Journal of Organometallic Chemistry, 321 (1987) 135–141
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SILICA-IMMOBILISED AMINE-PLATINUM COMPLEXES AS HYDROSILYLATION CATALYSTS

E.N. EJIKE and R.V. PARISH

Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD (Great Britain)

(Received September 22nd, 1986)

Summary

A simple method has been used to assess the efficiency of a variety of platinum-amine compexes anchored to silica and of anionic complexes supported on a silica-based ion-exchanger in the catalysis of the hydrosilylation of dec-1-ene by $(Me_3SiO)_2Si(H)Me$. In all cases, platinum was leached from the support, so that the catalyst became less active on each re-use. A rough correlation between extent of leaching and activity suggested that the effective catalysis was actually occurring homogeneously. The silane was responsible for the leaching.

Introduction

Hexachloroplatinic acid (Speier's catalyst) has long been used to catalyse the hydrosilylation of alkenes [1], although the active species involved has only recently been characterised [2]. Various other platinum complexes have been employed, including the ammines [3]. It therefore seemed likely that platinum-amine complexes immobilised on silica would be active and at the same time allow easy recovery of the platinum for re-use. Such materials are becoming of increasing interest [4–6]. We therefore decided to extend our previous studies with anchored phosphine complexes [7,8]. To our knowledge, there is only one report of the previous use of supported platinum-amine complexes for this type of catalysis [9].

Experimental

The following synthetic procedures are typical.

Silica-supported ligands

Silica gel (Grace ID112, 11.0 g) was dehydrated at 500 °C for 24 h and suspended in toluene (15 cm^3). 3-Aminopropyl-triethoxysilane (1.52 g) in toluene (15 cm^3) was added and the mixture was kept at 80 °C for 2 h and then refluxed for a further 4 h,

0022-328X/87/$03.50 © 1987 Elsevier Sequoia S.A.

after which ethanol was removed by distillation with a Dean and Stark apparatus. More toluene was added, and the distillation repeated. The solid was filtered off, Soxhlet-extracted with toluene for 3 h and finally washed with methanol and diethyl ether and dried at 70°C. (C, 2.7; H, 0.6; N, 0.7%).

Silica-supported platinum complexes

The silica-supported propylamine ligand (4.28 g) was suspended in water (20 cm^3) and methanol (8 cm^3). Sodium tetrachloroplatinate(II) (61 mg) in water (5 cm^3) was added and the mixture stirred for 24 h. The solid was filtered off and washed thoroughly with water, methanol and diethyl ether. (N, 0.6; Pt, 1.2%).

Tetrachlorobis(ethylene)diplatinum(II) (3.0 g, 5.1 mmol) in dichloromethane (10 cm^3) was treated with 3-aminopropyltrimethoxysilane (2.25 g, 12.6 mmol) in dichloromethane (10 cm^3). After 1 h the solvent was removed under reduced pressure, the residual gum dissolved in dichloromethane (25 cm^3) and chromatographed under nitrogen on silica gel which had been functionalised with trimethylchlorosilane. (Found: C, 25.0; H, 5.4; N, 2.7; Cl, 14.6; Pt, 37.1. Calc: C, 25.7; H, 5.4; N, 2.4; Cl, 13.8; Pt, 37.9%). This complex (0.3 g) in toluene (15 cm^3) was added to silica gel (ID112, 4.38 g) in toluene (25 cm^3) and the mixture was agitated for 24 h. The solid was filtered off and washed with toluene, dichloromethane, and diethyl ether. (C, 1.0; H, 0.5; N, 0.2; Pt, 2.4%).

Ion-exchange-supported anionic complexes

The silica-supported amine was treated with hydrochloric acid (0.1 mol dm^{-3}) and washed with water, methanol and n-heptane. The resulting supported ammonium salt (3.4 g) was packed into a column and treated with potassium (ethylene)trichloroplatinate(II) (Zeise's salt, 139 mg) in water (15 cm^3). The eluate was collected and passed down the column once more. The column was then washed with water until the eluate gave no reaction with silver nitrate. (C, 2.4; H, 0.7; N, 0.4; Pt, 1.2%).

Catalyst evaluation

All catalytic runs were performed with equimolar mixtures of dec-1-ene and heptamethyltrisiloxane, $(Me_3SiO)_2Si(H)Me$, (0.01 mol) and an amount of catalyst which contained 5×10^{-6} mol platinum. No solvent was used. Two procedures were employed for a crude evaluation of the activity of the catalysts.

