# The Photoelectron Spectra of Enneacarbonyl-$\mu_3$-methylidyne-tricobalt and some Derivatives

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The He(I) photoelectron spectra of compounds $[Co_3(CO)_9(CY)]$, Y = H, F, Cl, Br, I, $CH_3$, or $CF_3$, and some He(II) spectra are reported and assigned. Ionizations corresponding to the CY group can be picked out, and in particular the level of mainly bridge C $2p_\pi$ character is detected in all the compounds. The variations in ionization energy of this level and others are used to show that there is substantial delocalization of the $p_\pi$ levels of Y throughout the molecules. Calculations by the self consistent charge method are correlated with these measurements, and there is generally good agreement.

METAL cluster compounds are of wide interest as examples of metal–metal bonded systems, as homogeneous catalysts, and as possible models for heterogeneous catalytic sites.[1-3] Information on the electronic structures of such compounds should be useful as a basis for interpretation of a wide range of experimental observations. We have chosen to study the u.v. photoelectron spectra of the series [4] of cluster compounds $[Co_3(CO)_9(CY)]$. These compounds have high symmetry and contain a triply bridging carbon atom over the metal triangle [5] which is a potential model for adsorbed C-containing species on metal surfaces.[2,3] The large number of possibilities for the group Y mean that a variety of electronic effects can be studied. We report spectra of the compounds for which Y = H, $CH_3$, $CF_3$, F, Cl, Br, and I.

Approximate results from extended-Hückel calculations have been reported [6] for Y = H; we have used the self consistent charge (SCC) variation of this method [7] to carry out calculations on the compounds for which Y = H, F, $CH_3$, and $CF_3$.

## EXPERIMENTAL

The compounds were prepared and purified by standard literature methods.[8] Analytical and spectroscopic data showed no trace of impurities except in the iodo-compound, where substantial amounts of the chloro-compound were found to be present, in agreement with earlier reports.[8] Photoelectron (p.e.) spectra were run on a Perkin-Elmer PS16 spectrometer; internal calibration was performed using ionizations of argon, xenon, and methyl iodide.[9] The He(I) spectra were run using sample temperatures between 30 and 35 °C, giving count rates of *ca.* 300 counts $s^{-1}$, and He(II) spectra were run at *ca.* 40—45 °C, at *ca.* 100 counts $s^{-1}$. Except for the iodo-derivative, no ionization bands were detected which could be ascribed to impurities, and the spectra were constant in band intensity as the samples were run to exhaustion. The spectrum from the iodo-compound showed the presence of large amounts of molecular iodine and of $[Co_3(CO)_9(CCl)]$ initially. After evaporating the sample in the spectrometer for *ca.* 1.5 h the iodine spectrum disappeared and the spectrum obtained was consistent with that expected for a mixture of $[Co_3(CO)_9(CI)]$ and $[Co_3(CO)_9(CCl)]$. A significant region of the spectrum of the iodo-compound is free from interference by the chloro-compound.

*Calculations.*—The SCC program due to Hoffmann and co-workers [7] was employed without modification. The $[Co_3(CO)_9C]$ framework geometry was taken as the idealised $C_{3v}$ structure averaged over several compounds,[5] and standard single bond lengths and angles were used for C–Y.

## RESULTS AND DISCUSSION

*Assignments.*—The spectra are shown in Figure 1 (*a*)—(*h*), and the measured ionization energies (i.e.) are reported in the Table. In all the spectra there are two groups of ionizations which are relatively insensitive to the nature of the substituent Y. These occur between 7 and 9 eV,† bands 1 and 2, and between 14 and 18 eV, bands 5 and 6. By comparison with the many metal carbonyls which have been examined, bands 1 and 2 can readily be assigned as ionizations from mainly metal-localized orbitals, and bands 5 and 6 as from carbonyl-localized orbitals.[9-14] Band 5 contains ionizations from orbitals derived from 5σ and 1π of free CO, and band 6, ionizations from the 4σ levels. Although the overall appearance of these bands is very similar throughout the series there are small differences in i.e. which will be discussed below.

