744 *Inorg. Chem.* **1983**, *22*, 744-748

Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Padova, 35100 Padova, Italy,
and the Istituto di Chimica Generale ed Inorganica, Università di Torino, Torino, Italy

UV Photoelectron and Theoretical Studies of Organometal Carbonyl Clusters of Ruthenium and Osmium. μ-Hydrido-μ_3-Alkynyl Triangulo Cluster Compounds

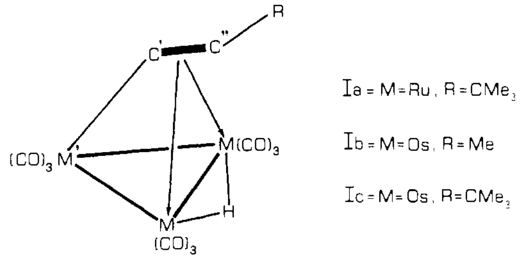
GAETANO GRANOZZI,*[1a] EUGENIO TONDELLO,[1a] RENZO BERTONCELLO,[1a] SILVIO AIME,[1b]
and DOMENICO OSELLA[1b]

Received May 7, 1982

The electronic structure of μ-hydrido-μ_3-alkynyl triangulo clusters of ruthenium and osmium is discussed on the basis of their He I excited vapor-phase photoelectron spectra and on the basis of CNDO quantum-mechanical calculations. The theoretical results contribute to the discussion of the highly complex PE spectra and provide novel insights into the bonding scheme of these molecules. The most interesting feature that emerges from this study is the inadequacy of the usual representation of the molecular structure with three metal-metal bonds since the μ-H-bridged metal atoms show a very low bond overlap population. On the other hand, the commonly accepted qualitative description of the alkynyl-cluster interactions, in terms of one σ bond and two weaker π interactions, receives strong support. Some selected features of the reactivity of these clusters are discussed on the basis of the emerging electronic structural picture.

Introduction

Reactions between the carbonyl clusters of Ru and Os and terminal alkynes occur mainly through an oxidative-addition pathway[2] and yield stable $HM_3(C_2R)(CO)_9$ derivatives (see I). The observation that compound I can also be obtained from acetylenic diols ($HOR_2C—C{\equiv}C—CR_2OH$) through a C—C σ-bond cleavage outlines the stability of the alkynyl fragment on an M_3 triangle.[2d]



I

Although the reactivity of these compounds has been extensively investigated,[3-6] spectroscopic studies have been limited to the observation of ^{13}C NMR spectra.[7] Among the reactivity studies, it has been shown that I reacts with strong protic acids to give mono- and dicationic adducts,[3] while with Lewis bases (phosphines and phosphites) mono- and disubstituted derivatives[4] have been obtained. On the other hand, treatment of Ia with KOH/EtOH gives rise to the anionic species $[Ru_3(C_2CMe_3)(CO)_9]^-$, whose X-ray structure shows that the basic structure of Ia has been maintained.[5] Besides the intrinsic interest in this chemistry, a better understanding of the bonding scheme in I can contribute to develop the approach based on the cluster-surface analogy.[8] Compound I can be envisaged as a model for the dissociative chemisorption of acetylenes on metallic surfaces involving C-H bond activation.

Table I. Ionization Energy Data (eV) for the Studied Organometal Carbonyl Clusters[a]

Ia	Ib	Ic
7.94 (A)	8.2 (A)	8.10 (A)
8.21 (B)	8.6 (B)	8.56 (B)
	8.82 (B')	8.8 (B')
9.10 (C)	9.4 (C)	9.3 (C')
9.5 (D)	9.90 (D)	9.5 (C)
		9.85 (D)
10.30 (E)	10.83 (E)	10.8 (E)
11.4 (F)	12.0 (F)	11.5 (F)
11.8 (G + H)	12.55 (G)	12.1 (G + H)
	13.08 (H)	

[a] Band labels are in parentheses.

Recently we have shown that vapor-phase UV photoelectron (PE) spectroscopy can be a valuable tool in the understanding of the electronic interactions in transition-metal carbonyl cluster derivatives, particularly when it is coupled with quantum-mechanical calculations.[9-12] In this paper we report the He I excited PE spectra of Ia-c[13] together with CNDO calculations; this study represents a development of our previous investigations concerning the M_2-CH_2[11] and M_3-CH[12] multicentered interactions.

Experimental Section

Compounds Ia-c were prepared according to the literature procedures.[2] We failed in an attempt to prepare the Ru analogue of Ib from $Ru_3(CO)_{12}$ and propyne: extensive polymerization of the alkyne has been noted to occur rapidly.

