

Preparation, X-ray structure, copolymerization with styrene of $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9\{\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2\}]$ and catalytic properties of the cluster/styrene copolymer [☆]

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Received 31 January 2005; received in revised form 10 June 2005; accepted 10 June 2005

Available online 10 August 2005

Abstract

The complex $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9\{\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2\}]$ derived from the replacement of a lightly-stabilizing NMe_3 ligand in $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9(\text{NMe}_3)]$ by allyldiphenylphosphine molecule was physico-chemically and X-ray structurally characterized and served further as a metal cluster monomer to be immobilized on a polymer surface. The copolymerization of this cluster monomer with styrene was studied. It was found that the cluster molecule, when copolymerized, maintains its integrity and the overall structure. The cluster copolymers obtained have been tested as catalysts for oxidative dehydrogenation and cyclohexenol hydroxylation reactions.

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Keywords: Osmium cluster; Allyldiphenylphosphine; Crystal structure; Cluster–styrene copolymer; Radical polymerization; Catalytic oxidation

1. Introduction

Since in much of its chemistry the *triangulo*-frame and overall structure of hydridocarbonyl carboxamido Os_3 clusters $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNR}'\text{R}'')(\text{CO})_9\text{L}]$ ($\text{R}' = \text{H}$, Alk; $\text{R}'' = \text{Alk}$, Ar; $\text{L} = \text{CO}$, amine, phosphine and other 2-e ligand) remain intact, they may be conveniently anchored to a polymer surface and then studied in a heterogeneous catalytic process without decomposition. The performance of catalysts is highly dependent,

among other factors, on the ancillary ligand L with which metal complex was modified. Phosphines are known to be strong coordinating moieties which undergo little to no dissociation from the metal in solution and they are widely used ligands in metal-complex homogeneous and heterogeneous catalysis due to their governing role in providing activity and selectivity (see for example [1]). In this regard, the complex modified with $\text{L} =$ allyldiphenylphosphine $\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2$ considered to be perspective as metal-complex monomer which may be immobilized to polymer by opening $\text{C}=\text{C}$ bond. On the other hand, recent publications show that complexes containing 3-electron bridging carboxamido ligands $\mu\text{-OCNR}'\text{R}''$ are capable to producing an activation of *N*-allylic substrates resulted in their double-bond

[☆] 64th Communications from “Synthesis and Reactivity of Metal-Containing Monomers” series. For 63 communication see [V. Berezovskii et al., Russ. Chem. Bull. 54 (2005) (in press)].

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[1,2]-migration and simultaneous intra-substrate hydrogen transfer [2]. While the catalytic properties of the mentioned complexes, in particular in alkene's oxidation, have not been yet examined, it is probably that mixed carboxamido:phosphine complex $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9\{\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2\}]$ (**1**) may have beneficial effects as anchored catalyst.

2. Results and discussion

2.1. Preparation and structure of $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9\{\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2\}]$ (**1**)

The complex $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9\{\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2\}]$ (**1**) was obtained as a major product by treatment of a dichloromethane solution of the labile NMe_3 -substituted complex $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9(\text{NMe}_3)]$ (**2**) with allyldiphenylphosphine at ambient temperature under a dry argon atmosphere. Small amounts of two side products, $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9(\text{PPh}_2)]$ and $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9(\text{PPh}_3)]$, have been also isolated as impurities from the reaction [3]. The complex **1** is red, air-stable crystalline solid. It has been characterized by spectroscopy and X-ray crystallography (Fig. 1).

The spectroscopic data for the complex in solution are fully consistent with the solid state structure. The high-field metal-hydride region of ^1H NMR spectrum of **1** (in CDCl_3) contains doublet from the bridging H at $\delta = -13.50$ with the value of μ -hydrogen-phosphorus coupling (J_{HP} about 10 Hz) being indicative of the phosphine ligand bonded equatorially to the H-bound osmium through phosphorus. In $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum, a singlet from phosphorus atom is observed at $\delta = 14.58$ relative to 85% H_3PO_4 as external standard.

