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Three-membered metallacycle $Cp_3Rh_3(\mu\text{-}CO)_3$ as a cluster and benzenoid system in reactions with 12-electron particles PPh_3M^+ (where M = Cu, Ag, Au) and CpM^+ (where M = Fe, Ru) *

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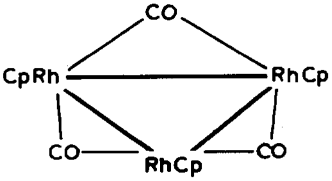
Abstract

The behaviour of the three-membered metallacycle $Cp_3Rh_3(\mu\text{-}CO)_3$ is similar to that of benzene and other benzenoids in reactions with 12-electron-particles CpM^+ (where M = Fe, Ru). Accordingly a hypothesis was made that $Cp_3Rh_3(\mu\text{-}CO)_3$ behaves as a typical benzenoid system. Cationic half-sandwich and sandwich clusters were synthesized during the interaction of $Cp_3Rh_3(\mu\text{-}CO)_3$ with cationic particles PPh_3M^+ (where M = Cu, Ag, Au) and $(CH_3CN)_4M^+$ (where M = Cu, Ag).

Introduction

The isolobality principle of Hoffmann [1] and the Wade rule [2] gave a powerful incentive for building bridges between two different fields of chemistry, namely organic and inorganic chemistry. The main incentive for this was the rapid development of organometallic chemistry after the discovery of ferrocene by Pauson and Kealy [3].

In summarizing the results of our researches on to the synthesis of multi-decker sandwiches [4–7] and cationic clusters [8], we remarked on the similarity of the behaviour of the three-membered metallacycle $Cp_3Rh(\mu\text{-}CO)_3$ (I) to that of such organic molecules as benzene. It made us regard the trirhodium cycle not only as a cluster but also as a benzenoid system.



(I)

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* This paper is dedicated to Professor P. Pauson.

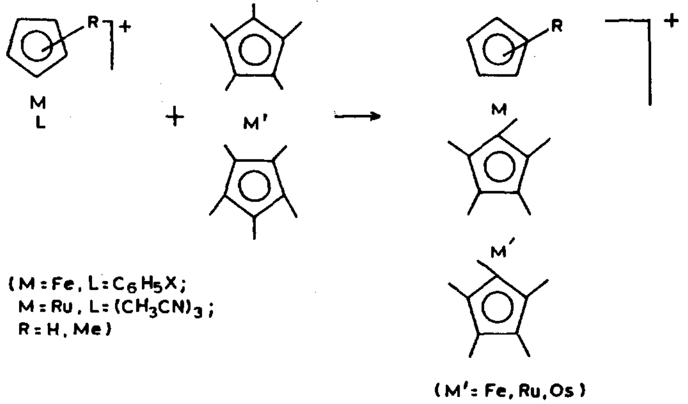
Results and discussion

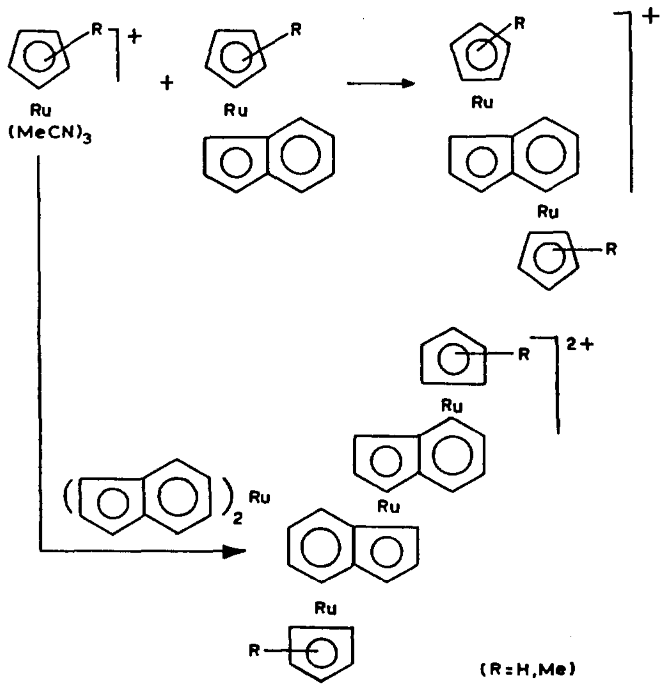
The addition of 12e$^-$ particles of type CpM$^+$ (where M = Fe, Ru) to arenes by the interaction of cationic complexes CpML$^+$ (where L = arene, $(CH_3CN)_3$) with aromatic compounds was studied previously * [9,10]:

$$CpML^+ + arene \rightarrow [CpMarene]^+ + L$$

(M = Fe, L = arene; M = Ru, L = $(CH_3CN)_3$)

We used this method to obtain previously unknown multi-decker cationic complexes—straight [4–6] and slipped [7]:





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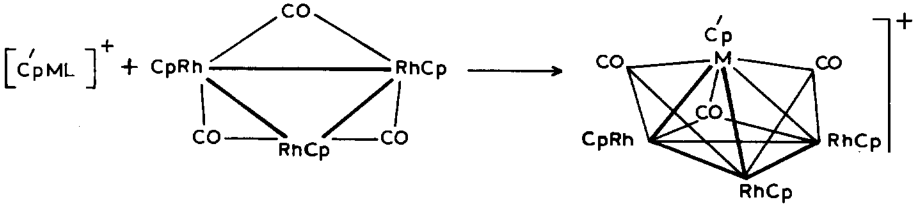
* The mechanism of these reactions has not been researched and therefore in talking about the attachment of 12e$^-$ particles, we are not sure that they are generated in a free state.

Moreover we showed that the mentioned 12e$^-$ particles easily attached not only to carbocyclic ligands in complexes, but under the same conditions they can be successfull added to the triangular metallacycle $Cp_3Rh_3(\mu\text{-}CO)_3$ with formation of earlier unknown cationic tetranuclear clusters of type II, the structure of which was proved by an X-ray diffraction study [8,11]:

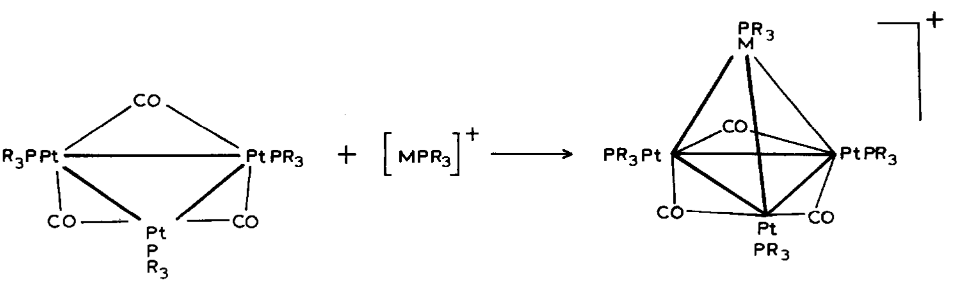


(I) (II)

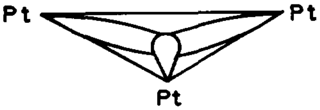
(M = Fe, L = $C_6H_5NO_2$, Cp' = C_5H_5, C_5Me_5 , Cp = C_5H_5 ;
M = Ru, L = $(CH_3CN)_3$, Cp' = C_5H_5 , C_5Me_5, Cp = C_5H_5)