Temperature-variation method

The reaction mixture (3.62 g) was placed in a tubular glass reactor fitted with a nitrogen inlet, a reflux condenser, a pivotted magnetic stirrer, and a thermometer. The reactor was placed in an air jacket and the whole apparatus was mounted in a heating bath. When temperature equilibrium had been reached, the catalyst was added, the temperature of the bath was raised at about 1°C/min, and the temperature of the reaction mixture monitored. There was usually an induction period during which the temperature of the mixture rose only slowly. When reaction began, there was a sharp increase in temperature. The temperature was monitored until it began to decrease, indicating that the exothermic reaction was complete. The final mixture was analysed by GLC.

Constant-temperature method

The glass reactor described above was placed in a jacket containing the vapour of a refluxing liquid of suitable boiling point. An equimolar mixture of the reagents was added and allowed to come to temperature equilibrium, the catalyst was added, and the temperature of the mixture was monitored. After a variable induction period, an exothermic reaction usually occurred, and temperature monitoring was continued until the exotherm was over. Samples for GLC analysis were withdrawn through a septum cap and quenched in a mixture of pyridine and dodecane (the latter provided an internal standard for the GLC analysis).

Results

The hydrosilylation reaction is highly exothermic, which provides a convenient method for rapid evaluation of catalysts. An equimolar mixture of dec-1-ene and $(Me_3SiO)_2Si(H)Me$ was brought to the desired initial temperature and the catalyst (containing 5×10^{-4} mol equivalents of platinum) was added. The temperature of the reaction mixture was then monitored with the surrounding bath temperature either constant or steadily raised; these methods are named constant-temperature or variable-temperature, respectively, referring to the applied temperature. After an induction period, the temperature of the mixture usually rose sharply as reaction commenced, and the time to reaction or the temperature at onset of the exotherm was used as a criterion of the activity of the catalyst. Induction periods were reproducible to about 30 s. The composition of the mixture was determined by GLC at the close of the reaction and sometimes at intervals throughout a reaction. The variable-temperature method is useful as an indicator of the gross properties of a range of catalysts while the constant-temperature method is well suited for closer comparisons of re-usability and deactivation.

Immobilised propylamine complexes

Two types of silica were mainly used (Grace ID112, 113) which have different surface areas. For the same composition (%N, %Pt), very similar results were obtained, indicating that particle-size and surface-area effects were unimportant. The major parameters of interest are therefore the platinum content, the N/Pt ratio, and the re-usability of the catalyst. Some samples of catalyst were treated with trimethylchlorosilane to block residual surface hydroxy groups; these materials exhibited the same activity as their untreated counterparts.

The uncomplexed ligand was inactive. For the platinum-treated catalyst, the activity increased and the induction period decreased as the N/Pt ratio decreased (see Table 1). Thus, the platinum-loading of the catalyst affects its reactivity, even though the same total amount of platinum was used in each run. There was also a correlation between the induction time and the time to complete reaction.

On re-use, many of the catalysts initially showed an increase in activity, and all showed a subsequent decline over 7–12 cycles. Although reactions became slower, there was no decrease in yield, which remained at ca. 95% until the final run in which the yield dropped to about 60%, indicating that deactivation was effectively complete (see Table 2).

The most likely cause of loss of activity is leaching of platinum from the support. All samples examined showed progressive loss of platinum, although considerable

TABLE 1

EFFECT OF N/Pt RATIO [a]

	Catalyst					
	Variable-temperature method			Constant-temperature method		
	C(1)	C(4)	C(14)	C(14)	C(16)	C(10)
%Pt	0.8	1.3	2.0	2.0	2.6	1.6
%N	0.3	0.3	0.3	0.3	0.4	0.8
N/Pt	5.2	3.2	2.1	2.1	2.7	7.0
Reaction time (min)	24	16	8			
Initiation temp. (°C)	45	40	37			
Induction time (min)				2	4	7
Time to completion (min)				4.5	7.5	12

[a] An amount of catalyst corresponding to 1×10^{-6} mol (Pt) was used in each case.

TABLE 2

CATALYST RE-USE

	Catalyst			
	C(9)	C(12)	C(14)	C(16)
Time to completion (1st run) (min)	2	4.5	4.5	7.5
Yield after 1st run (%)	95	95	95	95
Number of runs	12	11	12	7
Time to completion (last run, min)	12	11	12	11.5
Yield after last run (%)	65	62	65	60

quantities remained even when the catalyst had become inactive (Table 3). No detectable loss of nitrogen occurred. The proportion of platinum lost was less for higher initial N/Pt ratios. No reduction to metallic platinum was observed.

