The molecular and electronic structure of the coordinatively unsaturated triangular clusters $[RhM_2cp_3(CO)_5]$ (M = Mo, W)

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Abstract

The structures of the triangular clusters $[RhM_2cp_3(CO)_5]$ (M = W, Mo) have been determined by X-ray analysis. The isostructural clusters crystallize in the monoclinic space group $P2_1/n$ with $a = 16.378(2)$ (M = W), 16.389(2) (M = Mo); $b = 7.874(1)$, 7.932(1); $c = 16.052(2)$, 16.072(2) Å; $\beta = 113.67(1)$, 113.265(9)°; $D_{calc} = 2.92$, 2.18 g cm^{-3} for $Z = 4$. The structures were solved by direct methods and refined to $R = 0.031$ ($R_w = 0.035$) (M = W) and $R = 0.038$ ($R_w = 0.044$) (M = Mo). The non-symmetric molecules consist of a triangular RhM_2 core with two different Rh–M single bonds, the longer one being bridged by a carbonyl ligand, and an M–M double bond (2.650(0) (M = W), 2.653(0) (M = Mo) Å) semi-bridged by a carbonyl ligand. Thus, these clusters may be regarded as trimetallacyclopropenes. This view is in accord with the results of an EHT calculation, which furthermore underlines the importance of the bridging carbonyl ligands for the stability of these molecules.

Introduction

Recently, we reported on the synthesis and spectroscopic characterization of heteronuclear triangular $[RhM_2cp_3(CO)_n]$ clusters (M = Ni, $n = 2$; M = Fe, $n = 4$; M = Mo, W, $n = 6$) [1]. Our interest in these clusters was the intention of applying them as heterogeneous catalyst precursors in the CO hydrogenation reaction. Indeed, the $RhMo_2$ cluster appeared a good candidate for this purpose [1, 2]. In order to further characterize the clusters employed as catalyst precursors, single crystal X-ray analyses of the RhM_2 (M = Mo, W) clusters were carried out. It appeared that both these clusters are not electron precise (48 cluster valence electrons, c.v.e.) as indicated by the formula given above, but have one carbonyl ligand less, $[RhM_2cp_3(CO)_5]$, and represent therefore coordinatively unsaturated 46 c.v.e. species [3]. This unexpected result prompted an EHMO calculation to get a more detailed insight into the bonding properties of these clusters. The results of the structural analysis and of the molecular orbital consideration are presented here.

Experimental

The clusters $[RhM_2cp_3(CO)_5]$ (M = Mo, W) were synthesized as published [1]. Crystals, suitable for X-ray analysis, were obtained from methylene chloride solutions overlayered with diethyl ether at room temperature (M = Mo) and −30 °C (M = W), respectively.

Structure determination and refinement

The intensities of 3326 (3445) independent reflections were measured in the range $1.5 \leq \theta \leq 25°$ ($1.5 \leq \theta \leq 24.5°$) for $[RhW_2cp_3(CO)_5]$ and $[RhMo_2cp_3(CO)_5]$, respectively, with an Enraf-Nonius CAD-4 diffractomer with graphite-monochromatized Mo Kα radiation using $\omega/2\theta$-scan technique. Lattice constants were determined by least-squares refinement of setting angles of 25 reflections with $14.6 \leq \theta \leq 17.3°$ ($1.5 \leq \theta \leq 12°$). A total of 3013 (3236) reflections with $I \geq 2\sigma(I)$ was used for structure analysis. Corrections for Lorentz and polarization effects were carried out. All calculations were performed with the Enraf-Nonius SDP program package.

The structures were solved by MULTAN 11/82 [4] using 297 (288) normalized structure factors with

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0020-1693/91/$3.50

TABLE 1. Summary of crystal data and experimental details

	[$RhW_2cp_3(CO)_5$]	[$RhMo_2cp_3(CO)_5$]
Molecular formula	$RhW_2C_{20}O_5H_{15}$	$RhMo_2C_{20}O_5H_{15}$
Molecular weight (g mol^{-1})	805.94	630.12
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	16.378(2)	16.389(2)
b (Å)	7.874(1)	7.932(1)
c (Å)	16.052(2)	16.072(2)
β (°)	113.67(1)	113.265(9)
V ($Å^3$)	1896.0(2)	1919.5(2)
D_c (g cm^{-3})	2.92	2.18
Z	4	4
$F(000)$	1472	1216
μ(Mo Kα) (cm^{-1})	48.40	9.55
Crystal size (mm)	0.15×0.25×0.6	0.3×0.5×0.6
No. independent reflections	3326	3445
No. observed reflections ($\|F\| \geqslant 3.92\sigma(F)$)	3013	3236
Final difference synthesis peaks (e $Å^{-3}$)	1.93	1.13
Largest parameter shift	0.01	0.01
R	0.031	0.038
R_w	0.035	0.044

