the values in **1**, as is also that found in the simple stibine complex $\{Fe(CO)_4[Sb(t\text{-}Bu)_3]\}_3$, 2.547 (1) Å.[19]

The Sb atoms appear to apportion their five potential donor electrons, three to the central $Fe_2(CO)_6$ fragment and two to the outer $Fe_2(CO)_8$ fragments. This is in agreement with the isolobal principles used by Cowley et al. to describe the bonding in **2**[16] and the observed differences in the Sb–Fe distance in **1**. Each 34-electron diiron fragment is isoelectronic with $Fe_2(CO)_9$.

The acute Fe–Sb–Fe angles differ little whether involving inner or outer diiron units: inner average 69.25 (6)°; outer average 67.18 (6)°. These angles are similar to those found in $[Co_4(\eta^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+$ [average 70.1 (1)°], containing the related μ_4-$AsCo_4$ group,[3] and the $[Fe_2(CO)_8(\mu_4\text{-}E)Fe_2(CO)_6Cl]$ complexes, E = P or As.[2] The triangular Fe_2Sb planes in **1** have an inner/outer dihedral angle of 95.0 (1)° at Sb(1) and 85.1 (1)° at Sb(2) (if viewed from the same perspective). The expectation of more nearly perpendicular interplanar relationships is offset by intramolecular carbonyl repulsions between the $Fe_2(CO)_8$ units in the center of the complex; the O(22)···O(14) distance, 2.84 (1) Å, is within the sum of the van der Waals radii (3.04 Å).

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Registry No. **1**, 105859-91-4; $[Et_4N]_2[Fe_2(CO)_8]$, 26024-88-4; $[Cu(CH_3CN)_4][BF_4]$, 15418-29-8; $SbCl_3$, 10025-91-9.

Supplementary Material Available: Tables of bond distances, bond angles, and anisotropic temperature coefficients (3 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Electronic Structure of Nonacarbonylbis(μ_3-fluoromethylidyne)triiron by means of UV Photoelectron Spectroscopy and DV-Xα Quantum-Mechanical Calculations

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Mono- and bis(methylidyne) complexes have been the object of several experimental and theoretical investigations in the near past,[2-4] not least because of suggestions that discrete metal clusters may serve as models for miniature metal surfaces or highly dispersed supported catalysts.[5] Some of the authors have already focused their attention on the electronic structure of nonacarbonyl-substituted mono(methylidyne)tricobalt clusters $(\mu_3\text{-}CY)[Co(CO)_3]_3$ (Y = H, CH_3, CF_3, $COOCH_3$, F, Cl, Br, I),[4] obtaining an experimental evaluation, along the investigated series, of the interaction extent between the metal triangle and the apical carbon atom.

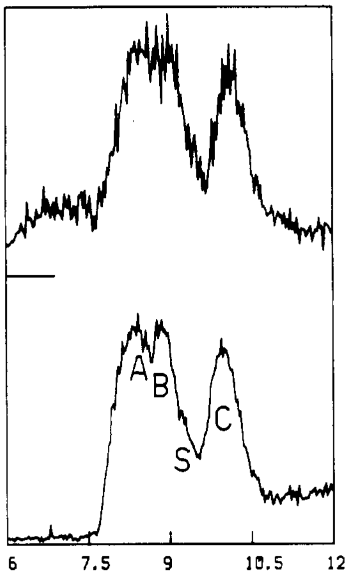

Figure 1. He I (below) and He II (above) excited PE spectra of $(\mu_3\text{-}CF)_2[Fe(CO)_3]_3$. PE bands are labeled alphabetically.

In agreement with the EAN rule,[6] a further CY ligand could be incorporated into the analogous Fe cluster, leading to the $(\mu_3\text{-}CY)_2[Fe(CO)_3]_3$ series. At present, as a matter of fact, only two complexes containing the $Fe_3(CY)_2$ moiety have been synthesized to our knowledge.[3a] Further, two iron clusters of the type $(\mu_3\text{-}CCH_3)(\mu_3\text{-}COR)[Fe(CO)_3]_3$ (R = CH_3, C_2H_5), which have been described recently, show interesting reactions with CO and acetylenes, respectively.[3b-d]

In this note we report an experimental and theoretical analysis of the electronic structure of $(\mu_3\text{-}CF)_2[Fe(CO)_3]_3$ combining He I/He II gas-phase UV photoelectron (PE) spectroscopy and Hartree–Fock–Slater first-principle DV–Xα calculations.[7]

$(\mu_3\text{-}CF)_2[Fe(CO)_3]_3$ has been prepared according to the literature methods.[3] Its He I/He II excited PE spectra were recorded on a Perkin-Elmer PS-18 spectrometer modified by inclusion of a hollow-cathode discharge lamp giving high output of He II photons. The spectrometer was connected on line with a MINC-23 computer (Digital Eq.). The ionization energy (IE) scale was calibrated by reference to admitted inert gases (Xe–Ar) and to the He $1s^{-1}$ self-ionization. A heated inlet probe system was used at 60–70 °C.

