Organometallics **1996,** *15,* 5723−5728 5723

Synthesis and Molecular Structure of Tetraruthenium Cluster Isomers with Different Electron Counts

Dario Braga* and Fabrizia Grepioni

Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2,
40126 Bologna, Italy

David B. Brown and Brian F. G. Johnson*

Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge, U.K.

Maria José Calhorda*

ITQB, R. Quinta Grande, 6, Apart. 127, 2780 Oeiras, Portugal, and IST, Lisboa, Portugal

Received April 11, 1996[⊗]

The two novel cluster species $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_8H_{10})$ (**1**) and $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2{:}\eta^2\text{-}C_8H_{10})$ (**2**) have been isolated from the thermolysis of $Ru_3(CO)_{12}$ in octane in the presence of cycloocta-1,3-diene. The two clusters are isomers of formula $Ru_4(CO)_{12}(C_8H_{10})$, differing only in the overall electron donation from the C_8H_{10} ligand to the cluster. Clusters **1** and **2** possess 60 and 62 electrons, respectively, and both are based on a butterfly framework of metal atoms, as shown by single-crystal X-ray diffraction experiments. The bonding interaction between the ligand and the cluster as well as the effect of the extra pair of electrons in **2** with respect to **1** has been investigated by extended Hückel molecular orbital calculations.

Introduction

Transition metal clusters showing the "butterfly" geometry are usually associated with a total of 62 valence electrons and may be seen as derived from the parent tetrahedral geometry by opening up of one M−M bond.[1] Butterfly clusters possessing 60 valence electrons are also known.[2] In these clusters the wings are flexible about the hinge, reflecting the steric requirements of the ligands. When there is no ligand bridging the wings, the butterfly can be flat, as in $[Re_4(CO)_{16}]^{2-}$.[3] We are now able to report on an unprecedented example of structural isomerism in which the same species, namely the butterfly cluster $Ru_4(CO)_{11}(C_8H_{10})$, has been isolated and fully characterized by crystallographic and spectroscopic methods as both its 60- ($Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_8H_{10})$) and 62-valence-electron ($Ru_4(CO)_{12}(\mu_4\text{-}\eta^2{:}\eta^2\text{-}C_8H_{10})$) forms.

Examples of cluster isomers of the same cluster core geometry which differ only in the number of electrons donated by one ligand are not common. Changes in electron donation from a given ligand are, for example, brought about by protonation reactions, which usually bring about a change in cluster geometry. This is the case, for instance, of the reversible interconversion of the cluster anion $[H_2Os_4(CO)_{12}I]^-$ into the neutral butterfly $H_3Os_4(CO)_{12}I$.[4] Two Fe_4 cluster conversions have also been reported: the dianion $[Fe_4(CO)_{13}]^{2-}$ undergoes reversible conversion into the monoanion butterfly $[Fe_4(CO)_{13}]^-$ on protonation,[5] and the reaction of $[Fe_4(CO)_{12}(COCH_3)]^-$ with acid produces $Fe_4H(CO)_{12}(COCH_3)$.[6]

In the case of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_8H_{10})$ (**1**) and $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2{:}\eta^2\text{-}C_8H_{10})$ (**2**), great advantage is taken of the flexibility of the cyclooctadiene ligand.

Results and Discussion

Synthesis and Structural Characterization. The thermolysis of $Ru_3(CO)_{12}$ in octane containing cycloocta-1,3-diene affords a range of products, in varying yields. Three Ru_4 butterfly complexes have been isolated and identified (see Experimental Section). The compound $Ru_4(CO)_{11}(C_8H_{10})$, which requires isomerization of the 1,3-diene to the 1,5-isomer, was characterized by Mason and Thomas,[7] whereas the two isomeric compounds $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_8H_{10})$ (**1**) and $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2{:}\eta^2\text{-}C_8H_{10})$ (**2**) have been prepared for the first time.

The solid-state molecular structures of **1** and **2** have been determined by single-crystal X-ray diffraction. Relevant structural parameters are reported in Table 1. Both compounds consist of a Ru_4 butterfly framework with three terminal carbonyls bonded to each ruthenium atom, as shown in Figure 1. Ru−Ru bond distances range from 2.698(1) (Ru(1)−Ru(4)) to 2.808(1) Å (Ru(2)−Ru(4)) in **1** and from 2.766(5) (Ru(3)−Ru(4)) to 2.890(5) Å (Ru(2)−Ru(3)) in **2**. The organic moiety in **1** is bound to the cluster in an alkyne fashion, seen for

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) For example see: (a) Keller, E.; Walters, D. *Chem. Berg.* **1984**, *117*, 1572. (b) Adams, R. D.; Horvath, I. T.; Segmüller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 1301. (c) Adams, R. D.; Wang, S. *Organometallics* **1985**, *4*, 1902.

