

CATALYTIC ACTIVITY OF RHODIUM(I) COMPLEXES CONTAINING POLY(SILOXY)ALKYLDIPHENYLPHOSPHINES*

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Kinetics of homogeneous hydrogenation of 1-heptene catalysed by rhodium(I) complexes prepared *in situ* from di- μ , μ' -chloro-bis(dicyclooctenylrhodium) and phosphine L (L = 2-(diethoxymethylsilyl)ethyldiphenylphosphine, 3-(diethoxymethylsilyl)propyldiphenylphosphine and their copolymers with diethoxydimethylsilane) have been studied at 64°C under normal hydrogen pressure. The dependence of the catalyst activity on the type of L (monomeric, polymeric, supported on silica) has been examined. The effects of Rh : P molar ratio, the concentration of phosphine groups in siloxane copolymers and of the method of catalyst fixation to support on catalyst performance are discussed.

In recent years an increasing attention has been paid to coordination bonding of homogeneous catalysts to organic and inorganic supports (for reviews see refs^{1,2}). Nevertheless, with the exception of polymerisation, these so called heterogenized catalysts have not yet been applied industrially. In addition to some advantages (the higher stability of catalysts³ and their increased activity due to suppression of conglomeration of reaction sites⁴), fixation to support has also some disadvantages connected with possible elution of a fixed complex by reaction medium⁵ and a certain nonuniformity of reaction sites. Similarly to heterogeneous catalysts, supported catalysts are also subject to transport phenomena (*e.g.* diffusion of reactants to reaction sites on support).

Within the framework of a systematic study of this problem, in a previous work⁶ we found that in addition to the effect of texture of the support and of loading, the decisive factor influencing catalyst activity is conglomeration of active sites. The present work is concerned with possibilities of suppression of this conglomeration.

EXPERIMENTAL

Chemicals. Rhodium(III) chloride (Safina, Vestec), diphenylchlorophosphine, allyl chloride, 1-heptene, 1,2-dibromoethane (Fluka, Buchs A.G.), methylchlorosilane, dimethylchlorosilane, vinylchlorosilane, methylhydrogenodimethylsiloxane copolymer (Synthesia, Kolín)

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and solvents (Lachema, Brno) were commercial products. The liquids were dried in usual way, distilled and deoxygenated before use. Silica (Kieselgel 100, 0.063–0.200 mm particle size, 10 nm medium pore diameter, specific surface 365 m²/g, Merck) was dried 5 h at 200°C/500 kPa. All manipulations were carried out under argon⁷. Di- μ , μ' -chloro-bis(dicyclooctadienerhodium)⁸, diphenylphosphine⁹, vinylidiphenylphosphine^{10,11}, (3-chloropropyl)methyldichlorosilane¹², methyldiethoxysilane¹³, dimethyldiethoxysilane¹⁴, (3-chloropropyl)methyldiethoxysilane¹⁵ and 2-(methyldiethoxysilyl)ethyldiphenylphosphine¹⁶ (M 1) were prepared by reported procedures as indicated.

3-(Methyldiethoxysilyl)propyldiphenylphosphine was obtained by the earlier described procedure¹⁷ based on the reaction of filtered solution of lithium diphenylphosphide (prepared from 290 g (1.3 mol) of diphenylchlorophosphine and 23.5 g (3.4 mol) of finely cut lithium in 1.5 l of tetrahydrofuran) with 335 g (1.6 mol) of (3-chloropropyl)methyldiethoxysilane at a temperature of 0°C. After removal of volatile products by distillation, 165 g (35% yield) of 3-(methyldiethoxysilyl)propyldiphenylphosphine (M 2) (b.p. 180°C/2.5 kPa, n_D^{20} 1.5460) were obtained. For C₂₀H₂₉O₂PSi (360.5) calculated: 66.6% C, 8.1% H; found: 66.0% C, 8.0% H.