Between these two main ionization regions there are other bands which vary substantially in energy and intensity as Y is changed; these have been labelled 3 and 4, although 4 has not been detected for all the compounds. These bands are considered to arise from ionizations of the CY group, and the CH compound will be considered first.

The p.e. spectrum of free CH has not been recorded, but by analogy [15] with HF, and [16] with OH, the sequence of ionization energies should be 1π (C $2p$) < 3σ(C $2p$–H) < 2σ(C $2s$–H). High-quality calculations [17] indicate orbital energies of 11.3, 12.4, and 22.6 eV respectively for these levels, although estimates of i.e. cannot be made directly from this because of open-shell effects. In the cluster compound the orbitals 1π and 3σ will be most directly concerned with binding the CH group to the metal triangle. For convenience in discussing the set of cluster compounds the 1π related levels will be denoted as $e(\pi)$; these orbitals should interact strongly with the metal atoms. The three levels of CH therefore become

† Throughout this paper: 1 eV ≈ 1.60 × $10^{-19}$ J.

Vertical i.p. (eV) of $[Co_3(CO)_9(CY)]$ complexes and proposed assignments *

| Band | Y = $CF_3$ | F | Cl | Br | I | H | $CH_3$ | Assignment |
|---|---|---|---|---|---|---|---|---|
| 1 | 8.38(3) | 8.18(5) | 8.11(5) | 8.02 | 7.92 | 8.12(9) | 7.99(8) | $Co_3(d)$ |
| 2 | 8.99(5) | 8.83(3) | 8.72(2) | 8.53 | 8.50 | 8.77(2) | 8.59(3) | $Co_3(d)$ |
| 3 | 10.54(2) | 10.13(2) | 9.85(6) | 9.63 | 9.30 | 10.31(5) | 9.95(1) | $(Co_3–C)e(\pi)$ |
| 4 | | | 12.55(5) | 11.56(6) | 10.81(2) | | | $X(np_\pi)$ |
| | | | | | | 12.62(9) | | $\sigma(C–H)$ |
| | | | | | | | 12.93(4) | $(CH_3)e$ |
| | | | | 12.70 | | | | $\sigma(C–Br)$? |
| 5 | | | | | 13—16 | | | $CO(5\sigma + 1\pi)$ |
| 6 | 17.97 | 17.94 | 17.80 | 17.80 | 17.91 | 17.81 | 17.77 | $CO(4\sigma)$ |

* Quantities in parentheses are standard deviations.