(2) For example see: (a) Uson, R.; Fornies, J.; Tomas, M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 1282. (b) Fox, J. R.; Gladfelter, W. L.; Tavanaiepour, I.; Abdel-Mequid, S.; Day, V. W. *Inorg. Chem.* **1981**, *20*, 3230.

(3) Churchill, M. R.; Bau, R. *Inorg. Chem.* **1968**, *7*, 2606.

(4) Puga, J.; Sánchez-Delgado, R.; Androllo, A.; Ascanio, J.; Braga, D. *Organometallics* **1984**, *4*, 2064.

(5) Manassero, M.; Sansoni, M.; Longoni, G. *J. Chem. Soc., Chem. Commun.* **1976**, 919.

(6) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1981**, *213*, 125. Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5621.

(7) Mason; K. K.; Thomas, J. *J. Organomet. Chem.* **1972**, *43*, C39.

Table 1. Relevant Structural Parameters (Å) for 1 and 2

1		2	
Ru(1)−Ru(2)	2.737(1)	Ru(1)−Ru(2)	2.770(4)
Ru(1)−Ru(4)	2.698(1)	Ru(1)−Ru(3)	2.850(4)
Ru(2)−Ru(3)	2.715(1)	Ru(1)−Ru(4)	2.872(5)
Ru(2)−Ru(4)	2.808(1)	Ru(2)−Ru(3)	2.890(5)
Ru(3)−Ru(4)	2.753(1)	Ru(3)−Ru(4)	2.766(5)
Ru(1)−C(1)	2.240(12)	Ru(1)−C(3)	2.05(3)
Ru(1)−−C(2)	2.259(11)	Ru(2)−C(3)	2.30(3)
Ru(2)−C(1)	2.185(11)	Ru(2)−C(4)	2.29(3)
Ru(3)−C(1)	2.256(12)	Ru(3)−C(2)	2.05(3)
Ru(3)−C(2)	2.229(12)	Ru(4)−C(1)	2.32(3)
Ru(4)−C(2)	2.174(13)	Ru(4)−C(2)	2.31(3)
C(1)−C(2)	1.45(2)	C(1)−C(2)	1.44(4)
C(1)−C(8)	1.55(2)	C(1)−C(8)	1.53(5)
C(2)−C(3)	1.50(2)	C(2)−C(3)	1.38(4)
C(3)−C(4)	1.31(2)	C(3)−C(4)	1.39(4)
C(4)−C(5)	1.50(2)	C(4)−C(5)	1.54(4)
C(5)−C(6)	1.52(3)	C(5)−C(6)	1.50(5)
C(6)−C(7)	1.52(2)	C(6)−C(7)	1.55(5)
C(7)−C(8)	1.53(2)	C(7)−C(8)	1.52(5)