Photoelectron spectra were run on a Perkin-Elmer PS-18 spectrometer using a heated inlet probe system. They were measured in the 65-85 °C temperature range with a count rate between 1500 and 3000 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.

Quantum-mechanical calculations were performed by a version of the CNDO method[14] suitable for transition-metal complexes. Ru

---

(1) (a) Università di Padova. (b) Univeristà di Torino.

(2) (a) Sappa, E.; Gambino, O.; Milone, L.; Cetini, G. *J. Organomet. Chem.* **1972**, *39*, 169-172. (b) Gambino, O.; Ferrari, R. P.; Chinone, M.; Vaglio, G. A. *Inorg. Chim. Acta* **1975**, *12*, 155-158. (c) Gambino, O.; Sappa, E. *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat.* **1973-1974**, *108*, 212. (d) Aime, S.; Milone, L.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1168-1169.

(3) Barner-Thorsen, C.; Rosenberg, E.; Saatjian, G.; Aime, S.; Milone, S.; Osella, D. *Inorg. Chem.* **1981**, *20*, 1592-1597.

(4) Jangala, C.; Rosenberg, E.; Skinner, D.; Aime, S.; Milone, L.; Sappa, E. *Inorg. Chem.* **1980**, *19*, 1571-1575.

(5) Barner-Thorsen, C.; Hardcastle, K. I.; Rosenberg, E.; Siegel, J.; Lanfredi, A. M. M.; Tiripicchio, A. *Inorg. Chem.* **1981**, *20*, 4306-4311.

(6) Castiglioni, M.; Gervasio, G.; Sappa, E. *Inorg. Chim. Acta* **1981**, *49*, 217-225.

(7) Aime, S.; Gambino, O.; Milone, L.; Sappa, E.; Rosenberg, E. *Inorg. Chim. Acta* **1975**, *15*, 53-56.

(8) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91-137.

(9) Ajò, D.; Granozzi, G.; Tondello, E.; Fragalà, I. *Inorg. Chim. Acta* **1979**, *37*, 191-193.

(10) Granozzi, G.; Tondello, E.; Bénard, M.; Fragalà, I. *J. Organomet. Chem.* **1980**, *194*, 83-89.

(11) Granozzi, G.; Tondello, E.; Casarin, M.; Ajò, D. *Inorg. Chim. Acta* **1981**, *48*, 73-76.

(12) Granozzi, G.; Tondello, E.; Ajò, D.; Casarin, M.; Aime, S.; Osella, D. *Inorg. Chem.* **1982**, *21*, 1081-1084.

(13) Some of the present results have been preliminarily communicated: Granozzi, G.; Tondello, E.; Aime, S.; Osella, D. EUCHEM Conference on the Challenge of Polynuclear Inorganic Compounds, Venice, Sept 28-30 1981; communication C9.