Figure 1, where bands have been labeled alphabetically, shows only the IE region below 12 eV. The higher IE one consists of

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Table I. Atomic Orbital Character for Ground-State $(\mu_3\text{-CF})_2[Fe(CO)_3]_3$

eigenvalue $-E$, eV	sym	TSIE, eV	exptl IE, eV	population						character[b]
				3 Fe						
				s	p	d	2 C	2 F	9 CO	
6.16	9e″[a]	8.49	8.40	0	3	52	16	8	21	(Fe–Fe)[a] + $Fe_3(\mu_3\text{-CF})_2$[b]
6.58	13e′	8.89		0	6	68	5	3	18	(Fe–Fe)[b]
6.58	10a″	8.89		0	4	72	2	1	21	3d t_{2g}-like MOs
6.94	12e′	9.23	8.90	0	5	68	5	2	20	
6.96	14a′	9.25		0	7	60	3	1	29	
7.37	13a′	9.68	9.20	0	1	73	4	4	18	
7.71	11e′	10.06	10.00	0	1	61	13	15	10	
7.74	8e″	10.08		0	1	59	11	19	10	
10.67	10e′	12.97		0	0	3	13	64	20	F lone pairs

[a] HOMO. [b] a = antibonding; b = bonding.

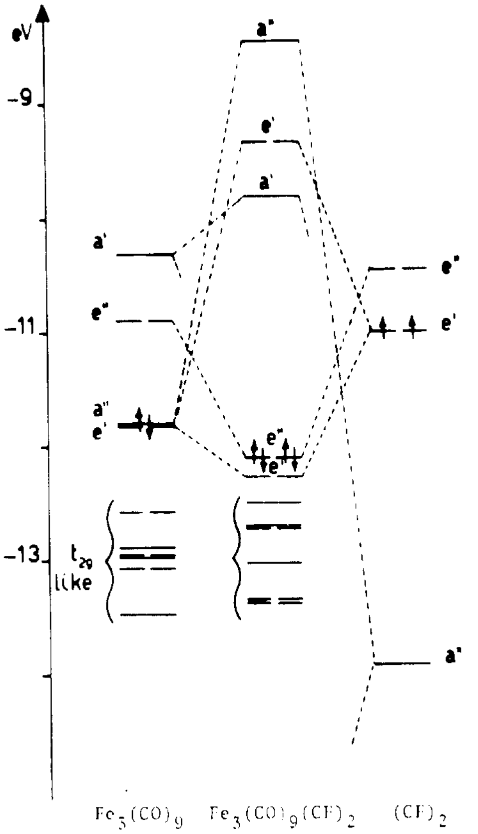

Figure 2. EHT orbital interaction diagram for $(\mu_3\text{-CF})_2[Fe(CO)_3]_3$.

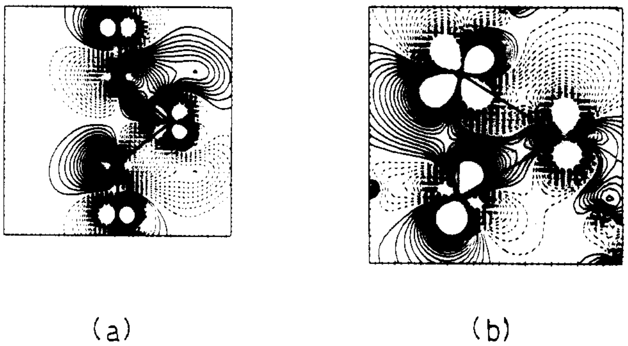

Figure 3. (a) Contour plot for one component of the 9e″ HOMO in the $Fe(CF)_2$ plane. The interval between successive contours is 0.038 $e^{1/2}/Å^{3/2}$. (b) Contour plot for one component of the 13e′ MO in the Fe_3 plane. The interval between successive contours is 0.038 $e^{1/2}/Å^{3/2}$.

a very broad and ill-resolved structure, centered at 14.2 eV, mainly due to ionizations from metal–CO σ-bonding molecular orbitals (MOs), 1π and 4σ CO-localized levels, and fluorine nonbonding MOs.[4] In Figure 1 at least three well-resolved bands (A, 8.40 eV; B, 8.90 eV; C, 10.00 eV) and one shoulder (S, 9.2 eV) can be detected. Reference to the He I spectrum of the isoelectronic cluster $(\mu_3\text{-CF})[Co(CO)_3]_3$[4] suggests that ionizations relative to the $Fe_3(CF)_2$ moiety are to be expected in this region.

