APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 7, 369–372 (1993)

Hydrosilylation of alkenes catalysed by rhodium complexes immobilized on silica via a pyridine group

Martin Čapka,* Marie Czakoová* and Ulrich Schubert†
* Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Rozvojová 135, CS-165 02 Prague 6, Czechoslovakia, and † Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, W-8700 Würzburg, Germany

2-(2-Trimethoxysilylethyl)pyridine, together with 3-methacryloxy)propyltrimethoxysilane, was used to prepare a series of rhodium carbonyl complexes bound to silica via a pyridine group. The rhodium complex $Rh_2(CO)_4Cl_2$ (Rh_2) was used as the starting compound, and the immobilized complexes were prepared by four different routes which yielded both surface-bonded complexes and complexes bonded within the silicate matrix. These complexes were efficient catalysts of hydrosilylation of octene by triethoxysilane. All the immobilized complexes were more than their homogeneous analogues and some could be re-used.

Keywords: Hydrosilylation, pyridine ligand, immobilized rhodium catalyst, sol–gel process

INTRODUCTION

Immobilization of soluble transition-metal complexes on solid supports has attracted increasing attention.[1,2] which indicates also the industrial importance of this operation. We have recently shown that in addition to traditional immobilization of the complexes on a support surface, the incorporation of the complex in the support matrix can be used as a promising alternative. Thus, for example, complexes bonded via tertiary phosphine[3] or acetylacetonate ligands[4] catalyse hydrogenation and hydrosilylation efficiently whilst catalysts containing pyridine groups rapidly lose their activity during carbonylation of methanol and rhodium is leached from the support.[5] For that reason, in the present work we centered on the question of whether the rhodium leaching mentioned for the pyridine-containing catalysts obtained by the sol–gel process is a general property, or is caused solely by the extreme conditions of a continuous liquid-phase arrangement of the carbonylation process which makes the rhodium leaching easier because of the cleavage of the spacer from the silicate matrix.

EXPERIMENTAL

Materials and determination of catalytic activities

Silic (Kieselgel 100, Merck), 1-octene, triethoxysilane, (3-methacryloxypropyl)triethoxysilane (compound **2**) (Fluka), 2-(2-trimethoxysilylethyl)pyridine (compound **1**) (Petrach) and solvents were commercial products. They were purified, dried and distilled as usual. Tetracarbonyl-μ,μ′-dichlorodirhodium(I) (abbreviated below to $\mathbf{Rh_2}$) was prepared as indicated in Ref. 6.

Hydrosilylation of 1-octene by triethoxysilane was performed in a glass reactor at 100 °C, and monitored as described in a previous paper.[4] When the catalyst was re-used, it was washed twice with hexane between runs.

Synthesis of the catalysts

Soluble catalysts were prepared by addition of 2-(2-trimethoxysilylethyl)pyridine (**2**) to a toluene solution of tetracarbonyl(μ,μ′-dichloro)dirhodium(I) ($\mathbf{Rh_2}$). They were immediately used, without isolation, in the hydrosilylation reactions.

Method (i)
To prepare catalyst **A**, a total of 2 g of silica (Kieselgel 100) was dried by heating to 200 °C/0.1 Pa for 4 h. then 5 ml of toluene was added with stirring, followed by a solution of 0.1 mmol of $\mathbf{Rh_2}$ (0.2 mmol Rh) and 0.4 mmol of the ligand **1** in 10 ml of toluene. The reaction mixture was stirred for 4 h. The immobilized catalyst was

0268–2605/93/060369–04 $07.00

Received 24 December 1992
Accepted 24 February 1993

washed with two 20-ml portions of each of toluene and tetrahydrofuran and then dried *in vacuo*. Elemental analysis: C, 2.3: N, 0.4: Rh, 0.5%. IR: ν(CO) 2082. 2005 cm^{-1}. UV: two broad bands with maxima at 294 and 251 nm.

Catalysts **B**, **C** and **D** were prepared by the same procedure, except that the molar ratio of **Rh$_2$** to the ligands **1** and **2** was 1:1:5, 1:2:5 and 1:3:2, respectively.