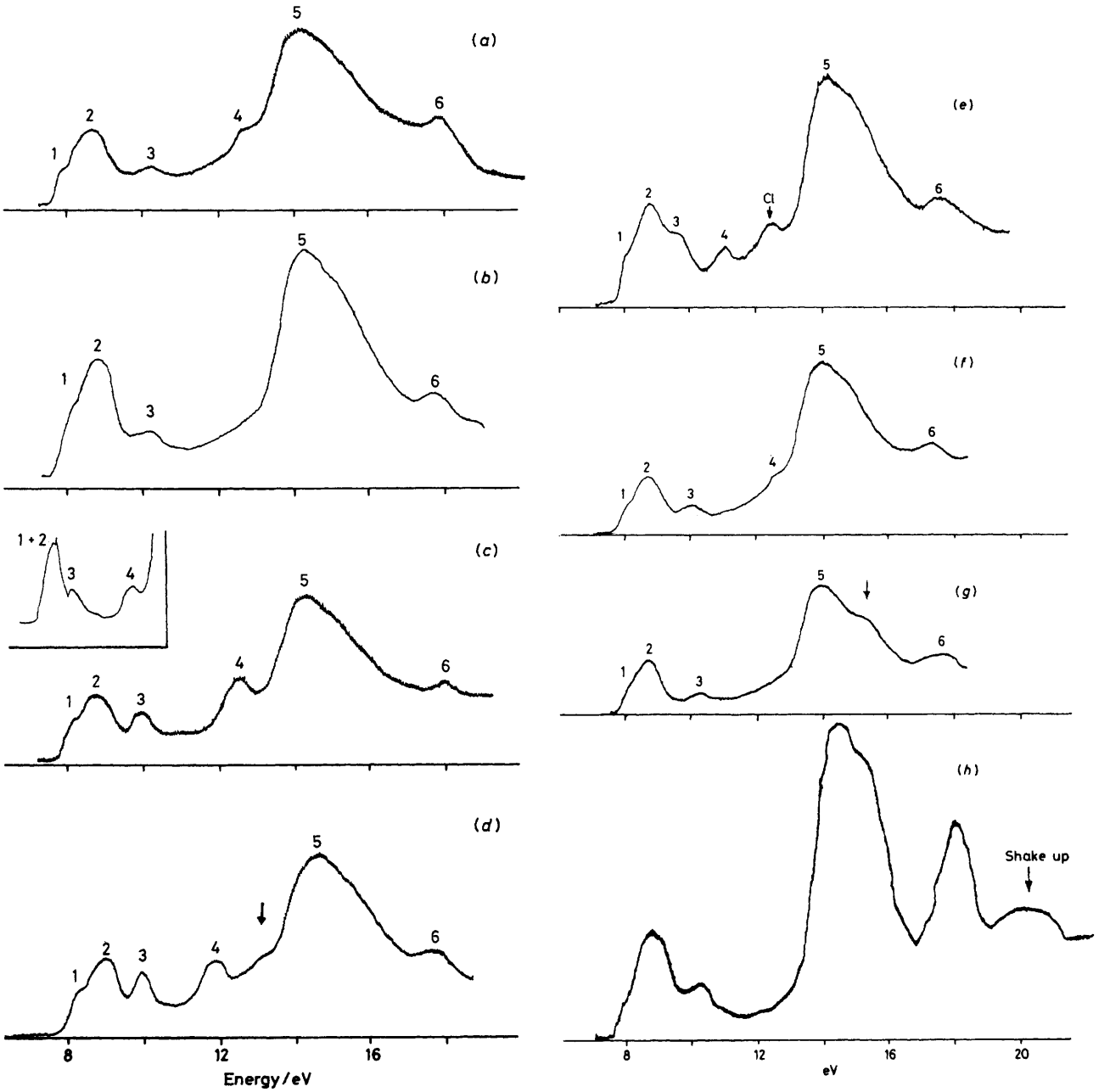


FIGURE 1 Photoelectron spectra of the compounds $[Co_3(CO)_9(CY)]$: (*a*) Y = H, He(I); (*b*) Y = F, He(I); (*c*) Y = Cl, He(I), insert He(II); (*d*) Y = Br, He(I); (*e*) Y = I, He(I), with substantial contamination from Y = Cl; (*f*) Y = $CH_3$, He(I); (*g*) Y = $CF_3$, He(I); (*h*) Y = $CF_3$, He(II). The arrowed bands are discussed in the text

M–C bonding [$e(\pi)$], mainly C $2p$–H with some C $2p$–M($3\sigma$), and mainly C $2s$–H($2\sigma$).

Orbitals with similar character are found in metal alkyls,[18,19] and ionize in the regions 9—11 (C–M), 12—14 (C $2p$–H), and 21—22 eV (C $2s$–H). Accordingly band 3, at 10.3 eV, is assigned as $e(\pi)$ and band 4, at 12.6 eV, as the $3\sigma$ derived level, in the CH complex. An orbital derived from $2\sigma$ is expected in the region of 21 eV and careful searches were made in this region of the He(II) spectrum. Unfortunately the well documented CO shake-up ionizations [13] occur between 18 and 26 eV and completely obscure this spectral region.

