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THE ALKYNE-CLUSTER INTERACTION IN A RUTHENIUM "BUTTERFLY" ACETYLENIC CARBONYL COMPLEX. AN UV-PES AND THEORETICAL STUDY

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Summary

The electronic structure of "butterfly" $Ru_4(CO)_{12}(R{-}C_2{-}R)$ cluster complexes is discussed on the basis of He(I) PE spectroscopy and CNDO quantum mechanical calculations. The theoretical results contribute to the discussion of the PE data and provide novel insights into the alkyne-cluster bonding scheme. The most interesting feature emerging from this study is the different roles of the "hinge" and "wing" ruthenium atoms: the former are involved in both donation and back-donation with the alkyne, whereas the latter are primarily involved in the donation only. This gives rise to a particularly stable arrangement, because the two highly polarizable Ru_3 triangles provide a mechanism for balancing the charges.

Introduction

We are interested in the gas-phase UV photoelectron spectroscopy (UV-PES) of alkyne carbonyl cluster complexes because of the possibility that further insight into the electronic features of these molecules may contribute to a better understanding of related chemisorption phenomena on catalytic metal surfaces [1,2].

In previous studies we investigated the UV-PE spectra of two μ_3-η^2-alkyne-cluster derivatives: $HM_3(CO)_9(C_2{-}R)$ (M = Ru, Os) [3] and $Fe_3(CO)_9(R{-}C_2{-}R)$ [4], which can be considered as models for chemisorption of terminal and internal alkynes, respectively, over a flat surface site [2]. These PE investigations, supported by CNDO calculations, provided a detailed description of the bonding system in these molecules, and enabled us to evaluate the relative importance of the alkyne donation to the cluster and metal cluster back-donation to the alkyne. We now report the

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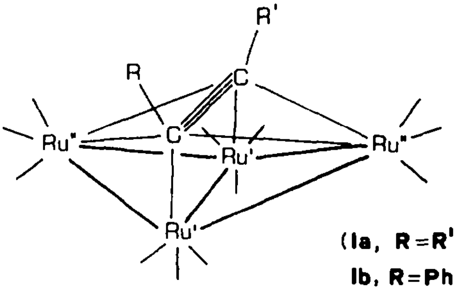
results of a CNDO and PE study of a "butterfly" ruthenium cluster derivative containing an alkyne in a μ_4-η^2 coordination mode (Ia, Ib). As was already suggested [2], this molecular arrangement can be viewed as a model for the chemisorption of alkynes over a step or kink site of a metal surface. The higher nuclearity of the complex considered in this study compared to those examined earlier [3,4] presents a challenge to the applicability of the gas-phase PE technique. The molecule under study has been classified as a 60 electron cluster [5] providing that the alkyne donates four electrons to the valence orbitals of the Ru_4 cluster. The bonding scheme can be qualitatively described as two σ-like bonds and two μ_2-type π interactions [6]. Within the PSEP (Polyhedral Skeletal Electron Pair) formalism, clusters Ia and Ib can be viewed as a closo-octahedron ($S = 7$, $n = 6$) in which the acetylenic carbon atoms occupy two basal vertices.



(Ia, R=R'=H;
Ib, R=Ph; R'=H)

Since alkynes usually add oxidatively to $Ru_3(CO)_{12}$ via cleavage of C–H bonds, giving rise to trinuclear hydrido derivatives [5,7], the title complexes are not readily obtained with most mono- and di-substituted alkynes [8]. A route to the synthesis of $Ru_4(CO)_{12}(H{-}C_2{-}Ph)$ (Ib) through the dehydrogenation of styrene in presence of $Ru_3(CO)_{12}$ was recently described [9].

Experimental

The title complex Ib was obtained according to the literature procedure [9] and its purity was checked by means of IR and NMR spectroscopy.

The He(I) excited PE spectrum was measured on a Perkin–Elmer PS 18 spectrometer using an heated inlet probe system. The ionization energy (IE) scale was calibrated by reference to peaks due to admixed inert gases (Xe, Ar) and to the $1s^{-1}$ He ionization. The IEs reported in Fig. 1 are the mean values from several runs.

Quantum mechanical calculations for Ia were performed by a version of the CNDO method [10] suitable for transition metal complexes. Ru semiempirical parameters were obtained [10] from atomic spectra whereas the C, O, H parameters are Pople's standard ones [11]. The geometrical data used in the calculations refer to previous X-ray structural determinations [12] approximated to C_{2v} symmetry. Gross atomic charges and bond overlap populations were obtained by Mulliken's population analysis [13] of the deorthogonalized [14] eigenvectors.