Weak bands at 1630 and 1634 cm^{-1} in IR (KBr pellet) and Raman spectra (CHCl_3 solution), respectively, are assigned the uncoordinated $\text{C}=\text{C}$. While examples of the allyl-to-1-propenyl type transformation are known for compounds containing a tetravalent phosphorus atom, viz., in both coordinated to metal $\text{P}(\text{CH}=\text{CH}-\text{CH}_3)\text{Ph}_2$ [4] and allylphosphonium salts upon refluxing in benzene [5] or in the presence of alkoxides, [6] the double bond shift and formation of 1-propenyl isomer $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9\{\text{P}(\text{CH}=\text{CHCH}_3)\text{Ph}_2\}]$ had not occurred with the cluster **1**. ^1H NMR spectrum displays the characteristic set of three multiplets (ratio 1:2:2) corresponding to the three groups of protons from the allylic fragment (CH multiplet at $\delta = 5.57$, four doublets of doublets from $\gamma\text{-CH}_2$ around $\delta = 5.06$, and $\alpha\text{-CH}'\text{H}''$ multiplet at $\delta = 3.45$). Comparison with the spectrum of free allyldiphenylphosphine ($\delta = 5.7$, 4.9 and 2.7 in CDCl_3) [4] show small difference in the δ values for β - and γ -protons, and the $\alpha\text{-CH}'\text{H}''$ multiplet is shifted ~ 0.7 ppm to lower field for the coordinated ligand. The two methyl groups in the bridging carboxamido ligand are non-equivalent due to hindered rotation about an amide $\text{N}-\text{C}$ bond and appear as two singlets at $\delta = 2.96$ and 2.41.

The molecular structure of **1** is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The crystallographic data, and details of the data collection and structure refinement procedures are summarized in Table 2. The backbone of the molecule is an Os_3 triangle with three metal–metal bonds.

The structure contains nine terminal carbonyl ligands. One of the $\text{Os}-\text{Os}$ edges is doubly bridged by the hydride and the carboxamido $\mu, \eta^2\text{-OCNMe}_2$ ligands, the latter 3-electron ligand being coordinated through both O and C atoms. The doubly bridged $\text{Os}(1)-\text{Os}(2)$ edge (2.9168(7) Å) is longer than the other two $\text{Os}-\text{Os}$ bonds ($\text{Os}(1)-\text{Os}(3)$ 2.8533(7) and $\text{Os}(2)-\text{Os}(3)$ 2.8822(8) Å). The $\text{Os}(1)-\text{Os}(3)$ distance is somewhat shorter relative to the another side edge (2.8533(7) vs. 2.8822(8) Å) as well as to an $\text{Os}-\text{Os}$ bond in $\text{Os}_3(\text{CO})_{12}$ (average 2.877 Å [7]). The $\text{Os}(1)$ and $\text{Os}(2)$ atoms of the edge spanned by bridging OCNMe_2 ligand lie virtually in plane with its O and C atoms. It is seen from Fig. 1 that the $\text{Os}(1)\text{Os}(2)\text{OC}$ plane is nearly perpendicular to the osmium triangle plane, similar to that reported for other related doubly bridged complexes [8], with the value of dihedral angle between the Os_3 and the Os_2OC planes 101.7°. The position of the bridging hydrogen atom is found experimentally. The equatorial carbonyl ligand attached to the H-bound osmium is opened out away from the $\text{Os}(1)-\text{Os}(2)$ and $\text{Os}(2)-\text{Os}(3)$ bonds as expected by the presence of the hydride, $\text{Os}(1)-\text{Os}(2)-\text{C}(21)$ 117.4(3)° and $\text{Os}(3)-\text{Os}(2)-\text{C}(21)$ 176.1(4)° in comparison with the corresponding angles for C(33) 92.1(4)°/153.2(4)° and C(31) 104.3(4)°/165.4(4)° in $\text{Os}(\text{CO})_4$ unit. The obtuse angle between the

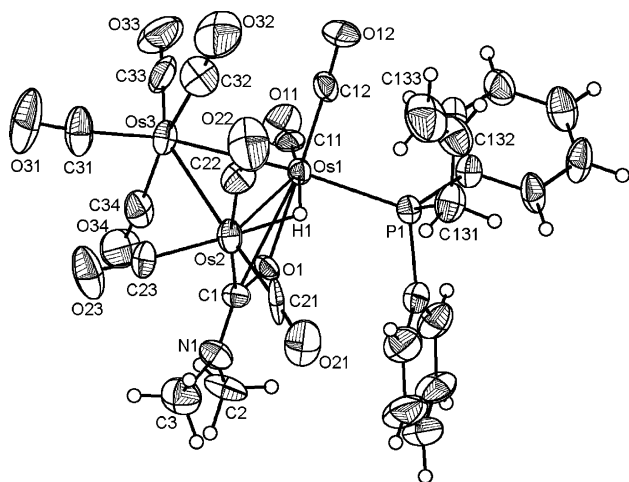


Fig. 1. Molecular structure of $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9\{\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2\}]$ (**1**) showing the atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level.