All these substrates, which along with benzene and other arenes included metallocenes and the trirhodium cluster $Cp_3Rh_3(\mu\text{-}CO)_3$, reacted with particles of type CpM^+ under practically the same conditions with the formation of respective cationic complexes. We therefore propose that the trirhodium cluster $Cp_3Rh_3(\mu\text{-}CO)_3$ is isolobal to benzene and is consequently a new type of benzenoid system. This is based on the fact that each rhodium atom in this metallacycle has a lone electron pair on d_{z^2}-orbital with axis perpendicular to the plane of the ring. If we take into account the closely similar sizes of trirhodium and benzene cycles (the radii of the circles circumscribing these cycles are 1.51 and 1.48 Å, respectively) it turns out that both cycles possess three orbitals similar in shape and extent and of the same symmetry with respect to the axis, perpendicular to the plane of the cycle and passing through its centre (one orbital σ-type and two orbitals π-type), on which there are six electrons. Therefore the supposition about the isolobality of the cluster $Cp_3Rh_3(\mu\text{-}CO)_3$ and of the benzene molecule seems to be quite reasonable.

At the same time Mingos and his collaborators used the analogous three-membered cycle consisting of platinum atoms $[(PR_3)_3Pt_3(\mu\text{-}CO)_3]$ in reactions with other 12e$^-$ particles of type R_3PM^+ (where M = Cu, Ag, Au), and they also obtained cationic tetrahedron clusters [12,13]:



In this work the behaviour of three-membered Pt_3-cycle was interpreted as the behaviour of a typical cluster, in which, during reaction with particles $MPPh_3^+$, the three-centre central molecular orbital takes the main part [14]:



However it should be noted that the role of six electrons of d_{z^2} lone pairs in coupling a tetrahedron cluster should be more marked in the Rh_3Ru cluster than in the Pt_3Au cluster.

In fact due to the rapid energy decrease of *d*-electrons of transition metal atoms on approaching the end of the row [15] the participation of d_{z^2}-electrons in bonding must be less in the case of platinum atoms than in the case of rhodium atoms. On the other hand, the energy hole between vacant *p*-orbitals and the other valent orbitals of metal atoms increases towards the end of the series of transition metals. As a result tangential $6p_x$- and $6p_y$-orbitals of gold atoms become ineffective and do not participate in bonding the cluster framework [16,17]. In particular only the σ-type combination from d_{z^2}-lone pairs of platinum atoms (molecular orbitals of metallacycle symmetry a_1^1) takes part to any extent in bonding of gold in the Pt_3Au cluster. The interaction of π-type combinations with $6p_x$- and $6p_y$-gold orbitals is completely ineffective because they are too high [14]. On the contrary, in the Rh_3Ru cluster all nine valent orbitals of ruthenium should be regarded as operating [18], and one can expect their effective interaction also with π-type combinations from d_{z^2}-lone pairs of rhodium atoms. In other words, this cluster can be described as a sandwich, in which ruthenium is connected with two rings: cyclopentadienyl and three-membered metallacycle. The coupling with each ring is performed by three generalized chemical bonds—one like a headlight σ-type and the other ones of two-petal π-type [19].

Those considerations accord with the results of the EHT calculations relating to Rh_3Ru and Pt_3Au clusters [20].

So, on interaction with cationic $12e^-$ particles CpM^+ (where M = Fe, Ru) the rhodium cluster $Cp_3Rh_3(\mu\text{-}CO)_3$ displays the properties of a benzenoid system of a new type.

At the same time it is also of interest to research the behaviour of the $Cp_3Rh_3(\mu\text{-}CO)_3$ cycle in reactions with cationic particles of copper subgroup $MPPh_3^+$ since it was known that these particles can be added to the Pt_3-clusters [12,13] and to a benzenoid system such as the cyclopentadienyl anion [21]. Indeed the rhodium cycle $Cp_3Rh_3(\mu\text{-}CO)_3$, which is simultaneously a cluster and a benzenoid system, adds these particles easily.

In the present paper we consider the reactions of trirhodium cycle $Cp_3Rh_3(\mu\text{-}CO)_3$ with the particles CpM^+ (M = Fe, Ru) and also with the particles PPh_3M^+ and $M(CH_3CN)_4^+$ (M = metals of copper subgroup). The experimental details of the reactions of particles CpM^+ are published in previous works [8,11], and the experimental details of the reactions of the particles PPh_3M^+ (M = Cu, Ag, Au) and the particles $M(CH_3CN)_4^+$ (M = Cu, Ag) are given below *.

