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Hydrosilylation of phenylacetylene catalyzed by metal complex catalysts supported on polyamides containing a pyridine moiety

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Abstract

The hydrosilylation of phenylacetylene with triethoxysilane catalyzed by polymer-supported Rh(I) and Pt(II) complexes has been investigated. Polyamides having the 2,5- and 2,6-pyridine moiety in their repeat units were used as the catalysts supports. The effect of the support structure, the type of solvent used, the substrate ratio and catalyst concentration on reaction selectivity were studied. X-ray photoelectron spectroscopy (XPS) was used to characterize the polymer supports and the supported catalysts before and after use. It was found that the selectivity of the hydrosilylation can be controlled by the chemical structure of the polymer support. When the reaction was catalyzed by Rh(I) attached to the polyamide with a pyridine substituted in the 2,6 position, $\beta(Z)$-vinylsilane was formed as the major product. Use of the same catalyst supported on the polymer with the 2,5-pyridine resulted in a reversal of the stereoselectivity and $\beta(E)$-vinylsilane was the major product. These results have been correlated with the reaction mechanism and the electron density on the rhodium centres. The binding energy for the Rh3d $5/2$ attached to the 2,6-py moiety was found to be lower by 1.03 eV than that for the Rh supported on the 2,5-py type polymer. Hydrosilylation using Pt(II) as the catalyst supported on the same series of polyamides proceeded in the usual manner of *cis* addition to give predominantly $\beta(E)$-vinyl product and the α-isomer. The only difference caused by the presence of the polymer support was the increased yield of α-product. Recycling tests demonstrated high stability of the supported catalysts during prolonged use. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polymer-supported catalysts; Phenylacetylene; Hydrosilylation; Stereoselectivity; Rh(I) catalysts; Pt(II) catalysts; X-ray photo-electron spectroscopy, XPS

1. Introduction

The vinylsilanes are versatile intermediates in organic synthesis. The simplest and most straightforward method for their preparation is the catalyzed hydrosilylation of alkynes. Among a variety of catalysts which promote the addition of hydrosilanes to carbon–carbon multiple bonds, platinum and rhodium compounds have been most effective. Several reviews and papers have discussed this process [1–13].

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Hydrosilylation of alkynes usually gives three addition products: α and two β stereoisomers *Z* and *E*.
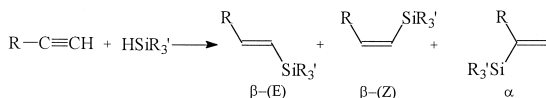
The selectivity of this reaction is difficult to control and depends on several factors such as the electronic and steric effects of the substituents on the alkyne and silane, the catalytic species involved and the type of solvent. This paper describes our results on hydrosilylation of alkynes where we use rhodium(I) and platinum(II) complexes as the catalysts supported on polyamide matrices containing a pyridine moiety. We investigated the effect of the polymer structure and reaction conditions on the selectivity of this reaction. This work continues our earlier studies on hydrosilylation of alkenes [14,15] and dienes [17] where the same catalytic systems were used.

2. Experimental

2.1. Materials

All solvents and reagents were of analytical or chemical grades. Benzene, ethanol, acetonitrile, tetrahydrofuran and cyclohexane were purified by standard methods. Phenylacetylene and triethoxysilane were commercial samples. $[RhCl(CO)_2]_2$ and $PtCl_2(PhCN)_2$ were synthesised using reported procedures in Refs. [18] and [19], respectively.
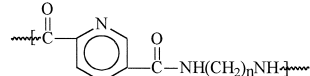
2.2. Polymer supports and supported catalysts

The polyamide supports were prepared by low temperature-interfacial condensation of 2,5- or 2,6-pyridine dicarboxylic acid chlorides and aliphatic diamines. Details of their synthesis
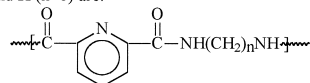
have already been described [14,15]. We retain the symbols used previously for the polymers:

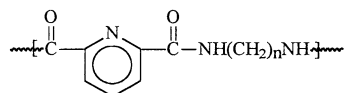Series 2,5-py E ($n = 2$) and H ($n = 6$) are:

Series 2,6-py E ($n = 2$) and H ($n = 6$) are:

The polymer-supported catalysts were prepared by reacting the soluble precursor complexes with the polymer [15,17]. Rh and Pt contents were determined by AAS spectroscopy.