Polysiloxanes containing diphenylphosphine groups. Copolymer of 2-(methyldiethoxysilyl)ethyldiphenylphosphine (M 1) with dimethyldiethoxysilane was obtained by cohydrolysis of these compounds in molar ratio 1 : 3 with boiling distilled water in toluene. A reaction flask equipped with a reflux condenser, a thermometer and a magnetic stirrer was charged with 8 g of dimethyldiethoxysilane and 7 g of 2-(methyldiethoxysilyl)ethyldiphenylphosphine in 50 ml of toluene. Then, 1.2 ml of deoxygenated water was added in one portion and the mixture was refluxed for 10 h; toluene and ethanol were distilled off, the distillation residue was freed from volatile products under high vacuum (2.5 Pa) at 180°C. By this way, 5.1 g of polymer P 1 were obtained which contained 7% P.

Copolymer of 3-(methyldiethoxysilyl)propyldiphenylphosphine with dimethyldiethoxysilane was prepared analogously, except that 2-(methyldiethoxysilyl)ethyldiphenylphosphine (M 1) was replaced by 3-(methyldiethoxysilyl)propyldiphenylphosphine (M 2) and the reaction time was only 8 h. The yield of polymer P 2 was 5.1 g and P content was 7 per cent.

2-(Diphenylphosphino)ethylmethyldimethylsiloxane copolymer (P 3) was prepared by UV light-induced addition of vinylidiphenylphosphine to the silicon-hydrogen bond of methylhydrogenodimethylsiloxane copolymer. A reactor equipped with a quartz tube containing 100 W UV quartz mercury lamp, a magnetic stirrer and a reflux condenser was charged with 16 g of methylhydrogeno-dimethylsiloxane copolymer, 6.9 g of vinylidiphenylphosphine, 40 ml of xylene and 1 ml of di-tert-butyl peroxide. The refluxing mixture was irradiated 48 h (6 \times 8 h) and the reaction course was followed by gas chromatographic analysis of unreacted vinylidiphenylphosphine. After removal of volatile products by distillation and residual traces by vacuum evaporation (180°C at 2.5 Pa), 18.5 g of the product (polymer P 3) were obtained, which consisted of 12.5 g of a milk white liquid phase and a yellowish solid portion. Only the liquid phase was used in further experiments (P content 1%).

Homogeneous catalysts were prepared *in situ* by the reaction of di- μ , μ' -chloro-bis(dicyclooctene-rhodium) with a solution of a polymer ligand in toluene in approx. 0.01M concentrations and Rh : P mol. ratios 1 : 1, 1 : 2, 1 : 3 and 1 : 20. The activity of these catalysts was tested immediately after their preparation.

Supported complexes were obtained by adsorption of preformed catalysts on macroporous silica or by coordination of Rh(I) to the support which was impregnated by the polymer ligand. The former procedure was used to prepare catalyst H 1; to 2 ml of catalyst solution (obtained by mixing 0.67 ml of 0.128M solution of 2-(diphenylphosphino)ethylmethyldimethylsiloxane copolymer

(P3) in toluene with 31 mg of $[\{\text{RhCl}(\text{cyclooctene})_2\}_2]$ in 7.9 ml of toluene) were added 20 ml of toluene and 1 g of macroporous silica and the mixture was stirred 2 h. Then, the solid phase was filtered off and washed twice with 10 ml portions of toluene. The filtrate and washings were colourless. Catalyst H 1, was dried under high vacuum at 50°C.

The same procedure was used to prepare catalyst H 2; 2 ml of catalyst solution (obtained by treatment of 4.2 ml of 0.041M solution of 3-(diphenylphosphino)propylmethyltrimethylsiloxane copolymer (P 2) in toluene with 31 mg of the cyclooctene-rhodium complex dissolved in 4.4 ml of toluene) were adsorbed on 1.5 g of macroporous silica.

Catalyst H 3 was obtained by the latter method. A total of 2.6 g of macroporous silica was mixed with 2 ml of 0.037M toluene solution of 2-(diphenylphosphino)ethylmethyltrimethylsiloxane copolymer P 3 in toluene. 10 ml of the solvent were added and the mixture was stirred for 2 h. After filtration and twofold washing with 10 ml of the solvent, the mixture was dried under high vacuum at 50°C. The so prepared support was added to a stirred solution of 26 mg of the cyclooctenerhodium complex in 20 ml of toluene. After 2 h-stirring, filtration and washing with toluene (2 . 10 ml), catalyst H 3 was dried under high vacuum at 50°C (Rh content = 0.3%).