0020-1669/83/1322-0744$01.50/0 © 1983 American Chemical Society

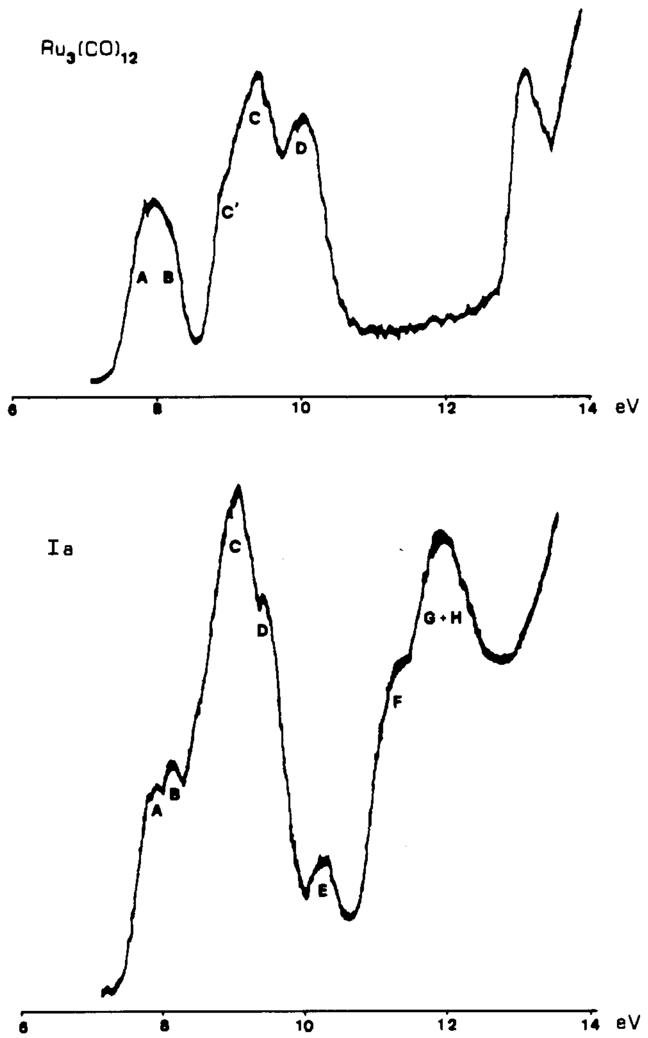


Figure 1. Low-energy region of the He I excited PE spectra of $Ru_3(CO)_{12}$ and Ia.

semiempirical parameters were obtained[14] from atomic spectroscopical data whereas the C, O, H parameters are Pople's standard ones.[15] The geometrical data used in the calculations refer to the neutron and X-ray structural determination of Ia[16] (C_s point group). The computed eigenvalues were related to the measured IEs with the assumption of the validity of Koopmans' theorem.[17] Atomic gross charges and overlap populations were obtained by Mulliken's population analysis[18] of the deorthogonalized[19] eigenvectors.

Results and Discussion

Preliminary Considerations. X-ray and neutron diffraction studies of Ia[16] have shown that the organic ligand is coordinated in a $\mu_3(\eta^2)$ perpendicular fashion.[20] The alkynyl ligand acts as a five-electron donor group through a σ M'–C' bond and two π bonds, whereas the μ-hydride lies below the metallic triangle opposite the organic fragment. In the empirical EAN formalism the title compounds have been classified as 48-electron clusters. Within the PSEP (polyhedral skeletal electron-pair) formalism, developed by Wade and Mingos,[21] cluster I can be viewed as a closo trigonal bipyramid ($S = 6$, $n = 5$), where the acetylenic carbon atoms occupy basal and apical vertices, respectively.[22] The shorter Ru–Ru distances in Ia[16] compared to those in $Ru_3(CO)_{12}$[23] might be due to optimization of overlap with the alkynyl fragment. Such "plastic" behavior of the metallic core can be related to the flat energy minima associated with the M–M potential curves.[24]