In one case (C(12)), the catalyst was examined during the induction period. The whole of the loss of platinum recorded in Table 3 occurred during the induction

TABLE 3

PERCENTAGE OF PLATINUM AFTER RE-USE AT 65°C

	Catalyst			
	C(16)	C(14)	C(8)	C(12)
Initial %Pt	2.6	1.9	1.5	1.8
After 1 run	1.5	1.1		1.4
2 runs	1.3	0.8 [a]	0.7	
3		0.7 [a]		
4			1.3	
7	1.1			
10		0.9	0.9	
12				1.2
% total Pt lost	58	53	40	33
Initial N/Pt	2.7	2.1	4.6	4.6
Final N/Pt	5.1	4.6	7.7	8.1

[a] Runs at 69°C.

period. No nitrogen was detected in the liquid products. Owing to the increased carbon and hydrogen contents mentioned below, it is not possible to make meaningful comparisons of the residual nitrogen content but, in all cases, the N/Pt ratio increased significantly.

The activity of the system also depended on the order in which the reagents were mixed. Normally, the silane and alkene were mixed and brought to reaction temperature before the catalyst was added. When the catalyst and decene were kept in contact for 30 min at 65 °C before the silane was added, the induction period was greatly extended and reaction was slow and incomplete. Conversely, when the catalyst was pretreated with the silane, reaction began immediately the decene was added, and reaction was rapid and complete. A fresh portion of the catalyst was left in contact with the silane for 24 h at room temperature and filtered off. Decene was added to the recovered silane at 39 °C and reaction commenced within a few minutes; the solid catalyst was not active at this temperature. However, pretreatment of decene with the catalyst gave an inactive liquid product. When the temperature of the silane-pretreatment was raised, the silane became active more rapidly: 1–2 h were sufficient at 60–70 °C. The solid catalyst recovered from these experiments was itself active, and showed shorter induction times than the untreated material. After the treatment with silane, the solid showed significantly increased carbon content (by a factor of about three), and the extra material could not be removed by thorough washing with organic solvents; the silane appears to be incorporated in some form into the solid.

Loss of platinum could be contained by mixing the uncomplexed ligand with the catalyst. For instance, catalyst C(16) lost 30% of its platinum in two cycles, and C(14) 25% in three cycles in the presence of added ligand compared to 50 and 63%, respectively in its absence. However, the addition of the ligand also resulted in an increase in activity, which contrasts with the effect of increasing N/Pt ratio within a given catalyst.

Immobilised diaminoethane complexes

The complexes of immobilised 1,2-diaminoethane showed considerably lower activity than those of analogous immobilised propylamine complexes (Table 4), and the yields were lower (ca. 55%). Leaching of platinum appeared to be negligible, at least as judged by the lack of catalytic activity in the liquid products. However, these catalysts became inactive after only three cycles of re-use.

Ion-exchange-supported anionic complexes

The immobilised propylamine ligand was converted to its hydrochloride and used

TABLE 4

CATALYSIS BY IMMOBILISED DIAMINOETHANE COMPLEXES

	Catalyst		
	C(19)	C(18)	C(17)
%Pt (initial)	2.9	5.0	5.3
Initial N/Pt	4.3	2.5	2.4
Induction time (min, 78 °C)	[a]	19	12

[a] Inactive below 120 °C.

TABLE 5

CATALYSIS BY IMMOBILISED ANIONIC COMPLEXES

	Catalyst			
	C(22)	C(23)	C(24)	C(25)
Anion [a]	Z	Z	T	T
%Pt	1.2	1.5	1.9	1.7
N/Pt	4.6	4.6	2.9	3.3
Induction time (min, 25 °C)	14	8	7	18

[a] Z = $[PtCl_3(C_2H_4)]^-$; T = $[PtCl_4]^{2-}$.

as an anion exchanger to support the anions $[PtCl_4]^-$ and $[PtCl_3(C_2H_4)]^-$. These materials were very active, having short induction times even at room temperature, but suffered severe leaching of platinum. This was indicated by the rapid discolouration of the liquid and by the catalytic activity of the separated products. Catalyst C(24) lost 53% of its platinum content during a single run. Leaching was again shown to be due to the silane: decene alone did not remove any platinum.

