changes in CD with solvent are less significant.

In $[Pt(NH_3)_2((S)\text{-dmbn})]^{2+}$ the quaternary carbon has an approximate trans relationship with the Pt. The vicinal coupling between the carbon and ^{195}Pt is therefore maximized, giving a value of 41 Hz. An axial carbon has a torsional angle with Pt of about 90° and therefore has a very small coupling with ^{195}Pt. In $[Pt(NH_3)_2(\textit{meso}\text{-bn})]^{2+}$ and $[Pt(NH_3)_2(ibn)]^{2+}$, the δ and λ conformations are equally populated, and hence the observed $^3J_{PtC}$ values, 27.3 and 22.4 Hz, respectively, are the averages of the values for the axial and equatorial methyls.[48] The methyl groups in $[Pt(NH_3)_2((R,R)\text{-bn})]^{2+}$ are predominantly, but not exclusively, in equatorial orientations, and have a value of 49.8 Hz for $^3J_{PtC}$.[48] A direct comparison of the $^3J_{PtC}$ values for the equatorial quaternary carbon in the dmbn complex and the equatorial methyl carbons in the above complexes is not possible because of the different substituent effects.

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Registry No. $[Co(NH_3)_4((S)\text{-dmbn})](NO_3)_{1.5}(ClO_4)_{1.5}$, 80145-88-6; *trans*-$[CoCl_2((S)\text{-dmbn})_2]ClO_4$, 80145-90-0; *trans*-$[CoCl_2((S)\text{-dmbn})_2]BPh_4$, 80145-91-1; Λ-$[Co((S)\text{-dmbn})_3]Cl_3$, 80225-17-8; Λ-$[Co((S)\text{-dmbn})_3](ClO_4)_{1.5}Cl_{1.5}$, 80225-15-6; $[Pt(NH_3)_2((S)\text{-dmbn})]Cl_2$, 80145-76-2; $K[Co(CN)_4((S)\text{-dmbn})]$, 58410-52-9; *trans*-dichlorotetrakis(pyridine)cobalt(III) chloride, 27883-34-7.

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Gas-Phase Helium I Photoelectron Spectra of Methinyltricobalt Enneacarbonyl Clusters

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The electronic structure of $Co_3(CO)_9CY$ clusters, where Y = H, F, Cl, Br, I, CH_3, CF_3, or $COOCH_3$, is discussed on the basis of their He I excited gas-phase photoelectron spectra. A qualitative energy level diagram has been afforded which allows a satisfactory discussion of the PE data. The most interesting feature of our interpretative model is the presence of a molecular orbital of e symmetry which accounts for a large portion of the interaction between the Co_3 triangle and the apical carbon atom C_{ap} and for the electron transmission from the apical substituent Y and the cobalt atoms via a resonance-type mechanism. In agreement with previous NQR and IR data, evidence for significant $Y \rightarrow C_{ap}$ π-bonding donation with Y = Cl, Br, or I is presented. The relationships existing between the present clusters and molecules of type $M_3(CO)_{12}$ and $(\mu\text{-}CH_2)[ML_n]_2$ have been stressed.

Introduction

Since it was suggested that transition-metal clusters can offer good models to mimic substrate–surface interaction,[2] a large number of spectroscopic studies have been devoted to this class of molecules.

Until now, however, few gas-phase photoelectron (PE) investigations have been carried out,[3] although these compounds often show good stability and volatility which make them suitable for PE investigations.

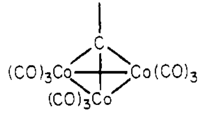
In order to get more information about the potentiality of this technique as applied to transition metal clusters and as a further development of our previous studies,[3a,4,5] we have undertaken a PE study of the series $Co_3(CO)_9CY$ (Y = H, F, Cl, Br, I, CH_3, CF_3, $COOCH_3$),[6] whose chemical and structural features have received widespread attention in the past 20 years.[7]

Table I. Ionization Energies (eV) of the $Co_3(CO)_9CY$ Clusters[a]

	band label					
cluster	A′ (S′)	A″	B′	B″	C′ (S″)	C″
H	8.75 (7.9)	10.23			14.0	18.0
CH_3	8.58 (7.9)	9.93			14.2 (12.7)	17.7
CF_3	8.96 (8.2)	10.40			14.3 (16.2)	17.9
$COOCH_3$	8.73 (8.1)	9.80	11.57		14.2	17.9
F	8.96 (8.2)	10.24			14.3	18.1
Cl	8.63 (7.9)	9.85	12.28		14.1	17.7
Br	8.73 (8.0)	9.80	11.55		14.2 (12.8)	17.9
I	8.76 (8.1)	9.77	10.94	12.46	14.1	17.8

[a] Values in parentheses refer to shoulders.