A band corresponding to band 3 occurs in all the spectra in Figure 1, and this is assigned as an ionization from $e(\pi)$ orbitals in all the cluster compounds; the variation in i.e. of this band is discussed below. For band 4 there are a number of possibilities. In the heavier halides band 4 is clearly very sensitive to the nature of the halogen, appearing at 10.8, 11.6, and 12.6 eV for Y = I, Br, and Cl. A corresponding band has not been detected for the fluoro-compound, but could be under the carbonyl ionization band at *ca.* 14 eV. For several sets of halides approximately linear correlations are found between the ionization potential (i.p.) of halogen orbitals and halogen electronegativity.[20] A similar plot can be made for band 4 of the heavier halides, and extrapolation to Y = F suggests an i.e. of 15.5 eV. By analogy with methyl halides [21] band 4 is assigned to ionization from the halogen $p_\pi$ orbitals. Confirmation of the halogen character of these levels is obtained from the He(II) spectra, an example of which is shown in the insert of Figure 1(*c*). The substantial decrease in intensity in relation to the metal levels is typical of ionizations of the heavier halogens.[9] In the methyl halides the halogen $p_\sigma$ level ionizes at *ca.* 3 eV higher i.e. than the $p_\pi$ levels, so in the chloro-compound the halogen $p_\sigma$ level is almost certainly under the carbonyl band at 14 eV. Unfortunately the region of the spectrum of the iodo-compound where the $p_\sigma$ level might be expected is obscured by the chloro-compound impurity. In the bromo-compound there is an indication of an additional ionization at 12.7 eV on the rising edge of the carbonyl band. This may be the halogen $p_\sigma$ level, although the $p_\pi - p_\sigma$ separation of 1.1 eV is substantially less than the 2.8 eV in methyl bromide.

In the $CH_3C$ compound the local environment of the $CH_3$ carbon is not unlike that of the carbon atom in ethane. In ethane [22] the average i.e. of the in-phase ($e_u$) and out-of-phase ($e_g$) combinations of the $CH_3$ $e$ orbitals, 13.5 eV, is slightly greater than that of the C–C bonding $a_{1g}$ orbitals at 13 eV. Corresponding $CH_3$ $e$ and C–C $a_1$ bonding orbitals in the cluster complex are expected to lie fairly close together, at slightly lower i.e. than in ethane because of the lower electronegativity of the metal atoms. Band 4 of the $CH_3C$ compound (12.9 eV) is assigned to a combination of these two ionizations, since there is no sign of a further band on the rising edge of the carbonyl ionization.

In the spectrum of the $CF_3$ compound there is no equivalent of band 4, but there is a distinct shoulder at *ca.* 15.7 eV on the high i.e. side of the main carbonyl band, which is marked with an arrow in Figure 1(*g*). In the He(II) spectrum, Figure 1(*h*), this shoulder is more intense. This can be assigned as the group of F $2p$ lone-pair levels observed in other $CF_3$ compounds.[23] Figure 1(*h*) also shows the strong carbonyl shake-up band. In this compound, the C $2s$ derived levels should be more readily detectable since the slight F $2p$ character in these orbitals is likely to increase the intensity of the corresponding ionizations. However, no corresponding band can be resolved, and the only detectable effect is that the merging of these ionizations with the shake-up processes gives one featureless band rather than the two separate shake-up bands observed for carbonyls.[13]

The spectra of the CH and $CCH_3$ compounds have a possible relationship to the spectra which have been assigned to CH and $C_2H_3$ species on metal surfaces; [24,25] these implications are discussed separately.[26]

*Trends in Ionization Energies and Experimental Evidence for Delocalization.*—Figure 2 shows a comparison of the measured levels for all the compounds. Band 4 has the sharpest variation and the change in i.e. of this band in the halides has already been used in support of the assignment of the band as ionization from