Hydrogenation was carried out on an apparatus described earlier¹⁸ (64°C and a constant hydrogen pressure of 115 kPa, *i.e.* pseudo-zeroth order in hydrogen). The reaction order with respect to catalyst was determined by van Hoff differential method¹⁹, that in alkene was determined by integral method under the assumption of first order.

TABLE I

Hydrogenation of 1-Heptene — the Reaction Order in Catalyst

Reaction temperature 64°C, hydrogen pressure 115 kPa; 1 ml of 1-heptene, $5 \cdot 10^{-4}$ — $2 \cdot 10^{-3}$ mmol Rh(I), 9 ml of toluene.

Monomer catalyst ^a	Molar ratio Rh : P	Reaction order	Polymer catalyst ^a	Molar ratio Rh : P	Reaction order
M 1	1 : 1	0.88; 1.1	P 1	1 : 1	1.07
M 1	1 : 2	1.05	P 1	1 : 2	1.27
M 1	1 : 3	1.04; 0.95	P 1	1 : 3	0.96; 1.21
M 2	1 : 1	1.05	P 2	1 : 1	0.84; 1.05
M 2	1 : 2	1.16	P 2	1 : 2	1.15; 1.21
M 2	1 : 3	0.84	P 2	1 : 3	1.05; 0.99
			P 3	1 : 1	1.19; 0.99
			P 3	1 : 2	0.85; 1.21
			P 3	1 : 3	0.03; 0.78

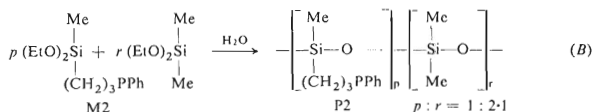
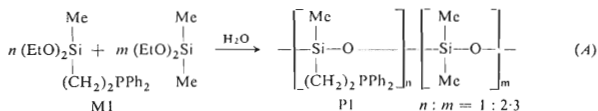
^a For designation see Experimental.

RESULTS AND DISCUSSION

With respect to the fact that metal complexes coordinately bound to soluble linear polysiloxanes have not yet been described, it was necessary to pay attention to their synthesis. For purposes of this work polysiloxanes containing only (dialkyl- and diarylphosphinoalkyl)methylsiloxo units (technical application of which was already reported¹⁶) were not suitable since neighbouring phosphine groups in chain could act as bidentate ligands.

It was therefore assumed that appropriate polysiloxanes can be obtained by co-condensation of dimethyldiethoxysilane with (diphenylphosphinoalkyl)methyldiethoxysilanes M1 and M2. This procedure is advantageous in that it makes possible to compare catalytic efficiency of complexes containing polymer ligands with that of compounds containing only monomer diphenylphosphinoalkylsiloxo units.

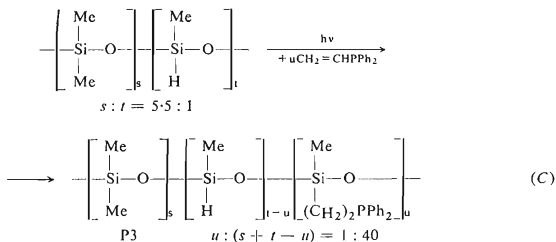
As synthesis of monomers of this type can be easily realized (M1 was prepared by literature procedure¹⁶ and unreported M2 was obtained by a modified method¹⁷) we checked the possibility of preparing polymer products by acid, neutral and basic hydrolysis and co-condensation with dimethyldiethoxysilane. As found by preliminary experiments, all three methods can be applied, the yields of high molecular products being 35 to 75%, the highest after prolonged alkaline hydrolysis. In order to avoid possible contamination, neutral hydrolysis has been chosen as a convenient method for synthesis of the ligands (Equations (A) and (B)).



With the use of threefold molar excess of diethoxydimethylsilane, polymers P1 and P2 were obtained containing 7% P (which corresponds to 2.3 and 2.1 dimethylsiloxo groups per one (diphenylphosphinoalkyl)methylsiloxo group, respectively). These are polysiloxanes with the high density of ligand groups.