Results and discussion

UV-PE data. Among the available derivatives, the Ib complex was found to be the most suitable for the PE experiment (Fig. 1). The quality of the spectrum obtained

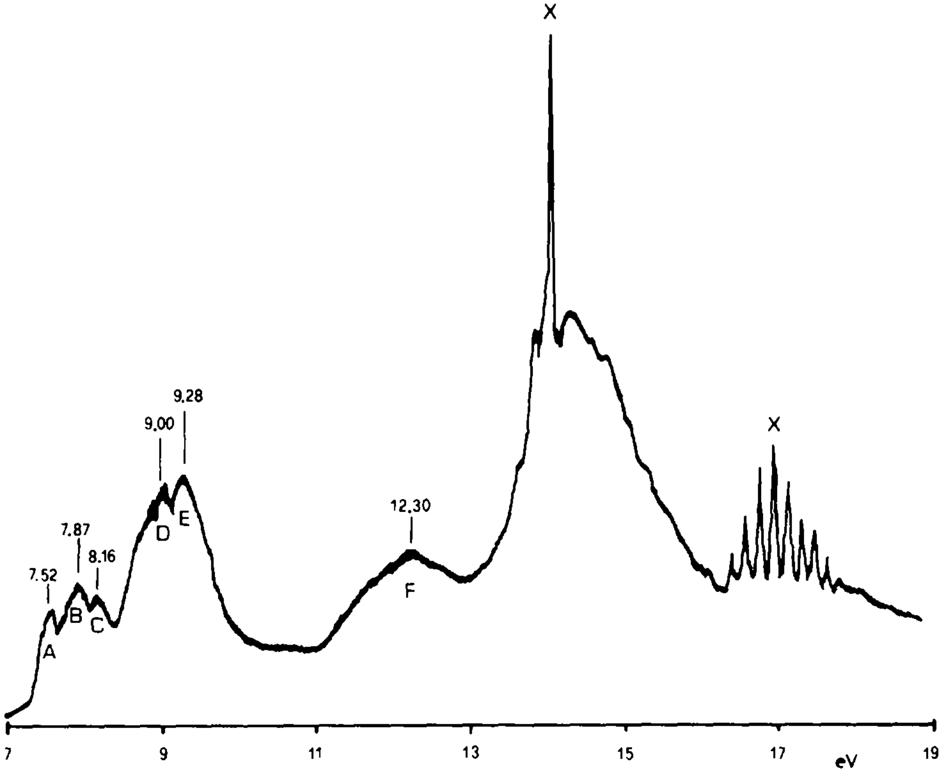


Fig. 1. He(I) excited PE spectrum of $Ru_4(CO)_{12}(Ph-C_2-H)$. Bands due to free CO are labelled as X.

was poorer than that of the related triangular clusters previously investigated [3,4]; the presence of free CO (labelled as X in Fig. 1) indicates that at the temperatures (110–130°C) necessary to obtain a sufficient count rate some decomposition of the sample takes place. However, spectral patterns obtained from different runs at various temperatures were identical in relative intensities and positions of the bands, indicating that the contribution of other volatile species to the spectrum is negligible.

Despite the large number of valence electrons in Ib we can readily assign the bands in Fig. 1 on the basis of purely comparative arguments. The available body of data on organometallic carbonyl clusters [3,4,15] allows us to divide the observed range of IE into three distinct regions (a = 6–10 eV; b = 10–13 eV; c = 13–18 eV). In region a are usually found the ionizations from nd metal based MOs having M–M bonding and non-bonding character. Region b contains ionizations from those MOs mainly localized on the organic portion of the molecule and representing cluster-substrate bonding interactions. Finally, region c (usually too complex for detailed assignments) corresponds to ionizations of the carbonyl group MOs (related to the 5σ, 1π and 4σ MOs in free CO) and of the inner levels of the organic substrates. Regions a and b, then, represent two spectral windows suitable for evaluating the mutual perturbations of the metallic and organic parts of the molecule, respectively. On this basis, bands A, B and C of Fig. 1 are related to Ru–Ru bonding MOs; the corresponding IEs (7.52, 7.87, 8.16 eV) can be compared with the Ru–Ru bonding IEs of $Ru_3(CO)_{12}$ (7.91 eV) [15d] and of $HRu_3(CO)_9(C_2-R)$ (7.94, 8.21 eV) [3].

