Nature of the Metal–Metal Bond in *Triangulo*-Ru₃(CO)₁₂ from UV Photoelectron Spectroscopy and Quantum Mechanical Calculations

D. AJÒ, G. GRANOZZI*, E. TONDELLO

Istituto di Chimica Generale ed Inorganica dell'Università, Via Loredan 4, 35100 Padua, Italy
and Laboratorio di Chimica e Tecnologia dei Radioelementi, 35100 Padua, Italy

and I. FRAGALÀ

Istituto Dipartimentale di Chimica e Chimica Industriale, V. le Andrea Doria 6, 95100 Catania, Italy

The HOMO nature of Ru–Ru bonds in triangulo-*Ru₃(CO)₁₂ has been evidentiated by He(I) photoelectron spectroscopy and CNDO calculations. The bonding features of the three membered ring are compared to Walsh's picture of the 'isoelectronic' ring of cyclopropane. Both 4d and 5s5p orbitals are significantly involved in the Ru–Ru bonds.*

Introduction

Many efforts have been devoted recently to theoretical and experimental investigations on the nature of the metal–metal bond [1] in polynuclear complexes. Such studies are interesting from both theoretical and applicative points of view, many of these compounds being good catalysts.

The combined use of quantum mechanical calculations and photoelectron spectroscopy (PES) proves to be a powerful tool in investigating the nature of the metal–metal bond. Nevertheless, very few papers [2] have appeared in the literature in which PE bands originating from metal–metal interactions are unequivocally assigned.

In this paper we report the He(I) PE spectrum of *triangulo*-Ru₃(CO)₁₂ together with the results of quantum mechanical calculations in the CNDO scheme.

The bonding features of the three membered cycle emerging from our calculations will be compared to those reported for the cyclopropane ring.

Experimental

A commercial sample was used after purification by sublimation *in vacuo*.

The PE spectra were run on a Perkin-Elmer PS 18 spectrometer using a heated inlet probe system. The

spectra were measured in the 85–110 °C temperature range and were calibrated by reference to peaks due to admixed inert gases and to the He 1s⁻¹ self-ionization. Depending on temperature, different amounts of free CO were detected together with a metallic mirror over the probe walls. However, the identical pattern of the spectra, both in relative intensities and positions of the peaks, led us to neglect the possible presence of different volatile species other than the title compound.

Quantum mechanical calculations were performed by a version [3] of the CNDO method suitable for compounds containing transition metals. Adopted parameters were taken from ref. 4 (for the Ru atoms) or are Pople's standard ones [5] (for the C and O atoms). D₃ₕ symmetry has been adopted with the molecular parameters reported in ref. 6. The computed eigenvalues were related to the measured ionization energies (IE's) through Koopman's approximation [7].
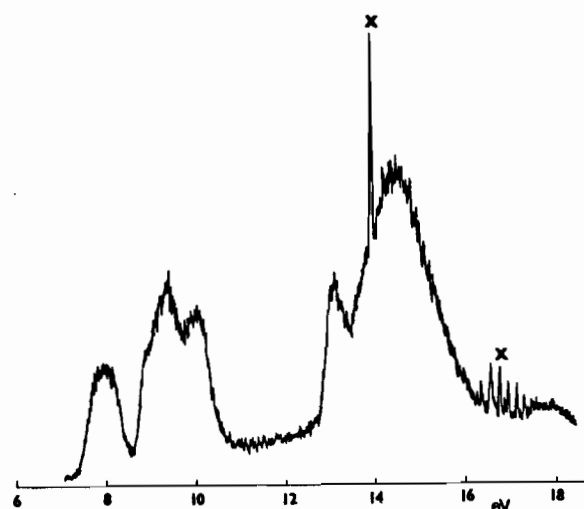

Fig. 1. He(I) photoelectron spectrum of Ru₃(CO)₁₂ recorded at 100 °C. Peaks due to free CO are labeled as X.

---

*Author to whom correspondence should be addressed.

TABLE I. Experimental Ionization Energies, Integrated Band Intensities and CNDO Results for $Ru_3(CO)_{12}$.