A trigonal-pyramidal structural core Co_3C (C_{3v} symmetry) was early inferred from chemical evidence[8] and IR measurements[9] and subsequently confirmed by several structural determinations.[7]



The peculiar arrangement of three Co atoms with the apical

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(1) (a) University of Padova. (b) CNR of Padova. (c) University of Torino.

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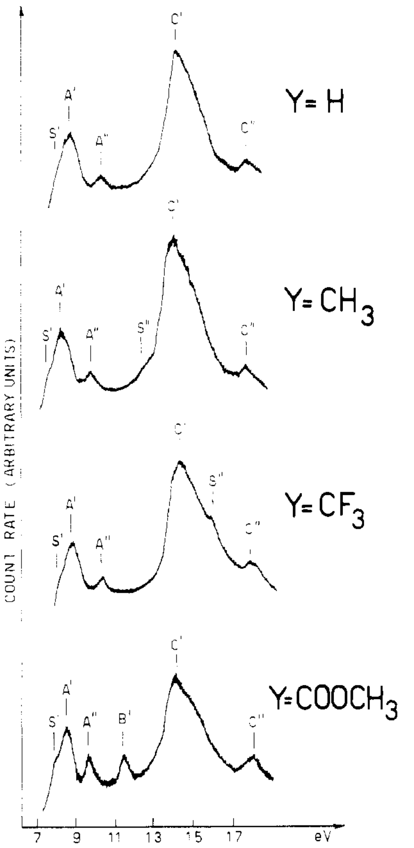

Figure 1. He I excited PE spectra of $Co_3(CO)_9CY$ clusters (Y = H, CH_3, CF_3, $COOCH_3$).

carbon atom has given rise to a long debate about the bonding mode in this system. Detailed studies have been reported concerning the spectroscopic properties (^1H and ^{13}C NMR,[10,11] NQR,[12] ESR,[13] UV-vis[13,14]) and electronic structure description (EHT calculations,[15,16] X-N deformation maps[17]) of such molecule, all pointing to a delocalized electronic system which involves the apical carbon atom. The view of the Co_3C cluster as an electron reservoir,[7c] strongly interacting with the substituents on the apical carbon atom, has received then strong support.

Due to the extreme complexity of the compounds examined, the following presentation of our PE data will be discussed on the basis of comparison arguments, following the spectral changes along the series of apical substituents, and a qualitative energy level diagram will be proposed.

Experimental Section

All the complexes were prepared according to the literature methods.[7] They were further purified by sublimation in vacuo.

PE spectra were run on a Perkin-Elmer PS-18 spectrometer using a heated inlet probe system. They were measured in the 35–45 °C temperature range with a count rate between 800 and 1500 counts/s. The ionization energy (IE) scale was calibrated by reference to peaks due to admixed inert gases (Xe, Ar). The IEs reported in Table I are the mean values over several distinct runs.

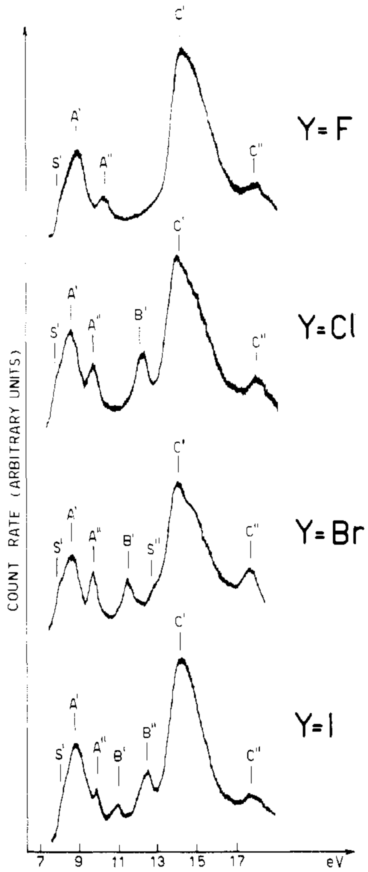

Figure 2. He I excited PE spectra of $Co_3(CO)_9CY$ clusters (Y = F, Cl, Br, I).