Bands D and E are similarly related to $4d$ non-bonding MOs which are only slightly perturbed by back-bonding interactions, with either the carbonyls or the alkyne. However, PE results on phenylacetylene [16] suggest that band E also includes the outer π ionizations of the phenyl ring. The actual IE values of these π ionizations cannot be extracted from the body of $4d$ ionizations, although this has been done for related Co clusters [15c]. In the cobalt systems the larger relaxation energies associated with $3d$ ionizations [17] shift the non-bonding IEs toward lower energy, allowing the phenyl bands to be detected separately.

In region *b*, we expect two ionizations originating from the π-alkyne orbitals mixed with suitable cluster orbitals: in fact we observe only a broad envelope (labelled F in Fig. 1) centered around 12.3 eV, to which the inner σ and π MOs of the phenyl ring also certainly contribute to some extent. This prevents the accurate determination of the alkyne π IEs. However, the low IE side of band F (11.07 eV) provides a threshold value for these ionizations; interestingly, this value is significantly higher than those previously observed for μ_3-η^2- and μ_2-η^2-alkyne complexes [4,15b,15e]. This shift toward higher IEs can be interpreted as evidence for an increased interaction between the alkyne and the metallic framework, although there may be other minor contributions to this shift [18].

A more detailed discussion of the various contributions to this interaction is given in the following paragraph on the basis of the results of the quantum mechanical calculations.

Theoretical data. The complexity of the title molecule prevents the use of accurate quantum mechanical approaches. We resorted, then, to the semiempirical CNDO method [10,11] which has been shown to be sufficiently accurate for describing the electronic structure of various related molecules [3,4,15d].

The eigenvalues and the population analysis of the 18 outermost occupied MOs of the model molecule Ia are shown in Table 1. The MOs are labelled according to the C_{2v} point group with the XZ plane containing the alkyne group.

The validity of the CNDO approach is supported by the satisfactory agreement between the experimental and calculated (through Koopmans' theorem [19]) IEs, especially when the relative energy ordering of the MOs is considered (Fig. 2). In particular, the CNDO results assemble the 18 outmost MOs into three groups whose overall order and character correspond to the assignments of the PE spectrum proposed on the basis of comparative arguments.

The highest metal–metal bonding character is associated with the three outermost occupied MOs ($26a_1$, $15a_2$, $20b_2$); the $26a_1$ HOMO relates almost uniquely to the Ru'–Ru' bond, while the other two are essentially Ru'–Ru'' bonding in character.

The twelve subsequent MOs lie within a 1.8 eV range; they almost are localized on the metallic centres (70–90%) and have predominant contributions from $4d$ AOs. They essentially represent non-bonding $4d$ MOs which are partially involved in back-bonding interactions with π^* carbonyl orbitals. They have counterparts in the MOs from $9e''$ to $9a_1'$ of $Ru_3(CO)_{12}$ [15d] and $36a'$ to $32a'$ of $HRu_3(CO)_9(C_2-CH_3)$ [3]. Minor contributions from alkyne carbon atoms are evident for some of these orbitals ($15a_2$, $20b_1$, $13a_2$); their symmetry properties indicate that some mixing with π^* alkyne MOs has occurred. The relatively high symmetry of Ia (C_{2v}) allows us to distinguish by symmetry arguments which of the alkyne frontier MOs is involved (see Table 2); such an analysis leads us to conclude that the inner $17b_1$ MO describes most of the back-bonding interaction with the π^* (||) MO. Because of

TABLE I

CNDO RESULTS FOR $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}H\text{-}C{\equiv}C\text{-}H)$ [a]

