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Synthesis and Properties of Rh_6- and Os_3-Cluster-Containing Monomers and Their Copolymers with Styrene

Svetlana I. Pomogailo, Gulzhian I. Dzhardimalieva,*
Viktoria A. Ershova, Sergei M. Aldoshin, Anatolii D. Pomogailo

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russia
E-mail:adpomog@icp.ac.ru

Summary: Cluster metal-containing monomers were obtained and characterized. Mono- and disubstituted products were obtained under mild conditions via the interaction of $Rh_6(CO)_{16}$ with 4-vinylpyridine (4-VPy) in the presence of trimethylamin-N-oxide. Substitution of labile acetonitrile ligand in $Rh_6(CO)_{15}NCMe$ by allyldiphenylphosphine ($AlPPh_2$) yields $Rh_6(CO)_{14}(\mu,\eta^2\text{-}PPh_2CH_2CH{=}CH_2)$ with formation of π-complex. The structures of $Rh_6(CO)_{15}(4\text{-}VPy)$, $Rh_6(CO)_{14}(\mu,\eta^2\text{-}PPh_2CH_2CH{=}CH_2)$ and $(\mu\text{-}H)Os_3(\mu\text{-}OCNM_2)(CO)_9PPH_2CH_2CH{=}CH_2$ have been determined by single-crystal X-ray diffraction studies, as well as by IR-, ^1H NMR spectroscopies. The Rh - Rh bond lengths are within 2.72÷2.80 Å. The copolymerization of cluster-containing monomers synthesized with traditional monomers has been studied. It was found that Rh_6- and Os_3-containing monomers did not change either the ligand surroundings or the structure of cluster monomer framework during polymerization reaction.

Introduction

The increasing interest in cluster-containing (co)polymers is nowadays based mainly on two aspects: (i) It is reasonable to expect that cluster or cluster complexes incorporated into the polymers would considerably modify polymer materials properties (adhesive, magnetic, thermal, etc.). (ii) Cluster-containing polymers are of great interest as catalysts for different reactions, combining the advantages both of homogeneous catalysts and heterogeneous ones (1). They may be obtained in two ways: by immobilization of cluster compounds on macroligands, or by polymerization reactions of some hypotetic monomers. One synthetic approach should include the introduction of polymerizable fragments into common type of

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clusters. To this end, recourse is made to the replacement of the intrinsic ligands of clusters by their analogues carrying multiple bonds, oxidative binding, addition of new groups on multiple M - M bonds under mild conditions, *etc.*

$Rh_6(CO)_{16}$ is widely used as a homogeneous catalyst in such reactions as hydroformylation, hydrogenation, *etc.* (2). We have succeeded in the synthesis of Rh_6 metal-containing monomers capable of radical copolymerization with several traditional monomers.

Synthesis and characterization of cluster-containing monomers

The $Rh_6(CO)_{16}$ cluster is known to be one of the most tolerant carbonyl clusters with respect to the substitution with various organic ligands. It was not until recently that new methods were developed (4) for the selective replacement of CO by nitrogen- and phosphorous-containing ligands, such as CH_3CN, PPh_3, Py, *etc.* In this work we used 4-vinylpyridine (4-VPy) and allyldiphenylphosphine ($AlPPh_2$) as unsaturated ligands.

Rh_6-containing Monomers with 4-VPy ligands. The reaction of $Rh_6(CO)_{16}$ with 4-VPy in the presence of N-trimethylaminoxide proceeds under mild conditions and results in the oxidation of coordinated CO to CO_2 (3):

$$Rh_6(CO)_{16} + 4\text{-VPy} \xrightarrow[-CO_2]{Me_3NO} \left\{ \begin{array}{c} Rh_6(CO)_{15}(4\text{-VPy}) \\ \mathbf{1} \\ Rh_6(CO)_{14}(4\text{-VPy})_2 \\ \mathbf{2} \end{array} \right. \qquad [1]$$

The main product of this reaction is the monosubstituted derivative $Rh_6(CO)_{15}(4\text{-VPy})$ (**1**). The disubstituted compound $Rh_6(CO)_{14}(4\text{-VPy})_2$ (**2**) is also produced in a small yield. Compounds **1** and **2** can be easily separated chromatographically and isolated as individual species.