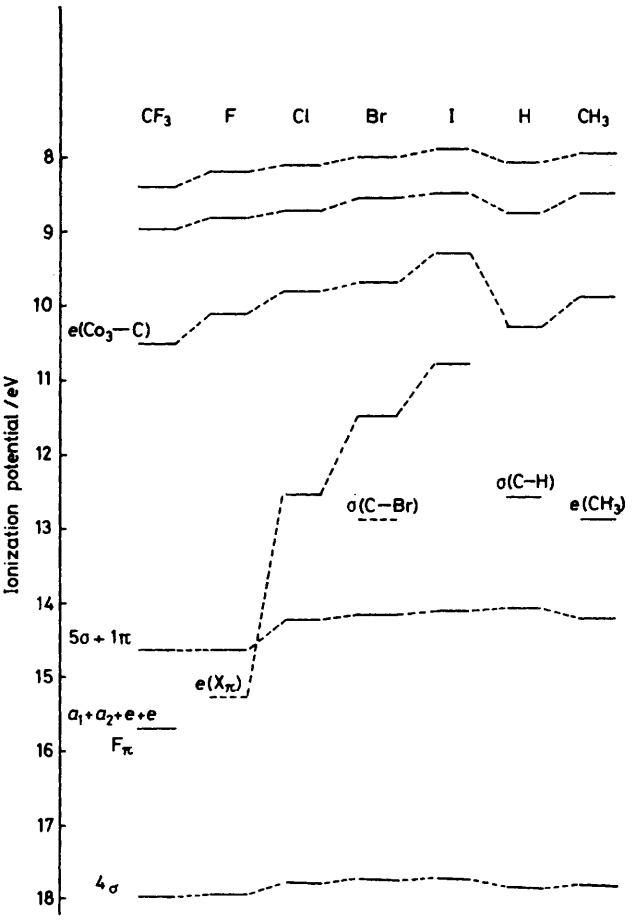


FIGURE 2 A comparison of energy levels measured from the spectra of Figure 1

halogen levels. However, the levels assigned as $e(\pi)$, metal–carbon bonding, are also quite sensitive to the nature of the substituent. Within the set of four halides the i.e. of this level follows the sequence expected on electronegativity grounds, but even in the fluoride this level is less stable than in the hydride. This strongly suggests that in addition to $\sigma$ electron withdrawal by the halogen atom there is a strong $\pi$ interaction between the two sets of $e$ levels on the halogen and carbon atoms. Evidence in support of this comes from the form and i.e. of band 4 in the spectra. In hydrogen or methyl halides the halogen $p_\pi$ ionization bands are sharp and show spin–orbit splittings comparable to the free-atom values.[15,21] In contrast, band 4 is broad, but even in the iodide shows no sign of splitting. In $CH_3I$ and HI the splittings are 0.62 and 0.67 eV respectively, and although band 4 in Figure 1(*e*) is broad, a splitting of this magnitude would readily be detected; any splitting would have to be less than 0.4 eV. Both the breadth of the bands, and this reduced spin–orbit coupling, indicate that the halogen $p_\pi$ levels are strongly bonding, and correspondingly delocalized.

Further evidence for this delocalization comes from the i.e. of band 4, which is 1.0—1.3 eV greater than that of the $p_\pi$ levels in the corresponding methyl halides,[21] although it might have been expected that the halogen atoms would withdraw more charge from the $Co_3C$ unit than from a $CH_3$ group. The pattern of levels for $e(\pi)$ (C–M) and $p_\pi$(X) exactly parallels that found for the $\pi$(C≡C) and $p_\pi$(X) levels in the halogenoacetylenes, where substantial delocalization of the halogen levels has been demonstrated from measurements of the spin–orbit splittings.[27] Finally, we note the substantial increase in intensity of band 3 through the sequence Y = H, F, Cl, Br, I, and the decrease in intensity of band 3 on changing to He(II) radiation [Figure 1(*c*)], both of which can be interpreted as the effect of halogen character in the nominally $e(\pi)$ (C–M) levels.