A first qualitative description of the bonding scheme can be obtained by dividing the whole molecular system into two interacting fragments: $[Fe(CO)_3]_3$ (I) and $(CF)_2$ (II), respectively. The electronic structure of I has been already discussed.[8] However, it is useful for the following discussion to make reference to the extended Hückel type (EHT) orbital interaction diagram reported in Figure 2, obtained by using literature parameters[9] and the actual structure of the title molecule.[10] The outermost occupied MOs of I, obtained by allowing the interaction of three $Fe(CO)_3$ fragments, consist of "t_{2g}-like" orbitals (2a′ + a″ + 2e′ + e″), strongly localized on the Fe atoms, and two almost degenerate MOs (e′ + a″) contributing to the Fe–Fe bond, while the LUMO (e″ in symmetry) is strongly Fe–Fe antibonding. The frontier MOs of II of relevance for interacting with I are also reported in Figure 2 and labeled according to C_{3h} symmetry. The a″ MO is the antisymmetric linear combination of the apical carbon lone pairs[11] while the e′ and e″ MOs are the symmetric and antisymmetric combinations of C–F antibonding π MOs.

In the whole cluster, the t_{2g}-like MOs are little affected with respect to I. On the contrary, the HOMO of I (a″, Fe–Fe bonding out of the symmetry plane) is dramatically destabilized by the interaction with the a″ MO of II, which points directly toward the center of the metal triangle. As a consequence, the HOMO of the whole cluster (e″) derives from the strong interaction between the LUMOs of the fragments.

The eigenvalues and the charge density analysis of the outermost nine MOs obtained by DV-Xα calculations are reported in Table I[12] together with experimental and theoretical (TSIE) ionization energies. The theoretical results completely fulfill the aforesaid qualitative analysis; in particular, both the 9e″ (HOMO) and 13e′ MOs describe (see Figure 3) the same type of interactions already anticipated by the EHT results; i.e., they are Fe–C_{apical} and Fe–Fe bonding, respectively. It is of relevance to note that only one Fe–Fe

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(11) The symmetric combination lies at −17.21 eV.

(12) Electronic structure calculations have been carried out on a VAX 11/750 minicomputer using the discrete variational (DV) Xα method.[7] Numerical atomic orbitals were used as basis functions. For iron, all orbitals through 4p were included; for C, O, and F, orbitals through 2p were used. Orbitals 1s–3p on iron and 1s on C, O, and F were kept frozen in the molecular calculations. Atomic orbital population were computed by using the Mulliken scheme.[13] More details about the used computational procedure can be found in ref 14. Experimental and theoretical IEs are compared by using the transition state (TS) procedure.[15] Geometrical parameters for the title compound were taken from ref 4 and idealized to C_{3h} symmetry.

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bonding MO (13e′) (a part from the smaller contributions from the inner t_{2g}-like MOs) is active in the present case, at variance with the isoelectronic cobalt cluster $(\mu_3\text{-CY})[Co(CO)_3]_3$.[4] However, we must remember that the overall cluster stability is ensured by the cluster–C_{apical} interactions.

The agreement between experimental and theoretical IEs is very good, in terms of both absolute and relative energies. We propose to assign band A to the ionizations from 9e″ (HOMO), 13e′, and 10a″ MOs. Band B, showing a smaller relative intensity with respect to band A, is related to the ionization from 12e′ and 14a′ MOs. Shoulder S on its higher IE side is associated with the 13a′ ionization event. Finally, band C is assigned to the ionization from two doubly degenerate MOs (11e′ and 8e″). The stabilization of these two MOs with respect to the other t_{2g}-like MOs is certainly due to bonding interactions with e′ and e″ MOs of II, as already proposed for the $(\mu_3\text{-CY})[Co(CO)_3]_3$ series.[2c,4]

Such an assignment is consistent also with the spectral pattern obtained by using the more energetic He II radiation.[16] Actually all the ionizations present in the region below 11 eV come from MOs significantly localized on the metal atoms so that only minor and undetectable variations could be expected on passing from the He I to the He II ionization source.[17]

Finally, the present bonding picture suggests that the electronegativity of the apical substituent is of relevance for the stability of the cluster. Actually, the significant localization of the HOMO on the apical substituents (see Table I and Figure 3a) shows that a strong electron-withdrawing substituent (as fluorine) removes charge density from an antibonding Fe–Fe region, enhancing at the same time the cluster–C_{apical} interaction.