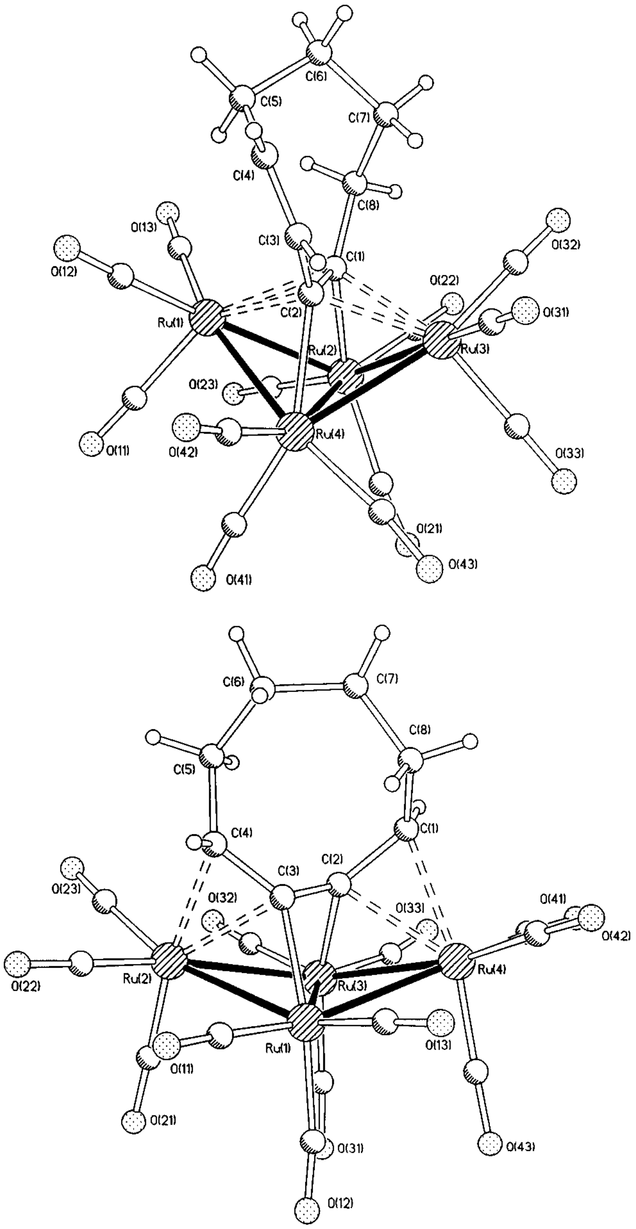


Figure 1. Solid state molecular structures of **1** (a, top) and **2** (b, bottom) showing the atomic labeling schemes.

many linear and ring systems previously,[8] the free olefinic bond (C(3)−C(4) = 1.31(2) Å) having no interaction with the cluster. The ligand in **2** has the 1,3-diene unit in the hinge of the cluster; *i.e.*, there are four carbon atoms involved in bonding in the hinge of the cluster (*cf.* two carbons in **1** and discussion below). The additional carbon atoms in the hinge have the effect of "opening up" the butterfly core by more than 20°, as shown by the intrawing angle, which changes from 115° in **1** to 150° in **2**.

Molecular Orbital Calculations. Extended Hückel molecular orbital calculations[9] were performed on model compounds of the two clusters. As mentioned above, the ligand in compound **1** can be thought to donate a total of four electrons to the cluster framework *via* interactions with the hinge atoms and the wingtip ruthenium atoms. Thus, the cluster has a total of 60 valence electrons, two less than the 62 valence electrons required for the butterfly structure.[10] If it is viewed as a *closo*-octahedral cluster (M_4C_2), it has 66 valence electrons, which is satisfactory for the four-metal/two-carbon geometry. In compound **2** the organic moiety apparently donates 6 electrons via 2 σ interactions with the hinge atoms and 2 π interactions with the wingtip atoms. This gives the cluster 62 valence electrons, which is satisfactory for the butterfly cluster.[10b]

The two clusters share the same $Ru_4(CO)_{12}$ core and differ in the opening angle. While the conversion from a tetrahedral cluster with a 60-electron count to a planar rhombus (64 electrons) across an average butterfly (62 electrons) has been widely studied,[10] the effect of varying the angle of the butterfly on the frontier orbitals of the cluster has received much less attention. A Walsh diagram[11] for the transformation of a closed butterfly into an open one is shown in Figure 2.

The opening of the butterfly is energetically unfavorable for the electron count of this fragment, though the potential energy is soft, as the HOMO is a molecular orbital having bonding character between the two ruthenium atoms in the wingtips. As they are moved away from each other, the bonding character decreases and the energy rises. This can be seen in the three-dimensional representation of this orbital shown with the Walsh diagram. If the two ruthenium atoms are allowed to approach further in order to reconstruct a tetrahedral geometry, the same trend is observed, a new metal−metal bond then being formed. The overlap population between the wingtip ruthenium atoms changes from 0.238 in the open to 0.249 in the closed

---

(8) For example see: (a) Aime, S.; Milone, L.; Osella, D.; Vaglio, G. A.; Valle, M.; Tiripicchio, A.; Tiripicchio Camellini, M. *Inorg. Chim. Acta* **1979**, *49*, 34. (b) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Will, G. J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1980**, 1190. (c) Adams, K. J.; Barker, J. J.; Charmant, J. P. H.; Ganter, C.; Klatt, G.; Knox, S. A. R.; Orpen, A. G.; Ruile, S. *J. Chem. Soc., Dalton Trans.* **1994**, 477. (d) Braunstein, P.; Rose, J.; Bars, O. *J. Organomet. Chem.* **1983**, *252*, C101.

(9) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179. (c) *Ibid.* **1962**, *36*, 3489.

(10) (a) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5304. (b) Halet, J.-F. In *Topics in Physical Organometallic Chemistry*; Gielen, M., Ed.; Freund: Tel Aviv, Israel, 1992; Vol. 4, pp 221−288. (c) Evans, D. G.; Mingos, D. M. P. *Organometallics* **1983**, *2*, 435. (d) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (e) Slovokhotov, Yu. L.; Struchkov, Yu. T. *Russ. Chem. Rev. (Engl. Transl.)* **1985**, *54*, 323. (f) Mingos, D. M. P. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; pp 11−120.

(11) Walsh, A. D. *J. Chem. Soc.* **1953**, 2260.