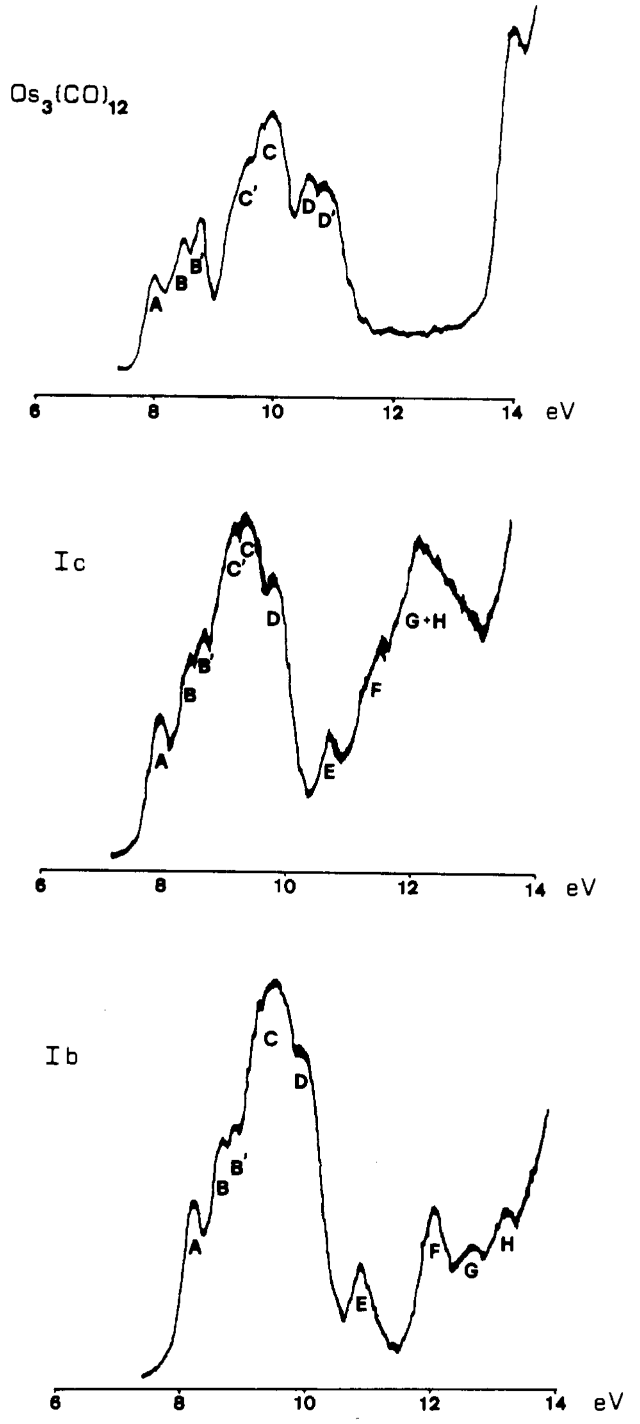


Figure 2. Low-energy region of the He I excited PE spectra of $Os_3(CO)_{12}$, Ib, and Ic.

---

(14) Tondello, E. *Inorg. Chim. Acta* **1974**, *11*, L5–L6.

(15) Pople, J. A.; Segal, G. A. *J. Chem. Phys.* **1966**, *44*, 3289–3296.

(16) Catti, M.; Gervasio, G.; Mason, S. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2260–2264.

(17) Koopmans, T. C. *Physica (Amsterdam)* **1933**, *1*, 104–113.

(18) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833–1846.

(19) Löwdin, P. O. *J. Chem. Phys.* **1950**, *18*, 365–375.

(20) Thomas, M. G.; Muetterties, E. L.; Day, R. O.; Day, V. W. *J. Am. Chem. Soc.* **1976**, *98*, 4645–4646.

(21) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66. (b) Mingos, D. M. P. *Nature (London) Phys. Sci.* **1972**, *236*, 99–102.

(22) It is interesting to note, however, that the same polyhedral arrangement is forecasted for $Fe_3(C_2R_2)(CO)_9$ regardless of the fact that this compound is described as a 46-electron coordinatively unsaturated cluster derivative.

(23) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655–2659.

(24) Vahrenkamp, H. *Angew. Chem.* **1978**, *17*, 379–392.

Table II. CNDO Results for $Ru_3(CO)_{12}$[a]

MO	eigenvalue, eV	% population 3 Ru	 6 CO_{ax}	 6 CO_{eq}	dominant character
$7a_2'$ (LUMO)	+0.05	86	3	11	Ru–Ru antibonding
$15e'$ (HOMO)	−7.38	86	7	7	Ru–Ru bonds
$10a_1'$	−7.48	69	18	13	
$9e''$	−9.25	89	6	5	4d metal-based MOs mainly maintaining atomlike character (nonbonding)
$14e'$	−9.33	87	0	13	
$2a_1''$	−9.39	86	7	7	
$8e''$	−9.84	83	11	6	
$6a_2''$	−10.12	83	13	4	
$9a_1'$	−10.29	92	0	8	
$13e'$	−15.65	22	44	34	onset of carbonyl MOs

[a] Reported up to 16 eV.

A convenient starting point for the forthcoming discussion is the photoelectron spectra reported for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$[9,25] (see Figures 1 and 2[26]). The bands labeled A and B have been assigned to ionizations from the two MOs (a_1' and e' in D_{3h} symmetry) representing the M_3 ring metal–metal bonding. Splitting in two components of band B in the case of $Os_3(CO)_{12}$, by operation of the spin–orbit coupling mechanism, supports the proposed assignment. Higher IE bands, labeled C and D, have been attributed to the 18 electrons occupying MOs having "d" lone-pair character that are partially involved in π-back-bonding interactions with the carbonyls.

These assignments have been sustantiated by the results of CNDO calculations on $Ru_3(CO)_{12}$,[9] whose outmost eigenvectors are also reported in Table II for comparative purposes. Recently, $X\alpha$–DV calculations on the same molecule showed an excellent agreement with our previous CNDO ones;[27] we are therefore encouraged to continue the use of the simpler CNDO scheme to study the organometal cluster derivatives reported herein.

UV PE Spectra. For comparison purposes with the parent carbonyl clusters, it is convenient to divide the PE spectra of Ia–c (Figures 1 and 2) into two portions (region a, up to 10 eV; region b, 10–14 eV). It is reasonable to say that region a should contain ionizations from the M_3 ring, whereas region b should mainly involve ionizations derived from the MOs representing the alkynyl substrate interacting with the metallic framework.