The catalysts **E**, **F** and **G** were prepared similarly to those described in previous work.[4,5]

Method (ii)

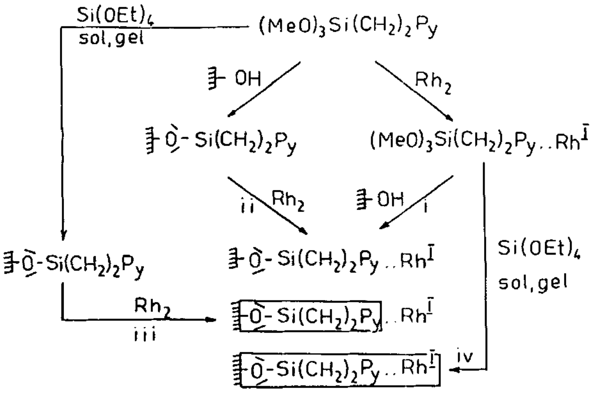
Catalyst **E** was prepared as follows. Toluene (20 ml) was added to 2.5 g of silica. After addition of 0.5 mmol of ligand **1** with stirring, the stirring was continued for 3 h. The mixture was allowed to stand overnight and then 0.125 mmol of **Rh$_2$** was added. The mixture was shaken for 5 h and allowed to stand for two days. Then the catalyst was filtered off, washed with toluene and acetone, and dried *in vacuo*.

Method (iii)

To prepare catalyst **F**, a total of 3 mmol of ligand **1**, 70 mmol of tetraethoxysilane and 39 ml of 0.2 M amonia was added to 300 ml of ethanol. The mixture was stirred at 70 °C for 70 h and then transferred into an open beaker. During seven days the solvent was allowed to evaporate in a hood; then the residual solvent was removed at 100 °C. The mixture was ground, washed with water and acetone, dried *in vacuo*, twice treated with an excess of trimethylethoxysilane in toluene, filtered, washed with acetone and dried *in vacuo* (yield 4.6 g). A total of 20 ml of toluene was added to 2 g of thus prepared support, followed by solution of 39 mg of **Rh$_2$** in 10 ml of toluene while the mixture was stirred. Stirring was continued for another 2 h, then the catalyst was filtered off, washed with acetone and dried *in vacuo*.

Method (iv)

For catalyst **G**, a solution of 165 mg **Rh$_2$** and 1.7 mmol of ligand **1** was added with stirring to 300 ml of ethanol, then 8 ml of tetraethoxysilane and 20 ml of 0.2 M ammonia were added. The mixture was stirred for 14 days and then transferred into an open beaker. The solvent was allowed to evaporate in a hood. The residual solvent was removed *in vacuo*, and the mixture was ground, washed with acetone and dried *in vacuo*.



Py = 2-pyridyl, Rh$_2$ = Rh$_2$(CO)$_4$Cl$_2$, ⫶ = surface bonded to silica, ⫶▭ = incorporated in silica matrix

Scheme 1

RESULTS AND DISCUSSION

The routes of catalyst preparation are depicted in Scheme 1 and the rhodium contents and carbonyl frequencies of the catalyst are presented in Table 1. It should be mentioned that the identity of the rhodium content in catalysts **A**–**E** is due to the fact that during their preparation purposely only such amounts of rhodium precursor were used as would achieve the desired 0.5% rhodium content. This means that the coordination capacity of the support was not fully utilized.

As shown previously,[4,5] in all the catalysts prepared the same type of rhodium complex is probably present, independently of the immobilization procedure.

To evaluate the effect of immobilization, the homogeneous rhodium complexes containing ligand **1** were first tested in solution. The data

Table 1. Physical properties of immobilized rhodium complexes

Catalyst	Method of preparation	Rhodium content (%)	ν(CO) (cm^{-1})[a]
A	(i)	0.5	2082, 2005
B	(i)	0.5	2081, 2007
C	(i)	0.5	2083, 2006
D	(i)	0.5	2082, 2007
E	(ii)	0.5	2082, 20011
F	(iii)	0.6	2081, 2012
G	(iv)	1.2	2086, 2012

[a] In Nujol null.

Table 2. Hydrosilylation of 1-octene (10 mmol) by triethoxysilane (10 mmol) catalysed by homogeneous complexes prepared *in situ* from $\mathbf{Rh_2}$ and **1**, at 100 °C

	Conversion (%)		
Rh: **1**	After 1 h	After 2 h	After 3 h
1:1	54	60	70
1:2	43	47	54
1:4	0	1	2

presented in Table 2 show that in comparison with other rhodium complexes[7] the catalysts exhibit moderate activity, which is markedly reduced by excess of the free ligand. This phenomenon is known in homogeneous catalysis, even in the case of silylated phosphines.[8] It is therefore unlikely that immobilization via two pyridine ligands bound to the support would enhance the catalyst efficiency.

However, Michalska and Osterszewski[9] recently proposed a bidentate coordination of the rhodium complex by one pyridine group and one oxygen-containing (carboxylic) anchoring ligand to form a five-membered metalacycle. This assumption has been advanced to explain favourable catalytic properties of the immobilized complex. For that reason a series of the anchored complexes differing in the rhodium : pyridine : carboxyl ratio was prepared by using the alkoxysilanes **1** and **2**. However, the results summarized in Table 3 demonstrate that this ratio does not exert any significant effect. Therefore a methacryloxypropyl ligand is probably not significantly associated with immobilized rhodium species.