Table 1
Selected bond lengths (Å) and angles (°) for $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9\{\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2\}]$ (**1**)

Os(1)–Os(2)	2.9168(7)
Os(1)–Os(3)	2.8533(7)
Os(2)–Os(3)	2.8822(8)
Os(1)–P(1)	2.356(3)
Os(1)–O(1)	2.121(7)
Os(1)–C(11)	1.87(1)
Os(2)–C(1)	2.10(1)
Os(2)–C(21)	1.88(1)
Os(2)–C(23)	1.85(1)
Os(3)–C(34)	1.94(2)
O(1)–C(1)	1.29(1)
P(1)–C(131)	1.84(1)
C(131)–C(132)	1.45(2)
C(132)–C(133)	1.31(2)
C(1)–O(1)–Os(1)	110.7(7)
Os(2)–Os(1)–Os(3)	59.92(2)
Os(1)–Os(2)–Os(3)	58.95(2)
Os(1)–Os(3)–Os(2)	61.13(2)
N(1)–C(1)–Os(2)	133.8(9)
C(21)–Os(2)–Os(1)	117.4(3)
C(23)–Os(2)–Os(1)	137.6(4)
C(21)–Os(2)–Os(3)	176.1(4)
C(23)–Os(2)–Os(3)	83.0(4)
P(1)–Os(1)–Os(2)	108.29(8)
P(1)–Os(1)–Os(3)	167.84(8)
O(1)–Os(1)–Os(3)	88.7(2)
O(1)–Os(1)–Os(2)	67.9(2)
C(31)–Os(3)–Os(2)	104.3(4)
C(31)–Os(3)–Os(1)	165.4(4)
C(33)–Os(3)–Os(1)	92.1(4)
C(33)–Os(3)–Os(2)	153.2(4)
C(12)–Os(1)–Os(3)	90.4(4)
C(12)–Os(1)–Os(2)	111.3(4)
C(22)–Os(2)–Os(1)	104.3(4)
C(22)–O(2)–Os(3)	92.0(4)
C(11)–Os(1)–Os(2)	143.7(3)
C(11)–O(1)–Os(3)	91.1(3)

Table 2
Crystallographic data for the complex **1**

Compound	1
Formula	$\text{C}_{27}\text{H}_{22}\text{NO}_{10}\text{Os}_3\text{P}$
F_w	1122.03
Crystal system	Monoclinic
Space group	$P2_1/c$, No. 14
a (Å)	14.5620(10)
b (Å)	10.5840(10)
c (Å)	20.521(2)
β (°)	96.530(8)
V (Å ³)	3142.3(5)
Z	4
D_x (g cm ⁻³)	2.372
μ (mm ⁻¹)	12.205
Crystal size (mm), color	$0.36 \times 0.24 \times 0.12$, orange
$2\theta_{\text{max}}$ (°)	50
Reflections total/unique	4767/4572
R_{int}	0.0346
Final residuals	
R_1 for 3217 $F_{\text{hkl}} \geq 4\sigma(F)$	0.0330
wR_2 for all data	0.0663
Goodness-of-fit for all data	0.787

Os₃ and the Os(1)HOs(2) planes is 145.1°. The lengths of the ordinary bond C(132)–C(133) 1.45(2) and the double bond C(131)–C(132) 1.31(2) are as expected for an allylic moiety.

2.2. Copolymerization of the complex **1** and styrene

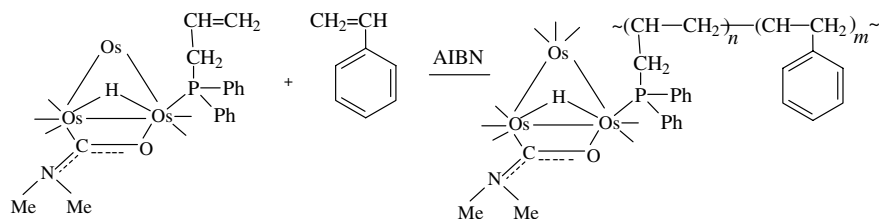
The specific character of structure of cluster monomers comes from their chemical behavior in polymerization reaction. As a rule, their homopolymerization proceeds with difficulty, except that formation of some oligomeric products was detected in a small yield [9]. Cluster monomers are best copolymerizing with traditional organic monomers [10,11]. The reactivity of cluster monomers toward copolymerization depends on the type of an unsaturated auxiliary ligand. For example, copolymerizability of cluster complexes bearing 4-vinylpyridine group is quite high. Copolymerization of 4-vinylpyridine complexes occurs even at their low concentrations (at 1–2 mol.%) in starting mixture of comonomers and results in the polymers modified abundantly (up to 12 wt.%) with the cluster units. At the same time, for many purposes, mainly for catalysis, copolymers with a low content of cluster fragments are just beneficial (the so-called low-percentage catalysts). In this regard, cluster monomers containing an allylic ligand, through which complex will be anchored to polymer, possess an advantage over those containing the vinyl group because allylic compounds are known to be less favorable to be polymerized due to the chain transfer degradation processes [12]. We have studied the copolymerization reaction of $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9\{\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2\}]$ (**1**) with styrene in the presence of azobisisobutyronitrile (AIBN) as an initiator (Scheme 1).