The stabilization of $e(\pi)$ in the $CF_3$ compound, to give a greater i.e. than in the F compound, probably reflects the lack of $\pi$ destabilization in the former, coupled with the strong $\sigma$-electron withdrawal by this group. In contrast, the $e(\pi)$ level in the methyl compound is substantially destabilized; here any inductive and conjugative effects operate in the same direction. Similar effects have been noted [9] in the series $[Mn(CO)_5Y]$.

Inspection of Figure 2 shows that the pattern of energy shifts of the $e(\pi)$ levels is also present for the metal levels and even for the CO $4\sigma$ levels. The most plausible interpretation of these shifts is that the delocalization effects noted above extend through the entire molecule, with a progressive diminution as the orbital localization site moves away from the bridge. At the bridging C atom, the $e(\pi)$ level shifts over a range of 1.2 eV, while the metal ionizations, bands 1 and 2, move over a range of 0.5 eV, and the CO $4\sigma$ levels only change by 0.15 eV. It has been suggested that there is appreciable double-bond character in the C–X bond of the halides, since the vibrational frequencies are unusually high.[5,28] Also nuclear quadrupole resonance (n.q.r.) spectra of the chloride [5] indicate substantial delocalization between Co and Cl; both these observations are in accord with the deductions from the p.e. spectra.

*Comparison with Calculation.*—The bonding in $[Co(CO)_9(CH)]$ has been discussed previously by Schilling and Hoffmann,[6a] and by Evans.[6b] Both discussions were based on extended-Hückel (EH) calculations using values for the Coulomb integrals for Co $3d$, $4s$, $4p$ atomic orbitals much reduced from the standard VSIE (valence state ionization energy) values,[29] to attempt to account for the effect of a molecular environment of these orbitals. The results of these two calculations are quite similar and we will consider only the former. Schilling and Hoffmann consider the build up of $[Co_3(CO)_9(CH)]$ from $Co(CO)_3$ units to $[Co_3(CO)_9]$, by interaction with CH. For $[Co_3(CO)_9]$ they propose a simple and intuitively attractive picture of the bonding. The $3d$ orbital-based molecular orbitals (m.o.s) are separated into two groups; one derived from the '$t_{2g}$' atomic orbitals (a.o.s) which are essentially M–M non-bonding; and at higher energy, a group derived from the '$e_g$' a.o.s which have some $4s$, $4p$ contributions and are M–M bonding, and resemble the Walsh orbitals of cyclopropane. In $[M_3(CO)_{12}]$ compounds the corresponding M–M bonding group is predicted to be the highest energy set of occupied orbitals, and the p.e. spectra of $[Re_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ have been interpreted as supporting this prediction.[14] In $[Co_3(CO)_9]$ there is an additional set of acceptor orbitals ($a_1 + e$) which can interact with an incoming ligand such as CH. Schilling and Hoffmann's calculation on $[Co_3(CO)_9(CH)]$ predicts that the $1\pi$ and $3\sigma$ orbitals of CH interact strongly with the acceptor orbitals, but the occupied $e$ m.o., with large C $2p_x$, $2p_y$ contributions, is at higher energy than all but one of the metal localized orbitals. This prediction is in apparent conflict with the interpretation of the p.e. spectrum proposed above, at least within the framework of Koopmans' approximation.[30]