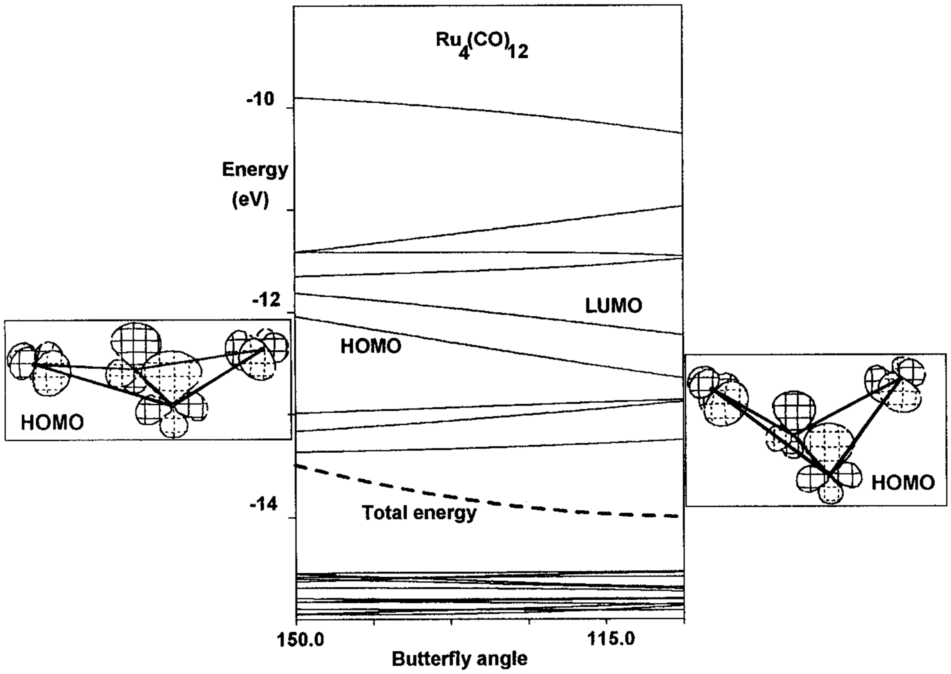


Figure 2. Walsh diagram and the change in total energy (same scale) for the conversion of an open-butterfly cluster into a closed one. The HOMOs of the limiting species are shown.

butterfly cluster. In these calculations the carbonyl groups were kept fixed as they are in the final clusters (see Experimental Section for further details), but it should be kept in mind that the orientation of the carbonyl groups determines the conclusions. By changing their orientation relative to the cluster framework, the cluster orbitals can rehybridize in a different way, to achieve better metal-metal bonds, for example.[12] Therefore, better overlap between frontier orbitals of the wingtip $Ru(CO)_3$ pyramidal fragments may be obtained as the butterfly is closed by adjusting these groups. From the previous results, one should expect clusters containing a closed butterfly in their core to be more stable, as they incorporate a more stable $Ru_4(CO)_{12}$ fragment. On the other hand, some of the empty orbitals are more stable for the open butterfly, which may therefore behave as a better acceptor toward incoming ligands.

The ligand in $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_8H_{10})$ (**1**) may be viewed as essentially an alkyne. In order to have the same model ligand in both clusters, we choose C_4H_4, which is here $H_2C{=}CHC{\equiv}CH$. This is a planar but bent ligand, and its internal angles reproduce those found for the $\mu_4\text{-}\eta^2\text{-}C_8H_{10}$ cycle. The coordination of acetylenes has been studied previously, and the orbitals of the bent ligand have been well described.[13] There are two sets of π and π^* orbitals, $\pi_\perp$ and $\pi_{||}$. While $\pi_\perp$ is localized in the acetylenic carbon atoms, $\pi_{||}$ forms with the other two carbon atoms of the neighboring C=C bond a butadiene type unit. Besides, due to the bending of the acetylene, there is a mixing between $\pi_\perp$ and a σ orbital having the same symmetry, giving them a better directionality to interact with the cluster. These orbitals are sketched on the right side of Figure 3, which shows the interaction of the organic ligand with the $Ru_4(CO)_{12}$ cluster core.

Two σ bonds are formed by donation of electrons from $\pi_\perp$ and $\pi_{//}$ to empty orbitals of the cluster fragment, while back-donation to $\pi_\perp{}^*$ also takes place. Strong bonds are thus formed between the two acetylenic carbons and the four ruthenium atoms, with Ru−C overlap populations ranging from 0.23−0.25 (wingtip atoms) to 0.43−0.44 (hinge atoms), as will be seen below. The carbon atoms in the olefin present an extremely small interaction with the closest rutheniums. This bonding model therefore supports the assigment of a 60-electron count previously made for the cluster. The analogous clusters containing a RC≡CR unit coordinated to $Ru_4(CO)_{12}$ have the same electron count, a C−C distance ranging between 1.45 and 1.47 Å, reflecting the weakening of this bond, and a butterfly angle between 114 and 116°.[8b,14] The HOMO−LUMO gap is large enough for these clusters to be electronically stable.