Cluster **1** has a poor solubility in styrene, and its concentration in the reaction mixture is less than 1 mole%. No appreciable period of induction has been observed for the copolymerization reaction. The reaction rate increases with concentration of the initiator (Fig. 2).

As expected, increase of AIBN concentration results in decrease of the copolymer-molecular weights (Table 3) from the high concentration of the active radicals. In organic solvent such as toluene, the same reaction of **1** with styrene leads to a decrease of the yield of the polymer, but percentage content of the cluster units in the copolymer chain is not changed.

A slope of the straight line from a graphical dependence of initial rate W_0 of the **1**/styrene copolymerization reaction on initiator concentration is near to 0.5 and so the rate of copolymerization is proportional to the square root of the initiator concentration to indicate a preferably bimolecular mechanism of the chain termination process.

Distribution of the molecular weight values for the **1**/styrene copolymer points toward a non-metal



Scheme 1.

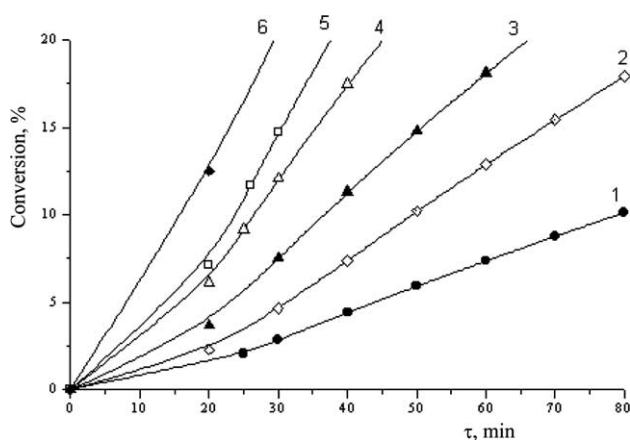


Fig. 2. Dependencies of the conversion degree of $[(\mu\text{-H})(\mu\text{-OCN-Me}_2)\text{Os}_3(\text{CO})_9(\text{CH}_2=\text{CHCH}_2\text{PPh}_2)]$ (**1**) on the reaction time at various AIBN concentrations upon copolymerization of **1** with styrene: curve 1, 0.07; 2, 0.39; 3 0.67; 4, 1.25; 5, 1.88; 6, 3.5 mole% of AIBN (70 °C, in bulk).

Table 3
Dependence of the average molecular weight of copolymer formed from styrene and cluster monomer **1**^a on initiator concentration

Concentration of AIBN (mol.%)	Content of Os in copolymer (wt.%)	\bar{M}_n ^b
0.07	1.7	108400
0.39	1.9	65000
0.67	2.1	40000
1.25	2.9	37000
1.88	1.6	32000
3.5	0.65	17000

^a The concentration of the **1** monomer was 0.6 mol.%.

^b \bar{M}_n is average molecular weight.

centered polymerization process, i.e., the osmium cluster monomer **1** behaves mainly like an allylic monomer, with its cluster substituent being intact, except it makes the chain-transfer degradation occurrence more probable and leads to a chain lengths shortening (Scheme 2).

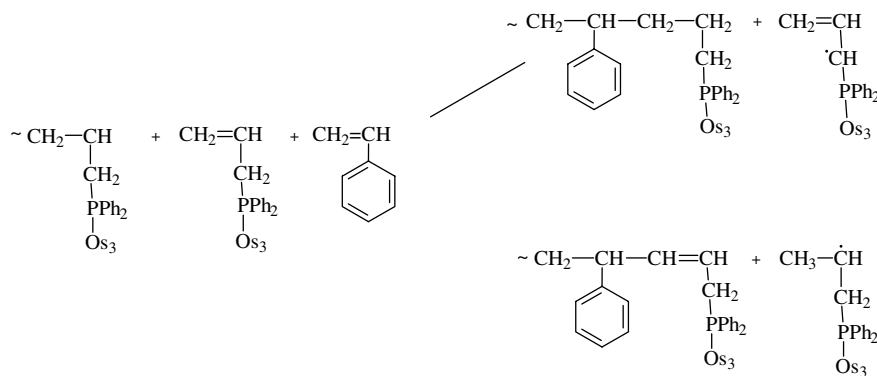
As follows from comparison of the IR spectra of **1**/styrene copolymer and complex **1**, the *triangulo*-frame and overall structure of the copolymerized cluster molecules are maintained. Near the same two main CO stretching frequencies are observed in the both spectra

