THE CATALYTIC OLIGOMERIZATION OF BUTADIENE ON COMPLEXES OF Rh(I)

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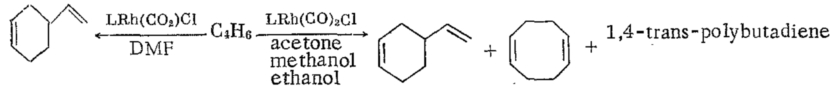
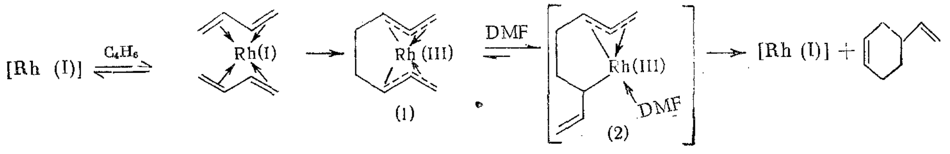
Complex catalysts open up new possibilities for the synthetic use of butadiene. Particular interest is presented by the preparation of linear and cyclic oligomers, which have been relatively inaccessible previously [1-3]. The selectivity of the oligomerization process depends strongly on the nature of the ion of the complex-forming agent and the ligands, the solvent, and the reaction conditions. In the present work we have studied the influence of these factors on the direction of the dimerization of butadiene. As catalysts we used complexes of Rh(I), of types (I), (II), and (III) having in the coordination sphere ligands easily displaced by butadiene: $LRh(CO)_2Cl$ (I), where L is benzotriazole (Ia), acridine (Ib), imidazole (Ic), benzimidazole (Id), or m-phenylenediamine (Ie); $H[Rh(ArCOO^-)Cl]$ (II), where $ArCOO^-$ represents the anion of N-phenylanthranilic acid (IIa) or that of Rhodamine C (IIb); and $Cl(CO)_2Rh-L-Rh(CO)_2Cl$ (III), where L is benzidine (IIIa) or m-phenylenediamine (IIIb).

The mobility of one of the carbonyl groups in complexes of types (I) and (III) is shown by the possibility of its displacement by amines and tertiary phosphines [4]. The lability of the carbonyl group is also confirmed in our experiments: when a solution of the complex (Ia) was treated with butadiene, in the IR spectrum of the initial complex, which had two ν_{CO} absorption bands at 2100 and 2025 cm^{-1}, the absorption at 2100 cm^{-1} disappeared and the second band shifted to 1950 cm^{-1}. The displacement of the aromatic part of the ligand by organic compounds capable of forming a bond of the π-donor type in the complexes (II) has been shown previously [5].

Experiments with catalysts of type (I) have shown that the direction of the process depends strongly on the nature of the solvent. In methanol, ethanol, and acetone, cycloocta-1,5-diene and 1,4-trans-polybutadiene (intense absorption band of $\delta_{trans-CH=CH-}$ at 964 cm^{-1}) [6] are formed in addition to 4-vinylcyclohexene:



Conversely, in dimethylformamide (DMF) solutions of the complexes a single oligomerization product is formed – 4-vinylcyclohexene. It may be assumed that in DMF solutions an intermediate bis-π-allyl complex of tervalent rhodium (1), formed in the reaction of the initial complex with two molecules of butadiene, is converted into the mono-π-allyl complex (2), which then decomposes with the formation of 4-vinylcyclohexene and Rh(I):



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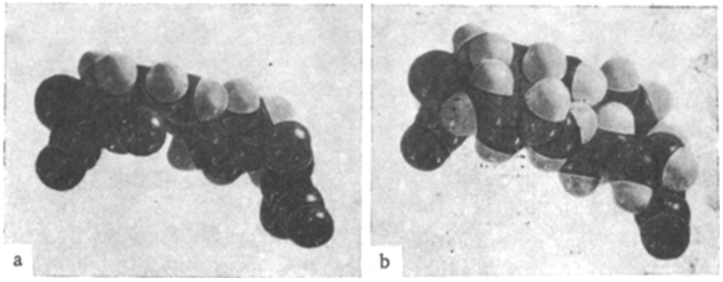


Fig. 1. Molecular models of the complex: a) (IIIa); b) butadiene-(IIIa).

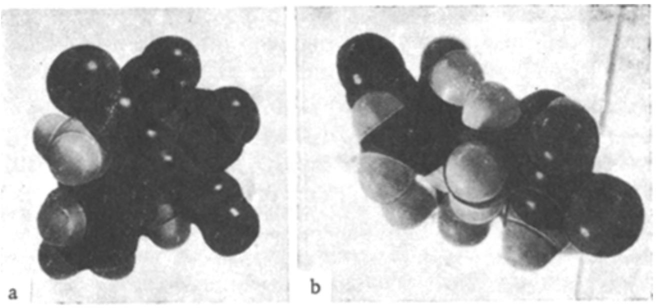
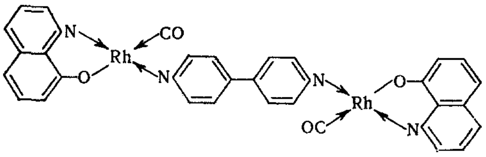


Fig. 2. Molecular models of the complexes: a) (IIIb); b) butadiene-(IIIb).

In solvents with a lower complex-forming capacity, the conversion (1) → (2) takes place more slowly, in consequence of which the polymeric product and cycloocta-1,5-diene are formed, in addition to 4-vinylcyclohexene.