The molecular structure of compound 1 . The compound **1** is an octahedral cluster of Rh atoms with eleven terminal and four μ_3 - bridging CO ligands. The 4-VPy substituent is linked to the Rh(3) atom and occupies the coordination site of the twelfth CO terminal ligand. The Rh - Rh bond lengths are within 2.736 -

2.787Å. The geometric parameters of the μ_3 -bridging CO ligands reveal a distinct asymmetry in the distribution of the Rh - Rh bond lengths caused by the non-equivalence of Rh atoms in the cluster due to the substitution of a 4-VPy ligand for a terminal CO ligand at the Rh (3) atom. The nitrogen N(21) atom in the 4-VPy ligand attached to the Rh(3) atom displays trigonal coordination. The Rh(3) - N(21) bond length is 2.19 Å. The vinyl group in **1** is in the plane of the pyridine ring and does not interact with the rodium cluster. The length of the double C=C bond is within its normal range (1.32(3) Å.).

Spectral characteristics of compounds 1 and 2. Spectral parameters of compounds **1** and **2** are listed in Table 1. The frequencies and relative intensities of IR adsorbtion bands in the carbonyl region of compounds **1** (2104, 2068, 2038, 1788 cm^{-1}) and **2** (2090, 2056, 2028, 1760 cm^{-1}) are the same as the relevant parameters for the derivatives of the parent cluster. ^1H NMR spectra of **1** and **2** contain multiplet signals from the α- and δ-protons in the pyridine cycle (AA`BB` spin system) and relevant signals from the vinyl protons; the overall ratio of intencities is 2:2:1:2).

Rh_6 -containing monomer with $AlPPh_2$-ligand (3). The interaction $AlPPh_2$ with $Rh_6(CO)_{15}NCMe$ proceeds under mild conditions at room temperature.

$$Rh_6(CO)_{15}NCMe + PPh_2CH_2CH{=}CH_2 \longrightarrow Rh_6(CO)_{15}PPh_2CH_2CH{=}CH_2 + MeCN$$

The IR-spectroscopy and TLC -monitoring of the reaction showed that at first the intermediate complex $Rh_6(CO)_{15}(\eta^1\text{-}PPh_2CH_2CH{=}CH_2)$ was formed. But in the coordination sphere of the carbonyl cluster there is the reactive $AlPPh_2$ ligand possesed the bidentate properties due to the double bond. This results in the formation of the yield $Rh_6(CO)_{14}(\mu,\eta^2\text{-}PPh_2CH_2CH{=}CH_2)$ product with additional π-coordination. As shown by X-ray study $AlPPh_2$ ligand substitutes CO in Rh_6-cluster with forming of Rh(2) - P (1.75 Å) bond as well as it is bound with cluster skeleton via vinyl group by π-bond. The Rh(4) - C(232) and Rh(4) - C(233) bond lengths are 2.368 Å and 2.319 Å, respectively. The Rh - Rh bond lengths are within

2.73÷2.80 Å, that are comparable to the ones of compound **1**. Thus, the compound **3** is an octahedral complex, in which AlPPh$_2$ ligand substitutes two terminal CO groups of the parent Rh$_6$-cluster with formation of π-complex (Fig.1).

Table 1. Spectral characteristics of $Rh_6(CO)_{15}(4\text{-VPy})$ (**1**) and $Rh_6(CO)_{14}(4\text{-VPy})_2$ (**2**)

Compound	IR spectrum ($CHCL_3$)		^1H ($CDCl_3$) spectrum
	ν(CO), cm^{-1}	ν(C=C), cm^{-1}	δ
1	2104 (w), 2068 (s), 2038 (av), 2010 (sh), 1788 (av.w)	1619 (av)	7.39 (m, 2H-α); 8.88 (m, 2 H-β); 6.68 (dd, 1H, -CH=CH$_2$,J = 10.74, 17.58 Hz); 6.10 (dd, 1H, -CH=CH$_2$, J = 17.54 Hz); 5.68 (dd, 1H, -CH=CH$_2$, J = 10.81 Hz)
2	2090 (av), 2056 (s), 2028 (av), 1619 (av), 1760 (av.w)	1619 (av)	7.35(m, 2H-β); 8.81(m, 2H-α); 6.65(m, 1H, -CH=CH$_2$); 6.06 (dd,1H, -CH=CH$_2$, J = 10.89 Hz); 5.63 (dd, 1H, -CH=CH$_2$, J = 10.89 Hz)

