmetry.

(32) The oxidation step should remove one electron from the 9e″ HOMO (bonding (antibonding) with respect to the Fe–C_{apical} (Fe–Fe) interaction) in II–IV and one electron from the MO of symmetry e′ in I accounting for the direct Fe–Fe interaction.