Bands A and B in the spectrum of Ia are probably related to the first band in the PE spectrum of $Ru_3(CO)_{12}$; i.e., they represent ionizations from the Ru–Ru bonding MOs. The lower symmetry (C_s) of Ia with respect to that of the parent carbonyl (D_{3h}) can qualitatively explain the observed splitting. The relative intensity ratio between A + B and C + D bands in Ia indicates that A + B represents only ionizations corresponding to four electrons in place of the expected six electrons; this is an experimental indication that the bonding of the ruthenium ring in the organometal cluster is rather different when compared to that in the parent carbonyl molecule. In the same spectral region of Ib and Ic (Figure 2) we find three bands (A, B, B′). Noting the results found for Ia and for a series of derivatives obtained by oxidative addition of an internal alkyne to $Os_3(CO)_{12}$ (namely, μ_3-allenyl and μ_3-allyl derivatives)[28] and bearing in mind that the low molecular symmetry does not allow the presence of degenerate e′ MOs, we propose to relate bands A, B, and B′ in Ib and Ic to three distinct MOs, all having bonding Os–Os character, which are to be related with the $a_1' + e'$ Os–Os MOs of $Os_3(CO)_{12}$.[25] The body of these results suggests that a smaller perturbation is induced on the M_3 ring in osmium clusters than in ruthenium ones, in accordance with the well-known higher Os–Os bond strength.

If bands C and D, in both Ru and Os derivatives, are related to bands C and D of the parent $M_3(CO)_{12}$, then they represent ionizations from MOs maintaining metal "d" character (essentially nonbonding with some mixing with carbonyl $2\pi^*$ MOs). With respect to the binary carbonyls, there is a smaller C–D separation and an overall shift toward lower IEs. The former effect probably depends on the loss of pseudooctahedral symmetry around the metallic atoms whereas the latter can be interpreted, in the chemical shift picture, as reflecting larger electron densities on the metallic centers; the absence of three carbonyl groups in comparison to the situation for the parent binary carbonyls may account for a large portion of this shift.

The low intensity of band E, which has been found almost unshifted in the spectra of Ia–c, has to be related to one ionization. A criterion for the assignment of this band is suggested by the observation that it is invariably present in other related organometal M_3 clusters of Ru and Os with a μ-H bridge, independent of the organic substrate.[28] Therefore, it is reasonable to assign band E to an ionization from a molecular orbital mainly localized on the HM_3 moiety; it can be related either to a three-center two-electron M–H–M MO[29,30] or to a stabilized "d" metallic lone pair.[31]

An attempt to get some more insight into the nature of this band E was made by recording the He II excited PE spectra. Very slight changes in the relative intensity pattern of bands A–E have been found, which allow us to assess similar contributions from *n*d AOs to all of these bands. This evidence would support the assignment of band E to an ionization from an orbital with strong d character; preferential interaction with the bridging hydride would concur with the stabilization of this lone pair in character MO.

Moving to spectral region b, we note that only Ib exhibits three resolved bands, labeled F–H. In Ia and Ic, this spectral region is markedly obscured by the typical ionizations of the σ(C–C) and σ(C–H) levels of the *tert*-butyl group. In the following we shall confine our discussion to Ib only. We expect to find, on the basis of qualitative arguments, ionizations from two π alkynyl-M_2 bonds and from two σ bonds (C′–Os′ and C″–CH_3) in this region. The only pertinent literature data useful to recall in this context are those relative to the free methylacetylene;[33] the two bands at 10.37 and 14.6 eV have been assigned to the two degenerate π bonds and to the σ C–CH_3 bond, respectively. The shift of the former toward lower IE (by 1.02 eV) with respect to the acetylene peak has been attributed to hyperconjugative and inductive effects of

---

(25) Green, J. C.; Mingos, D. M. P.; Seddon, E. A. *Inorg. Chem.* **1981**, *20*, 2595–2602.

(26) The spectral region up from 14 eV consists of a very broad and featureless envelope containing the ionizations from levels primarily localized on the carbonyl groups (5σ, 1π, 4σ MOs of free carbon monoxide). Since this spectral region is not of relevance for the purposes of this paper, it has been omitted from Figures 1 and 2.

(27) Manning, M. C.; Trogler, W. C. *Coord. Chem. Rev.* **1981**, *38*, 89–138.

(28) Granozzi, G.; Bertoncello, R.; Aime, S.; Osella, D. *J. Organomet. Chem.* **1982**, *229*, C27–C30.

(29) Churchill, M. R.; De Boer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843–1853.

(30) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176–183.

(31) Recently, low-intensity features in the 11.5–12.5-eV region have been assigned to M–H–M bonds in other hydrido carbonyl clusters.[25,32] Since in our spectra this region is obscured by bands associated with alkynyl-based MOs, we cannot exclude the presence of a similar feature also in this case. However, it would be not unreasonable to observe some shift in the signal for the M–H–M bond on going from simple unsubstituted hydrido carbonyls to organometal carbonyl derivatives.