The second cluster presents a much wider butterfly and a different coordination of the organic ligand. Keeping C_4H_4 as a model, it will now bind as $H_2C{=}C{=}C{=}CH_2$, but in a distorted fashion. In the cluster, it belongs to the ring, which somehow determines its geometry. The central C−C unit is bent, as the acetylenic moiety in cluster **1**, and also twisted. In order to more fully understand the bonding capabilities of this ligand, the frontier orbitals of the linear model ligand (two $\pi_\perp$ from the central C=C, four $\pi_{//}$ from the butadiene) were first obtained and their evolution after bending and twisting was examined. The first movement, bending the outer CH_2 groups from 180° to 120°, leaves the ligand planar. The character of the orbitals is mainly preserved, though, as in the acetylene case, the bending forces a mixing of a σ molecular orbital into the $\pi_\perp$ set, changing its directionality. In the second step, the CH_2 groups are moved away from each other (45°) in opposite directions, keeping a 2-fold symmetry

---

[12] Hoffmann, R.; Schilling, B. E. R.; Bau, R.; Kaesz, H. D.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1978**, *100*, 6088.

[13] Calhorda, M. J.; Hoffmann, R. *Organometallics* **1986**, *5*, 2179, 2181.

[14] (a) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1417. (b) Basu, A.; Bhaduri, S.; Sharma, Jones, K. P. G. *J. Organomet. Chem.* **1987**, *328*, C34.

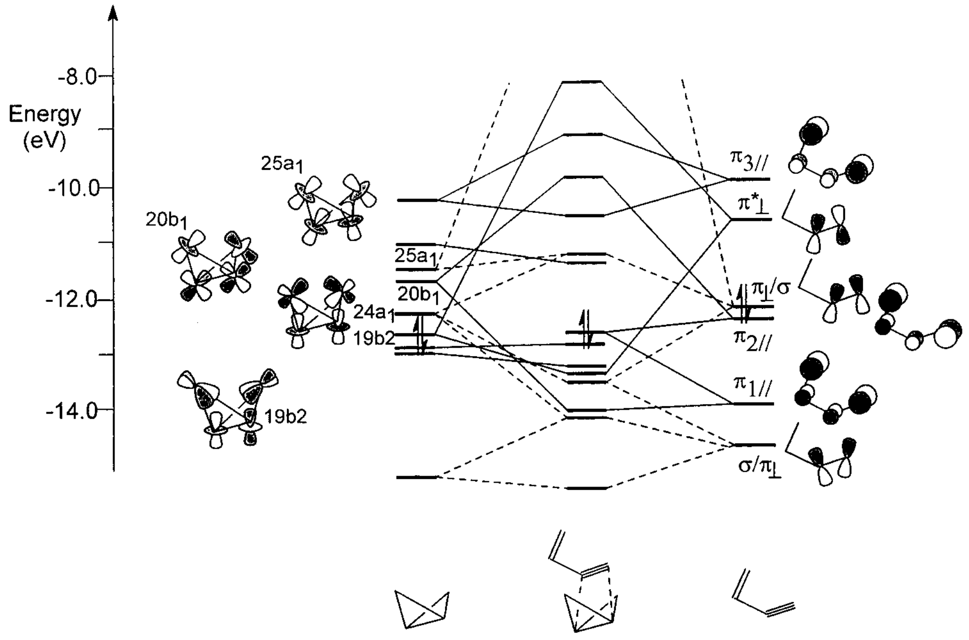


Figure 3. Interaction between a $H_2C{=}CHC{\equiv}CH$ model ligand and the $Ru_4(CO)_{12}$ cluster in $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_8H_{10})$ (**1**).