(2045, 2002 for **1** and 2043, 2008 cm^{-1} for the polymer). The bands attributed to the stretching vibrations of polystyrene units are also observed in the IR spectrum of the polymer (1601, 1493, 758, 689 cm^{-1}).

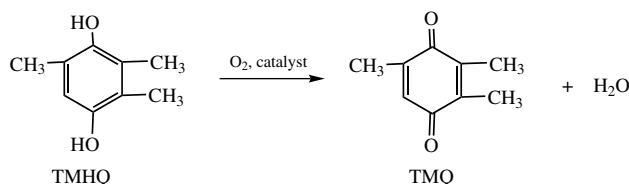
2.3. Oxidative dehydrogenation of 2,3,6-trimethyl-1,4-hydroquinone in the presence of the **1**/styrene copolymer as catalyst

The reaction of oxidative dehydrogenation of 2,3,6-trimethyl-1,4-hydroquinone (TMHQ) into 2,3,6-trimethyl-1,4-quinone (TMQ) under oxygen of the air was chosen for two reasons as a model reaction in examining of catalytic properties of **1**/styrene copolymer (Scheme 3). The first reason is that no side products have been observed in the literature in the reaction with another catalysts in water-methanol media [13]. The second reason is that TMQ plays a role of intermediate compound in the synthesis of α -tocopherol (vitamin E), and α -tocopherol can be prepared from TMQ by its hydrogenation. As synthetic methods of TMQ producing, a few catalytic reactions have been also described. 2,3,6-Trimethylbenzene can be oxidized with hydrogen peroxide in the presence of Cu^{2+} and Co^{2+} complexes with Schiff bases as ligands and gives TMQ contaminated with diphenone, diphenquinone and tar by-products [14]. Being coated on aluminum oxide or silica surfaces, it can be also oxidized with per-acids to TMQ in yields of about 20%.

It was found that the **1**/styrene copolymer is capable of producing an activation the TMHQ oxidative dehydrogenation reaction under oxygen of the air. It was shown also that this catalyzing polymeric material can be used repeatedly without loss in its activity (Table 4) with maintenance both of percentage Os-content and the cluster structure. It follows from comparison of IR data both for **1** and the polymeric catalyst registered before and after the reaction. Such a catalyst may be considered as heterogenised homogeneous catalyst [15]. The advantage of such catalysts over conventional homogeneous catalysts is that they are influenced to a less extent by catalytic poisons, and their catalytic activity remains near the same through a number of experiments. The catalysts are easily returnable from the reaction media and can be further subjected to studying, if necessary, or to reusing.



Scheme 2.



Scheme 3.

Table 4
Catalytic oxidation of TMHQ into TMQ in the presence of **1**/styrene copolymer

Run ^a	Initial reaction rate (mole/L h)	Specific activity (mole/(g-atom of Os) h)
1	0.32 ± 0.02	188
2	0.31 ± 0.02	182
3	0.30 ± 0.02	177
4	0.30 ± 0.02	177
F5	0.29 ± 0.02	177

^a The catalyst – 7.4×10^{-5} mole/L ([Os] = 1.71%), the substrate – 66 mmole/L, 10 mL water–methanol (1:1), 50 °C.

2.4. Oxidation of cyclohexene by hydrogen peroxide or *tert*-butylhydroperoxide (TBHP) in the presence of the **1**/styrene copolymer catalyst

Studying of catalytic oxidation of cyclohexene (CH) in the presence of the **1**/styrene copolymer showed that the process leads mainly to formation of unsaturated alcohols with the major product (52–65% yields) being cyclohexenol (CHol) (Table 5).

Cyclohexenone (CHone) and cyclohexene oxide (OCH) are obtained in much smaller yields (0.8–2.5%). Most likely, the catalytic oxidation of cyclohexene goes through initial formation of cyclohexenehydroperoxide (CHHP) and then proceeds as an autocatalytic process [16]. Traces of carboxyl-containing products as well as small quantities of bicyclohexenyl and bi(2-cyclohexene-4-hydroxy-1-yl) were also detected in the reaction mixture. Kinetic measurements and their implication in considerations regarding formation of these products are to be published elsewhere.