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Registry No. $(\mu_3\text{-CF})_2[Fe(CO)_3]_3$, 94621-00-8.

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(16) The low-IE region (6.5–8.0 eV) of the He II spectrum suffers from high noise and low resolution because of the photoelectrons originated from the orbitals at ~15 eV by operation of a small amount of the He IIβ radiation (48.40 eV).

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Reinvestigation of the Molecular Structure of Gaseous Tetrabromooxotungsten(VI), $WOBr_4$, by Electron Diffraction

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The P=O and P=S bond lengths in the phosphoryl and thiophosphoryl halides, PYX_3, have been found to be significantly shorter in the fluorides[3,4] than in the chlorides[3,4] or bromides.[5] As is seen from Table I, a similar situation is found in the oxo tetrahalides of tungsten,[6-8] WOX_4, where the W=O bonds are shortest in the tetrafluoride.[6] However, in the corresponding sulfo and seleno tetrafluorides[9,10] and tetrachlorides[11] the W=S and W=Se bonds are longer in the fluorides.

Table I. Bond Lengths (r_a) and Bond Angles in Tungsten Tetrahalides

	r(W=Y)/ Å	r(W—X)/ Å	∠(Y=W—X)/ deg	ref
WOF_4	1.666 (7)	1.847 (2)	104.8 (6)	6
$WOCl_4$	1.684 (11)	2.280 (3)	102.4 (13)	7a
	1.683 (15)	2.279 (3)	102.6 (15)	7b
$WOBr_4$	1.684 (6)	2.437 (3)	102.8 (11)	this work
WSF_4	2.104 (7)	1.847 (3)	104.5 (11)	9
$WSCl_4$	2.086 (6)	2.277 (3)	104.2 (5)	11
$WSeF_4$	2.226 (7)	1.853 (5)	105.0 (7)	10
$WSeCl_4$	2.203 (4)	2.284 (3)	104.4 (3)	11

One of the unsettled matters in these bond length comparisons is the position of the bromine-containing compounds in the phosphorus and tungsten series. For example, in the phosphoryl compounds the P=O bond length (r_g) in the chloride, 1.449 (5) Å,[1] is the same as that in the bromide, 1.445 (7) Å,[5] to within the uncertainties of the measurements, and in the sulfuryl compounds the difference between the lengths of the S=O bonds in the bromide (1.894 (4) Å[5]) and in the chloride (1.885 (5) Å[5]) is of marginal significance. In tetrabromooxotungsten(VI) the W=O bond length at 1.695 (25) Å[8] appears not to be significantly different from that in the chloride (1.684 (11) Å,[7a] 1.683 (15) Å[7b]), but the large uncertainties associated with the measurements cloud the issue. Our special interest in compounds of this type has led us to reinvestigate the structure of $WOBr_4$ in an attempt to improve the precision of the measurement of the W=O bond distance and thereby to settle the question of any difference between it and the corresponding distance in the chlorine compound.

Experimental Section

Tungsten(VI) bromide was made by allowing $W(CO)_6$ to react at 0 °C with an excess of dry bromine in an all-glass vacuum line. The mixture was kept at 0 °C and the excess bromine pumped away. The results of tungsten and bromine analyses of the product agreed with theory for WBr_6. A sample of WBr_6 was placed in an evacuated tube, and a quantity of resublimed Sb_2O_3 sufficient to give a W:Sb molar ratio of 3:2 was added under dry nitrogen. The resulting mixture was pumped while being maintained at 0 °C for 3 h, after which the tube was sealed and placed in a furnace at 180 °C, where it remained for 2 days. The tube was opened under an inert atmosphere, and the contents were sublimed twice with use of evacuated sublimation tubes. The first sublimation removed $SbBr_3$ to give the desired $WOBr_4$. The second (resublimation) led to a purified, air-sensitive product that had tungsten and bromine analyses in accord with theory for $WOBr_4$. Small quantities of $WOBr_4$ were loaded under an inert atmosphere into glass ampules fitted with break-seals. The ampules were evacuated and sealed. For a diffraction experiment an ampule was connected via glass tubing and a Swagelok coupling to the apparatus. The whole of the tubing between the break-seal and the apparatus was heated to approximately 250 °C under evacuated conditions for 1.5 h before the break-seal was opened. At the end of the experiment there was no evidence for the formation of any tungsten blue that would have indicated product decomposition or reaction.

The electron-diffraction photographs were made in the Oregon State apparatus at nozzle temperatures of 295–305 °C. Other experimental conditions as well as the various analytical procedures were similar to those described for WSF_4.[6] Data from two plates at the long camera (75

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