For comparative purposes we also prepared a polysiloxane having phosphine groups in low concentration (polymer P3). This was obtained by the reaction of vinyl-diphenylphosphine with the Si—H bonds of methylhydrogenodimethylsiloxane copolymer. UV light-induced radical addition (Eq. (C)) yielded polymer P3 containing 1% P (corresponding to approx. 1 (diphenylphosphinoethyl)methylsiloxo

unit per 40 dimethylsiloxo units).



Reaction of prepared monomer and polymer ligands with di- μ , μ' -chloro-bis-(dicyclooctenerhodium) was used for the *in situ* synthesis of complexes of Wilkinson type. Since their catalytic behaviour has not yet been reported we studied first the kinetics of hydrogenation. Kinetic measurements were carried out at 64°C, and van t'Hoff differential method¹⁹ was used to determine the reaction order in the catalyst by means of graphical treatment of initial reaction rates. The reproducibility of data was on the level usual for kinetic measurements of homogeneously catalysed reaction²⁰. With regard to this fact, data summarized in Table I show that the reaction is first order in the catalyst, in agreement with data reported for tris(triphenylphosphino)chlororhodium(I) complex²¹. Within experimental errors, the reaction order is not influenced by the number of methylene groups between phosphorus and silicon (compare M 1 and M 2, P 1 and P 2), the inclusion of the monomer ligand to the polysiloxane chain (compare M 1 and P 1; M 2 and P 2) and by the density of phosphine groups on the polysiloxane chain (compare P 1 and P 3). Furthermore, it is not affected also by the molar ratio of phosphine groups to rhodium, the fact which is surprising from the mechanistic point of view.

As far as the reaction order in the alkene is concerned, it was assumed that we deal here with first-order reaction. This assumption was verified by a good agreement of the conversion curve with the integral form of the first-order equation for all the catalysts, again in harmony with literature data for related rhodium-phosphine complexes^{7,21-13}. Rate constants for hydrogenation of 1-heptene in dependence on the ligand are presented in Table II. From comparison of the activity of catalysts it becomes evident that with increasing excess of monomer ligand the activity decreases, in accordance with the mechanism proposed for triphenylphosphine analogues^{21,22} which involves formation of a vacant coordination site by ligand dissociation. The high activity of the catalysts with Rh : P molar ratio equaling to 1 : 1 is worth mentioning. When compared to the usual ratios 1 : 2 or 1 : 3, the catalysts are approximately twice as active. Whether this phenomenon is characteristic of (di-

alkoxymethylsilyl)alkyldiphenylphosphines as ligands is under further investigation. Solutions of the catalysts containing monomer ligands are generally unstable, gradually lose their activity and after three days they become inactive.

If the previous results are compared with data for catalysts containing polymer ligands one can state that in the case of the ligand with the high density of phosphine groups (P 1 and P 2), the activity of such catalysts is practically the same as those with monomer ligands. This holds also for the dependence of the hydrogenation rate on the excess of the ligand. On the other hand, they exhibit greater resistance against desactivation processes (*e.g.* only 5% decrease in the activity was observed after 5 days). This indicates that also here, coordination of more than one phosphine ligand to rhodium atom could not be completely excluded. It seems likely that this coordination may take place not from the same chain, but, which is more probable also from another polysiloxane chain. In comparison with monomer rhodium complexes, however, the mutual interaction of active sites is less probable, which accounts for prolonged life time of the catalysts with polymer ligands.

Another situation has been observed for a polymer ligand with low density of phosphine groups on polymer chain (polymer P 3). In this case coordination of more phosphine groups to transition metal atom is less probable. Consequently the activity

TABLE II

Rate Constants k (in $\text{l mol}^{-1} \text{ min}^{-1}$) for Hydrogenation of 1-Heptene Catalysed by Rhodium Complexes Containing Monomer (M) or Polymer (P) Phosphine Ligands

Reaction temperature 64°C, hydrogen pressure 110 kPa, 1 ml of 1-heptene, 9 ml of toluene.