The effect of the method of synthesis of the immobilized complexes (Scheme 1) on their catalytic performance was also studied. All these complexes are very good catalysts for hydrosilylation of alkenes by triethoxysilane (Table 4). They make it possible to use lower catalyst concentrations without isomerization of the unreacted alkene, compared with the complexes bound to organic polymers.[10]

Table 3. Hydrosilylation of 1-octene (10 mmol) by triethoxysilane (10 mmol) catalysed by immobilized catalysts **A**–**D** (5×10^{-4} mmol Rh), at 100 °C

		Conversion (%)		
Catalyst	Ratio Rh:N:COOR	After 1 h	After 2 h	After 3 h
A	1:2:0	53	70	74
B	1:1:5	60	74	76
C	1:2:5	59	67	70
D	1:3:2	60	74	77

Table 4. Re-use of immobilized catalysts (5×10^{-4} mmol Rh) in hydrosilylation of 1-octene (10 mmol) by triethoxysilane (10 mol) at 100 °C

		Conversion (%)				
Catalyst (method)	Run no.	After 10 min	After 30 min	After 60 min	After 120 min	After 180 min
A (i)	1	53	59	66	73	76
	2	0	17	50	55	61
	3	0	2	3	4	5
E (ii)	1	65	72	80	86	87
	2	14	52	56	61	66
	3	0	1	3	6	9
F (ii)	1	65	58	60	61	67
	2	1	9	19	22	29
	3	0	0	1	3	3
G (iv)	1	0	59	64	68	72
	2	0	1	3	5	7
	3	0	0	0	0	0

It is of interest that in comparison with homogeneous analogues, immobilization by all three methods resulted in an increase of catalytic activity. This finding can be ascribed as being most likely due to the fact that immobilization restricts significantly the possible deactivation of the intermediates due to dimerization as well as being due to the absence of the rate-retarding effect of competing free ligand.[11–13]

Catalysts having surface-bound rhodium complexes (**A**, **E**) are more active (especially at the beginning of the reaction) than the matrix-caged complex (**G**). This result can be explained by the fact that in the latter case, the accessibility of the metal complex is more difficult for the bulky triethoxysilane (the porosity of the catalyst was not determined and not optimized). The same finding was observed in hydrogenation and hydrosilylation catalysed by rhodium complexes immobilized via 2,4-pentanedionato anchoring ligands.[4] Worth mentioning is not only the activity of the catalysts but also the instability upon re-use. It was possible to use catalysts **A** and **E** twice in succession, but in the third run they lost their activity. We did not find any traces of rhodium in the reaction products and washing liquids, so we conclude that the loss of the catalyst activity is due to its deactivation during handling.

Summarizing, the present catalysts offer promising alternative types of immobilization. They are more active compared with both homogeneous analogues and complexes immobilized on organic polymers. Naturally, until now it is difficult to determine the mechanism of the action of the immobilized species, and therefore a more detailed study is under way.

Acknowledgement The support of the Alexander-von-Humboldt Foundation, Bonn, which made possible M. Čapka's stay in Würzburg, is gratefully acknowledged.

REFERENCES

1. Pitmann, C U Jr In: *Comprehensive Organometallic Chemistry*, vol 8, Wilkinson, G (ed), Pergamon Press, New York, 1982, p 253

2. Hartley, F R *Supported Metal Complexes*, D Reidel, Dordrecht, 1985

3. Schubert U, Egger, C, Rose, K and Alt, C *J. Mol. Catal.*, 1989, 55: 330

4. Čapka, M, Czakoová, M, Urbaniak W and Schubert, U *J. Mol. Catal.*, 1992, 74: 335

5. Čapka, M, Schubert, U, Heinrich B and Hjortkjaer, J *Collect. Czech. Chem. Commun.*, 1992, 57: 2615

6. McCleverty J A and Wilkinson G *Inorg. Synth.* 1966, 8: 211

7. Dickson, R S, *Homogeneous Catalysis with Compounds of Rhodium and Iridium*, D Reidel, Dordrecht, 1985, p 108

8. Kavan, V and Čapka, M *Collect. Czech. Chem. Commun.*, 1980, 45: 2100

9. Michalska, Z M and Osterszewski, B *J. Organomet. Chem.*, 1986, 299: 259

10. Michalska, Z M, Osterszewski, B and Zientarska, J *J. Mol. Catal.*, 1989, 55: 256

11. Čapka, M *Collect. Czech. Chem. Commun.*, 1990, 55: 2803

12. Allum, K G, Hancock, R D, Howell, I V, McKenzie, S, Pikethly, R C and Robinson, J *J.Organomet. Chem.*, 1975, 87: 201

13. Allum, K G, Hancock, R D, Howell, I V, Pitkethly, R C and Robinson, J *J. Catal.*, 1976, 43: 322