2.3. Catalytic reactions

All the reactions were carried out under nitrogen using freshly distilled dry solvent and liquid reagents. A typical procedure for the hydrosilylation of phenylacetylene was as follows. Polymer-supported catalyst (0.0014 mmol metal) was placed in a dried reaction vessel thoroughly flushed with nitrogen. A solvent (0.5 ml), hydrosilane (1.5 mmol) and phenylacetylene (1.5 mmol), were added successively with a syringe. The mixture was stirred at 80°C and the progress of the reaction was monitored using a Hewlett-Packard 5890 II gas chromatograph equipped with a thermal conductivity detector, and a column of 6 ft of 10% OV-101 and 6 ft of 10% OV-225 on 100–120 mesh Chromosorb W HP.

Products were separated using an Alltech HPLC with an Adsorbosil C18 Column (10 μm packing, 250 mm × 10 mm) and pentane–iso-propanol 98.2 v/v at a flow rate of 0.5 cm^3/min. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker MSL 300 or a Bruker AC 200 spectrometer. Chemical shifts are given downfield from internal tetramethylsilane.

2.4. Spectroscopic data of products

α-Triethoxysilylstyrene. ^{1}H NMR ($CDCl_3$): δ 7.58–7.32 (m, H_{aromat}, 5H), 6.14 (d, $J = 3$ Hz, C=CH, 1H), 5.96 (d, $J = 3$ Hz, C=CH, 1H), 3.83 (q, $J = 7$ Hz, OCH_2, 6H), 1.20 (t, $J = 7$ Hz, CH_3, 9H).

β-*cis*-Triethoxysilylstyrene. ^{1}H NMR ($CDCl_3$): δ 7.58–7.26 (m, H_{aromat}, C=CHPh, 6H), 5.54 (d, $J = 16$ Hz, C=CHSi, 1H), 3.81 (q, $J = 7$Hz, OCH_2, 6H), 1.20 (t, $J = 7$ Hz, CH_3, 9H).

β-*trans*-Triethoxysilylstyrene. ^{1}H NMR ($CDCl_3$): δ 7.58–7.26 (m, H_{aromat}, C=CHPh, 6H), 6.16 (d, $J = 19.1$ Hz, C=CHSi, 1H), 3.81 (q, $J = 7$ Hz, OCH_2, 6H), 1.20 (t, $J = 7$ Hz, CH_3, 9H).

2.5. X-ray photoelectron spectroscopy measurements

X-ray photoelectron spectroscopy (XPS) measurements were made on a VG ESCALAB 210 spectrometer with an Al K_α ($h\nu = 1486.6$ eV) X-ray source. The pressure in the spectrometer chamber was about 5×10^{-9} mbar. Samples were pressed into pellets under a pressure of 100 kbar for 10 min before use. Survey spectra were recorded for all samples in the binding energy range 0–1400 eV with a step of 0.5 eV. High-resolution scans for the C 1s, N 1s, O 1s, Cl 2p, Rh 3d and Pt 4f core level spectra were recorded with a step of 0.05 eV and dwell time of 200 ms. The analyser pass energy was set at 20 eV. A take-off angle of 90° was used in all XPS studies. To avoid possible X-ray-induced metal reduction in the polymer host [20] measurements were made with a reduced power of the X-ray source to 10 kV, 10 mA. Curve fitting was performed using the ECLIPSE data system software. This software describes each of the components of a complex envelope as a Gaussian–Lorentzian sum function; a constant G/L ratio 0.3 was used. The background was fitted using a nonlinear model function proportional to the integral of the elastically scattered electrons (Shirley background).

The most characteristic of the C1s peaks, attributed to the carbonyl group $>$C=O, was used as the reference peak for all the binding energy (BE) values recorded. A value of BE = 287.90 eV for the above peak was arbitrarily taken as the mean value for several polymer containing carbonyl groups [21]. Some carbonyl groups are involved in the coordination to the

Table 1
Characteristics of the polyamide supports and supported catalysts

Sample symbol[a]	Crystallinity[b] (%)	Surface area[c] (m^2/g)	Micropore volume[c] (%)	Mean pore radius (Å)	Rh content[d] (wt.%)	Pt content[d] (wt.%)
2,5-py E	30	91.7	14	$20^{b,c}$,	1.31	1.46
2,5-py H	35	19.0	24.5	$20^{b,c}$	1.38	3.00
2,6-py E	20	47.9	11.6	$< 10^e$	1.62	2.34
2,6-py H	26	4.4	24.2	8.8^e	1.40	0.99

[a] For the preparation and characterization of the supports and supported catalysts see Refs. [13–15].
[b] Determined by SAXS.
[c] Determined by BET.
[d] Determined by AAS method.
[e] Determined by ISEC.

metal centres, however, taking into account the low percentage of these, it was assumed that the electronic state of the $C_{C=O}$ 1s remains fairly stable. The N 1s peaks were fitted into two major peaks at 399.36 and 399.88 eV assigned to pyridine and amide nitrogens respectively, having an area ratio of 1:2. We give the BE values obtained from the curve fittings with the accuracy of 0.01 eV in order to show more clearly the changes in the system.