(32) Wong, K. S.; Dutte, T. K.; Fehlner, T. P. *J. Organomet. Chem.* **1981**, *215*, C48–C52.

(33) Ensslin, W.; Bock, H.; Becker, G. *J. Am. Chem. Soc.* **1974**, *96*, 2757–2762.

Table III. CNDO Results for $HRu_3(\mu_3\text{-}C'{\equiv}C''\text{-}CH_3)(CO)_9$[a]

MO	eigenvalue, eV	% population							dominant character
		Ru							
		2 Ru	Ru'	H	9 CO	C'	C''	CH_3	
29a'' (LUMO)	+1.37	41	46	0	13	0	0	0	Ru–Ru antibonding
28a'' (HOMO)	−6.99	54	31	0	8	1	5	1	Ru–Ru' bonds
37a'	−7.22	48	32	0	13	5	2	0	
36a'	−8.46	53	19	10	5	3	7	3	4d metal-based MOs mainly maintaining atomlike character (nonbonding)[b]
27a''	−8.63	82	5	0	10	1	2	0	
35a'	−8.87	46	41	1	12	0	0	0	
26a''	−8.92	84	3	0	8	4	1	0	
25a''	−9.02	72	17	0	11	0	0	0	
34a'	−9.09	56	30	0	13	0	1	0	
33a'	−9.38	47	39	0	12	2	0	0	
24a''	−9.42	27	60	0	12	0	0	1	
32a'	−9.83	61	17	7	13	1	1	0	
31a'	−10.07	45	25	15	14	0	1	0	
23a''	−13.47	19	7	0	15	24	21	14	π C'≡C'' interacting with bridged Ru atoms
30a'	−13.87	10	9	1	8	27	22	23	
29a'	−14.71	9	16	0	13	40	14	8	Ru'–C' σ bond

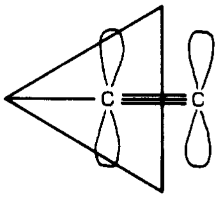
[a] Reported up to 16 eV. [b] 36a', 32a', and 31a' have Ru–H–Ru character also.

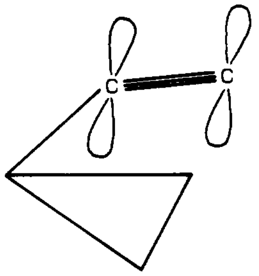
the methyl group.[33] Due to the lack of further pertinent PE data for use as a comparative assignment criterion, safe assignments for all F–H bands cannot be produced at the moment. Nevertheless, we can tentatively suggest rational assignments, which are based on the perturbations that are expected for the methylacetylene MOs and on the relative intensity ratio found among bands F, G, and H ($\simeq$2:1:1). We propose to relate band F in Ib to the band found at 10.37 eV in the free methylacetylene, i.e., to the two π C≡C bonds interacting with the two bridged Os atoms. The shift toward higher IE should account for alkyne donation to the Os centers and for partial cancellation of the methyl hyperconjugative effect. The latter effect can be expected because of the partial rehybridization of C'' found by the molecular structure determination of Ia.[16] For a similar reason, with the effect acting in the opposite direction, band H is to be related to the σ C–CH$_3$ bond. Consequently, we propose to assign band G to the σ Os'–C' bond. The theoretical results (Table III), which will be discussed in the following section, are consistent with the assignments proposed above.

Theoretical Data. Eigenvalues and eigenvectors of the 15 outermost occupied MOs and of the LUMO of $HRu_3(\text{-}C'{\equiv}C''\text{—}CH_3)(CO)_9$ are reported in Table III. Bearing in mind the complexity of this molecule, we can obtain a satisfactory agreement between the computed (via Koopman's theorem) and experimental IEs, as in the case of $Ru_3(CO)_{12}$.[9]

Orbitals 28a'' and 37a' (Table III) are the only two MOs maintaining a net Ru–Ru' bonding character. Simultaneously, however, 28a'' displays antibonding character with respect to two bridged Ru atoms. Analysis of the separate 5sp and 4d atomic contributions to these two MOs indicates that both are to be related with the 15e' HOMO of $Ru_3(CO)_{12}$ (Table II) since the 10a$_1$' MO of $Ru_3(CO)_{12}$ has a large contribution from the 5sp AOs, which is not present in either of the 28a'' and 37a' MOs presently analyzed. The 10a$_1$' MO of the parent carbonyl is strongly stabilized by the interaction with the bridging hydride, giving rise to the 36a' MO. The H 1s AO interacts preferentially with the a$_1$' type Ru–Ru MO of $Ru_3(CO)_{12}$ mainly because the spatial characteristics of this MO (with lobes pointing out of the M_3 plane) allow good overlap.

