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Preliminary communication

UV PHOTOELECTRON SPECTRA OF SOME ORGANOMETALLIC CARBONYL OSMIUM CLUSTERS

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Summary

The He(I) excited PE spectra of $HOs_3(\mu_3\text{-L})(CO)_9$ (L = allenyl, allyl) and of $HOs_3(\mu_2\text{-vinyl})(CO)_{10}$ are presented. Some gross spectral features are discussed on the basis of a direct comparison with previous results for $Os_3(CO)_{12}$ and the alkynyl corresponding cluster derivative. Large perturbations in the Os—Os bonding levels are induced by the bridging hydride and the interaction with the organic substrate.

The reactions of $M_3(CO)_{12}$ (M = Ru, Os) with alkenes and alkynes have been widely investigated in the last decade, and several derivatives which involve the organic substrate interacting with two or more metallic centres, have been characterized [1]. These compounds are of additional interest because it has been suggested that they can represent good models for the chemisorption phenomena on metallic surfaces [2]. The observation that most of these compounds are very stable and highly volatile prompted us to undertake a comprehensive study of their electronic structures by means of gas-phase UV photoelectron spectroscopy (PES). Application of this technique to cluster-containing compounds has been shown to be very valuable in elucidating of the bonding schemes and electronic structures [3—8].

We previously investigated the PE spectra of $HM_3(\mu_3\text{-C}{\equiv}\text{CR})(CO)_9$ cluster derivatives [9] (M = Ru, Os; R = CH_3, t-Bu) in which the alkynyl ligand acts as a $5e^-$ donor group; with the aid of CNDO type calculations it was possible

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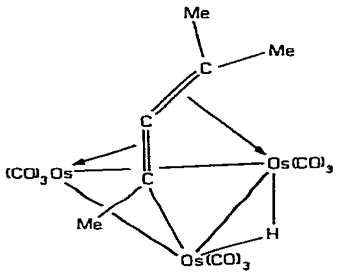
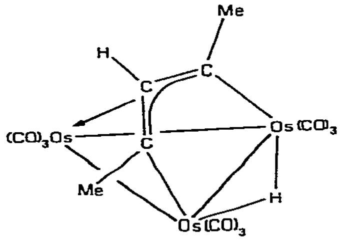
to assign the PE bands completely and discuss the bonding scheme in such compounds.

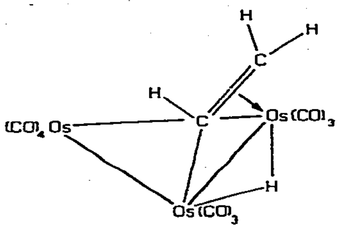
We now report some preliminary He(I) PE results for the related tri-osmium derivatives, I—III. The organic substrate acts formally as a $5e^-$ donor group in I and II, whereas in compound III it donates $3e^-$ to the cluster.



I



II



III

The low ionization energy (IE) region (up to 14 eV) of the spectra of I, II and III is shown in Fig. 1. The higher IE region is not included because the broad and ill resolved structures typical of the metal carbonyl systems preclude discussion. As it can be clearly seen, the spectra show a very complex band pattern, so that a complete assignment of all the ionizations is a very hard task at the moment. Nevertheless, we can indicate some gross features which can be discussed with reasonable confidence by direct comparison with previous results for $Os_3(CO)_{12}$ [6] and the alkynyl derivative [9].

The bands labelled A and B in Fig. 1 can be reasonably assigned to ionizations from MOs which mainly represent Os—Os bonds: the significant difference observed on going from $Os_3(CO)_{12}$ to I, II and III is an indication of the large perturbations induced by the bridging hydride and the organic substrates on the trimetallic triangle.

It is interesting to note that different ligands (namely σ-allenyl in I; di-σ-allyl in II; σ-vinyl in III) cause marked changes in the spectral pattern of the Os—Os ionizations.

By similar arguments we relate bands C and D to ionizations from MOs having 5*d* "lone-pair" character and partly involved in back-donation with the carbonyls. The overall shift toward lower IEs of these ionizations with respect to the parent $Os_3(CO)_{12}$ can be interpreted as evidence of larger electron density on the metallic centres, which, in turn, can be related to the net balance of electronic charge following the replacement of carbonyl groups in the oxidative addition of the unsaturated ligands.

Band E is present in the spectra of all three compounds studied and in that of the alkynyl derivatives [9], independent of the organic substrate. Thus we suggest assignment of band E to the ionization from the three-center two-electrons $\mathrm{Os}\overset{\mathrm{H}}{\diagup\;\diagdown}\mathrm{Os}$ bond. In the case of III, the high intensity of band E indicates that it must contain some other contribution, which likely is to be related to ionization of the organic moiety.

The higher IE region includes ionizations from MOs representing interaction

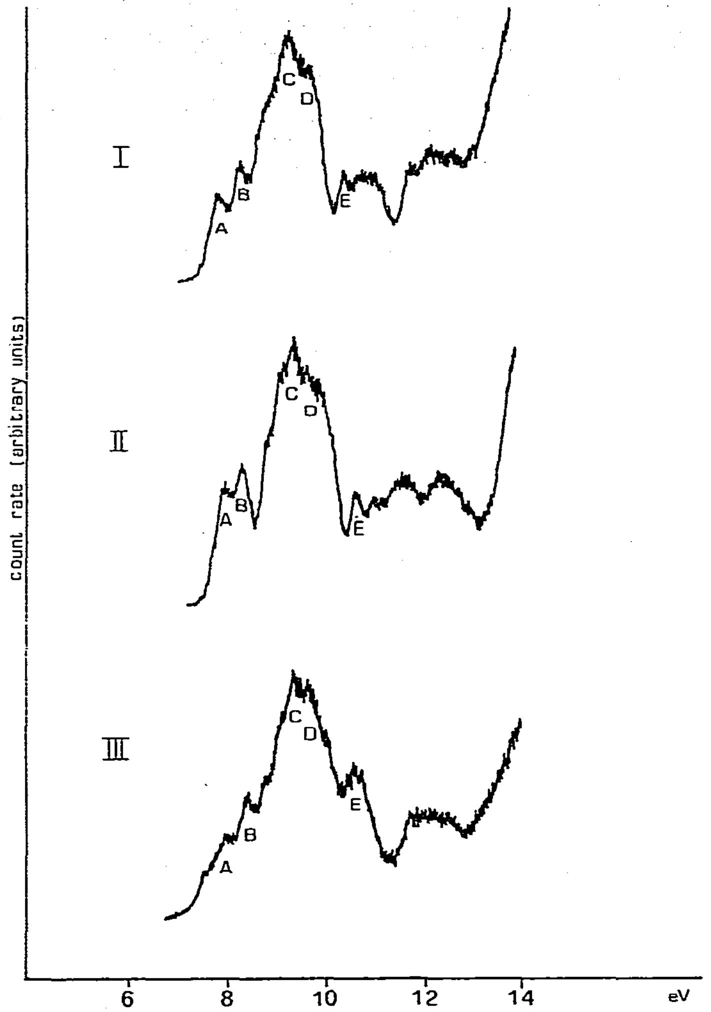


Fig. 1. He(I) excited PE spectrum of $HOs_3(allenyl)(CO)_9$ (I), $HOs_3(allyl)(CO)_9$ (II) and $HOs_3(vinyl)(CO)_{10}$ (III).

of the organic substrate with the metallic triangle. Analysis of this region based on purely qualitative considerations of the electronic structures of these cluster derivatives would be unproductive. Quantum mechanical calculations are in progress, and will be included, together with additional data for He(I) and He(II) spectra of related Ru clusters, in a full paper.

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