3. Conclusion

The cluster-containing monomer $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_9\{\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2\}]$ is a molecular compound that include a framework of metal atoms, which are separated by short distances permitting direct metal–metal interaction. Such a framework is surrounded by a polymerizable ligand.

The copolymerization of cluster-containing monomers is the most promising approach to obtaining a high degree of uniformity and integrity of polynuclear formations in the polymers. This method is expected to be one of the ways of preparing novel structurally organized catalysts for different reactions.

4. Experimental

4.1. General techniques

Syntheses were performed under an inert atmosphere of argon. Solvents were purified by standard methods prior to use [17]. *tert*-Butyl hydroperoxide (TBHP) was used after removing water, acetone and methanol admixtures by pumping-out. Infrared spectra were recorded in cyclohexane or from KBr pellet on a Specord 75-IR spectrometer using CaF₂ cell. The Raman spectrum was registered in CHCl₃ solution on a Triplemate, Spex (USA) spectrometer measured with excitation at 633 nm. ¹H and ³¹P{¹H} NMR spectra were recorded on a Bruker DPX-250 spectrometer using CDCl₃ as solvent and calibrated against internal TMS (¹H) or external 85% H₃PO₄ (³¹P). Mass spectra were obtained on a MX-1310 mass spectrometer at 50 eV. Preparative thin layer chromatography (TLC) was carried out on commercial Merck plates (Kieselgel 60 F₂₅₄). The cluster $[(\mu\text{-H})\text{Os}_3(\mu\text{-OCNMe}_2)(\text{CO})_{10}]$ was prepared according to the published procedure [18]. Allyldiphenylphosphine was prepared from the allyl bromide and LiPPh₂ according to the literature procedure [19]. Me₃NO · 2H₂O were prepared by the literature method [20].

Table 5
Hydroperoxide oxidation of cyclohexene with **1**/styrene copolymer

Oxidizing agent	[Os] · 10 ⁴ (mole/L)	Solvent	[CH] (mole/L)	T (°C)	Yields of products (%)		
					OCH	CHone	CHol
H ₂ O ₂	5	CH ₂ Cl ₂	2.0	30	0.8	47	52
TBHP	3.5	CH ₂ Cl ₂	2.1	30	0	48	52
TBHP	0.82	benzene	4.1	50	2.5	25	62.5 ^a
TBHP	0.87	toluene	4.1	50	1.8	25.7	65.0 ^a

^a The other products: carboxyl-containing products, bicyclohexenyl and bi(2-cyclohexene-4-hydroxy-1-yl).

4.2. Preparation of [(μ-H)Os₃(μ-OCNMe₂)(CO)₉(NMe₃)] (**2**)

A solution of [(μ-H)Os₃(μ-OCNMe₂)(CO)₁₀] (41 mg, 0.044 mmol) in diethyl ether (5 cm³) was treated with a methanolic solution (1 cm³) of Me₃NO · 2H₂O (9 mg, 0.081 mmol) and then stirred at ambient temperature for an additional time. The reaction was monitored by TLC (hexane–CH₂Cl₂ 2:1, v/v) and stopped as soon as starting material (*R_f* 0.7) had disappeared (2 h), along with a single band of product (*R_f* 0.5) being present on TLC plate. The solution was then diluted with hexane (5 cm³) and filtered successively through two short silica columns in order to remove residual Me₃NO. Removal of the solvent under reduced pressure gave orange-red crystalline powder of the cluster [(μ-H)Os₃(μ-OCNMe₂)(CO)₉(NMe₃)] (**2**) (40 mg, 96%). IR (ν(CO), C₆H₁₂, cm⁻¹): 2094m, 2048s, 2016s, 2005vs, 1974w, 1994s, 1966m, 1924m. ¹H NMR (CDCl₃, δ, ppm): 3.21 (s, 3H, NMe), 2.97 (s, 9H, NMe₃), 2.93 (s, 3H, NMe), -12.63 (s, 1H, μ-H). This product was used in the following steps without further purification.