MO	Eigenvalue (eV)	Population (%)					Dominant character
		2 Ru′	2 Ru″	2 C	2 H	12 CO	
$26a_1$ HOMO	−6.26	50	34	2	1	13	Metal–metal bonding MOs
$15a_2$	−6.31	40	45	5	0	10	
$20b_2$	−6.84	44	42	0	0	14	
$20b_1$	−8.12	43	35	9	2	11	4*d* metallic MOs mainly maintaining atom-like character (non-bonding)
$19b_2$	−8.56	72	15	1	0	12	
$19b_1$	−8.56	83	3	0	0	14	
$25a_1$	−8.67	50	37	1	0	12	
$14a_2$	−8.73	64	23	0	0	13	
$24a_1$	−8.99	81	2	0	0	17	
$18b_1$	−9.03	48	31	1	0	20	
$23a_1$	−9.13	19	65	1	0	15	
$18b_2$	−9.28	1	89	0	0	10	
$17b_2$	−9.46	11	78	1	0	10	
$22a_1$	−9.58	18	71	1	1	9	
$13a_2$	−9.85	17	66	4	0	13	
$17b_1$	−10.58	35	1	27	15	22	Cluster to alkyne back-donation MO (see text)
$21a_1$	−13.63	11	5	67	6	11	π alkyne MOs involved in the alkyne to cluster donation
$16b_2$	−13.64	6	25	45	0	24	

[a] Reported up to 14 eV.

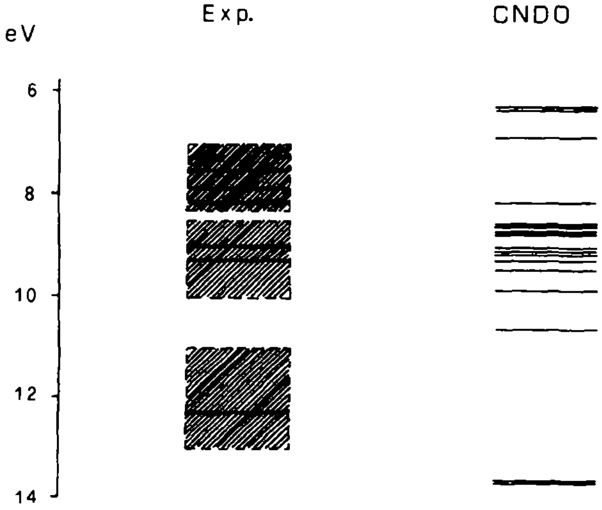
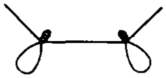
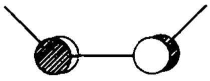
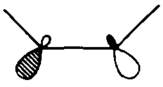
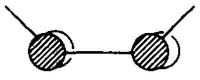


Fig. 2. Comparison between the computed IEs for Ia and the experimental IEs of Ib.

TABLE 2

SYMMETRY PROPERTIES OF FRONTIER ALKYNE MOs IN C_{2v} SYMMETRY [a]

Symmetry	Alkyne MO [b]	Schematic description
a_1	$\pi\ (\parallel)$	
a_2	$\pi^*(\perp)$	
b_1	$\pi^*(\parallel)$	
b_2	$\pi(\perp)$	

[a] Axes choice so that XZ plane contains the alkyne group. [b] $\parallel$, $\perp$ refer to the alkyne plane.

overlap arguments, this back-donation mainly involves Ru′ atoms, as indicated by the overlap population analysis of this specific MO (Ru′–C = $0.15e^-$; Ru″–C = $0.04e^-$). The π^* (‖) was also found to be the main π-acceptor orbital in $Fe_3(CO)_9(RC_2R)$ by the CNDO calculations and the corresponding MO was detected as a separate band at 9.86 eV in its PE spectrum [4]. In the present case, however, we have no spectral evidence for a similar separate band which can be attributed to the $17b_1$ MO. Differences in the electronegativities of iron and ruthenium may contribute to the shift in this band.

The two quasi-degenerate $21a_1$ and $16b_2$ inner MOs represent the $\pi(\parallel)$ and $\pi(\perp)$ alkyne MOs (Table 2) mixed with suitable cluster orbitals; it is of interest to note that this mixing is considerably larger for the $16b_2$ MO (Table 1). This means that a large portion of the alkyne to cluster charge transfer involves donation from $\pi(\perp)$ to Ru″ type metal atoms.

