

**Preliminary communication**

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**ELECTRONIC STRUCTURE OF SOME METHINYLTRICOBALT  
ENNEACARBONYLS BY MEANS OF ULTRAVIOLET PHOTOELECTRON  
SPECTROSCOPY**

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(Received December 2nd, 1980)

**Summary**

The He(I) excited photoelectron spectra of  $\text{Co}_3(\text{CO})_9\text{CY}$  (where  $\text{Y} = \text{CH}_3, \text{F}, \text{Cl}$ ) are presented, and assignments of the bands to the ionization events are made on the basis of qualitative arguments. The photoelectron data agree with the representation of this cluster as an electron sink capable of  $\pi$ -interaction with the substituent Y.

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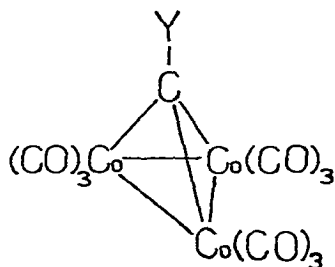
The methinyltricobalt enneacarbonyls  $\text{Co}_3(\text{CO})_9\text{CY}$  (where Y is halogen, alkyl, aryl, etc.) represent an example of a three-point attachment of an aliphatic carbon atom to a cluster of metal atoms. A structure based on a trigonal pyramidal  $\text{Co}_3\text{C}$  cluster ( $\text{C}_{3v}$  symmetry) was predicted from chemical evidence [1,2] and IR measurements [3] and subsequently confirmed by several X-ray structural determinations [4]. These compounds are very stable and highly volatile, thus suitable for study by gas-phase photoelectron (PE) spectroscopy.

The He(I) excited PE spectra of  $\text{Co}_3(\text{CO})_9\text{CY}$  (I,  $\text{Y} = \text{CH}_3$ ; II,  $\text{Y} = \text{F}$ ; III,  $\text{Y} = \text{Cl}$ ) are presented. Additional studies of the PE spectra of this type of compound and related quantum mechanical calculations are in progress in our laboratories and will be the subject of a forthcoming full paper.

The low ionization energy (IE) region (up to 13 eV) of the spectra of I and II shows two distinct bands (see Fig. 1). A further definite shoulder in the lower IE side of the first band is present in both spectra. Moreover, the region of the

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- (I)  $Y = \text{CH}_3$   
 (II)  $Y = \text{F}$   
 (III)  $Y = \text{Cl}$

spectrum of I around 12.7 eV shows a broad shoulder, probably due to ionizations from the  $\sigma(\text{CH})$  MOs of the methyl group.

The spectrum of III shows two new features when compared to those of I and II: the second band at 9.85 eV has a higher relative intensity and a further prominent band is present at 12.28 eV. This latter band lies in the region where

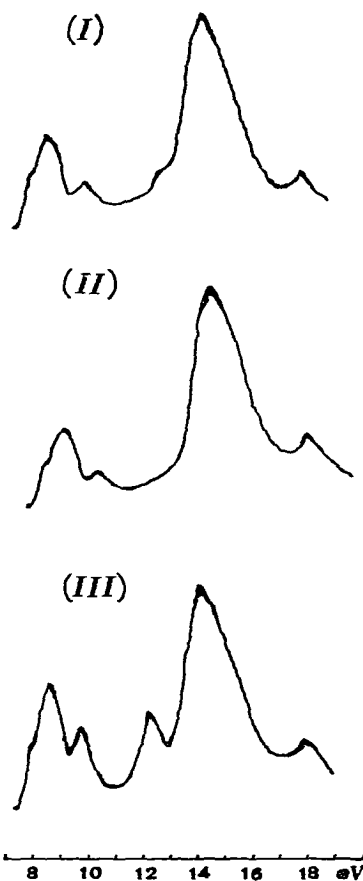


Fig. 1. He(I) excited PE spectra of  $\text{Co}_3(\text{CO})_9\text{CY}$  (I,  $Y = \text{CH}_3$ ; II,  $Y = \text{F}$ ; III,  $Y = \text{Cl}$ ).

ionizations from the  $3p$  non-bonding chlorine orbitals usually occur. The rather high IE value is an indication of an extensive  $\text{Cl} \rightarrow \text{C}_{\text{ap}} \pi$ -bonding interaction, in agreement with other spectroscopic evidence [5]. There is no doubt about assigning the first band in all the three spectra to ionizations from MOs characterized by their high contribution from  $3d$  cobalt atomic orbitals. Based on intensity considerations and on results on similar compounds [6, 7, 8], we assign the lower IE shoulder to ionizations from MOs contributing to the ring Co—Co metal bonding and the main band to MOs maintaining  $3d$  atom-like character (i.e. non-bonding with some contribution from carbonyls). Consistently, the second band in all the spectra is related to MOs containing the six electrons engaged in the bonds between the metal ring and the apical carbon atom. A large degree of delocalization over the Y substituent was indicated by NQR and NMR measurements [5, 9], so that small shifts and changes in relative intensity of this band must reflect the contribution from the substituent.

Finally, we comment briefly on the two broad and ill resolved structures which are present in the spectral region beyond 13 eV in all the spectra (see Fig. 1). These are primarily due to ionizations from the metal—CO bonding and the CO  $1\pi$  levels. In the case of II this band must also include the ionizations from the  $2p$  non-bonding fluorine orbitals.

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