Exp.	Intens.	Calc.[a]	Symm.	Assign.
7.91	3.0	7.38 7.48	e' a_1'	Ru–Ru ring bonds
8.90 9.30 10.01	8.1	9.25 9.33 9.39 9.84 10.12 10.29	e'' e' a_1'' e'' a_2'' a_1'	4d lone pairs of Ru atoms (e'', a_1'', a_2'' out-of-ring plane) (e', a_1' in-the-ring plane)
13.08 14.54	16.5	15.65 16.47 16.73	e' a_1' e''	ligand MOs

[a]Reported up to 17 eV.

Results and Discussion

The PE spectrum of $Ru_3(CO)_{12}$ is shown in Fig. 1. The low IE region (up to 12 eV) contains two well resolved bands. The second of them is clearly split into two components and presents a relevant shoulder on the low energy side. The higher IE region consists of two bands centered at 13.08 and 14.54 eV. The peaks due to free CO are labeled as X in Fig. 1.

The experimental IEs are compared in Table I with the quantum mechanical results.

$Ru_3(CO)_{12}$ is diamagnetic and each Ru atom has a d^8 configuration in a pseudo-octahedral environment so that 24 electrons ionizing from MOs mainly composed by the 4d orbitals of Ru atoms are to be detected. Furthermore, on the basis of qualitative arguments 18 electrons (6 per Ru atom) should ionize from MOs having d lone pair character (6 in the ring plane and 12 out of plane). The 6 remaining electrons should be engaged in the ring bonding. Moreover, by analogy with other organometallic clusters [1], the HOMO–LUMO nature of the metal–metal bonds should in principle be inferred.

These qualitative expectations are fulfilled by the spectral pattern of Fig. 1. As a matter of fact, the relative integrated band intensities in the 7–12 eV spectral region (Table I) confirm the assignment of the single band at 7.91 eV to the ring Ru–Ru bonds and the assignment of the bands at 8.90, 9.30 and 10.01 eV to MOs having d lone pair character.

CNDO calculations (Table I) corroborate these assignments since they point out the quasi-degeneracy between the MOs (topmost e' and a_1') mainly contributing to the ring metal bonds and the spread over 1 eV of the d lone pair MO's. Moreover, the calculations also confirm that the LUMO's (a_2', e') correspond to the antibonding partners of the Ru–Ru ring MO's.
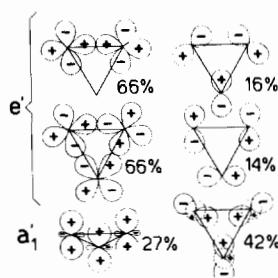

Fig. 2. Atomic orbital contributions to the upmost e' and a_1' MO's separately for 4d and 5s5p orbitals of Ru atoms.

The bands between 12. 5 and 17 eV, as for all the other metal carbonyls [8], are primarily due to ionizations from the metal–CO σ bonding levels and the CO 1π levels. Ionizations from 4σ MO's are probably out of the range detectable by the He(I) radiation source.

It is worthwhile to discuss further the composition of the e' and a_1' MO's which contribute mainly to the ring metal–metal bond and compare it with the results of calculations on the cyclopropane ring [9]. Such a ring can be regarded to some extent as being isoelectronic with the $Ru_3(CO)_{12}$ one since in both cases 6 electrons are involved in the overall bonding of the cycle. In Fig. 2 the atomic orbital contributions to the upmost e' and a_1' MOs are detailed separately for 4d and 5s5p atomic orbitals of Ru atoms. As can be seen, the 4d atomic orbitals contribute substantially to the metal–metal bonding.

The bonding picture emerging from our calculations is very similar to that proposed by Walsh [10] for cyclopropane, obviously apart from the presence of 4d orbitals. The a_1' MO provides electron density inside the three membered ring whereas the e' MO

TABLE II. Atomic Charges and Relevant Bond Overlap Populations for $Ru_3(CO)_{12}$.

Atomic Charges		Overlap Populations					
Ru	+0.155	Ru–C_{ax}	0.356	Ru–Ru	5s–5s	0.026
C_{ax}	+0.338	Ru–C_{eq}	0.345		5s–5p	0.072
O_{ax}	−0.374	$(C–O)_{ax}$	1.010		5s–4d	0.036
C_{eq}	+0.319	$(C–O)_{eq}$	1.014		5p–5p	0.059
O_{eq}	−0.360				5p–4d	0.070
					4d–4d	0.041
					Total	0.304

provides a substantial contribution to the electron density outside the ring.