3. Results and discussion

The reactions were carried out in benzene with an equimolar ratio of phenylacetylene and triethoxysilane in the presence of the rhodium (I) or platinum(II) catalysts immobilized on the polyamides having the 2,5- and 2,6-pyridine moiety in their repeat units. The metal sites were introduced into the polymers by ligand exchange using soluble $[RhCl(CO)_2]_2$ or $PtCl_2(PhCN)_2$ complexes as precursors. The synthesis of polymer supports and supported catalysts are reported elsewhere [14–17]. Selected properties of these are collected in Table 1.

3.1. Rhodium catalyzed reactions

It is well known that the hydrosilylation of alkynes catalyzed by rhodium (I) complexes provides a unique route to *cis*-vinylsilanes [2,3].

The results of the hydrosilylation catalyzed by the supported rhodium complex are summarized in Table 2 and Fig. 1. The most important observation is that the selectivity of the hydrosilylation is dependent on the chemical structure of the polymer support. When the rhodium catalyst was attached to the 2,6-py type polyamide (*Z*)-vinylsilane was obtained as the major product. Use of the same catalyst supported on the 2,5-py type polymer resulted in a reversal of the

Table 2
Results of phenylacetylene hydrosilylation with triethoxysilane using polymer-supported rhodium catalysts in benzene
Reaction conditions: catalyst preswelled in the reaction medium for 24 h prior to reaction; temperature 80°C, time 8 h, solvent: benzene, alkyne/catalyst mol. ratio $1/1 \times 10^{-3}$ for entries 1–19.

Entry	Catalyst	Alkyne/silane mole ratio	Product distribution[a]		
			α	β-(Z)	β-(E)
1	homogeneous system	1/1	12	57	31
2	2,5-py E/Rh	1/1	25	21	54
3	2,5-py H/Rh	1/1	26	14	60
4	2,6-py E/Rh	1/1	17	51	32
5	2,6-py H/Rh	1/1	9	73	18
6	homogeneous system	5/1	5	84	11
7	2,5-py E/Rh	5/1	17	45	38
8	2,5-py H/Rh	5/1	6	79	15
9	2,6-py E/Rh	5/1	6	80	14
10	2,6-py H/Rh	5/1	5	84	11
11	homogeneous system	1/5	21	9	70
12	2,5-py E/Rh	1/5	43	16	41
13	2,5-py H/Rh	1/5	39	9	52
14	2,6-py E/Rh	1/5	41	4	55
15	2,6-py H/Rh	1/5	31	36	33
16	2,6-py E/Rh[b]	1/1	18	47	35
17	2,6-py E/Rh[c]	1/1	17	48	35
18	2,5-py H/Rh[b]	1/1	28	15	57
19	2,5-py H/Rh[c]	1/1	27	15	58
20	2,5-py E/Rh[d]	1/1	21	36	43
21	2,5-py H/Rh[d]	1/1	20	40	40
22	2,6-py E/Rh[d]	1/1	30	58	12
23	2,6-py H/Rh[d]	1/1	10	78	12

[a] Determined by GLC.
[b] After 2 h.
[c] After 4 h.
[d] Alkyne/catalyst mol ratio $1/2.4 \times 10^{-4}$ for entries 20–23.

stereoselectivity and (*E*)-vinylsilane became predominant ((Table 2, entries 4, 5 and 2, 3), respectively). No isomerization of products from *cis* to thermodynamically more favorable *trans* isomer occurred. The *Z/E* product ratio, which was established at the early stages of the reaction, remained fairly stable as the reaction proceeded (Table 2, entries 3, 4, 16–19).