Results

The He I excited PE spectra of $Co_3(CO)_9CY$ (Y = H, F, Cl, Br, I, CH_3, CF_3, $COOCH_3$) are shown in Figures 1 and 2. The pertinent PE data are reported in Table I.

For discussion purposes, the spectra can be conveniently divided in three distinct regions (I, 7.5–10.5 eV; II, 10.5–13.0 eV; III, 13.0–19.0 eV).

All the spectra show two distinct bands (labeled A′, A″) in region I. A defined shoulder S′ is clearly seen in the lower IE side of band A′ in all the cases. Small IE shifts and intensity changes are found for bands A′ and A″ along the series. On the contrary, region II appears quite different according to the actual substituent Y. A single band (B′) is evident when Y = Cl, Br, or $COOCH_3$ whereas a further band (B″) is present when Y = I.

In the third region two broad bands (C′ and C″) are always present. In some cases shoulders (S″) are evident either in the lower or in the higher IE sides of band C′.

Discussion

He I PE spectra of transition-metal carbonyls present two typical features:[18] beyond 13 eV, the ionizations from levels primarily localized on the carbonyl groups (1π, 5σ, 4σ MOs), whereas at lower IEs (7–10 eV) the ionizations from MOs having predominant contributions from *n*d metallic AOs.

Reference to the spectra of simpler related molecules[19] suggests that the ionizations relative to Y apical substituents are to be expected beyond 10.5 eV, that is, in the spectral regions II and III defined previously.

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As a starting point, then, we can assume that A′, A″, and S′ bands of region I represent ionizations mainly originating from the Co_3C core fragment, also in tune with the relative invariant pattern of this spectral region along the series.

The bands of region II we take to represent ionizations peculiar to the Y apical substituent, some of which are obscured in region III by the broad bands C′ and C″, which are typical of carbonyl levels. We discuss hereafter the detailed assignments separately for the different cluster fragments.

Ionizations of the Y Substituents. In the He I range two kinds of ionization are expected when Y = F, Cl, Br, or I, i.e., ionization from the halogen *n*p lone pairs (representation e in the C_{3v} point group) and ionization from the σ C–Y bonding MO (representation a_1).

The former occurs within energy ranges typical of each halogen atom.[19] Actually bands B′ when Y = Cl, Br, or I lie within these ranges, and they are to be assigned to ionizations from such nonbonding e MOs.[20] In the case of Y = F, this ionization is obscured by the broad band C′; only when Y = CF_3 is a shoulder S″, which can be associated to this kind of ionization, intense enough to be detected. The actual IE values of band B′ lie in proximity of the higher IE boundary of the IE ranges typical of each halogen atom. This is an indication for electron deficiency on Y, which in turn can be related to $Y \rightarrow C_{ap}$ π-bonding donation. This is also in agreement with the ^{35}Cl NQR,[12] and IR[7,9] results on $Co_3(CO)_9CCl$ which predict a significant amount of π character in the Cl–C_{ap} bond.

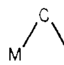
Band B″ when Y = I can be associated to the a_1 σ(C–Y) MO, mainly on the basis of comparison with the same ionization in methyl iodide.[21] The higher electronegativities of F, Cl, and Br shift this ionization in region III under band C′. The shoulder S″ when Y = Br may represent this ionization.

Analogously, ionizations from σ(C–C) and σ(C–H) MOs when Y = H, CH_3, CF_3, or $COOCH_3$ are not resolved, their typical IE region being at the boundary of regions II and III. The shoulder S″ at 12.7 eV when Y = CH_3 might represent such ionizations. An alternative assignment of this shoulder will be proposed in the next paragraph.

Band B′ in the spectrum of Y = $COOCH_3$ originates from two MOs, usually referred to as n_0 and π_2, which represent the in-plane lone pair of the carbonyl oxygen and the nonbonding antisymmetric carboxylic π MO, respectively.