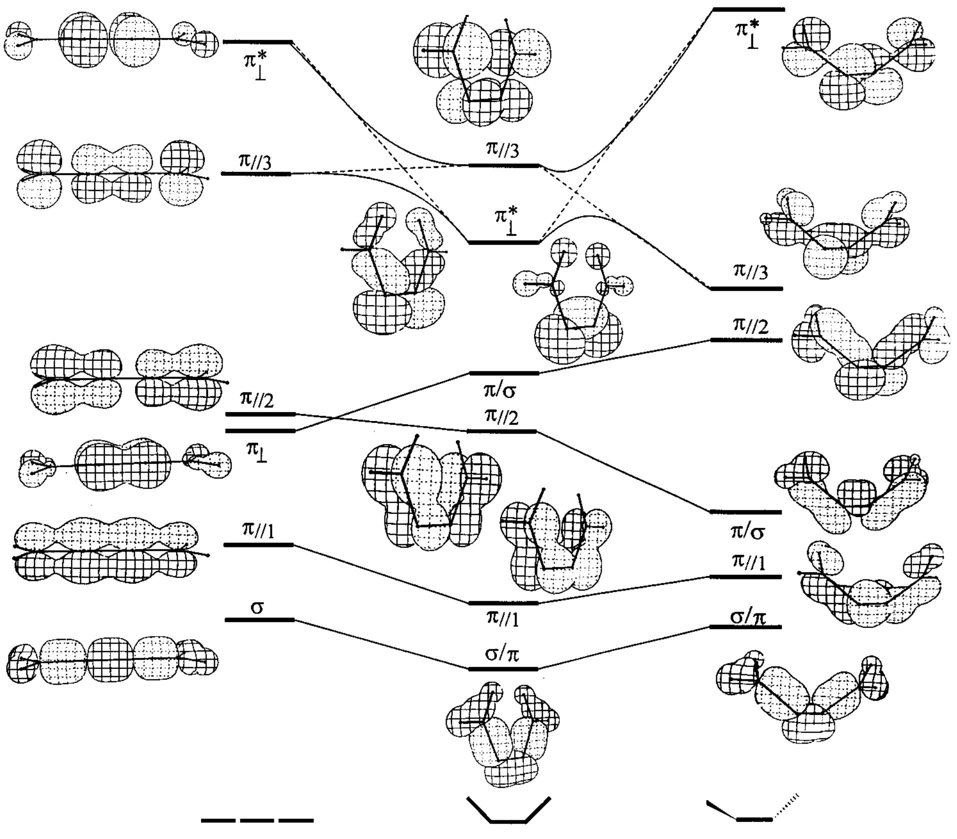


Figure 4. $H_2C{=}C{=}C{=}CH_2$ model ligand and its frontier orbitals along distortion.

axis. This leads to mixing of many orbitals, but we assigned their main character for simplicity. The energy increases first by 1.23 eV and then decreases by 1.20 eV, which means that the final ligand arrangement is barely less stable than the linear configuration. The three geometries and the molecular orbitals are shown in Figure 4.

The distorted ligand interacts with the $Ru_4(CO)_{12}$ fragment, as depicted in Figure 5. More than one orbital of the ligand is used for each type of interaction, as a result of both the low symmetry (only one 2-fold axis) and the orbital overlap reasons. For instance, σ/π and π/σ mix to provide a better match for 53, but they behave as a two-electron donor in a three-orbital interaction; an almost nonbonding orbital also results.

Considering in this way the interactions shown in Figure 5, it would appear that three pairs of electrons are donated by the ligand onto empty orbitals of the ruthenium carbonyl fragment. One can be assigned to the π/σ ligand orbital and might be interpreted as a σ-bond between the central C=C group and the hinge ruthenium atoms; the other two can be considered to use the two lower butadiene-like orbitals and can be envisaged as σ bonds from the outer C=C groups to the

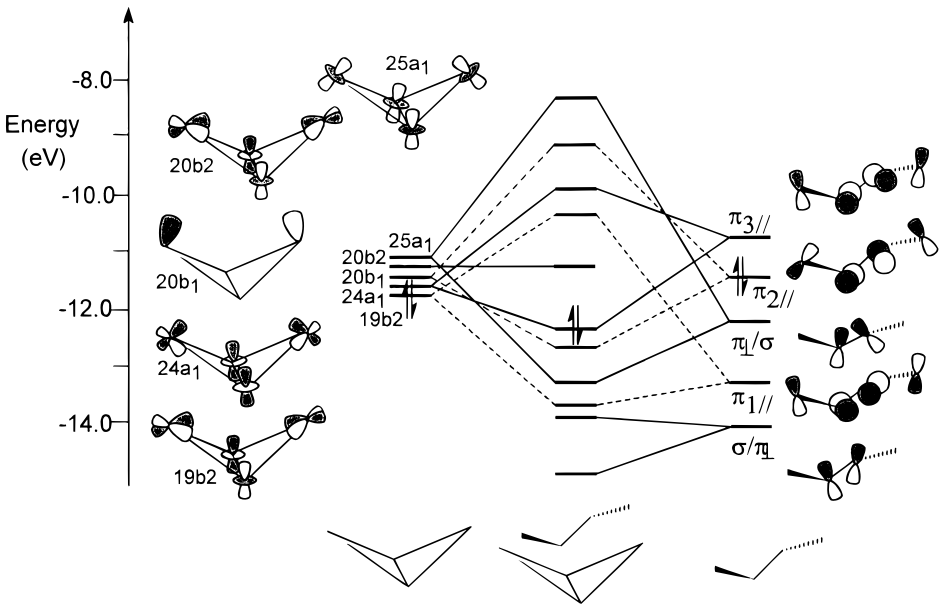
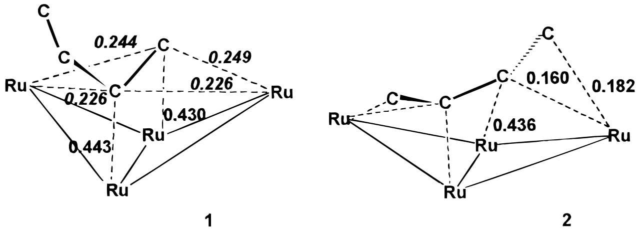


Figure 5. Interaction between a $H_2C{=}C{=}C{=}CH_2$ model ligand and the $Ru_4(CO)_{12}$ cluster in $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{:}\eta^2\text{-}C_8H_{10})$ (**2**).