From Table 2 it can be seen that the distribution of addition products is also affected by the alkyne to silane ratio and catalyst concentration.
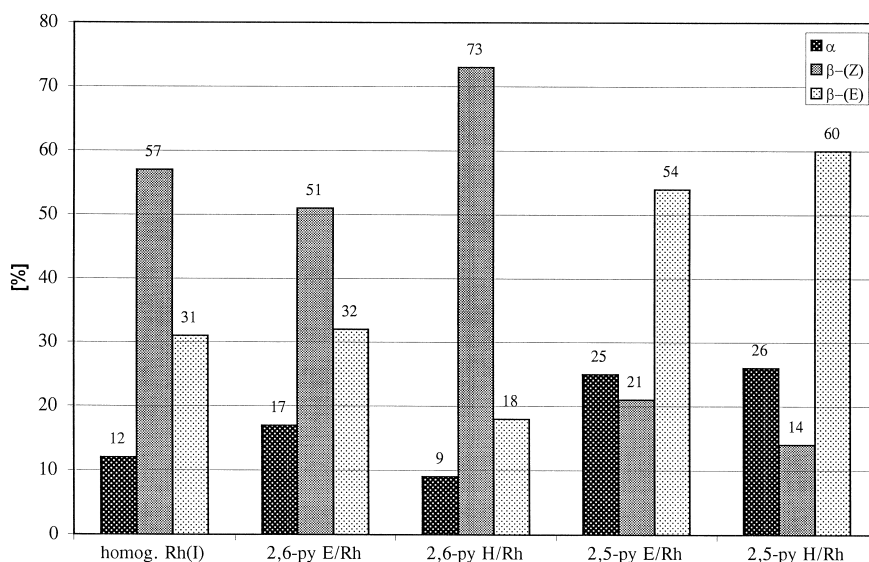
Fig. 1. Selectivity in the hydrosilylation of phenylacetylene by triethoxysilane in benzene using polymer-supported rhodium catalysts.

The use of 5 equiv. excess of phenylacetylene increased formation of the (Z)-vinyl product for all rhodium catalysts, including those supported on 2,5-py E and H polymers (entries 6–10). The opposite effect was observed when the alkyne/silane ratio was reversed, i.e., (E)-vinylsilane and α-isomer were formed as the main products (entries 11–15).

We can also see from Table 2 that a lower catalyst concentration increases the yield of (Z)-vinyl silane for all four catalyst studied (Table 2, entries 20–23).

In order to get more information on the influence of polymer swelling on the reaction selectivity, experiments were carried out where polymeric catalysts were preswelled in the reaction medium for 24 h prior to the reaction. The results in Table 3 clearly show that the product distribution is greatly influenced by the polymer morphology. For example, for the 2,6-py H/Rh catalysts which exhibit high crosslinking and a very poor porous structure, preswelling did not exert any effect on the reaction products, whereas for the 2,5-py H/Rh system with larger pores higher proportions of the (E)-vinylsilane were obtained. Presumably in the preswelled

state the steric and electronic factors are becoming more significant and create better conditions for the formation of the *trans* product. On the basis of these results all catalytic reactions were carried out at constant conditions with preswelled catalysts.

Figs. 2 and 3, and Table 4 illustrate the effect of different solvents (benzene, ethanol, acetonitrile and THF) on the selectivity of hydrosilylation. It appears that the specific (Z)- and (E)-selectivity of the 2,6-py/Rh and 2,5-py/Rh catalysts, respectively, are independent of the

Table 3
The effect of catalyst preswelling on the hydrosilylation of phenylacetylene with $HSi(OEt)_3$ using supported rhodium catalysts
Conditions: as in Table 2, except that there was no preswelling for values in parentheses.

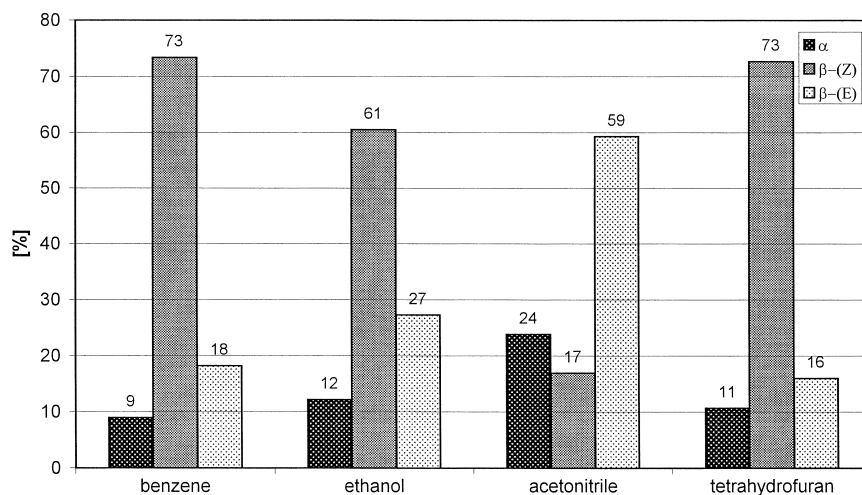| Catalyst	Product distribution (%) swelled (non-swelled)		
	α	β-(Z)	β-(E)
2,5-py E/Rh	25 (22)	21 (36)	54 (42)
2,5-py H/Rh	26 (25)	14 (25)	60 (50)
2,6-py E/Rh	17 (16)	51 (50)	32 (34)
2,6-py H/Rh	9 (10)	73 (76)	18 (14)

Fig. 2. Hydrosilylation of phenylacetylene with triethoxysilane using 2,6-py H/Rh catalyst in different solvents.

type of the solvent used with one exception. In the reaction catalyzed by Rh/2,6-py E and H polymer in acetonitrile the stereoselectivity was reversed from (Z) to (E)-mode. This result was in agreement with the results of Takeuchi and Tanouchi [10,11]. They found that the nitrile solvents can change the hydrosilylation stereos-

electivity by promoting the dissociation of a chloro ligand; this generates a cationic rhodium complex, an active species in E-selective conditions.

