

SILICA-SUPPORTED CATIONIC RHODIUM(I) COMPLEXES AS HYDROGENATION CATALYSTS

Vladimír ZBÍROVSKÝ and Martin ČAPKA

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

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Cationic silica-supported Rh(I) complexes prepared from Rh(COD)(acac) and phosphines of the type $(C_2H_5O)_3Si(CH_2)_nP(C_6H_5)_2$ ($n = 1, 3$) in the presence of *p*-toluenesulphonic acid were found to be efficient catalysts for hydrogenation of alkenes, alkadienes, and *Z*- α -acetamidocinnamic acid at 40°C and normal hydrogen pressure. Kinetic measurements showed that the most efficient catalysts are obtained at the P : Rh mol. ratio = 2. When this ratio was ensured for each molecule of the immobilized complex, such catalysts were three to four times more active than their homogeneous analogues.

In recent years, homogeneous catalysts coordinately bound to insoluble supports have become increasingly the subject of research and application^{1,2}. These the so called heterogenized catalysts can be prepared with advantage *via* anchoring to functionalized inorganic supports and the catalysts of this type has been systematically studied³⁻⁷ in our laboratory. We have found that the restrictive factor of the application of these catalysts is their solubilization due to the cleavage of the bond between the polymer bound ligand and transition metal⁷. This cleavage takes place especially in the case of neutral Wilkinson type catalysts where vacant coordination site is formed by dissociation of the neutral ligand⁷.

For the above reasons, in the present work we have studied hydrogenation activity of cationic rhodium(I) complexes which are supposed⁸ to retain neutral ligands during catalytic cycle. Inorganic supports and silylsubstituted phosphines enabled us to use the way of heterogenization differing substantially from the procedures used so far for anchoring transition metal complexes to organic polymers⁹⁻¹³.

EXPERIMENTAL

Chemicals. Unsaturated hydrocarbons (Fluka AG, Buchs), rhodium trichloride (Safina, Vestec), *p*-toluenesulphonic acid (Lachema, Brno), *Z*- α -acetamidocinnamic acid (Léčiva, Modřany) were commercial products purified by usual procedures. (1,5-Cyclooctadiene)rhodium(I) 2,4-pentanedionate was prepared by modified Cramer method¹⁴, (triethoxysilyl)methyldiphenylphosphine³ and 3-(triethoxysilyl)propyldiphenylphosphine¹⁵ were prepared by reported procedures. All manipulations were made under argon¹⁶.

Phosphinated Silicas

The support used was Kieselgel 100 (Merck), 0.063–0.2 μm particle size, 100 \AA mean pore diameter, surface area 365 m^2/g . The silica was dried at 180°C/5 mm Hg for 5 h before use. All the subsequent operations were made under argon. The support was functionalized in the following way: 10 g of dried silica was placed into a reaction flask, 60 ml of dry toluene were added, followed by 14 mmol of (triethoxysilyl)methyldiphenylphosphine (or 6.6 mmol of (3-triethoxysilyl)propyldiphenylphosphine) dissolved in 30 ml of the same solvent under stirring. The reaction mixture was refluxed for 6 h, then 50 ml of toluene were distilled off and 60 ml of dry toluene added. The support was filtered off, washed four times with 70 ml portions of toluene and dried at room temperature *in vacuo* for 6 h.

Catalysts and Hydrogenation Procedure

Homogeneous catalysts were prepared *in situ*, using solutions of (1,5-cyclooctadiene)rhodium(III) 2,4-pentanedionate, a given (trialkoxysilyl)alkyldiphenylphosphine and *p*-toluenesulphonic acid which were mixed in the mentioned sequence. The solutions contained 0.057 mmol of a given compound in 1 ml of ethanol–toluene mixture (1 : 1 v/v) and the Rh : *p*-toluenesulphonic acid mol. ratio was 1 : 1.1. The catalysts so prepared were immediately used in hydrogenation experiments. Rh : P mol. ratios tested are given in Tables I and II.

Heterogenized catalysts were prepared by two procedures. Procedure A. To 0.205 g (0.658 mmol) of the rhodium pentanedionate dissolved in 5 ml of tetrahydrofuran, 0.7 mmol of *p*-toluenesulphonic acid dissolved in the same volume of the solvent were added. After several minutes of stirring, the solution was added to a suspension of 10 g of phosphinated silica in 30 ml of toluene. The mixture was shaken for 1 h, the supported catalyst was filtered off, washed twice with 70 ml of tetrahydrofuran and twice with 70 ml of toluene and then dried at room temperature *in vacuo* for 8 h. The Rh content in both catalysts was 0.6 per cent.