Evidence for the different roles played by the two types of ruthenium atoms emerges also from the analysis of the electron density distribution obtained from the CNDO atomic charges and overlap populations (Fig. 3). The charge differences between Ru′ and Ru″ atoms should be noted: Ru′ atoms have higher positive charges because of their strong back-bonding interactions with the alkyne, while Ru″ atoms, which mainly receive electrons form the alkyne, have significantly higher electron densities. The difference in the electronic charge between Ru′ and Ru″ is

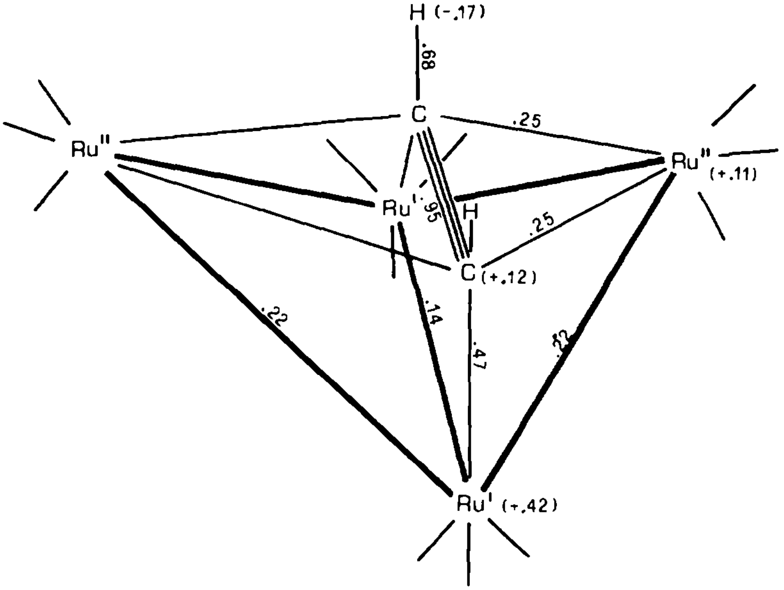


Fig. 3. Gross atomic charges and bond overlap populations of Ia (electrons).

much larger than that observed for the different ruthenium atoms in Ru_3 organometal clusters [3]. In this context a detailed analysis of the bond overlap populations is also quite instructive. In Table 3 we give the bond overlap populations of the Ru′-C and Ru″-C couples of atoms divided into the contributions due to the a_1, b_1, a_2, b_2 MOs. Referring back to Table 2 and using the informations in Table 3 it can be seen that there is a difference in the balance between the donation/back-donation interaction in the two inequivalent Ru′ and Ru″ sites. In the Ru′-C bond both donation and back-donation mechanisms contribute to a similar extent. On the other hand, the Ru″-C interaction arises primarily from an alkyne to Ru″ donation.

The small overall negative charge localized on the alkyne group ($-0.10e^-$) is consistent with this picture; this value is much lower than that found in $Fe_3(CO)_9(HC_2H)$ [4], where the back-donation was found to play a more important role in the bonding. In the present case the efficient charge donation to Ru″ atoms tends to relieve the alkyne of the negative charge. Furthermore, since both the donation and back-donation mechanisms tend to reduce the C≡C bond overlap population [18], the value of this parameter obtained in this case ($0.95e^-$) is significantly lower than any value so far calculated for μ_3-η^2 systems [3,4] using the same CNDO formalism *. In this sense our CNDO calculation reproduces the structural evidence of the enhanced activation of the μ_4-η^2 coordinate alkyne when compared to the μ_3-η^2 and μ_2-η^2 alkynes [20].

In conclusion, the results suggest that this particularly stable arrangement must be favoured by a sort of synergic mechanism in which the alkyne mainly donates

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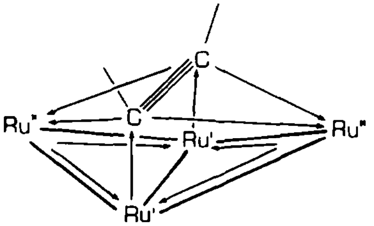
* C≡C bond overlap population for a free acetylene in a molecular geometry identical to that found in the cluster derivative [12] amounts to $1.41e^-$.

TABLE 3

ALKYNE-CLUSTER OVERLAP POPULATIONS DIVIDED INTO THE FOUR a_1, b_1, a_2, b_2 SETS (in electrons)

Couple of atoms	a_1	b_1	a_2	b_2	Total
Ru′–C	0.19	0.23	0.02	0.03	0.47
Ru″–C	0.05	0.03	0.03	0.14	0.25

charge to Ru″ atoms while receiving charge from Ru′ atoms (see structure A). The two highly polarizable Ru_3 triangles can then serve to balance these charge shifts. This mechanism is expected to be even more efficient in the case of the chemisorbed alkyne over a step site of a metal surface, where the presence of supporting metal atoms around the step site makes it even more polarizable.



(A)

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