Chart 1. Ru−C Overlap Populations



wingtip ruthenium atoms. No back-donation appears to be involved in the bonding. Indeed, the Ru−C overlap populations reflect this description, as can be seen in Chart 1, comparing the bonding pattern of cluster **1**.

It should be kept in mind that cluster **2** contains a 2-fold symmetry axis and therefore only a half-molecule needs to be described. While in terms of formal electron counting the ligand in **2** donates three electron pairs (formally three double bonds) and the ligand in **1** only two (the triple bond), two stronger bonds to the hinge ruthenium atoms and the pairs of weaker bonds to the wingtip rutheniums are formed.

Conclusions

In this paper we have illustrated a rare example of cluster isomeric pairs which differ in the coordination mode and hence, in the electron contribution to the cluster orbitals, of the unsaturations on the carbocyclic ligand. Isomer **1** shows the more conventional $\mu_4\text{-}\eta^2\text{-}C_8H_{10}$ bonding mode, while in cluster **2** the ligand shifts to a less common $\mu_4\text{-}\eta^2\text{:}\eta^2\text{-}C_8H_{10}$ mode of coordination. Since the two clusters are isomers, it would be interesting to find an interconversion pathway. In order for this to occur the ligand must undergo a 1,3-shift, change its shape, and shift the carbon atoms binding to the ruthenium atoms. This process is too complicated to be addressed by the calculations adopted in this work. However, it has been established that **1** readily converts to **2** on heating in hexane. This conversion probably involves a hydride transfer first to the metal core and then back to the organic moiety, as is known to happen in many other instances.

Experimental Section

Thermolysis of $Ru_3(CO)_{12}$ (250 mg) in octane (25 mL) containing cycloocta-1,3-diene (5 drops) for 4 h results in the formation of a deep red-brown solution. Removal of the solvent *in vacuo*, followed by thin-layer chromatography on silica using dichloromethane/hexane (1/4 v/v) as eluent results in the isolation and identification of three cluster complexes: the known compound $Ru_4(CO)_{11}(C_8H_{10})$[7] and the two isomers $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_8H_{10})$ (**1**) and $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{:}\eta^2\text{-}C_8H_{10})$ (**2**), this latter isomer being the main product. The mixture was separated by TLC using hexane/dichloromethane (5/1); compounds were eluted in the order **1** and then **2**; yields 6% and 24%, respectively. Anal. Calcd for both **1** and **2**: C, 28.36; H, 1.18. Found for **1**: C, 30.91; H, 2.79. Found for **2**: C, 30.05; H, 1.71. Compound **1** was very oily and may have retained solvent.

Spectroscopic data for **1**: IR (ν_{CO} cm^{-1}; CH_2Cl_2) 2091(w), 2065 (s), 2033 (vs), 2009 (m); positive FAB mass spectrum 846 amu (calcd 846). ^1H NMR ($CDCl_3$) δ 6.5 (d, 1H, $J^d = 11$Hz), 4.8 (dt, 1H, $J^d = 11$, $J^t = 9$ Hz), 3.65 (br s, 2H), 1.90 (br s, 2H), 1.15 (s, 2H).

Spectroscopic data for **2**: IR (ν_{CO} cm^{-1}; CH_2Cl_2) 2090 (w), 2062 (m), 2034 (vs), 2011 (m); positive FAB mass spectrum 848 amu (calcd 846). ^1H NMR ($CDCl_3$) δ 4.3 (q, 2H, $J^q = 4.5$ Hz), 2.4 (t, 2H, $J^t = 12$ Hz), 2.0 (t, 2H, $J^t = 8$ Hz), 1.4 (t, 4H, $J^t = 9$ Hz).