Table 4 also indicates that the yields of either (Z)- or (E)-products achieved in these solvents (except acetonitrile) were higher with polymer-
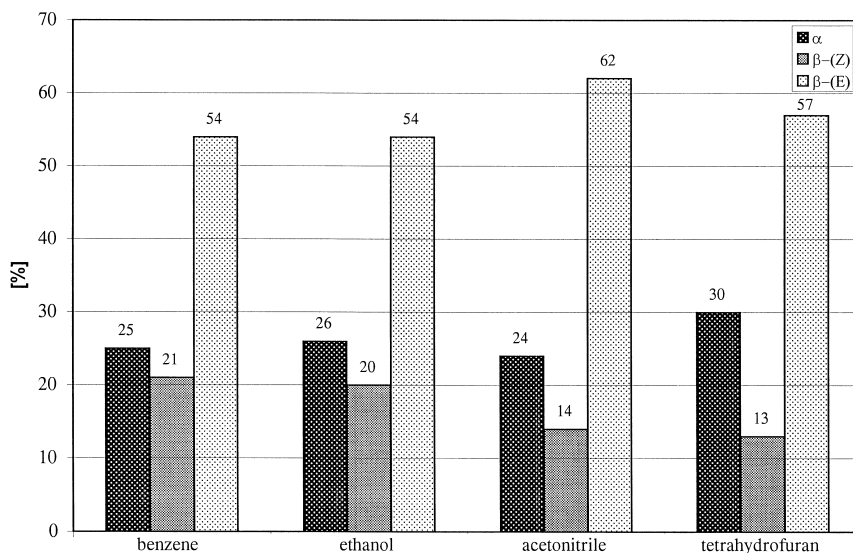

Fig. 3. Hydrosilylation of phenylacetylene with triethoxysilane using 2,5-py E/Rh catalyst in different solvents.

Table 4
Hydrosilylation of phenylacetylene with HSi(OEt)$_3$ catalyzed by polymer-supported rhodium catalysts in different solvents at 80°C
Conditions: see Table 2.

Catalyst Rh/support	Product distribution (%)											
	Benzene			Ethanol			THF			Acetonitrile		
	α	β-(Z)	β-(E)	α	β-(Z)	β-(E)	α	β-(Z)	β-(E)	α	β-(Z)	β-(E)
Homogeneous system	12	57	31	13	51	36	17	48	35	23	18	59
2,6-py H	9	73	18	12	61	27	11	73	16	24	17	59
2,6-py E	17	51	32	9	70	21	15	59	26	19	15	66
2,5-py H	26	14	60	26	28	46	29	19	52	25	18	57
2,5-py E	25	21	54	26	20	54	30	13	57	24	14	62

immobilized catalysts than in the homogeneous systems.

4. XPS studies

To shed more light in the catalytic properties of the rhodium species attached to the 2,5-py and 2,6-py polyamides we have studied the electronic state of the metal centres and of polymer donor functions by XPS for all of the catalytic systems. Tables 5 and 7 give the binding energy values for the freshly prepared catalysts and for the samples after one and several catalytic runs. It also includes the BE data of the nitrogen- and oxygen-donor functions for the pure, unloaded polymer supports.

4.1. Rhodium catalysts

The XPS results summarized in Table 5 clearly show that the three possible coordination sites participate in the rhodium linking to the polymer support. This was proved by the increase of the binding energy BE for N_{py} 1s, N_{amide} 1s and $O_{C=O}$ 1s electrons after the rhodium precursor attachment. It was also revealed that the BE for the Rh $3d_{5/2}$ attached to the 2,6-py type polymers was lower by 0.31 to 1.03 eV than that observed for the rhodium

Table 5
Binding energy values (eV) for supported rhodium catalysts and pure polymer supports
All binding energy values referenced to C 1s = 287.90 eV of the >C=O group.
FWHM values ranged from 1.5 to 2 eV.