TABLE 2. Atomic parameters of [$RhMo_2cp_3(CO)_5$]: final fractional coordinates and isotropic equivalents of the anisotropic thermal parameters for the non-hydrogen atoms with e.s.d.s in parentheses

Atom	x	y	z	B^a
Rh	0.02414(3)	0.01832(6)	0.33433(3)	2.068(9)
Mo(1)	−0.12690(3)	0.09382(7)	0.17120(4)	2.44(1)
Mo(2)	0.03026(3)	0.21442(7)	0.18928(3)	2.14(1)
O(1)	−0.1518(3)	0.0020(8)	0.3470(3)	4.4(1)
O(2)	−0.1385(3)	0.4733(7)	0.2130(3)	5.2(1)
O(3)	0.0042(4)	−0.1284(7)	0.0900(4)	5.2(1)
O(4)	−0.1036(4)	0.3722(9)	0.0097(4)	6.3(2)
O(5)	0.0280(4)	0.3549(7)	0.4176(4)	4.8(1)
C(1)	−0.1182(4)	0.0360(9)	0.2952(4)	3.0(1)
C(2)	−0.1272(4)	0.332(1)	0.2021(5)	3.6(2)
C(3)	0.0038(4)	−0.003(1)	0.1282(4)	3.3(2)
C(4)	−0.0572(4)	0.308(1)	0.0781(5)	3.7(2)
C(5)	0.0290(4)	0.2264(9)	0.3849(4)	2.9(1)
C(6)	−0.2042(7)	−0.133(1)	0.0787(7)	6.4(3)
C(7)	−0.2130(6)	0.017(2)	0.0259(6)	6.5(3)
C(8)	−0.2599(6)	0.131(1)	0.0510(7)	6.5(3)
C(9)	−0.2797(5)	0.059(1)	0.1206(7)	6.1(3)
C(10)	−0.2452(6)	−0.100(1)	0.1361(6)	5.8(2)
C(11)	0.1470(4)	0.3997(9)	0.2738(5)	3.5(2)
C(12)	0.1864(4)	0.238(1)	0.2828(5)	3.5(2)
C(13)	0.1752(4)	0.182(1)	0.1956(5)	4.2(2)
C(14)	0.1307(4)	0.312(1)	0.1321(5)	4.1(2)
C(15)	0.1138(4)	0.4455(9)	0.1803(5)	3.4(1)
C(16)	0.0361(5)	−0.2534(9)	0.3020(9)	3.9(2)
C(17)	0.0230(5)	−0.2541(9)	0.3836(5)	4.4(2)
C(18)	0.0921(5)	−0.167(1)	0.4475(5)	4.5(2)
C(19)	0.1534(5)	−0.121(1)	0.4071(6)	4.5(2)
C(20)	0.1193(4)	−0.1785(9)	0.3184(5)	3.5(2)

[a] Defined as $(4/3)[a^2(B1,1)+b^2B(2,2)+c^2(B3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc\cos(\alpha)B(2,3)]$.

TABLE 3. Atomic parameters of [$RhW_2cp_3(CO)_5$]: final fractional coordinates and isotropic equivalents of the anisotropic thermal parameters for the non-hydrogen atoms with e.s.d.s in parentheses

