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LETTERS TO THE EDITOR

Binuclear Rhodium Organometallic Complexes as Catalysts of the Liquid-Phase 1-Octene Oxidation

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The reaction of catalytic liquid-phase oxidation of olefins by molecular oxygen belongs to the most promising processes of organic synthesis and is a subject of numerous publications (see [1–3] for example). We have shown recently [4] that mononuclear rhodium organometallic complexes are active catalysts of the 1-octene oxidation by molecular oxygen. In this communication we present preliminary results of studying catalytic properties of complexes containing several metal centers, namely binuclear complexes of rhodium (+1), rhodium (+3), iridium (+1), palladium (+2), and triad complexes containing the ruthenium (+2) complex *trans*-$[Ru(py)_4(CN)_2]$ as a central unit and rhodium (+1) or palladium (+2) complexes as terminal fragments.

The oxidation was carried out in a glass reactor with a temperature-controlled jacket and a magnetic stirrer [5]. Pressure of oxygen was 90 kPa, solvent chlorobenzene. Initial oxidation rate (W_0) was determined from the oxygen absorption curve by the extrapolation of the obtained dependence to a zero time. As earlier [4, 5], reactions were carried out in the presence of *tert*-butyl hydroperoxide (TBHP) synthesized as described in [5]. 1-Octene and chlorobenzene were of Aldrich production.

The results of studying catalytic activity of compounds **I–V, VII** obtained earlier and of new complexes **VI, VIII** are given below {W_0 values at 333 K; [TBHP] 0.05 M; [catalyst] 0.005 M; (Allyl) π-allyl ligand, (Cod) cycloocta-1,5-diene, and (Acac) acetylacetone residue}. For comparison the activity of complex **IX** [Rh(Acac)(PPh$_3$)(CO)] (*c* 0.01 M), which is the most active of mononuclear complexes [4], is also presented. To have comparable data, the concentration of binuclear complexes per one metal atom is given. The concentration of triad complexes **VII, VIII** was 0.0033 M.

Catalyst	$W_0\times10^5$, mol l^{-1} s^{-1}
$[Rh(CO)_2Cl]_2$ (**I**)	9.2
$[Rh(\mu\text{-}OOCPh)(COOMe)(CO)(PPh_3)]_2$ (**II**)	9.9
$[Rh(Allyl)_2Cl]_2$ (**III**)	10.6
$[Ir(Cod)Cl]_2$ (**IV**)	9.7
$[Pd(Allyl)Cl]_2$ (**V**)	0.4
$[(Cod)Rh(\mu\text{-}Cl_2)Rh(PPh_3)(CO)]$ (**VI**)	10.3
$[(CO)_2ClRh(CN)Ru(Py)_4(CN)RhCl(CO)_2]$ (**VII**)	3.1
$[(Allyl)ClPd(CN)Ru(Py)_4(CN)PdCl(Allyl)]$ (**VIII**)	0.4
$[Rh(Acac)(PPh_3)(CO)]$ (**IX**)	6.5

These data point to the fact that binuclear complexes of rhodium **I–III, VI** exhibit a higher activity as compared to mononuclear complexes studied earlier [4], for example, compared to complex **IX**. A high activity is also characteristic of binuclear iridium complex **IV**. It suggests that the reason of higher activity of binuclear complexes is the ability of chloride and carboxylate bridges to be split in a reaction medium under the action of solvent and/or substrate molecules. For cyanide bridges in complexes **VII, VIII** such ability is not characteristic. Low

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† Deceased.

activity of both binuclear **V** and triad **VIII** palladium complexes points to a determining influence of the metal nature on the catalytic activity of the complexes.

The most active complex **III** in the series of compounds under study was used for the determination of the dependence of the 1-octene oxidation rate on the catalyst concentration. The data obtained on carrying out the reaction under the same conditions, but at a lower temperature (313 K), are given below.

III$\times 10^5$, mol l^{-1}	2.5	7.5	38	75	220	500
$W_0\times 10^5$, mol l^{-1} s^{-1}	3.2	11.0	11.2	12.5	13.5	16.0

These data show that a high catalytic activity of complex **III** is observed even at the concentration of 7.5×10^{-5} M and increases slightly as the temperature increases further.

Complexes **I–V** and **VII** were synthesized by the procedures [6–11].

[(Cod)Rh(μ-Cl$_2$)Rh(PPh$_3$)(CO)] (VI). To a weighed sample of 0.106 g of [Rh(PPh$_3$)(CO)Cl]$_2$ [12] a solution of 0.185 g of [Rh(Cod)Cl]$_2$ [13] in 6 ml of chloroform was added. The suspension was stirred with a magnetic stirrer up to complete dissolution of the initial complex. The solvent was removed in vacuo, a residue was ground with hexane at –30°C, filtered off, washed with hexane (–30°C), and dried. Yield 0.27 g (92%). IR spectrum (CHCl$_3$), cm^{-1}: ν(CO) 1980. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 4.42 (2H, CH, Cod), 3.94 (2H, CH, Cod), ~2.5 m (4H, CH$_2$, Cod), ~1.8 m (4H, CH$_2$, Cod), 7.8–7.4 (15H, Ph, PPh$_3$). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: ($^1J_{\text{CRh}}$, $^2J_{\text{CP}}$, Hz): 184.29 (CO, 81.3, 17.5). ^{31}P NMR spectrum (CDCl$_3$), δ, ppm: ($^1J_{\text{CRh}}$, $^2J_{\text{CP}}$, Hz): 46.48 (PPh$_3$, 175.9, 17.5). Found, %: C 47.79; H 4.02; Cl 10.31. $C_{27}H_{27}Cl_2\cdot OPRh_2$. Calculated, %: C 48.03; H 4.03; Cl 10.05.

Complex **VI** in the CHCl$_3$ solution is in a dynamic equilibrium with initial complexes.

[(Allyl)ClPd(CN)Ru(Py)$_4$(CN)PdCl(Allyl)] (VIII). To a solution of 0.117 g of *trans*-[Ru(Py)$_4$(CN)$_2$] [14] in 3 ml of chloroform a solution of 0.091 g of [PdCl(Allyl)]$_2$ [10] in 5 ml of chloroform was added. The mixture was stirred for 15 min, then the solvent was removed, the reaction product was carried on a filter, washed with ether, and dried up in vacuo. Yield 0.198 g (95%). IR spectrum (CHCl$_3$), cm^{-1}: ν(CN) 2098. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 8.58 d (8H, CH, Py), 7.65 t (4H, CH, Py), 7.16 t (8H, CH, Py), 5.49 m (2H, CH, Allyl), 3.4 d (2H, CH$_2$, Allyl), 3.89 d (2H, CH$_2$, Allyl), 2.86 d (2H, CH$_2$, Allyl), 2.82 d (2H, CH$_2$, Allyl). Found, %: C 40.21; H 3.59; N 10.11. $C_{28}H_{30}Cl_2N_6Pd_2Ru$. Calculated, %: C 40.26; H 3.62; N 10.06.

Conditions of measuring spectral characteristics of the compounds see [4].

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