Procedure B. A solution of 0.134 g (0.431 mmol) of the rhodium pentanedionate dissolved in 10 ml of ethanol–toluene mixture (1 : 1 v/v) was placed into a flask and then 0.469 g (1.293 mmol) of

TABLE I

Hydrogenation of unsaturated substrates (7 mmol) catalysed by $[(\text{SiO}_2)_x-\text{O}-\text{SiCH}_2\text{PPh}_2]_x \cdot \text{Rh}(\text{COD})^+ \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ (0.028 mmol); $p_{\text{H}_2} = 176 \text{ kPa}$, temperature 40°C, 5 ml of ethanol, 5 ml of toluene

Substrate	Initial reaction rate, $\mu\text{mol min}^{-1}$	Product distribution, %		
		diene	alkene	alkane
1,3-Cyclooctadiene	39	81	16	3
1,5-Cyclooctadiene	29	87	12	1
1-Heptyne	58	67 ^a	32	1
1-Heptene	145	—	51	49

^a 1-Heptyne.

(triethoxysilyl)methyldiphenylphosphine, and 0.082 g (0.421 mmol) of *p*-toluenesulphonic acid, both dissolved in the same solvent mixture were added in the mentioned sequence. After addition of the phosphine, the reaction mixture turned dark orange and this colouration further deepened when the acid was added. The solution was poured into a suspension of 8.66 g of the dried, non-functionalized silica in 35 ml of toluene and the mixture was shaken for 1 h. Then, the solvents were distilled off under reduced pressure at temperature not exceeding 30°C. Then 60 ml of toluene were added, the supported catalyst was filtered off, washed with 60 ml of toluene and dried in high *vacuo* at room temperature for 8 h. The same procedure was used to prepare the catalyst containing 3-(triethoxysilyl)propyldiphenylphosphine as ligand. The metal content in both catalysts was 0.5 per cent.

Hydrogenation rates at constant hydrogen pressure were determined using the apparatus described elsewhere¹⁷. The rate of hydrogenation of unsaturated hydrocarbons was determined by the method of initial reaction rates, the conversion and product distribution was analysed by

TABLE II

Hydrogenation of *Z*- α -acetamidocinnamic acid (7 mmol) catalysed by homogeneous complexes of the type $[(\text{SiO}_2\text{-ligand})_x\text{Rh}(\text{COD})]^+ \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ (0.028 mmol); reaction conditions see Table I

Rh : P mol. ratio	k (min ⁻¹)	
	$(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_2\text{P}(\text{C}_6\text{H}_5)_2$	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2$
1 : 1	54	74
1 : 1.5	101	122
1 : 2	141	124
1 : 3	2	0
1 : 4	1	0

TABLE III

Hydrogenation of *Z*- α -acetamidocinnamic acid (7 mmol) catalysed by heterogenized cationic complexes of the type $[(\text{SiO}_2\text{-ligand})_x\text{Rh}(\text{COD})]^+ \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ (0.028 mmol); reaction conditions see Table I.

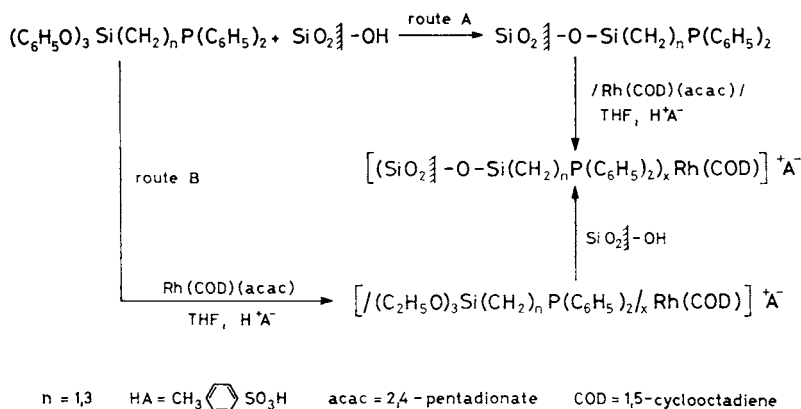
Procedure	k (min ⁻¹)	
	$\text{SiO}_2\text{-O-SiCH}_2\text{PPh}_2$	$\text{SiO}_2\text{-O-Si}(\text{CH}_2)_3\text{PPh}_2$
A	82 (45 ^a , 9 ^b 49 ^c)	13
B	424	544

^a Second run; ^b third run; ^c the catalyst exposed to air for 20 h.

gas chromatography. The hydrogenation of *Z*- α -acetamidocinnamic acid was found to follow first order kinetics at least to one half-time. Therefore, integral form of first-order kinetic equation was used to determine rate constants. As in all the experiments the catalysts were used in the same amount and the order of the reaction in the catalyst was not verified, the rate constants given in Tables II and III are not divided by catalyst concentration.