Ionizations of the Co_3C Core. Two different EHT calculations on $Co_3(CO)_9CH$ have been recently reported.[15,16] However, EHT-type calculations usually do not give a reasonable agreement with PE experimental data. Due to the lack of any reliable quantitative MO result, we prefer to propose tentative assignments going on in a pure qualitative way by developing a level diagram (Figure 3) representing ionization energies rather than MO eigenvalues, mainly derived on the basis of PE data previously obtained for strictly related molecules such as $Ru_3(CO)_{12}$[3a,3d] and $(\mu\text{-}CH_2)[(\eta^5\text{-}C_5H_5)Mn(CO)_2]_2$.[5] The basal and lateral triangular faces of the trigonal-pyramid Co_3C can be, indeed, qualitatively related either to the M_3 or to the

triangles present in these two molecules. The lowest IE band in the spectrum of $Ru_3(CO)_{12}$[3a,3d] has been assigned to the ionizations from the two quasi-degenerate MOs (a'_1 and e′ in D_{3h} symmetry) representing the ring metal–metal bonding. In the case of $(\mu\text{-}CH_2)[(\eta^5\text{-}C_5H_5)Mn(CO)_2]_2$ three distinct bands (at 6.75, 8.45, and 10.36 eV) were assigned[5] to the three MOs (27a, 26b, and 22a in C_2 symmetry) that describe the three-membered ring bonding; 27a HOMO represents a bonding M–M interaction, 26b represents bonding



interactions with a marked antibonding M–M character, whereas 22a MO is mainly localized on the methylene carbon atom and looks like a lone pair pointing toward the center of the three-membered ring.

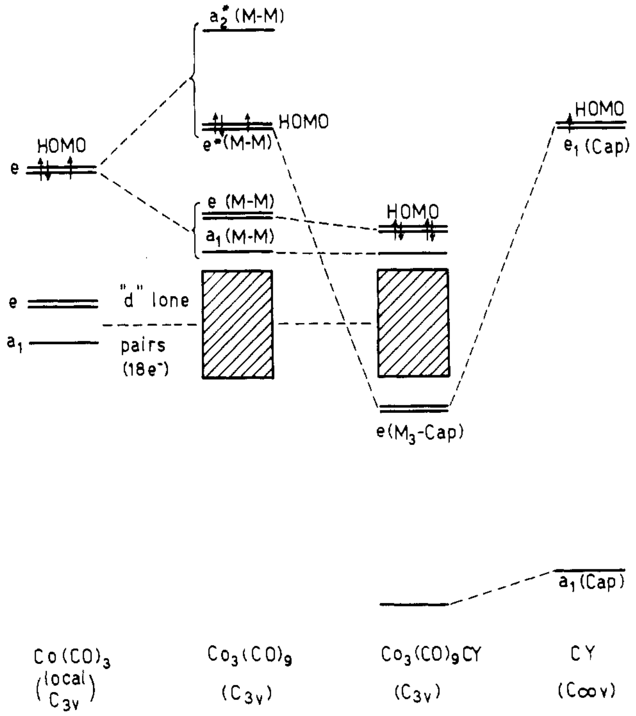


Figure 3. Qualitative energy level diagram for $Co_3(CO)_9CY$ and its constitutive fragments. Y substituent MOs not directly interacting with the $Co_3(CO)_9$ fragment have been omitted for clarity.

The level diagram reported in Figure 3 is obtained by building up the whole cluster from its constituent fragments. $Co_3(CO)_9$ levels are derived from those of three $Co(CO)_3$ fragments[15,16] with the assumption that the e HOMO of each $Co(CO)_3$ group is mainly perturbed during the formation of the metallic triangle, giving rise to e(M–M) and a_1(M–M) bonding and to e*(M–M) and a^*_2(M–M) antibonding MOs. With the assumption for Co atoms the formal (d^9) oxidation state is 0, we have three electrons on the HOMO e*(M–M). The $a_1(C_{ap})$ and $e_1(C_{ap})$ MOs of the C–Y fragment ($C_{\infty v}$) represent respectively a low-lying electron pair mainly localized on the apical carbon atom, pointing toward the center of the Co_3 triangle, and the p_x, p_y degenerate carbon set interacting with Y via a π mechanism. On the basis of previous results,[5] it is likely that the main source of interaction between the two fragments is the mixing between the two HOMOs e*(M–M) and $e_1(C_{ap})$, giving rise to the $e(M_3\text{–}C_{ap})$ bonding MO, while the $a_1(C_{ap})$ MO remains essentially localized on the apical carbon atom. The $e(M_3\text{–}C_{ap})$ MO should also maintain a remarkable M–M antibonding character.[22] From this level diagram the following tentative assignments can be proposed: shoulder S′ is related to ionizations from a_1(M–M) and e(M–M) bonding MOs, band A′ to six MOs ($2\ a_1 + a_2 + 3\ e$) maintaining metal-like character (i.e., nonbonding), and band A″ to the $(M_3\text{–}C_{ap})$ bonding MO. The ionization from $a_1(C_{ap})$

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(20) No spin–orbit coupling effect has been detected when Y = Br or I.