The nine MOs from 27a'' to 31a' (Table III) are essentially nonbonding in character and are mainly localized on the 4d metallic AOs. Some admixture with 2π* carbonyl MOs indicates their involvement in the back-bonding interactions with the carbonyls. They find their counterpart in the MOs from 9e'' to 9a$_1$' (Table II) of $Ru_3(CO)_{12}$. As a whole they are slightly destabilized with respect to the corresponding MOs of $Ru_3(CO)_{12}$, in agreement with the experimental findings discussed in the previous section. Among them, 32a' and 31a' show significant Ru–H–Ru bonding character. The 23a'' and 30a' MOs, close in energy, are mainly localized on the bridged Ru atoms and the organic C' and C'' carbon atoms. Inspection of the relative eigenvectors reveals π-bonding C'≡C'' contributions with nodal planes lying in the molecular symmetry plane and perpendicular to it:





These two MOs mainly represent the π C'≡C'' bonds interacting with the two bridged Ru atoms; the 30a' MO, however, shows a significant Ru'–C' σ-bonding character because the spatial arrangement of the alkynyl fragment on the metallic triangle tends to mix the two contributions (Ru'–C' σ and Ru_2—C'≡C'' π) in a' type MOs. The subsequent 29a' MO, in turn, is localized on the Ru' and C' atoms and describes mainly the Ru'-C' interaction.

A final consideration concerns the 29a'' LUMO. As already found in $Ru_3(CO)_{12}$ (Table II), this orbital is metal–metal antibonding. Interestingly enough, the alkynyl fragment does not contribute to this MO and the destabilization with respect to the 7a$_2$' LUMO of the parent carbonyl (Table II) may be ascribed to second-order perturbation effects either from the carbonyl network or from the organic portion itself.[34]

The atomic gross charges and overlap populations (Figure 3) obtained from the CNDO eigenvectors allow us to discuss the electronic density distribution and to gauge the interaction strengths in the cluster, because these quantities can be compared with those of $Ru_3(CO)_{12}$ (Figure 4). In accord with the interpretation of the experimental data, each ruthenium atom bears a larger electron density with respect to the parent

---

(34) It is important to recall that the 7a$_2$' LUMO of $Ru_3(CO)_{12}$ represents in-plane antibonding Ru–Ru contributions so that first-order perturbation induced by the removal of one axial carbonyl per Ru atom in the formation of the organometal cluster is expected to be negligible.

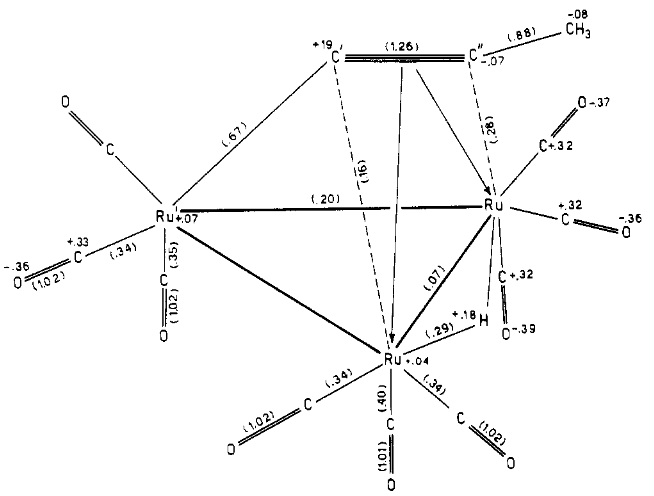


Figure 3. CNDO atomic charges and bond overlap populations of $HRu_3(-C{\equiv}C{-}CH_3)(CO)_9$.