Atom	x	y	z	B^a
Rh	0.02625(4)	0.0199(1)	0.33473(4)	2.01(1)
W(1)	−0.12736(2)	0.09611(5)	0.17359(2)	2.323(7)
W(2)	0.03003(2)	0.21209(5)	0.18914(2)	2.017(7)
O(1)	−0.1489(4)	−0.003(1)	0.3505(4)	4.2(2)
O(2)	−0.1429(5)	0.478(1)	0.2107(7)	5.4(2)
O(3)	0.0017(6)	−0.127(1)	0.0850(5)	4.8(2)
O(4)	−0.1074(6)	0.378(1)	0.0106(5)	5.5(2)
O(5)	0.0265(5)	0.345(1)	0.4199(5)	4.6(2)
C(1)	−0.1191(5)	0.034(1)	0.2973(6)	2.4(2)
C(2)	−0.1315(6)	0.335(2)	0.2020(7)	3.8(3)
C(3)	0.0045(6)	0.000(2)	0.1260(6)	3.1(2)
C(4)	−0.0576(7)	0.312(2)	0.0787(7)	3.9(3)
C(5)	0.0282(6)	0.226(1)	0.3863(6)	2.8(2)
C(6)	−0.1996(8)	−0.134(2)	0.0789(9)	5.5(3)
C(7)	−0.2093(9)	0.011(2)	0.0258(8)	5.9(4)
C(8)	−0.2600(8)	0.128(2)	0.0496(9)	5.7(4)
C(9)	−0.2816(7)	0.062(2)	0.122(2)	5.7(4)
C(10)	−0.2440(8)	−0.106(2)	0.1371(9)	5.3(3)
C(11)	0.1452(6)	0.399(1)	0.2746(7)	3.2(2)
C(12)	0.1870(6)	0.235(1)	0.2843(8)	3.5(2)
C(13)	0.1766(6)	0.178(2)	0.1964(7)	3.5(2)
C(14)	0.1302(6)	0.309(2)	0.1317(7)	3.7(2)
C(15)	0.1123(6)	0.448(1)	0.1810(7)	3.3(2)
C(16)	0.0361(7)	−0.255(1)	0.3001(8)	3.7(3)
C(17)	0.0232(8)	−0.254(1)	0.3837(8)	4.4(3)
C(18)	0.0947(8)	−0.171(2)	0.4498(8)	4.3(3)
C(19)	0.1561(7)	−0.122(2)	0.4079(9)	4.2(3)
C(20)	0.1217(7)	−0.174(7)	0.3183(8)	3.6(2)

[a] Defined as $((4/3)[a^2(B1,1)+b^2B(2,2)+c^2(B3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)])$

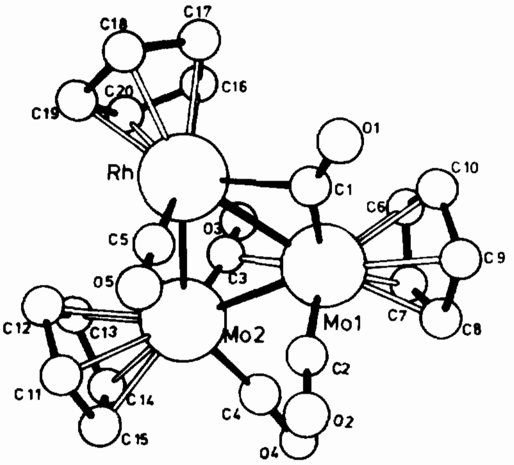


Fig. 1. Molecular structure of [$RhMo_2cp_3(CO)_5$].

$E \geqslant 1.690$ (1.699). From 32 phase sets developed, the E map corresponding to the set with the highest combined figure of merit revealed the three heavy atoms of the molecules. The position of the other non-hydrogen atoms were subsequently localized in difference Fourier maps. Full-matrix least-squares procedure minimized $\Sigma\omega(\Delta F)^2$. An absorption correction was applied for [$RhW_2cp_3(CO)_5$] using the program DIFABS [5] ($\theta_{max} = 25°$, $\mu_{min} = -4.22°$, $\mu_{max} = 23.87°$). Application of the absorption correction reduced the height of final difference Fourier peaks from 5.06 e $Å^{-3}$ to an average of 1.93 e $Å^{-3}$. R decreased from 0.048 for the uncorrected data to 0.031 after correction with DIFABS. For [$RhMo_2cp_3(CO)_5$] no absorption correction was applied. Positions of hydrogen atoms were calculated. Further experimental detail are given in Table 1. The final atomic parameters of the clusters under study are given in Tables 2 and 3.

EHT calculation method

For quantum chemical model calculations the extended Hückel molecular orbital method was applied using a PC version of Hoffmann's ICON program [6]. The ionization energies, exponents, and coefficients were obtained from the literature [7]:

EHT parameters

		H_{ii}	ζ_1	c_1	ζ_2	c_2
Rh	5s	−8.09	2.135			
Rh	5p	−4.57	2.100			
Rh	4d	−12.50	5.540	0.55613	2.400	0.61172
W	6s	−8.26	2.340			
W	6p	−5.17	2.310			
W	5d	−10.37	4.980	0.66827	2.070	0.54222
C	2s	−21.40	1.625			
C	2p	−11.40	1.625			
O	2s	−32.20	2.275			
O	2p	−14.80	2.275			

Results and discussion

Molecular structure of [$RhM_2cp_3(CO)_5$] (M = Mo, W)

The [$RhM_2cp_3(CO)_5$] (M = Mo, W) clusters exist as discrete molecules in the solid state with non-unusual intermolecular contacts.