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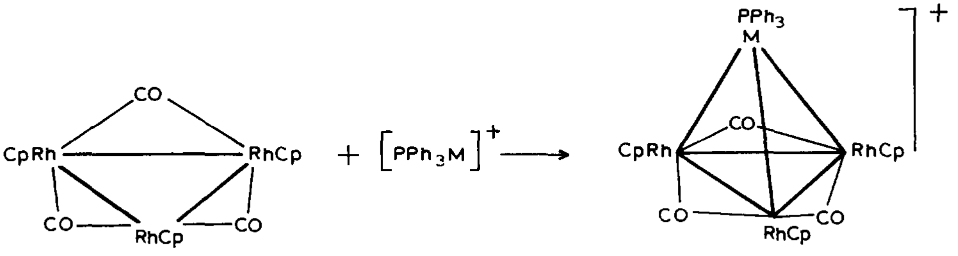
* For preliminary communication see ref. 22.

On studying 12e$^-$ PPh$_3$M$^+$ reactions (M = Cu, Ag, Au) with the three-membered Cp$_3$Rh$_3$(μ-CO)$_3$ cycle we have found that, as in the case of triplatinum (PR$_3$)$_3$Pt$_3$(μ-CO)$_3$ cycle, the cationic tetranuclear clusters IIIa–c are formed:



(I)

(IIIa : M = Cu ; IIIb: M = Ag; III c = Au)

In order to the generate MPPh$_3^+$ particles the separation of haloid-anions from M(PPh$_3$)X (M = Cu, Ag; X = I; M = Au; X = Cl) compounds with the help of TlPF$_6$ was chosen as a method. The reactions were conducted in CH$_2$Cl$_2$ at 20 °C under an inert atmosphere. The resulting cationic clusters IIIa–c are brown, small-crystalline substances, stable in a solid state in the air and decomposing in solution; in polar solvents the velocity of decomposition is greater. The initial trirhodium complex Cp$_3$Rh$_3$(μ-CO)$_3$, identified by its IR spectrum, is one of the decomposition products.

The structure of the clusters IIIa–c was confirmed by elemental analysis and also by IR, ^{1}H and ^{31}P NMR spectroscopy (Table 1).

In ^{1}H NMR spectra (in CD$_3$NO$_2$ solution) of these compounds two groups of signals with the same intensities are present and they correspond to protons of the cyclopentadienienyl (δ = 5.9 ppm) and phenyl (δ = 7.6–7.7 ppm) rings. In ^{31}P NMR spectra (CH$_3$NO$_2$ solution), PF$_6^-$ anion signals in the range of positive δ P values are also observed. For IIIa, c (M = Cu, Au) compounds these signals are singlets and for IIIb (M = Ag) clusters the splitting of ^{31}P signal is split into two doublets at ^{107}Ag and ^{109}Ag atoms. The obtained values of the constants $^1J(^{109}$AgP) 580 Hz and