| Entry	Sample	N 1s		O 1s	Cl $3p_{3/2}$	Rh $3d_{5/2}$
		N_{py}	N_{amide}			
1	polymer 2,6-py E	399.36	399.88	531.47		
2	2,6-py E/Rh before use	399.50	400.02	531.63	198.05	309.57
3	2,6-py E/Rh after 1st run	399.29	399.81	531.35	197.95	309.06
4	2,6-py E/Rh after several runs	399.50	400.02	531.59	198.10	309.56
5	polymer 2,6-py H	399.35	399.87	531.58		
6	2,6-py H/Rh before use	399.54	400.05	531.64	198.27	309.27
7	2,6-py H/Rh after 1st run	399.26	399.78	531.44	197.96	309.00
8	2,6-py H/Rh after several runs	399.34	399.86	531.49	198.25	309.11
9	polymer 2,5-py E	399.22	399.74	531.33		
10	2,5-py E/Rh before use	399.36	399.88	531.46	197.26	309.88
11	polymer 2,5-py H	399.39	399.91	531.67		
12	2,5-py H/Rh before use	399.82	400.34	531.97	198.43	310.30
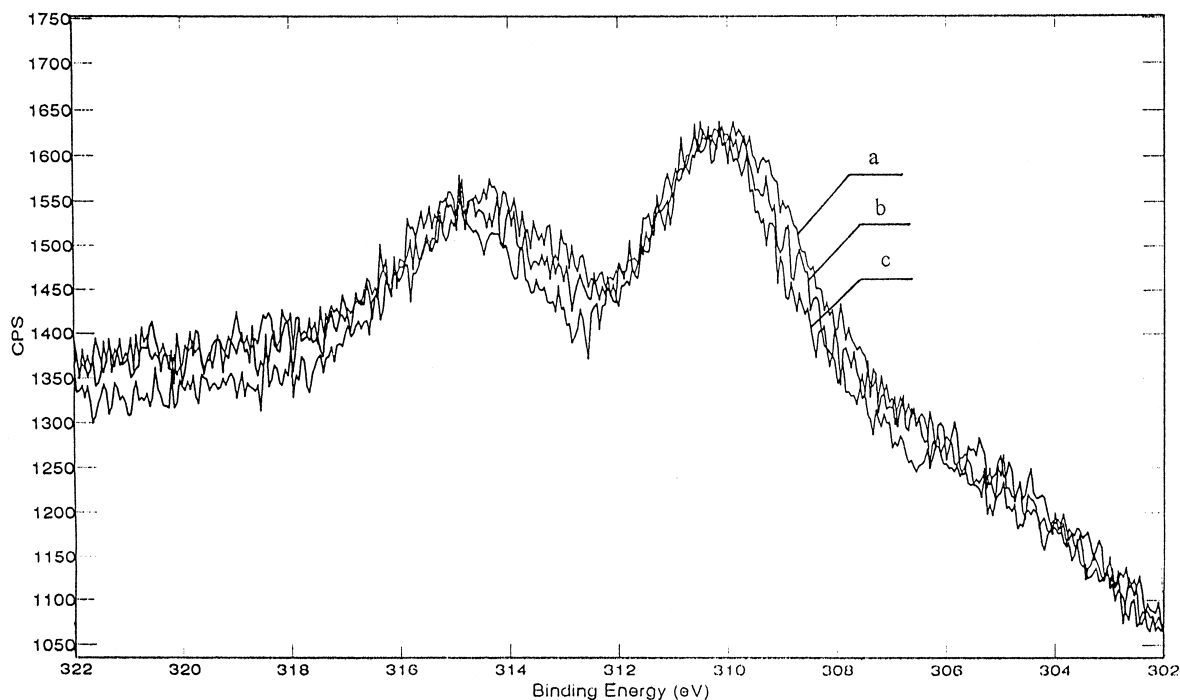
Fig. 4. Rhodium 3d XPS spectra for the catalyst 2,6-py E/Rh as (a) before use, (b) after one, (c) after several runs.

supported on the 2,5-py polymers. (Table 5, entries 2, 6, 10 and 12). These results are in excellent agreement with the electronic effects of the polymeric ligands. The pyridine ring substituted with the amide groups in the 2,6-positions is considered as the better electron donating moiety than that substituted in the 2,5-positions, where the electron density is more dispersed. This was confirmed by the semiempirical PM3 method.