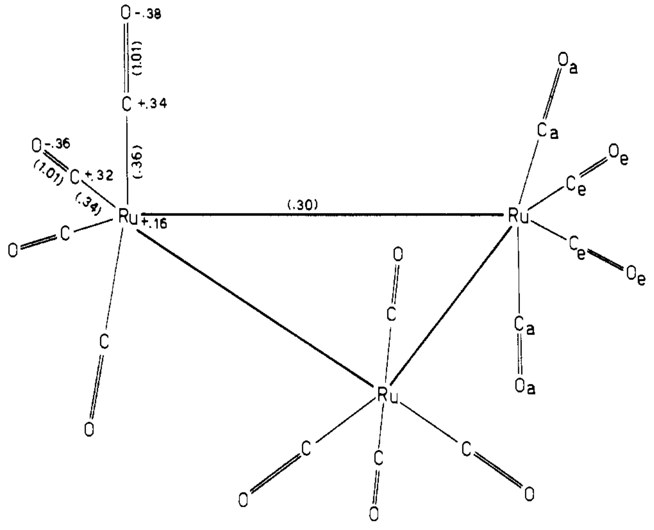


Figure 4. CNDO atomic charges and bond overlap populations of $Ru_3(CO)_{12}$.

carbonyl. It is not possible, however, to evaluate which of the two factors, i.e., the removal of one axial carbonyl or the interaction with the electron-rich alkynyl fragment, plays the major role in determining such electron enrichment of the metallic centers. Note the change of overlap populations within the metallic framework in the cluster. The two Ru′–Ru bonds carry a smaller overlap population with respect to $Ru_3(CO)_{12}$ whereas the bridged Ru–Ru overlap is particularly small (Figure 3). These results illustrate the inadequacy of the usual representation of the molecular structure of Ia with three metal–metal bonds.

Concerning the alkynyl–cluster interactions, the Ru′–C′ couple of atoms presents the largest overlap population (Figure 3); this feature is in line with the commonly accepted qualitative description of the bonding in such compounds on the basis of one Ru′–C′ stronger bond and two weaker π interactions. It is instructive to compare the C′≡C″ overlap population (1.26 e) with the value computed for a free acetylene (C≡C distance 1.20 Å) and for a distorted acetylene whose C≡C distance was assumed to be 1.31 Å (as in the cluster). In the former we found an overlap population of 1.82 e and in the latter a value of 1.50 e. These results demonstrate that the C≡C bond order reduction caused by the donation and back-donation mechanisms is of the same magnitude of that consequent to the elongation of the C≡C bond distance.

Finally, notice the marked difference in the atomic charges of C′ and C″ (which are reflected in the ^{13}C chemical shifts[7]); the positive atomic charge of C′ reflects the strong charge donation to Ru′. This charge polarization could play a role in the chemical reactivity of the bound unsaturated organic substrate.

The electronic structure of the title molecules suggests to us some rationalizations for selected features of their reactivity in comparison to that of $Ru_3(CO)_{12}$.

(i) Electrophilic addition of protic acids: On the assumption that protonation of $Ru_3(CO)_{12}$ occurs on one edge of the M_3 cluster, as has been shown unambiguously for $Os_3(CO)_{12}$,[35] the ready protonation (and stability of the product) of Ia with respect to that of $Ru_3(CO)_{12}$ can be accounted for in terms of increased electron charge density on the metallic centers in I.

(ii) Nucleophilic addition of PR_3: Although it has been found[4] that Ia gives mainly mono- and disubstituted PR_3 derivatives by CO displacement, their formation may occur through the intermediacy of a 1:1 adduct (initial addition of a PR_3 molecule to the positively charged C′). Actually, an adduct of this type has been recently obtained and fully characterized for Ib.[36] In this type of reaction $Ru_3(CO)_{12}$ behaves in a very different way, showing a cluster-breakdown–cluster-re-formation pathway. Only trisubstituted derivatives have been isolated.[37] This difference in the reaction pattern can be mainly related to the fact that the nucleophilic addition of the Lewis base to $Ru_3(CO)_{12}$ occurs into the low-energy highly accessible LUMO, which has a high metal–metal antibonding character. In the case of I, the combined effect of a higher energy LUMO and the presence of a novel electrophilic center (C′) allows an alternative pathway which also gives substituted products.

Acknowledgment. The authors thank the Consiglio Nazionale delle Ricerche (CNR Rome) for generous financial support to this study and Johnson Matthey Ltd. for a loan of $RuCl_3$ and OsO_4.

Registry No. Ia, 57673-31-1; Ib, 84192-57-4; Ic, 57673-30-0; Os, 7440-04-2; Ru, 7440-18-8.

---

(35) Koridze, A. A.; Kizas, O. A.; Astakhova, M. M.; Petrovskii, P. V.; Grishin, J. K. *J. Chem. Soc., Chem. Commun.* **1981**, 853–855.

(36) Deeming, A. J., personal communication.

(37) (a) Põe, A.; Twigg, M. V. *Inorg. Chem.* **1974**, *13*, 2982–2985. (b) Põe, A.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860–1866.