The molecular structure of both isostructural clusters is presented on the example of the $RhMo_2$ compound in Fig. 1 which also contains the atomic numbering scheme. Selected bond distances and bond angles are summarized in Tables 4 and 5, respectively. The non-symmetric molecules of [$RhM_2cp_3(CO)_5$] consist of a triangular RhM_2 core with three different metal–metal distances. Each metal atom bears one η^5-cp ligand and one terminal CO ligand. Both types of ligands are normal bonded to the metal atoms in every respect. Both Rh–M distances are in the range expected for single bonds. The Rh–M(1) bonds are elongated compared with the Rh–M(2) bonds by 0.05 (M = W) and 0.032 (M = Mo) Å, respectively, and are bridged by the carbonyl ligands C(1)O(1). An inspection of the bridge bond distances M(1)–C(1) and Rh–C(1) compared with the M(1)–C(2) and Rh–C(5) distances of the terminal carbonyl ligands attached to these metal atoms reveals that this bridge is very much closer to M(1) than to the Rh atom. The coordination sphere around the metal atoms may be approximately described, including the metal–metal bonds and in the case of the Rh atom the carbonyl bridge bond as well, as four-legged piano-stool geometry (coordination number 7). The unsaturation of these 46 c.v.e. molecules is apparent in the M(1)–M(2) distance of 2.650(0) (M = W) and 2.653(0) (M = Mo) Å, respectively, which is considered to be in the range of a double bond, see for example ref. 8. Thus, the clusters under study may be considered as trimetallacyclopropene derivatives [9]. Beside the C(1)O(1) group bridging the RhM(1) bond there is another carbonyl ligand (C(3)O(3)) which may be regarded as semi-bridging the M(1)–M(2) bond. The M(1, 2)–C(3) distances differ markedly by 0.76 (M = W) and 0.66 (M = Mo) Å, respectively, with the shorter distance to M(2). As a criterion to recognize a semi-bridging carbonyl group the 'asymmetry parameter' α, defined as $\alpha = (d_2 - d_1)/d_1$ where d_2 is the longer M–C(0) distance, has been suggested [10]. Carbonyl groups with $0.1 \leqslant \alpha \leqslant 0.6$ are considered semi-bridging. The α values for M(2)–C(3)...M(1) are 0.399 (M = W) and 0.340 (M = Mo). Both planes defined by the metal atoms and the (semi-)bridging carbonyl ligands are declined to opposite sites from the plane through the three metal atoms with dihedral angles of 154.4, 156.3° (Rh, M(1), C(1); M = W, Mo) and 85.9, 87.5°

TABLE 4. Selected bond distances of [RhM$_2$cp$_3$(CO)$_5$] (M = W, Mo) with e.s.d.s in parentheses

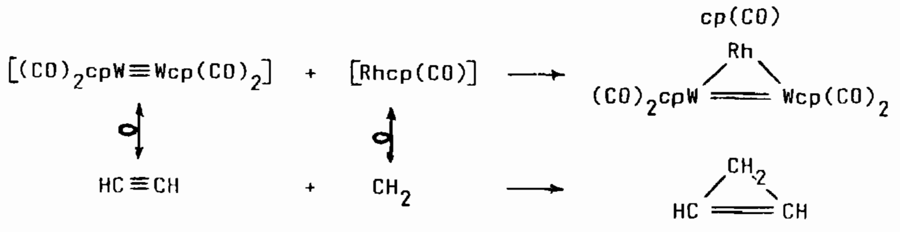
Atoms	Distance (Å)		Atoms	Distance (Å)	
	M = W	M = Mo		M = W	M = Mo
Rh–M(1)	2.856(0)	2.869(0)	M(1)–M(2)	2.650(0)	2.653(0)
Rh–M(2)	2.806(0)	2.837(0)			
Carbonyl groups					
Rh–C(1)	2.212(4)	2.167(4)	C(1)–O(1)	1.178(6)	1.196(5)
M(1)–C(1)	1.997(5)	1.995(4)			
M(1)–C(3)	2.672(5)	2.612(4)	C(3)–O(3)	1.187(7)	1.168(5)
M(2)–C(3)	1.909(6)	1.949(5)			
M(1)–C(2)	1.940(7)	1.957(5)	C(2)–O(2)	1.163(8)	1.158(6)
M(2)–C(4)	1.944(6)	1.942(5)	C(4)–O(4)	1.190(7)	1.178(6)
Rh–C(5)	1.817(6)	1.827(4)	C(5)–O(5)	1.151(7)	1.150(5)
Cyclopentadienyl rings					
Ring 1 (C(6)–C(10))			Ring 2 (C(11)–C(15))		
C–C(average)	1.416(11)	1.382(9)	C–C(average)	1.437(8)	1.418(7)
M(1)–C(average)	2.333(6)	2.323(5)	M(2)–C(average)	2.354(5)	2.353(4)
Ring 3 (C(16)–C(20))					
C–C(average)	1.427(9)	1.405(7)			
Rh–C(average)	2.279(5)	2.273(4)			