The pure H-type polymers show higher BE values for $O_{C=O}1s$ than those of the *E* type. We believe that this increase is due to hydrogen bonding that usually occurs in the polyamides. Generally, H-type polyamides of both series have a higher proportion of hydrogen bonds and higher crystallinity (see Table 1) than the *E*-type polymers. The hydrogen bond formation via carbonyl oxygen lowers the oxygen electron density and in consequence increases the binding energy.
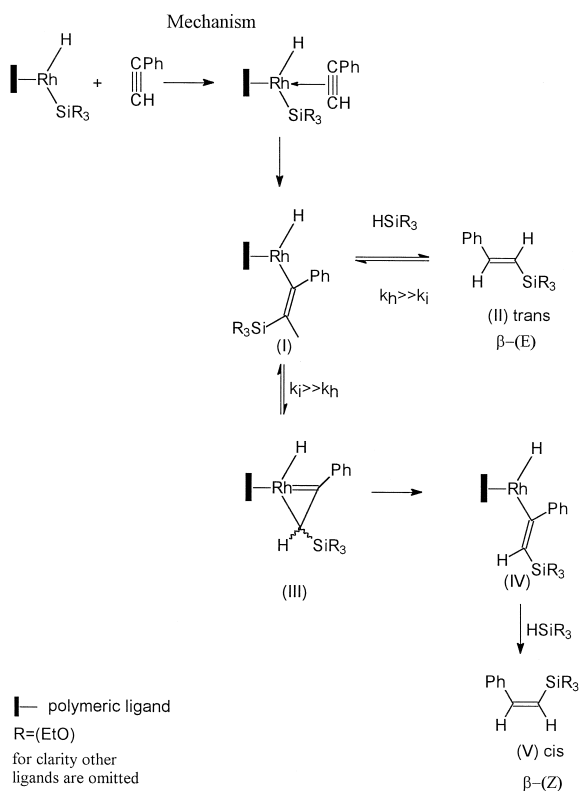
Fig. 4 shows the BE spectra for the rhodium 3d level supported on the 2,6-py E polymer. It can be seen that the peaks from the freshly prepared catalyst (a) and those obtained after one (b) and several catalytic cycles (c) are identical. These results provide evidence for high stability of the rhodium supported systems during the recycling experiments.

5. Reaction mechanism

To account for the dependence of the selectivity of the rhodium systems on the type of the polymer support used, it is necessary to discuss the reaction mechanism in conjunction with the XPS data.

The mechanism of the alkyne hydrosilylation catalyzed by polymer-supported rhodium catalysts studied here follows that proposed by Ojima et al. [2,3,5], Speier 4 and Tanke and Crabtree [6 7] (Scheme 1). It involves the initial insertion of the alkyne into a Rh–Si bond to give a (*Z*) vinylrhodium intermediate (I). This intermediate can either add another hydrosilane

Scheme 1. Mechanism.

less hindered isomer (IV) and to the final *cis*-product ($k_i > k_h$).

On the other hand, the lower donating ability of the ligand 2,5-[HNCOpyCONH] is responsible for the lower electron density on the rhodium (entries 10 and 12). Such a situation disfavors isomerization of the intermediate (I) and facilitates the addition of the hydrosilane molecule and subsequent reductive elimination of *trans*-product (II) ($k_h > k_i$).

On the basis of this discussion it is clear that the excess of the phenylacetylene favors stabilization of the carbene intermediate and increases the yields of *cis*-isomer as observed here (Table 2, entries 6–10). The excess of hydrosilane on the other hand reversed the stereoselectivity of the reaction giving rise to the higher yields of the *trans*-isomer and α-product (Table 2, entries 11–15). It has already been reported [5] that a low catalyst concentration favors isomerization as an intramolecular process vs. the reductive elimination as a bimolecular process, thus leading to the higher yield of *cis*-vinyl isomer. We observed the same trend when the concentration of the supported catalyst was four times lower than that usually regarded as standard (Table 2, entries 20–23). Similar reasoning can be used to explain why the use of the 2,6-py H/Rh catalyst gives the highest yield of the *cis*-vinylsilane. In the H-type support the donor functions that bind the rhodium to the polymer are separated by hexamethylene spacers and therefore the catalytic sites are more isolated than those separated by short ethylene chains. Presumably this ''diluting'' effect on the *cis*-product formation is stronger than that raised by crosslinking which decreases the electron density on the oxygen and might increase the BE for the Rh 3d.

5.1. Platinum-catalyzed reactions

The addition of triethoxysilane to phenylacetylene with 2,5-py and 2,6-py polymer-supported platinum (II) catalysts proceeded in the usual way by *cis* addition to give (*E*) and α

molecule to give the *trans*-vinyl product (II) or isomerize to the less sterically congested (*E*)-vinylrhodium intermediate (IV) via the η^2-vinyl carbene complex (III). From (IV) the final *cis*-vinyl product is formed through oxidative addition of hydrosilane and reductive elimination. Which route will prevail depends on the stabilizing effect of the ligands.