RESULTS AND DISCUSSION

Although immobilized rhodium(I) complexes turned out to be in general useful catalysts, the heterogenized cationic ones were found to be unstable, undergoing easily decomposition to the metal⁹⁻¹³. As it has been proposed^{8,18} that two coordinated phosphine ligands are present in catalytically active species during the whole catalytic cycle, we have believed that the reason of the low activity and instability of the heterogenized cationic complexes is the fact that the analogs of homogeneous catalysts were not in fact introduced on support surface. In other words, in the above cases the rhodium was bonded to the surface only by one polymer-bound ligand. Therefore, we have studied immobilization of these complexes using silyl substituted alkylidiphenylphosphines and silica which makes it possible to anchor the complexes by two procedures (Scheme 1).



SCHEME 1

Procedure A is widely used and involves the synthesis of the phosphinated support (by reaction of silica with trialkoxysilylalkylidiphenylphosphine in toluene), coordination of (1,5-cyclooctadiene)rhodium(I) 2,4-pentandionate in the presence of a strong acid. In the light of interesting results obtained recently by Reiss and Hettflejš^{19,20} in the synthesis of rhodium(I) arenesulphonate complexes, we have used *p*-toluenesulphonic acid in place of strong inorganic acids usually applied for preparing cationic complexes. The reaction was found to proceed practically instantaneously. The number of coordinated phosphine ligands is affected by steric effects and by the

density of phosphine groups at the coordination site of a given rhodium atom and not by the total P : Rh mol. ratio. One can assume that this ratio equals to 1 rather than to 2, which results in nonuniformity of the active sites.

By contrast to procedure *A*, procedure *B* provides conditions for active species of uniform structure. It involves preformation of soluble cationic rhodium(I) complex containing ω -triethoxysilylalkyldiphenylphosphines as ligand, followed by anchoring the so prepared complex to unmodified silica.

As cationic rhodium(I) complexes of the above type have not so far been reported, it was necessary to pay attention also to the properties of homogeneous analogues.

As demonstrated by the results given in Table I, the cationic complexes catalyze hydrogenation of alkenes, alkynes and dienes and as far as their hydrogenation activity is concerned, in the case of alkenes their behaviour is analogous to the complexes reported by Reiss and Hetflejš¹⁹. The product distribution shows that dienes and alkynes are preferentially hydrogenated compared to monoenes, in accordance^{21,22} to other Rh complexes of the type $[\text{Rh}(\text{diene})\text{L}_2]^+$.

It has been shown¹⁹ that cationic rhodium(I) complexes with monodentate tertiary phosphines do not catalyze hydrogenation of *Z*- α -acetamidocinnamic acid. It is thus worth mentioning that the use of ω -triethoxysilylalkyldiphenylphosphines results in efficient catalysts (Table II), the catalytic activity of which depends strongly on the ligand to metal mol. ratio, the most efficient ones being those corresponding to $[\text{Rh}(\text{diene})\text{L}_2]^+$. The ligand to metal ratio affects not only the activity but also the stability of the catalysts. The complexes with Rh : P mol.ratio = 1 : 1 are extremely sensitive to minute amounts of oxygen and undergo easily decomposition to metallic rhodium.

From this aspect, also the results obtained in hydrogenation of *Z*- α -acetamidocinnamic acid catalysed by heterogenized catalysts (Table III) should be analyzed. The catalysts prepared by procedure *A* (which does not ensure Rh : P mol. ratio = = 1 : 2) are less efficient than the homogeneous analogues. Although they could be exposed to air, their activity rapidly decreased on recycling due to decomposition to metallic rhodium, quite analogously to the reported catalysts⁹⁻¹³.

However, dramatic change has been observed when using procedure *B* involving preformation of the complex in solution and its subsequent anchoring to silica, which ensures excess of the phosphine ligand in each molecule of the immobilized complex. In this case, the catalysts exhibited the activity which was three to four times that found for homogeneous analogue, although the catalytic effect of heterogenized catalysts is unfavourably affected by transport phenomena.

This justifies our assumption about the possibility to ensure the desired stoichiometry of each molecule of the immobilized complex. These results are not in discrepancy with our earlier finding²³ that the catalysts prepared by procedure *B* are less efficient than those obtained by procedure *A*. In the just mentioned case²³ we immobilized neutral rhodium(I) complexes which are known to undergo²⁴ dimerization

and deactivation already in the course of their anchoring. Such a situation does not occur with cationic rhodium(I) complexes, which makes it possible to utilize to advantage the preformed soluble complex. The higher catalytic activity of the complexes bound to the surface by the longer chain spacer (Table III) is in harmony with the view²⁵ that the longer spacer ensures formation of surface complexed of the desired stoichiometry as well as with our recent results⁶ obtained in hydrogenation of *Z*- α -acetamidocinnamic acid catalysed by rhodium(I) complexes supported on silica *via* alkyldimethyl ligands.

Summarizing, cationic rhodium(I) complexes bound to inorganic supports *via* alkoxysilylsubstituted phosphines and prepared by the procedure ensuring the stoichiometry of catalytic sites exert considerably higher activity than their soluble analogues and should be used also in the study of chiral anchoring ligands.

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