4.3. Preparation of [(μ-H)Os₃(μ-OCNMe₂)(CO)₉(PPh₂CH₂CH=CH₂)] (**1**)

Cluster **1** (196 mg, 0.2 mmol) in CH₂Cl₂ (5 cm³) and allyldiphenylphosphine (0.05 cm³, 0.23 mmol) were mixed and stirred under dry argon atmosphere at r.t. for 15 h, after which the mixture was subjected to preparative TLC using hexane–diethyl ether (7:1, v/v) as eluent. The major band (*R_f* 0.6) was extracted with CH₂Cl₂ and the extract was filtered. Removal of a solvent under reduced pressure gave reddish-orange crystalline solid which was then recrystallized repeatedly (4–5 times) from hexane–CHCl₃ (1:2 v/v) to give red crystals of spectroscopically individual complex [(μ-H)Os₃(μ-OCNMe₂)(CO)₉(PPh₂CH₂CH=CH₂)] (**1**) (136 mg, 61%). IR (ν(CO), C₆H₁₂, cm⁻¹): 2088m, 2044s, 2009vs, 1995m, 1984w, 1974w, 1942w; 1630w (ν(C=C), KBr). ¹H NMR (CDCl₃, δ, ppm): 7.51 (m, 10H, Ph), 5.57 (m, 1H, =CH–), 5.12 (dd, 1H, ³J = 10.3 Hz, *J_{gem}* = 3.6, ⁴J = 1.1 Hz, =CHH_{cis}), 5.00 (ddd, 1H, ³J = 16.8 Hz, *J_{gem}* = 3.6, ⁴J = 1.3 Hz, =CHH_{trans}), 3.45 (m, 2H, *J_{gem}* = 13.6, ³J = 7.2,

⁴J = 1.3 Hz, *J_{HP}* = 11 Hz, –CH'H''), 2.96 (s, 3H, NMe), 2.41 (s, 3H, NMe), -13.50 (d, 1H, *J_{HP}* = 10.0 Hz, μ-H).

4.4. X-ray crystallography

Crystals of the complex **1** was grown from cyclohexane–CH₂Cl₂ solution at room temperature.

Diffraction data were measured by the standard technique on Nonius CAD4 diffractometer at room temperature using Mo Kα radiation. An empirical correction for absorption was applied to the data using the 3 azimuthal scan curves. The structure was solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms by full-matrix least-squares using SHELX97 program package. The bridging hydrogen atom was found on a final difference electron density map and included into refinement with fixed *U_{iso}* = 0.05 Å [2]. The rest hydrogen atoms were refined geometrically. CCDC 252202 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

4.5. Copolymerization of [(μ-H)Os₃(μ-OCNMe₂)(CO)₉(PPh₂CH₂CH=CH₂)] (**1**) with styrene

Radical copolymerization of **1** with styrene was carried out in bulk or in toluene in the presence of AIBN (0.07–3.5 mol.%). The monomer [(μ-H)Os₃(μ-OCNMe₂)(CO)₉(PPh₂CH₂CH=CH₂)] (0.02 g, 1.78 × 10⁻⁵ mole), styrene (0.3 g, 0.003 mole), and AIBN were placed in glass ampoule. The mixture was degassed by freeze-thaw cycles to remove the oxygen from the reaction mixture completely. The ampoule was then sealed in vacuum and heated at 70 °C for 3 h. The copolymer formed was dissolved in 5 mL of benzene and precipitated with 20 mL of ethanol, then dried at 30 °C under vacuum. The yield: 0.22–0.24 g (72–78%). Os, found (0.65–2.9 wt.%), *M_n* = 17,000–108,400 Da, IR (KBr): 3468, 3026, 2922, 2043, 2008, 1602, 1494, 1438, 1371, 1182, 1029, 907, 757, 698, 540 cm⁻¹.

4.6. Oxidative dehydrogenation of 2,3,6-trimethyl-1,4-hydroquinone

The experiments were carried out in the thermostating three-neck flask provided with seal and condenser at stirring in 10 mL water–methanol solution (1:1 vol.) at 50 ± 0.2 °C. Initial concentration of the substrate 2,3,6-trimethyl-1,4-hydroquinone was 66 mmole/L. The air was feeded with the rate of 6.2 L/h and the rate of stirring was 2 s^{-1} that provided the carrying out of the process in the kinetic region. Before reaction the Os-copolymer catalyst (0.08 g, the content of Os is 1.71%, $\overline{M}_n = 108,000$) was aged in water–methanol solution (1:1 vol.) for 24 h. The initial rate for oxidizing dehydrogenation was 0.3 mole/L h. The kinetic measurements were carried out by control sampling followed by the analysis of the content of TMHQ. The concentration of substrate were analyzed by GLC.