TABLE 5. Selected bond angles of [RhM$_2$cp$_3$(CO)$_5$] (M = W, Mo) with e.s.d.s in parentheses

Atoms	Angle (°)		Atoms	Angle (°)	
	M = W	M = Mo		M = W	M = Mo
Rh–M(1)–M(2)	61.14(1)	61.67(1)			
Rh–M(2)–M(1)	63.04(1)	62.91(1)			
M(2)–Rh–M(1)	55.82(1)	55.42(1)			
Rh–M(1)–C(1)	50.5(1)	49.0(1)	M(2)–M(1)–C(1)	108.4(1)	106.9(1)
Rh–M(1)–C(2)	95.3(2)	95.3(2)	M(2)–M(1)–C(2)	76.7(2)	73.9(1)
Rh–M(1)–C(3)	71.3(1)	71.3(1)	M(2)–M(1)–C(3)	42.0(1)	43.4(1)
Rh–M(2)–C(3)	84.1(2)	81.7(1)	M(1)–M(2)–C(3)	69.6(2)	67.2(1)
Rh–M(2)–C(4)	136.3(2)	135.4(1)	M(1)–M(2)–C(4)	73.8(2)	72.8(1)
M(1)–Rh–C(1)	44.2(1)	44.0(1)	M(2)–Rh–C(1)	97.4(1)	96.3(1)
M(1)–Rh–C(5)	94.2(2)	95.1(1)	M(2)–Rh–C(5)	84.0(2)	82.0(1)
Rh–C(1)–O(1)	120.3(4)	121.5(3)			
Rh–C(5)–O(5)	177.2(5)	176.2(4)			
			Rh–C(1)–M(1)	85.3(2)	87.0(2)
M(1)–C(1)–O(1)	154.1(4)	151.2(3)			
M(1)–C(2)–O(2)	172.4(6)	171.4(4)			
M(1)–C(3)–O(3)	122.7(5)	124.3(4)	M(1)–C(3)–M(2)	68.3(3)	69.5(3)
M(2)–C(3)–O(3)	168.8(5)	166.3(4)			
M(2)–C(4)–O(4)	176.4(5)	173.6(4)			

(M(1), M(2), C(3); M = W, Mo), respectively. The M–M–cp (centroid) angles are highly different (M(2)–M(1)–cp 39.76, 37.89°; M(1)–M(2)–cp 5.96, 3.68° (M = W, Mo)).

The structures under study reveal that the coordinative unsaturation as the striking feature of these clusters should be caused by the steric crowding of the ligand sphere around the metal core. The solid state structures also explain some spectroscopic observations [1]. The two bridging CO ligands reveal themselves in the IR spectra with bands at 1750, 1830 (M = W) and 1752, 1838 (M = Mo) cm^{-1}, respectively. The molecules are fluxional at room temperature in solution but are rigid at 193 K as shown



Scheme 1.