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should occur at higher IE in region III, mainly because of the positive charge expected on the carbon atom.[23] Shoulder S″ in the spectrum of Y = CH_3 could represent this ionization, as an alternative to what was proposed previously.[24]

An experimental support to the assignment of band A″ to the $e(M_3–C_{ap})$ MO is derived from the trend of IE (A″) along the series of Y substituents. With Y = H assumed as a gauge, we note (Table I) that the IE is much more affected by π-donor (i.e., Cl, Br, I, CH_3) than by σ-acceptor (CF_3, F) acceptor substituents. This is an indication for the symmetry properties of the ionized MO mainly because π effects of the Y substituent can only influence e type MOs, at least if only the first-order perturbation is invoked. Furthermore, the larger relative intensity of band A″ when Y is a π donor can be tentatively explained on the basis of involvement of the apical substituent Y in the $e(M_3–C_{ap})$ MO. As a matter of fact, the assumption of the Gelius model[25] for the photoionization cross section and the differences in atomic cross section between metallic 3d and halogen np AOs[26] can account qualitatively for the increased cross section of the $e(M_3–C_{ap})$ MO.

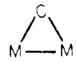
Conclusions

The present PE study shows the high potentiality of the gas-phase PE technique even for very complicated systems such as those reported in this paper. Although the discussion of the PE data is based on qualitative arguments, some interesting informations concerning the electronic structure of the Co_3C framework can be gained. The interaction between the metal triangle and the apical carbon atom, which was already recognized[16,27] to play a determinant role for the stability of the whole cluster, is now for the first time somewhat gauged from the position of band A″ which was assigned to the ionization from a molecular orbital representing the bonding interaction between the metal triangle and the apical carbon atom. The metal–metal antibonding character attached to the same MO can account for the minor role of metal–metal bond in stabilizing the cluster.

This feature is supported by the observation of the fragmentation pattern in the mass spectra of these compounds,[27] which shows a preferential cleavage of cobalt–cobalt rather than $Co–C_{ap}$ bonds. The MOs whose ionizations give rise to bands S′ and A′ constitute the electron reservoir localized on the $Co_3(CO)_9$ fragment that has been already proposed on the basis of other spectroscopic measurements.[7c] These MOs are only slightly perturbed by the apical substituents.

Furthermore, the electron transmission from Y to cobalt, which was shown to follow a resonance-type mechanism,[11,12] can be also discussed on the basis of these PE results. The localized and low-lying nature of the $a_1(C_{ap})$ MO suggests that σ active apical substituents should transmit only slightly their electronic effects to the metal triangle. On the other hand, the behavior of the A″ band along the series strongly indicates noticeable π-conjugation effects of Y and allows us to ascribe the operation of large portion of the electronic transmission to the $e(M_3–C_{ap})$ MO.

Finally, we wish to stress the strong relationship between the present clusters and complexes of the $(\mu\text{-}CH_2)[ML_n]_2$ type.[5] A satisfactory qualitative description of the Co_3C clusters can be obtained simply by assuming that the cluster is assembled from three triangular pieces.



Acknowledgment. This work was partially supported by the Italian Consiglio Nazionale delle Ricerche (CNR) (Grant CT80.02550.03).

Registry No. $Co_3(CO)_9CH$, 15664-75-2; $Co_3(CO)_9CCH_3$, 13682-04-7; $Co_3(CO)_9CCF_3$, 18433-88-0; $Co_3(CO)_9CCOOCH_3$, 36834-85-2; $Co_3(CO)_9CF$, 18433-91-5; $Co_3(CO)_9CCl$, 13682-02-5; $Co_3(CO)_9CBr$, 19439-14-6; $Co_3(CO)_9CI$, 41749-34-2.

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(23) The large difference in the ^{13}C NMR chemical shift of methylene and methine carbon atoms in $(\mu\text{-}CH_2)[(\eta^5\text{-}C_5H_5)Mn(CO)]_2$[28] and the present clusters[11] can be qualitatively interpreted on the basis of different carbon atomic charges. This seems to us a satisfactory explanation for the higher IE of $a_1(C_{ap})$ MO in our complexes with respect to the IE of the 22a MO in the manganese dimer.[5]

(24) Consider that, unique within the set of apical substituents here investigated, CH_3 has a σ-releasing electronic effect which may shift ionization $a_1(C_{ap})$ toward lower IE.

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