Discussion

Supported platinum-amine complexes are effective catalysts for the hydrosilylation reaction, and can be re-used through several cycles. In most cases, there was an increase in activity after the first run, followed by progressive loss of activity. This suggests that the complex(es) present on the support are not themselves directly involved in the catalysis, but require to be activated. Pretreatment experiments established that the silane is the activating entity, the alkene had no effect. The same process is presumably occurring during the induction period. The silane became incorporated into the solid during reaction or pretreatment, and may reasonably be presumed to be associated with the platinum. The activation process is likely to involve oxidative-addition of the silane to platinum(II), generating a hydrido-silyl-platinum(IV) complex as the active entity.

In every case, however, catalytic activity is accompanied by leaching of the platinum into solution, and this is the most likely cause of the loss of activity on re-use. More fundamentally, there appears to be a correlation between activity and extent of leaching, and it seems likely that the effective catalysis is actually occurring in the solution, and not on the support. The leached material is catalytically active in the absence of the solid catalyst. It was not possible to determine if only platinum is leached or whether the propylamine ligand also goes into solution (no nitrogen was detected in the liquid products, but the amount would in any case be very small), but there was always a significant increase in N/Pt ratio during the leaching process. Independent experiments showed that platinum(II) complexes of $(MeO)_3Si(CH_2)_3NH_2$, $Ph(CH_2)_3NH_2$, and Bu^nNH_2 were effective homogeneous catalysts but were less active than $K_2[PtCl_3(C_2H_4)]$. The silane is the responsible agent for leaching, and it seems possible that the leaching and activating effects are the same. In this case, assuming that the ligand is not leached, the reaction of the bound platinum complex with the silane may involve cleavage of the anchoring Pt–N bond, perhaps assisted by the high *trans*-influence of hydride or silyl ligands [10]. The soluble species so formed is stable in the presence of the alkene (but decomposes to metallic platinum in its absence), and may become partially re-bound to the immobilised ligand. This would explain both the activation of the catalyst in the first cycle and the enhancing effect of added immobilised ligand. The silica-immobilised phosphine ligand used previously by us [8] was resistant to leaching by $Me_3Si[SiH(Me)O]_nSiMe_3$ but was leached by ethanol. This observation reinforces the view that, in the present case, platinum is removed preferentially.

It is noticeable that not all the platinum is leached, but that which remains is inactive. There may be a correlation here with the observed lack of reactivity of the immobilised diaminoethane complex. The species formed when $[PtCl_4]^{2-}$ reacts with the immobilised propylamine ligand are not known; this will to some extent depend on the spacing of the amine groups on the silica surface. Initially, monosubstitution of chloride in $[PtCl_4]^-$ will occur; on the basis of the normal *trans*-effect this would be followed by formation of the *cis*-disubstituted complex. There might also be some chloride-bridged dimers with one nitrogen ligand per platinum. The concentration of the mono-amine complexes would presumably be greater at the higher platinum-loadings. Assuming the ligand to remain firmly bound, it would appear that the monoamine complexes can be leached and activated but the *cis*-diamine complex has low activity, like the diaminoethane complex. The two ion-exchanged anionic complexes were both extremely active and heavily leached. Evidently, the leaching process can take anionic species into solution. Possibly, the alkene acts as a neutral ligand in stabilising these species.

Acknowledgements

We are grateful to the University of Benin for a research scholarship and to Dow Corning for financial and material assistance.

References

1 J.L. Speier, J.A. Webster, and G.H. Barnes, J. Am. Chem. Soc., 79 (1957) 974.
2 R.A. Benkeser and J. Kang, J. Organomet. Chem., 185 (1980) C9.
3 H.J. Kollmeier and R.D. Langenhagen, Eur. Pat. EP75703 (1983) [Chem. Abs. 99 (1983) 39272].
4 D.C. Bailey and S.H. Lange, Chem. Rev., 81 (1981) 109.
5 J.P. Collman and L.S. Hegedus, Principles and Applications of Organo-transition Metal Chemistry, University Science Books, California, 1980, p. 370.
6 L.L. Murrell, in J.L. Burton and R.L. Garton (Eds.), Advanced Materials in Catalysis, Academic Press, New York, 1977, Chap. 8.
7 J. Dwyer, H.S. Hilal and R.V. Parish, J. Organomet. Chem., 228 (1982) 191.
8 R.V. Parish and M.I. Vania, J. Organomet. Chem., 263 (1984) 139.
9 B. Marciniek, Z.W. Kornetka, and W. Urbaniak, J. Mol. Catal., 12 (1981) 221; Z.W. Kornetka, J. Bartz, and B. Marciniec, Polish Pat., PL 115645 B2 (1982).
10 R.N. Haszeldine, R.V. Parish, and J.H. Setchfield, J. Organomet. Chem., 57 (1973) 279.