Rh : P molar ratio	Ligand	Rh(I) conc. mmol/l	k	Ligand ^a	Rh(I) conc. mmol/l	k	Ligand ^b	Rh(I) conc. mmol/l	k
1 : 1	M 1	0.5	10.3	P 1	1	12.5	P 3	0.2	10.5
1 : 2	M 1	2	6.2	P 1	2.2	7.1	P 3	1	10.4
1 : 2	M 1 ^c	1	0	P 1 ^d	2.2	6.8	P 3 ^d	1	9.7
1 : 3	M 1	1	4.3	P 1	0.5	4.8	P 3	0.5	6.8
1 : 20	M 1	1	0	P 1	1	0.5	P 3	0.3	5.6
1 : 20							P 3 ^e	0.3	5.2
1 : 1	M 2	1	11.8	P 2	1	10.5			
1 : 2	M 2	2	7.1	P 2	0.3	5.1			
1 : 2	M 2 ^c	2	0	P 2 ^d	0.5	4.8			
1 : 3	M 2	0.5	4.9	P 2	0.5	4.7			

^a High density of phosphine groups. ^b Low density of phosphine groups. ^c Catalyst activity after 3 days. ^d 5 days. ^e 10 days.

of the catalyst, being at Rh : P molar ratio = 1 : 1 comparable to the previous cases, remains unaffected by increasing molar ratio to 1 : 2. Further excess of phosphine groups leads to a decrease in the activity, but even at Rh : P molar ratio = 1 : 20 the activity is higher than that of the other complexes with the 1 : 2 molar ratio. Also the life time of these catalyst solutions is substantially longer compared to the previously discussed catalysts.

In order to obtain information about the role of mobility of polysiloxane chains, we have introduced these catalysts in small concentrations into a macroporous inorganic support and examined their activity (Table III). The supported catalysts prepared by adsorption of the complex performed *in situ* in solution catalysed the hydrogenation at a rate ($5 \text{ l mol}^{-1} \text{ min}^{-1}$) which was not dependent upon Rh : P molar ratio and did not decrease with recycling the catalyst. With respect to the high activity of the catalyst H 3 fixed to the same support, it seems improbable that this striking similarity in hydrogenation rates is exclusively due to transport phenomena. We believe that it results rather from dimerisation of active sites and, to some extent, also from inaccessibility of some rhodium atoms located in narrow pores, both processes taking place during synthesis of supported catalysts which requires rather long reaction time.

The highest effectiveness — distinctly exceeding that of the previous complexes — has been found for the catalyst which was obtained by coordination of the rhodium-cyclooctene complexes to the support impregnated by the polysiloxane having low

TABLE III

Rate Constants k (in $\text{l mol}^{-1} \text{ min}^{-1}$) for Hydrogenation of 1-Heptene Catalysed by Rhodium Complexes Fixed to Supports

For conditions see Table II.

Catalyst ^a	Ligand	Rh : P molar ratio	Rh(I) conc., mmol/l	k
H 1	P 3	1 : 1	1.8	4.6
H 1 ^b	P 3	1 : 1	1.8	4.7
H 1 ^c	P 3	1 : 1	3.2	4.4
H 2	P 2	1 : 2	2	5.2
H 2 ^d	P 2	1 : 2	2	4.9
H 3	P 3	1 : 1	0.5	15.8

^a H 1, H 2 — catalysts prepared in solution were introduced onto silica, H 3 — silica was treated with P 3 and then Rh(I) was coordinated from solution. ^b Reaction components from preceding experiment were distilled off and the catalyst reduced. ^c The catalyst used after 10 days ageing.

^d Reaction components from preceding experiment were removed by filtration, the catalyst was dried *in vacuo* and reused.

density of phosphine groups (P 3). The reason can be sought for again in the different extent of dimerisation of active sites, which here should be relatively small not only due to mild synthesis preventing such dimerisation and conglomeration but also due to sufficient immobility of polysiloxane chain preventing coordination of phosphine groups from different chains to the same metal atom.

Summarising, this work shows that the success in forming active catalysts can be achieved by the choice of such conditions for their synthesis and application by which desactivation processes are minimised. We believe that one of the promising routes is the use of siloxanes containing sufficiently separated ligands, the flexibility of which is further reduced by adsorption on a macroporous support.

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