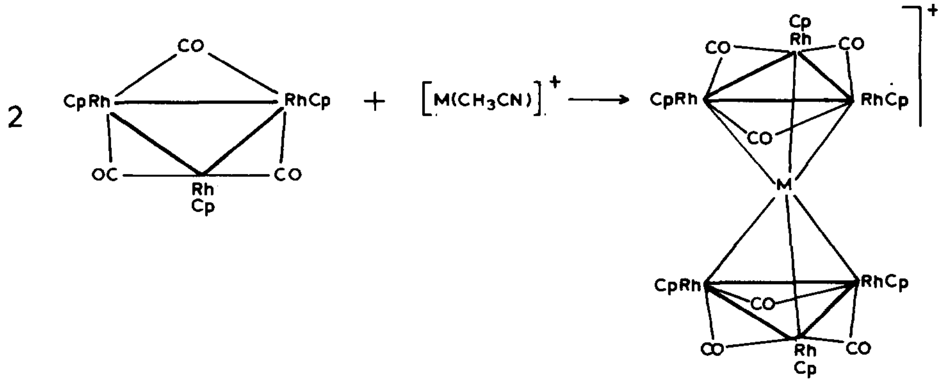
Table 1

	Compound		
	IIIa	IIIb	IIIc
M	Cu	Ag	Au
Yield (%)	18	44	25
Anal. Found (calc.) (%)			
C	40.39 (40.84)	38.94 (39.20)	36.60 (36.27)
H	2.78 (2.85)	2.71 (2.74)	2.53 (2.53)
P	6.18 (5.86)	5.57 (5.44)	–
Formula	$C_{36}H_{30}CuF_6O_3P_2Rh_3$	$C_{36}H_{30}AgF_6O_3P_2Rh_3$	$C_{36}H_{30}AuF_6O_3P_2Rh_3$
IR (CH$_2$Cl$_2$) ν(CO) (cm^{-1})	1866vs, 1820s	1868vs, 1818s	1866vs, 1817s
^{1}H NMR (CD$_3$NO$_2$) δ (ppm)	5.89 (s, Cp, 15H); 7.63 (s br, Ph, 15H)	5.85 (s, Cp, 15H); 7.67 (s br, Ph, 15H)	5.86 (s, Cp, 15H); 7.68 (s br, Ph, 15H)
^{31}P NMR (CH$_3$NO$_2$) δ (ppm)	−143.5 (sept, PF$_6$); 1.4 (s, PCu)	−143.5 (sept, PF$_6$); 18.0 (d d, PAg, $^1J(^{109}$AgP) 580, $^1J(^{107}$AgP) 503 Hz)	−143.5 (sept, PF$_6$); 37.6 (s, PAu)

$^1J(^{107}AgP)$ 503 Hz are close to those of phosphine complexes of silver and their $^1J(^{109}AgP)/^1J(^{107}AgP)$ ratio is approximately 1.15, which corresponds to the ratio of their gyromagnetic constants $\gamma^{109}Ag/\gamma^{107}Ag$ [23].

In IR spectra of IIIa–c complexes two $\nu(CO)$ absorption bands 1870 and 1820 cm^{-1}, typical for μ_2-CO groups, are observed. The $\nu(CO)$ values (1866–1868 and 1817–1820 cm^{-1} in CH_2CI_2) are 25–30 cm^{-1} greater than those of the $\nu(CO)$ values of initial $Cp_3Rh_3(\mu\text{-}CO)_3$ cluster, under 1840 and 1790 cm^{-1}, and this conforms well with the cationic nature of the IIIa–c complexes. So, unlike what happens in the clusters, obtained in the reactions of $Cp_3Rh_3(\mu\text{-}CO)_3$ with cationic particles of iron subgroup CpM^+ (where M = Fe, Ru), CO ligands in these compounds preserve their μ_2-bridge position in relation to the rhodium atoms, which is explained by the different electron demands of these two metal groups.

The choice of the three-membered metal cycle of $Cp_3Rh_3(\mu\text{-}CO)_3$ for the reactions with cationic particles turned out to be very successful, and if this cycle is to be considered as a ligand, the above cationic complexes can be named "half-sandwich clusters". To obtain "sandwich clusters" on the base of Rh_3-cycle I we also used tetrakisacetonenitrile cationic complexes of copper and silver $M(CH_3CN)_4^+$, following Venanzi [24] and Mingos [25] *. It was found that in these cases the reactions proceed under soft conditions (20 °C) in the same solvent, namely CH_2CI_2. As a result new heteronuclear cationic clusters IVa, b were obtained [26]. It should be noted that these cationic clusters IVa, b can also be considered as sandwich complexes:



The sandwich cationic clusters are red-brown substances, stable in the solid state in air. They slowly decompose in polar solvents, such as acetone and nitromethane. Their solubility in CH_2CI_2 is slight and they are precipitated from solution in the process of synthesis. The identification of their structure also offers no difficulties; it is confirmed by elemental analysis and by IR and ^1H NMR spectra (Table 2). The data of IR-spectra firmly testify to the presence of μ_2-coordinated CO ligands. In IR spectra the absorption bands of carbonyl groups are observed under 1810 and 1860 cm^{-1} (in CH_3NO_2 solution) and their position differs little from those of the absorption bands in half-sandwich clusters IIIa–c in spite of the fact that different solvents are used. In ^1H NMR spectra of both complexes (in CD_3NO_2 solution) only one band from the signal of cyclopentadienyl rings is observed, and the nature

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* In the above-mentioned works the term "sandwich clusters" is applied.

Table 2

	Compound	
	IVa	IVb
M	Cu	Ag
Yield (%)	30	46
Anal. Found (calc.) (%)		
C	31.90 (31.23)	31.06 (30.26)
H	2.22 (2.18)	2.31 (2.11)
Formula	$C_{36}H_{30}CuF_6O_6PRh_6$	$C_{36}H_{30}AgF_6O_6PRh_6$
IR (CH_3NO_2) ν(CO) (cm^{-1})	1860vs, 1810s	1860vs, 1810s
^1H NMR (CD_3NO_2) δ (ppm)	6.04 (s, Cp)	6.02 (s, Cp)

of the metal (Cu δ -6.04 or Ag δ -6.02 ppm) does not significantly affect its position. These data permit the structure of IVa, b to be defined as symmetrically constructed cationic sandwich clusters.

Thus, the use of the $Cp_3Rh_3(\mu\text{-}CO)_3$ cluster—as a benzenoid system of new type—facilitated formation of a bridge between sandwiches with carbocyclic ligands and sandwiches whose main framework consists entirely of metal atoms.

Experimental

The reactions were performed under dry argon in dry solvents. IR-spectra were recorded on a UR-20 spectrophotometer ^1H and ^{31}P NMR spectra on a Bruker WP 200 SV instrument using TMS and H_3PO_4 85% as standards respectively.

1. The synthesis of compounds IIIa–c

0.207 g (0.6 mmol) of $TlPF_6$ in 20 ml of CH_2Cl_2 were added to a mixture of 0.189 g (0.3 mmol) of $Cp_3Rh_3(\mu\text{-}CO)_3$ and 0.35 mmol of $M(PPh_3X)$ (M = Cu, Ag, X = I; M = Au, X = Cl) and stirred for 2 h at 20 °C, then 30 ml of $(C_2H_5)_2O$ were added. The precipitate was filtered, rapidly washed with CH_2Cl_2 (5 × 10 ml) for separation of the initial cluster $Cp_3Rh_3(\mu\text{-}CO)_3$. Complexes IIIa–c are considerably less soluble in this solution than $Cp_3Rh_3(\mu\text{-}CO)_3$, but long washing can greatly decrease the yield of clusters IIIa–c. The residue on the filter was extracted with acetone by small portions. IIIa–c were precipitated from the obtained solution by adding ether, filtered, and rapidly washed with CH_2Cl_2 (3 × 5 ml). After double precipitation from acetone by ether, analytically pure product was obtained in the form of bronze or red-brown crystals. In Table 1 are listed the yields and data of the elemental analyses.

2. The synthesis of compounds IVa, b

20 ml of CH_2Cl_2 were added to a mixture of 0.189 g (0.3 mmol) of $Cp_3Rh_3(\mu\text{-}CO)_3$ and 0.15 mmol $M(CH_3CN)_4^+PF_6^-$ (M = Cu, Ag), stirred below 20 °C for 4 h; the precipitate was filtered, washed with CH_2Cl_2 (5 × 10 ml) for the separation of the initial metallacycle. The precipitate was dissolved in acetone and ether was added. The resulting precipitate was filtered, washed with CH_2Cl_2 (4 × 5 ml) and analytically pure product (IVa, b) was obtained in the form of red-brown powders. In Table 2 are listed the yields and data of the elemental analyses.

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