TABLE 6. σ and π parts of metal–metal bond orders in $[RhW_2cp_3(CO)_5]$

	M–M bond	n (M–M)				
		σ		π		σ/π
$[W_2cp_2(CO)_4]$	W(1)–W(2)	d_{z^2}–d_{z^2}	0.0573	d_{yz}–d_{yz}	0.0575	
		p_z–d_{z^2}	0.0453	d_{xz}–d_{xz}	0.0410	
		d_{z^2}–p_z	0.0328			1.35
$[RhW_2cp_3(CO)_5]$	W(1)–W(2)	d_{z^2}–d_{z^2}	0.0572	d_{yz}–d_{yz}	0.0324	
		p_z–d_{z^2}	0.0437	d_{xz}–d_{xz}	0.0426	
		d_{z^2}–p_z	0.0317			1.70
	W(1)–Rh	d_{z^2}–d_{z^2}	0.0341			
		p_z–d_{z^2}	0.0214			
		d_{z^2}–p_z	0.0249			∞
	W(2)–Rh	d_{z^2}–d_{z^2}	0.0435			
		p_z–d_{z^2}	0.0329			
		d_{z^2}–p_z	0.0264			
		d_{z^2}–s	0.0254			∞

by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The appearance of three signals for the cp ligands in the low temperature spectra is in accord with the absence of any symmetry in the solid state structures.

EHMO analysis

The electronic structure of $[RhM_2cp_3(CO)_5]$ (M = W, Mo) has been studied by molecular orbital calculations on the extended Hückel level. Both clusters are nearly identical in their electronic properties. For the sake of clarity only the tungsten derivative will be discussed in the following section.

The nature of the metal–metal bonds in $[RhW_2cp_3(CO)_5]$ has been analysed in terms of the bonding between the $[W_2cp_2(CO)_4]$ and $[Rhcp(CO)]$ fragments. Beside the structural consideration (see above), also in view of the isolobal analogy between $[W_2cp_2(CO)_4]$ and acetylene on the one hand, and between $[Rhcp(CO)]$ and the methylene group on the other, the cluster $[Rhcp_3W_2(CO)_5]$ may be considered as cyclometallapropene formally built up by cycloaddition of the two metal fragments (Scheme 1).

Semi-empirical quantum chemical calculations have been reported for the rhodium [11] as well as for the tungsten fragment [12, 13]. In accordance with the 18 electron rule, the W–W bond in $[W_2cp_2(CO)_4]$ may be formally regarded as a triple bond. This bond order should be reduced $3 \rightarrow 2$ on going from $[W_2cp_2(CO)_4]$ to $[RhW_2cp_3(CO)_5]$. This consideration is well reflected by the EHT calculations. In Table 6 σ and π parts of the metal–metal bond orders in $[W_2cp_2(CO)_4]$ and $[RhW_2cp_3(CO)_5]$ are compared. In every case the metal–metal bond axis is directed along the z axis of the coordinate system and the metal atoms are located in the yz plane. The multiple tungsten–tungsten bond in $[W_2cp_2(CO)_4]$ is realized by σ interactions between the orbitals $5d_{z^2}$ and $6p_z$, and by π interactions via the $5d_{yz}$ and $5d_{xz}$ orbitals. There are no δ bonds between the tungsten orbitals $5d_{x^2-y^2}$ or $5d_{xy}$.

The σ to π ratio of the W–W bond increases by combining the fragments. For geometrical reasons, especially the W $5d_{yz}$ orbitals, responsible for the W–W π interaction in $[W_2cp_2(CO)_4]$, are now involved in the bonding to the rhodium atom. The bond orders of the two Rh–W bonds differ largely: the W(1)–Rh bond, bridged by CO, is much weaker than the W(2)–Rh bond. Figure 2 shows the molecular orbital

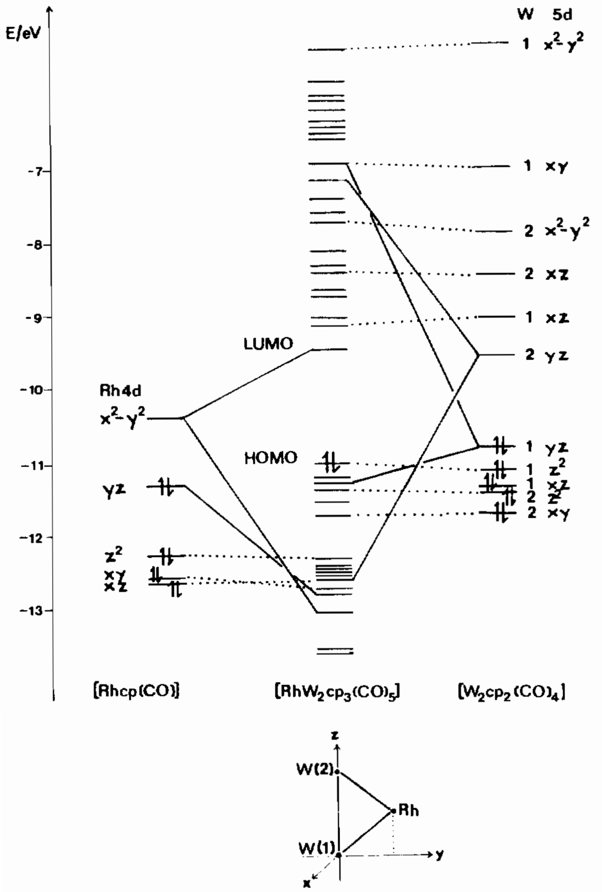


Fig. 2. Molecular orbital scheme of [$RhW_2cp_3(CO)_5$].