Diffraction Experiments. X-ray measurements were made on a Stoë Stadi-4 four-cycle diffractometer. Data were collected at room temperature for compound **1** and at 150 K for compound **2**. An Oxford Cryosystems low-temperature device was used for the low-temperature determination. Diffraction data were corrected for absorption by azimuthal scanning of high-χ reflections. Absorption correction: minimum and maximum correction are 0.879 and 1.097 for **1** and 0.885 and 1.092 for **2**. All non-H atoms in **1** were allowed to vibrate anisotropically, whereas in **2** only the ruthenium atoms were refined anisotropically. The low-temperature data collection on the crystal of **2** could not prevent rapid decay under X-ray exposure (>40%), thus accounting for the limited data set and for the relatively low accuracy of the data on this species. SHELX93[15] was used for data treatment and refinement based on F^2. Crystal data and details of measurement

Table 2. Crystal Data and Details of Measurements for 1 and 2

	1	**2**
formula	$C_{20}H_{10}O_{12}Ru_4$	$C_{20}H_{10}O_{12}Ru_4$
M_r	846.56	846.56
temp (K)	293(2)	150(2)
cryst system	orthorhombic	monoclinic
space group	$Pna2_1$	$P2_1/n$
a (Å)	18.788(4)	8.990(7)
b (Å)	9.773(2)	16.19(2)
c (Å)	13.113(3)	17.43(2)
β (deg)		103.86(7)
V (Å^3)	2407.7(9)	2463(5)
Z	4	4
F(000)	1608	1608
D_{calcd} (g cm^{-3})	2.335	2.283
λ(Mo Kα) (Å)	0.710 69	0.710 69
μ(Mo Kα) (mm^{-1})	2.523	2.466
θ range (deg)	2.5−25	2.5−25
octants explored ($h_{min}-h_{max}$, $h_{min}-k_{max}$, $l_{min}-l_{max}$)	0−22, 0−11, 0−15	−8 to +8, 0−15, 0−16
no. of measd rflns	2806	2348
no. of unique reflns used in refinement	2227	2241
no. of refined params	325	165
GOF on F^2	1.068	1.075
R_1 (on F, $I > 2\sigma(I)$)	0.0442	0.0785
wR_2 (on F^2, all data)	0.1072	0.1664

are reported in Table 2. Fractional atomic coordinates are deposited as Supporting Information.

Molecular Orbital Calculations. All the molecular orbital calculations were done using the extended Hückel method[9] with modified H_{ij}'s.[16] The basis set for the metal atom consisted of *n*s, *n*p, and $(n - 1)$d orbitals. The s and p orbitals were described by single Slater-type wave functions, and the d orbitals were taken as contracted linear combinations of two Slater-type wave functions. Standard parameters were used for H, C, and O, while those for Ru were the following (H_{ii}/eV, ζ): 5s, −10.40, 2.078; 5p, −6.89, 2.043; 4d, −14.90, 5.378, 2.303 (ζ_2), 0.5340 (C_1), 0.6365 (C_2). Three-dimensional representations of orbitals were drawn using the program CACAO.[17]

Idealized models having C_{2v} symmetry in the $Ru_4(CO)_{12}$ core were used, based on the geometries of the clusters $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_8H_{10})$ (**1**) and $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2{:}\eta^2\text{-}C_8H_{10})$ (**2**). The butterfly angles were taken as 150 and 115°, respectively. The $Ru(CO)_3$ fragments were half-octahedrons (its orbitals are described in detail in ref 18). Their orientation was optimized for both clusters at an angle between the 3-fold axis and the center-of-the-butterfly-Ru of 146°. The cyclic ligands were modeled with C_4H_4 groups, as the remaining part of the cycle is saturated and is too far away from the cluster to impose any steric constraints besides the topology of the ring. The angles inside C_4H_4 were thus the same as in the real ligands. The final model for **1**, $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_4H_4)$, has no symmetry, while that of **2**, $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2{:}\eta^2\text{-}C_4H_4)$, has C_2 symmetry. The following distances (Å) were used: Ru−Ru, 2.80; Ru−C(CO), 1.89; C−O, 1.13; C−C, 1.40; C−H, 1.08. The C−C group directly bound to the butterfly was 2.078 Å above the axis of the butterfly.

Acknowledgment. Financial support by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica is acknowledged. B.F.G.J., D.B., and F.G. thank NATO for a travel grant. The ERASMUS project "Crystallography" is acknowledged for student exchange (D.B.B). D.B.B. and B.F.G.J. thank the EPSRC, ICI (Wilton). D.B., F.G., and M.J.C. acknowledge the CNR (Italy) and JNICT (Portugal) for joint financial support.

Supporting Information Available: Tables of crystal data, anisotropic thermal parameters, fractional atomic coordinates, and all bond lengths and angles and a figure giving another view of **2** (8 pages). Ordering information is given on any current masthead page.

OM9602825

---

[15] Sheldrick, G. M. SHELX93, Program for Crystal Structure Determination; University of Gottingen, Göttingen, Germany, 1993.

[16] Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

[17] Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 39.

[18] Albright, T. A.; Whangbo, M.-H.; Burdett, J. K. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.