It is known that butadiene polymerizes in solutions of Rh(III) salts in water, methanol, ethanol, and DMF [7]. We have found that in a methanolic solution of $RhCl_3$ previously treated with CO, 4-vinylcyclohexene is formed in addition to polybutadiene. A solution of $RhCl_3$ in DMF treated in the same way converts butadiene into 4-vinylcyclohexene only. Apparently, in these cases dicarbonyl derivatives of Rh(I) are formed which change the course of the reaction.

The heating of $RhCl_3$ in DMF, which leads to the formation of unstable dicarbonyl derivatives of Rh(I) [8] also excludes the polymerization reaction. Solutions of $Rh_2(CO)_4Cl_2$ (IV) behave similarly. At the same time, the replacement of one of the carbonyl groups in complexes of type (I) by amines leads to the complete loss of catalytic activity. Thus, the complex (V) having only one firmly bound carbonyl group on each rhodium atom proved to be catalytically inactive:



(V)

Hence, the presence of two carbonyl groups in the coordination sphere of the Rh(I), one of which is displaced by butadiene during the catalytic process enables the oligomerization of butadiene to take place in addition to polymerization. The direction of the oligomerization of butadiene on complexes of type (II) is practically independent of the solvent. Reactions in solutions of the complex (IIa) in DMF and solutions of (IIIb) in ethanol lead to the formation of 4-vinylcyclohexene. Apparently, in the reaction of these complexes with butadiene the dynamically bound aromatic part of the ligand liberates three vacancies in the coordination sphere of the metal, which enables only three double bonds of two molecules of butadiene to be coordinated, and these cyclize into 4-vinylcyclohexene.

The use as catalyst in the oligomerization of butadiene of the complex (IIIa) in DMF leads to the formation of a product of linear oligomerization, octa-1,3,7-triene, in addition to 4-vinylcyclohexene, while

TABLE 1. Characteristics of the Complexes Synthesized

Complex	$\frac{\text{Found}}{\text{Calculated}}$, %				IR spectrum, cm^{-1}	
	C	H	N	Cl	ν_{NH} bound	ν_{CO}
1a	31,23 30,88	1,90 1,60	13,09 13,36	11,36 11,27	3190	2100 2025
1b	47,51 48,00	2,51 2,40	3,20 3,70	8,99 9,55	—	2100 2030
1c	22,79 22,86	1,80 1,52	10,62 10,62		3190	2100 2036
1d	34,43 34,56	1,77 1,60	8,77 8,96	11,36 11,30	3200	2100 2040

in the presence of (IIIb) cycloocta-1,5-diene is formed. It may be assumed that the appearance of appreciable amounts (up to 10-15% calculated on the butadiene that reacted) of these substances is due to the concerted action of the two active centers of the binuclear complexes due to their suitable steric arrangement.

In actual fact, a consideration of molecular models of complex homogeneous catalysts (Figs. 1 and 2) shows the possibility of the realization of a doublet mechanism, leading in the case of the complex (IIIa) to octa-1,3,7-triene and in the case of the complex (IIIb) to cycloocta-1,5-diene. The formation of 4-vinylcyclohexene on complexes of type (III), and also the comparatively low yields of octatriene and cycloocta-1,5-diene can be explained by the partial decomposition of the complexes under the reaction conditions with the formation of mononuclear particles.

EXPERIMENTAL METHOD

The complexes (Ia)-(Id) were obtained by heating (IV) [9] with the corresponding ligands in benzene to 40-50° at a molar ratio of (IV) to ligand of 1 : 2. The complex (Ia) precipitated when the solution was cooled. The complexes (Ib)-(Id) were precipitated by the addition of heptane. The characteristics of the complexes (Ia)-(Id) are given in Table 1. The complexes (Ie), (IIIa), and (IIIb) were obtained as described previously [10], and so was (V) [11]. Complex (IIa) was obtained as described in [12] and (IIb) in a similar manner to [13].

The oligomerization of butadiene was performed in a 50 ml autoclave at 40-80°. The amount of catalyst was 10^{-4}-10^{-5} mole in 15-20 ml of solvent. The ratio of catalyst to butadiene was 1 : 1000. The reaction time was 6-16 h. The reaction products were analyzed by the GLC method using a "Khrom-3" chromatograph with a column 120 × 0.5 cm filled with 20% of polyethylene adipate and 5% of steric acid on Spherochrome at a column temperature of 120° with a rate of feed of carrier gas (Ar) of 4 liters/h.

The 4-vinylcyclohexene was isolated by fractional distillation, bp 130-131°; n_D^{20} 1.4620. The NMR spectrum, taken on a INM-C-60 instrument, agreed completely with that given in [14].

CONCLUSIONS

1. Complexes of the general formula $LRh(CO)_2Cl$, where L is benzotriazole, acridine, imidazole, or benzimidazole, have been synthesized.

2. In the presence of catalytic amounts of the complexes $LRh(CO)_2Cl$ in ethanol, methanol, and acetone, butadiene is converted into a mixture of 4-vinylcyclohexene, cycloocta-1,5-diene, and 1,4-trans-polybutadiene. In DMF solutions, the sole reaction product is 4-vinylcyclohexene.

3. In solutions of binuclear complexes of Rh(I) in DMF, in addition to 4-vinylcyclohexene, on the complex with p-phenylenediamine cycloocta-1,5-diene is formed and in the presence of the benzidine complex octa-1,3,7-triene is formed. Their formation may be connected with a doublet mechanism of the action of the two catalytically active centers of the binuclear complex catalyst.

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