TABLE 7. Metal–carbon and carbon–oxygen bond orders and CO charges in [$RhW_2cp_2(CO)_5$]

M	*i*	*n*[M–C(*i*)]	*n*[C–O(*i*)]	Q_{CO}
W(1)	3	0.18		
W(1)	4	0.08		
Rh	5	0.84	1.181	−0.07
W(1)	2	0.95	1.044	−0.53
W(2)	4	0.88	1.038	−0.41
W(1)	1	0.79	1.015	−0.54
W(2)	3	0.95	0.984	−0.65

scheme of the cluster. It is evident from the correlation that the most significant bonding contributions originate from the tungsten $5d_{yz}$ and from the rhodium $4d_{yz}$ as well as $4d_{x^2-y^2}$ orbitals. There is a significant energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 1.59 eV.

According to the results of the single crystal X-ray analyses, the carbonyl ligands of the cluster are of terminal, bridging and semi-bridging type. The semi-bridging mode of C(3)O(3) is supported by the results of the overlap population analysis. Table 7 lists the metal–carbon and carbon–oxygen bond orders as well as the charges on the CO ligands. A distinct overlap appears between the carbon atom (3), terminally bonded to W(2), and W(1). In accordance with the backbonding concept of carbon monoxide, coordinated to transition metal atoms, the carbon–oxygen bond is weakened by interaction of CO with an increasing number of metal atoms. This is reflected in a decreased C–O overlap and an increased negative charge on the semi-bridging and bridging carbonyl ligands C(3)O(3) and C(1)O(1). The calculated bond orders are consistent with the IR spectra of the clusters in CH_2Cl_2 solution (see above).

The stability of the heteronuclear cluster is closely related to its non-symmetric geometry. It can be demonstrated by model calculations on clusters with hypothetically idealized structures that the metal to metal bonds are necessarily supported by the bridging and semi-bridging carbonyl groups to ensure a stable cluster arrangement. In Fig. 3 the energetical consequences of the step by step transformation of a terminal CO group, coordinated on tungsten, into a carbonyl ligand, bridging one of the W–Rh bonds, are shown. The starting point is a model cluster with two equidistant Rh–W bonds and exclusively terminal bonded carbonyl ligands in an idealized ligand arrangement (bond distances, M–C–O and C–M–O angles*). The planes defined by the atoms of the $W(CO)_2$ fragment are perpendicular to the plane formed by the metal atoms. Whereas a binding energy

$$\text{b.e.} = (E_{[W_2cp_2(CO)_4]} + E_{[Rhcp(CO)]}) - E_{[RhW_2cp_3(CO)_5]}$$

of 1.73 eV has been evaluated in the case of [$RhW_2cp_3(CO)_5$] in a geometry, as determined by X-ray analysis (structure e), the terminal coordination of all carbonyl groups leads to an energetical destabilization of about 11 eV (structure a). A more favourable configuration can be found by rotating the $W(CO)_2$ groups around the W–W bond. In structure b one of each W–C–O bond axis is located near the plane of the metal core. The other W–C–O group stands almost perpendicular to it. For further stabilization of the molecule the metal–carbon separation of the bridging carbonyl ligand has to be optimized (structure c) and steric constraints, caused by the interaction of the carbonyl oxygen with the cyclopentadienyl ligands have to be removed (structure d). Structure d is a hypothetical cluster with one bridging and four terminal carbonyl ligands. The

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*Bond distances (Å) in the idealized geometry: W–W = 2.65, Rh–W = 2.83, W–C = 1.94, Rh–C = 2.21, C–O = 1.18, W–cp = 2.00, Rh–cp = 1.93, C_{cp}–C_{cp} = 1.43, C_{cp}–H = 1.00. Angle W–C–O = 180°, angle C–W–C = 90°.