4.7. Oxidation of cyclohexene by tert-butylhydroperoxide

Hydroxylation of cyclohexene (CH) was carried out in an argon atmosphere in benzene at 30–50 °C. The concentrations of CH were 2.0–4.1 mole/L. Products of the catalytic CH oxidation were analyzed by GLC and on a YEOL YMS D 3000 chromatomass spectrometer.

Acknowledgments

This work was financially supported by the Russian Foundation for Basic Research (Projects 03-03-06628 and 04-03-32634).

References

- [1] A. Caiazzo, R. Settambolo, L. Pontorno, R. Lazzaroni, J. Organomet. Chem. 599 (2000) 298.
- [2] (a) V.A. Ershova, S.V. Tkachev, A.V. Golovin, L.Ya. Al't, Mendeleev Commun. (1998) 208;
(b) V.A. Ershova, A.V. Golovin, V.M. Pogrebnyak, J. Organomet. Chem. 658 (2002) 1–2,147.
- [3] V.A. Ershova, A.V. Golovin, L.A. Shekudyakova, P.P. Semyanikov, S.I. Pomogailo, A.D. Pomogailo, Russ. Chem. Bull., Int. Ed. (2000) 1448.
- [4] A. Jegorov, F. Tureček, J. Organomet. Chem. 379 (1989) C5.
- [5] G. Bushi, H. Wuest, Helv. Chim. Acta 54 (1971) 1767.
- [6] T. Keough, M. Grayson, J. Org. Chem. 29 (1964) 631.
- [7] M.R. Churchill, B.G. BeBoer, Inorg. Chem. 16 (1977) 828.
- [8] (a) A.J. Deeming, Adv. Organomet. Chem. 26 (1986) 1;
(b) R.D. Adams, N.M. Golenbeski, J.P. Selegue, Inorg. Chem. 20 (1981) 1242;
(c) K.A. Azam, R. Dilshad, S.E. Kabir, M.A. Mottalib, M.B. Hursthouse, K.M.A. Malik, Polyhedron 19 (2000) 1081;
(d) B.K.-M. Hui, W.T. Wong, J. Chem. Soc., Dalton Trans. (1998) 447;
(e) A.V. Virovets, V.A. Ershova, N.V. Podberezskaya, V.A. Maksakov, Metalloorg. Khim. 4 (1991) 932 [Organomet. Chem. USSR, 4 (1991) (Engl. Transl.)];
(f) A. Vega, E. Spodine, A. Arce, J. Manzur, A.M. Garcia, M.T. Garland, Acta Crystallogr., Sect. C 55 (1999) 322.
- [9] A.D. Pomogailo, V.S. Savost'yanov, Synthesis and Polymerization of Metal-Containing Monomers, CRC Press, Boca Raton, 1994.
- [10] N.M. Bravaya, A.D. Pomogailo, V.A. Maksakov, V.P. Kirin, V.P. Grachev, A.I. Kuzaev, Russ. Chem. Bull. 44 (1995) 1062.
- [11] S.I. Pomogailo, G.I. Dzhardimalieva, V.A. Ershova, S.M. Aldoshin, A.D. Pomogailo, Macromol. Symp. 186 (2002) 155.
- [12] Kh.S. Bagdasar'yan, Theory of Radical Polymerization, Nauka, Moscow, 1966.
- [13] V.G. Kharchuk, A.B. Shishmakov, O.V. Koryakova, V.V. Satarova, L.A. Petrov, Zh. Org. Khim. 70 (2000) 993.
- [14] R.S. Drago, J. Goul, A. Zolombeck, D.K. Straub, J. Am. Chem. Soc. 102 (1980) 1033.
- [15] A.D. Pomogailo, Catalysis by Polymer-Immobilized Metal Complexes, Gordon & Breach, London, 1998.
- [16] S.N. Kholuiskaya, A.D. Pomogailo, N.M. Bravaya, S.I. Pomogailo, V.A. Maksakov, Kinetics and Catalysis 44 (2003) 831.
- [17] A.J. Gordon, R.A. Ford, The Cemist's Companion, Wiley, New York, 1972.
- [18] A. Mayr, Y.C. Lin, N.M. Boag, C.E. Campe, C.V. Knobler, H.D. Kaesz, Inorg. Chem. 23 (1984) 4640.
- [19] M.A. Marhur, W.H. Myers, H.H. Sisler, G.E. Ryschkewitsch, Inorg. Syn. 15 (1974) 128.
- [20] K. Weygand, G. Hilgetag, Organisch-Chemische Experimentierkunst, Johann Ambrosius Barth Verlag, Leipzig, 1964.