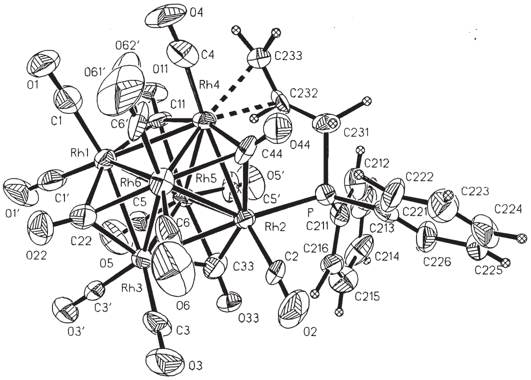
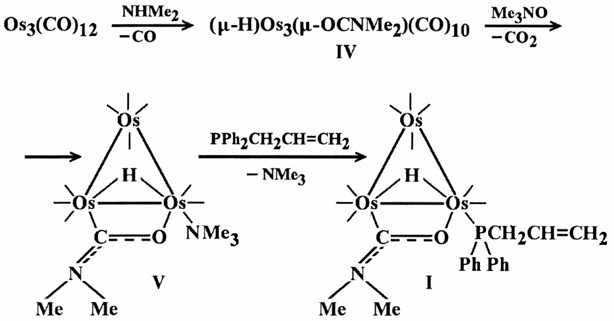


Figure 1. Molecular structure of $Rh_6(CO)_{14}(\mu,\eta^2\text{-}PPh_2CH_2CH{=}CH_2)$

The synthesis of the Os_3-monomer complex (μ-H)Os_3(μ-$OCNM_2$)$(CO)_9PPH_2CH_2CH=CH_2$ was carried out on the following scheme:[6]



The stability of the complex (μ-H)Os_3(μ-$OCNM_2$)$(CO)_9PPH_2CH_2CH=CH_2$ with respect to isomerization, ligand chelating, and other transformations in solution were investigated. No transformation of the complex were observed in the course of the synthesis or upon heating in solution.

The copolymerization of cluster-containing monomers.

Note that to the present time all attempts to homopolymerize cluster-containing monomers have not been successful. For the time being, the only way for making them participate in polymerization conversions is through copolymerization with conventional monomers. In this case, the units of the latter in the resulting products significantly predominate over those of the cluster monomers. Thus, the content of Os clusters in copolymers with styrene and acrylonitrile was 0.1-1.0 mol% [5]. The copolymerization of **1** with styrene proceeds much easier, and the content of the cluster monomer may be as high as 10 %. The previous studies of polymerization transformation of **3** showed that in spite of the existing of π-coordination with the participation of the multiple bond the latter was able to open. The copolymer of **3** with styrene is obtained.

Some properties of copolymers of styrene with Ph_2Pall and their macrocomplexes with $Rh_6(CO)_{15}CH_3CN$ are given in Table 2. Using IR-spectroscopy it is confirmed that the cluster fragments remain in the copolymers. The stretching frequencies of terminal and bridging CO of monosubstituted derivatives of $Rh_6(CO)_{16}$ (2064-2066 and 1794-1802 cm^{-1}) are observed in the spectrum of the macrocomplex. The absorbtion band at 2294 cm^{-1} corresponded to the stretching frequencies of the CN –group of coordinating acetonitrile is disappeared.

Table 2. The molecular - weight characteristics of copolymers of styrene with diphenylallylphosphine and immobilized $Rh_6(CO)_{15}CH_3CN$ cluster

Copolymers of Ph_2PAll (M_1) and styrene (M_2)				Macrocomplexes			
M/M_2 (mole)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w / \overline{M}_n$	Rh (wt. %)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w / \overline{M}_n$
1:1	9600	26200	2,70	1,12	9300	36100	3,88
1:3	20700	52900	2,55	7,57	22300	90500	4,06
1:7,5	25600	95600	3,73	7,29	60200	204200	3,39
1:40	80000	169000	2.11	5.43	56000	140000	2,5

Conclusion

Cluster-containing monomers represent a new generation of metal-containing monomers the studies of which are on early stage. All attempts to homopolymerize cluster-type monomers have not been succeccful. For the time being, the only way for making them participate in polymerization conversions is through copolymerization with the conventional monomers. Cluster-containing polymer products are characterized by high purity, product integrity, and structural homogeneity.

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