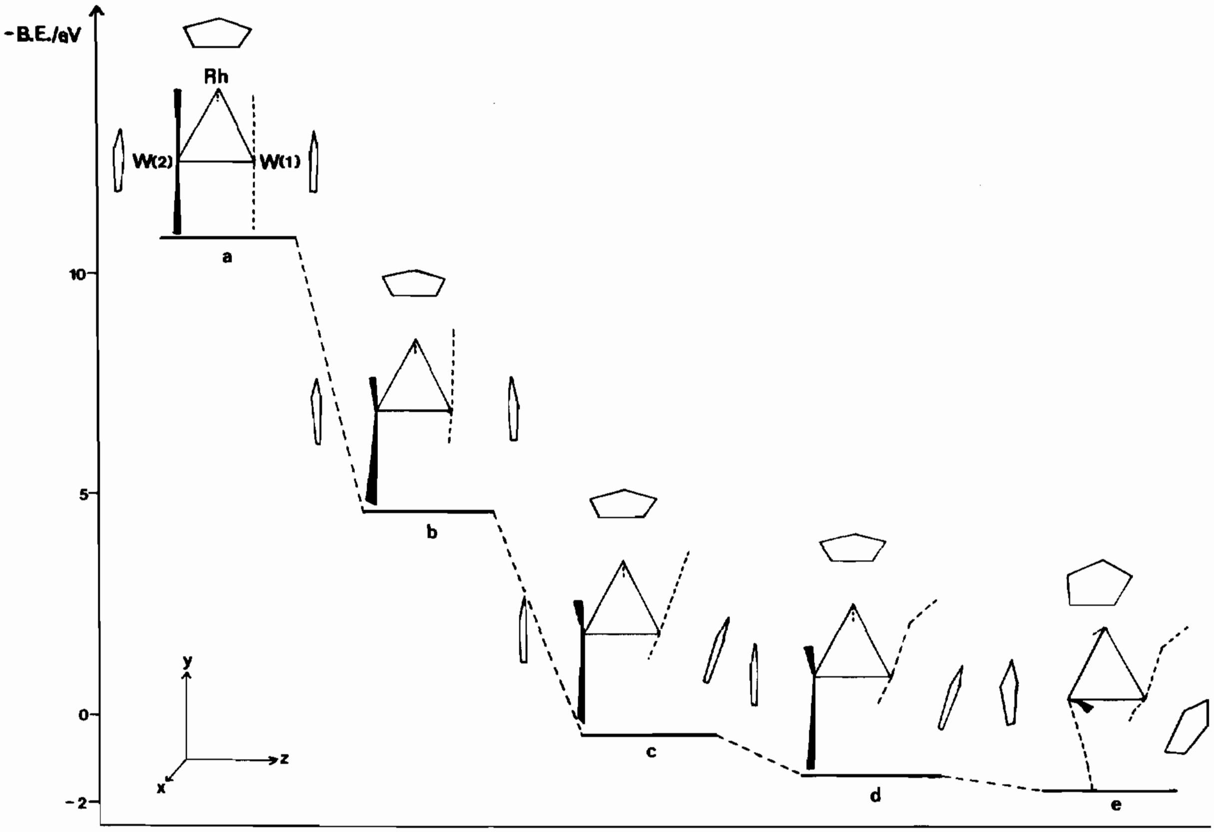

Fig. 3. Binding energy of [$RhW_2cp_3(CO)_5$] (e) and of cluster model with idealized geometry (a–d).

gain of binding energy, obtained by rotating one terminal ligand into a bridging position, is accompanied by an increased Rh–W overlap. In structure a the fragments [Rhcp(CO)] and [$W_2cp_2(CO)_4$] exist almost independently side by side. For the Rh–W(1) as well as for the Rh–W(2) bond an overlap n(Rh–W) of about 0.09 has been calculated. The transformation of structure a into structure d is accompanied with a decreased π interaction between the W $5d_{yz}$ orbitals ($\Delta n(W(1)-W(2)) = -11\%$), caused by the motion of one of each CO on W(1) and W(2) into the plane of these orbitals. The C(1)O(1) ligand is directed to the triangle of the metal atoms and forms the W(1)–Rh bridge without significant change in the W(1)–Rh overlap ($n(W(1)\text{–}Rh) = 0.1$). At the same time the W(2)–Rh overlap increases twofold from 0.09 in structure a to 1.19 in structure d.

Supplementary material

Further details of the crystal structure investigation are available from author G.W. on request.

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