One of the reasons for this disagreement with experiment is the choice of Coulomb integral values. Although an improvement on VSIE values, the values used by Schilling and Hoffmann were not optimized enough to account for the effects of the molecular environment on the atomic orbitals. We have performed self-consistent charge (SCC) calculations on the molecules with Y = H, $CH_3$, F, and $CF_3$, and have repeated Hoffmann's calculation for Y = H. The details of the calculational method have been described previously.[31] The comparison between the EH and SCC results illustrates the need for the full consistent charge calculations. Using Hoffmann's parameters we find the m.o. energy order he describes, and we also find that the cobalt atoms carry a small negative charge (−0.17), and that there is no bonding electron density between cobalt atoms [overlap population (o.p.) 0.04]. In contrast, in the SCC calculation the cobalt atoms are positively charged (+0.84), there is definite bonding between them (o.p. 0.40), and there are also substantial changes in the eigenvalue

sequence. This is not to suggest that the SCC calculations are without significant defects; the Coulomb integral values for all cobalt a.o.s are similar and very low in energy at −16.5 eV. As a result the final set of m.o.s is *ca.* 7 eV below the experimental values (Hoffmann's are *ca.* 3 eV below as are Evans'). We have commented on this defect previously [31] and it has been found by other authors using EH techniques.[32] In the following we shift the highest occupied molecular orbital (h.o.m.o.) of $[Co_3(CO)_9(CH)]$ to agree with experiment and apply the same magnitude shift to all other molecules. For $[Co_3(CO)_9(CH)]$ the SCC calculation predicts a group of m.o.s composed predominantly of metal 3*d* a.o.s spread over 1.6 eV, which is similar to the overall width of bands 1 + 2 of approximately 1.8 eV. With this small spread of energies there is no clear breakdown into an '$e_g$' and '$t_{2g}$' group; all the a.o.s are mixed with all others in the various m.o.s. However, from Figure 3 it is seen that

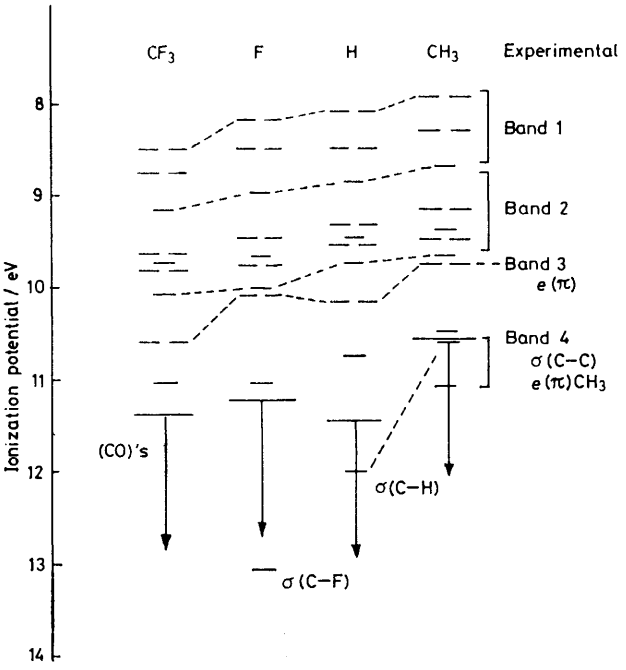


FIGURE 3 Energy levels calculated for the compounds $[Co_3(CO)_9(CY)]$ using the SCC method. The eigenvalues have all been shifted by the addition of 6.7 eV for comparison with Figure 2

the five highest-energy orbitals are separated from, and more spread than, the rest, and that this pattern is followed by the other compounds. This grouping could account for the form of bands 1 and 2. The variation of the energy of the highest orbital follows that of the experimental energies of band 1 very closely.