The a_1' MO seems to be closer to Walsh's picture (sp² hybrid orbitals toward the centre of the cycle) than in cyclopropane itself [9], wherein a largely predominant 2s character has been shown for the corresponding a_1' MO. As a consequence, in cyclopropane a_1' is a low energy lying MO, in contrast with the HOMO nature and the quasi-degeneracy with e' in $Ru_3(CO)_{12}$.

The 4d atomic orbitals contribute to a greater extent to e' than to a_1' MO, essentially with σ type bonds although some π character is present due to a bending of *ca*. 15° from the internuclear axes. These σ contributions originating from the 4d orbitals result in an overall 'less bent' electronic distribution than in cyclopropane.

Atomic charges and bond overlap populations obtained by Mulliken's population analysis [11] of the deorthogonalized [12] CNDO eigenvectors are reported in Table II. The total Ru–Ru bond population is 0.304, a remarkable value when compared both with the other bonds in the molecule and with the previously reported data on binuclear decacarbonyl complexes [13]. This strong Ru–Ru interaction agrees well with the appearance in the mass spectrum [14] of $Ru_3(CO)_{12}$ of the species corresponding to the progressive loss of the carbonyl groups yielding eventually the bare Ru_3^+.

Finally, analysis of the contributions to the total Ru–Ru bond population (Table II) shows that the 5s5p and 4d atomic orbitals contribute to a comparable extent to the Ru–Ru bonds.

Conclusions

Simple qualitative arguments, the He(I) PE spectrum and CNDO calculations combined indicate the HOMO character of metal–metal bonds in the *triangulo* organometallic cluster $Ru_3(CO)_{12}$. In particular, a_1' and e' MO's mainly contributing to the ring Ru–Ru bonds appear to be nearly degenerate. Both 4d and 5s5p orbitals are significantly involved in the Ru–Ru bonds. The participation of the 4d orbitals to ring bonding decreases the bent bond character with respect to cyclopropane.

A high stability of the three membered cycle can be inferred from the remarkable overlap population between the metal atoms.

Note added in proof:

While this manuscript was being processed a short communication on PE spectra of this compound appeared: J. C. Green, E. A. Seddon and D. M. P. Mingos, *Chem. Comm.*, 94 (1979).

References

1 H. Vahrenkamp, *Angew. Chemie (Engl. Edit.)*, *17*, 379 (1978).
2 a) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard and D. W. Turner, *Discuss. Faraday Soc.*, *47*, 112 (1969).
   b) J. C. Green and A. J. Hayes, *Chem. Phys. Letters*, *31*, 306 (1975).
   c) C. D. Garner, I. H. Hillier, M. F. Guest, J. C. Green and A. W. Coleman, *Chem. Phys. Letters*, *41*, 91 (1976).
3 D. A. Brown, W. J. Chambers and N. J. Fitzpatrick, *Inorg. Chim. Acta Rev.*, *6*, 7 (1972).
4 E. Tondello, *Inorg. Chim. Acta*, *11*, L5 (1974).
5 J. A. Pople and G. A. Segal, *J. Chem. Phys.*, *44*, 3289 (1966).
6 M. I. Bruce and F. G. A. Stone, *Angew. Chem. (Engl. Edit.)*, *7*, 427 (1968).
7 For a critical review see: K. Wittel and S. P. McGlynn, *Chem. Rev.*, *77*, 745 (1977).
8 C. Furlani and C. Cauletti, *Struct. Bonding*, *35*, 119 (1978) and references therein.
9 E. Kochanski and J. M. Lehn, *Theor. Chim. Acta*, *14*, 281 (1969).
10 A. D. Walsh, *Trans. Faraday Soc.*, *45*, 179 (1949).
11 R. S. Mulliken, *J. Chem. Phys.*, *23*, 1833 (1955).
12 P. O. Löwdin, *J. Chem. Phys.*, *18*, 365 (1950).
13 D. A. Brown, W. J. Chambers, N. J. Fitzpatrick and S. R. M. Rawlinson, *J. Chem. Soc. A*, 720 (1971).
14 R. B. King, *J. Am. Chem. Soc.*, *88*, 2075 (1966).