For Y = H, a degenerate pair of orbitals strongly localized on the carbon atom, corresponding to the 1π pair of CH, are predicted *ca.* 0.4 eV lower in energy than the lowest-energy m.o. assigned to band 2. This is in excellent agreement with the position of band 3 in Figure 1(*a*), and also with the experimental assignment of this band as $e(\pi)$. From Figure 3 the onset of carbonyl ionizations is expected *ca.* 3.2 eV above the first i.e. for all compounds, which compares with *ca.* 5 eV for the leading edge of band 5 in the spectra. The SCC calculation places one metal orbital between the $e(\pi)$ orbitals and the first carbonyl orbital for all four molecules. Although this orbital could provide a possible assignment of band 4 for Y = H it is not a tenable one as the band should also be present for Y = F, but is not. The calculation also places an m.o. with significant σ(C–H) contribution 3 eV below $e(\pi)$, 0.6 eV into the group of carbonyl orbitals; this could equally well account for band 4 and would be in agreement with the experimental assignment. The calculation also places σ(C–H) contributions in a number of $a_1$ m.o.s in the carbonyl region, and hence cannot be claimed either to agree or to disagree with the experiment. However, we note that a recent calculation [33] using the Hartree–Fock–Slater method on the CH group above a triangle of Ni atoms also gives a separation $e(\pi) - 2\sigma$ of *ca.* 3 eV, which tends to support the empirical assignment. For Y = F, the $e(\pi)$ pair of m.o.s is predicted below the metal ionizations, at slightly higher energy than found for Y = H, agreeing with the observations on band 3. No σ(C–F) orbital is predicted until 1.3 eV below the onset of carbonyl ionizations, directly under the peak of these ionizations, and hence the lack of a band 4 is expected.

For $Y = CH_3$, the pattern of orbitals in bands 1 and 2 is calculated to be identical to that for Y = H. The C $2p_\pi$ a.o.s now contribute significantly to a number of (nearly) degenerate m.o. pairs and their contribution to the orbitals corresponding to band 3 is reduced. A consequent increase in metal contribution to these m.o.s causes an increase in the energy of these orbitals, and band 3 is predicted to be very close to the high i.e. tail of band 2. These orbitals giving rise to band 3 also contain some contribution from $H_3C$ *e* a.o.s. Two possible interpretations for band 4, with $Y = CH_3$, are offered by the calculation. A σ(C–C) orbital is predicted at the same energy as the highest-energy carbonyl orbitals, and a $H_3C$ *e* pair of m.o.s 0.4 eV lower in energy. The $Y = CF_3$ compound does not resolve this optional assignment, since the fluorination effect stabilizes both the $F_3C$ *e* and σ(C–C) orbitals well into the carbonyl region, and hence no band 4 is expected for this compound. The stabilization of the $F_3C$ *e* a.o.s also means that orbitals corresponding to band 3 are as strongly localized on the carbon atom as were the corresponding orbitals for Y = H, and band 3 is predicted at a somewhat higher i.e. than the band of Y = H; this agrees well with the experiment. The shifts in i.e. of band 3 in all four compounds are in excellent agreement with the calculated eigenvalues, and this provides additional evidence in favour of the assignment given earlier. However, we note that the predicted separation of the metal levels from the other levels is rather too small; this may be the result of differential relaxation on ionization.

*Conclusions.*—The bands in the p.e. spectra of the compounds $[Co_3(CO)_9(CY)]$ can be assigned as ionization of mainly metal, carbonyl, or CY levels on empirical grounds. The trends in i.e. have been used to show the

existence of substantial delocalization of the π-type Y orbitals to the C bridge and to the rest of the molecule, and for Y = halogen there is evidence for C–Y π bonding by the ' π lone pairs ' of the halogen. Calculational results show very good correspondence with experiment for the compounds considered. The experimental assignments of bands 1, 2, and 3 are supported in all cases, although no ' $e_g$ ', ' $t_{2g}$ ' distinction in the two groups of metal ionizations is found. Band 4 is somewhat more problematic. Its absence for Y = F, $CF_3$ is expected from the calculations, and there is no evidence to doubt the experimental assignment for Y = H, $CH_3$; however, equally well there is none to support it uniquely.*

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* After the submission of this manuscript a note on three of the spectra reported above appeared (G. Granozzi, S. Agnolin, M. Casarin, and D. Osella, *J. Organomet Chem.*, 1981, **208**, C6). The results and conclusions are similar to ours.

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