Considering the steric and electronic effects of the polymeric ligands it is evident that the 2,6-[HNCOpyCONH] group is a better electron donating moiety than the 2,5-[HNCOpyCONH]. This was confirmed by the XPS measurements of the binding energy for the Rh 3d 5/2 which showed the lower BE values for 2,6-py E and H/Rh catalysts (Table 5, entries 2 and 6). The electron density transmitted from the 2,6-py ligand to the rhodium stabilizes the carbene intermediate and facilitates its rearrangement to the

Table 6
Hydrosilylation of phenylacetylene with $HSi(OEt)_3$ catalyzed by polymer-supported platinum catalysts in different solvents
Conditions: see Table 2.

Catalysts	Solvent	Product distribution (%)		
		α	β-(Z)	β-(E)
Homogeneous system	benzene	28	0	72
2,5-py E/Pt		36	0	64
2,5-py H/Pt		32	0	68
2,6-py E/Pt		32	0	68
2,6-py H/Pt		43	0	57
Homogeneous system	ethanol	27	0	73
2,5-py E/Pt		28	0	72
2,6-py H/Pt		28	0	72
Homogeneous system	acetonitrile	26	0	74
2,5-py E/Pt		30	0	70
2,6-py H/Pt		29	0	71
Homogeneous system	tetrahydrofuran	27	0	73
2,5-py E/Pt		44	0	56
2,6-py H/Pt		41	0	59

products [12,13]. The only difference in the distribution of products between the polymer-supported systems and the homogeneous system was a higher portion of the regioisomer α for the supported systems. A 44% yield of this isomer was obtained in THF, a solvating solvent (Table 6). There are reports that the formation of the α-isomer is favored by the bulky substituents both on alkyne and silane [9]. It is very likely that the steric hindrance around the metal centres by polymeric and $HSi(OEt)_3$ ligands is responsible for the increase of α-isomer.

6. XPS measurements on platinum catalysts

Contrary to the results obtained for the rhodium systems, the immobilization of the platinum precursors $PtCl_2(PhCN)_2$ on the polymers of the 2,6-py and the 2,5-py series did not cause any change in the BEs of their nitrogen and oxygen functionalities. A slight increase of the BE for these elements can be observed only for samples used for several runs. The BE of the Pt $4f_{7/2}$ was found to be virtually constant for all catalytic systems studied. However, the BE for the platinum on 2,5-py H was found to be higher by 0.17 eV than that for the Pt attached to the 2,6-py H polymer; this is a similar trend to that observed for the rhodium systems (Table 7, entries 4 and 8).

XPS of the platinum catalysts did not show any peak that can be attributed to the metallic state. The platinum remained on the 2 + oxidation state; however, greater peak widths were observed for the reused samples.

7. Catalyst stability

The stability of the supported rhodium catalysts was studied over nine repeated catalytic runs. The data presented in Table 8 show that the reaction stereoselectivity remains constant

Table 7
Binding energy values (eV) for supported platinum catalysts

Entry	Sample	N 1s		O 1s	Cl $3p_{3/2}$	Pt $4f_{7/2}$
		N_{py}	N_{amide}			
1	2,6-py E/Pt before use	399.17	399.69	531.22	198.38	72.67
2	2,6-py E/Pt after 1st run	399.36	399.88	531.45	198.39	72.80
3	2,6-py E/Pt after several runs	399.44	399.96	531.56	198.94	72.84
4	2,6-py H/Pt before use	399.31	399.83	531.41	198.50	72.73
5	2,6-py H/Pt after 1st run	399.54	400.06	531.70	199.01	73.02
6	2,6-py H/Pt after several runs	399.46	399.98	531.70	199.02	72.90
7	2,5-py E/Pt before use	399.24	399.76	531.32	198.29	72.72
8	2,5-py H/Pt before use	399.40	399.92	531.61	198.35	72.90

Table 8
Stability tests of the polymer-supported rhodium catalysts during prolonged use in the hydrosilylation of phenylacetylene with triethoxysilane in benzene
Conditions: see Table 2.

Catalyst	Run	Phenylacethylene conversion after 4 h (%)	Product distribution (%)			Rh content[a] (at.%)
			α	β-(Z)	β-(E)	
2,6-py E/Rh	1	73	16	49	35	0.64
	3	71	16	52	32	
	5	69	15	51	34	
	9	67	15	51	34	0.62
2,6-py H/Rh	1	65	8	74	18	0.71
	3	60	10	76	14	
	5	59	9	75	16	
	9	55	11	75	14	0.60

[a]By XPS.

during prolonged use. It was also observed that the reaction rate decreased with time and this was related to the metal loss from the support.

8. Conclusions

The results of this study have demonstrated that by choice of suitable donor functions incorporated in the polymer matrix it is possible to control the stereoselectivity of hydrosilylation. Using a poorer electron donating moiety such as 2,5-[HNCOpyCONH], we were able to reverse the specific rhodium *cis*-selectivity to the less common *trans*-selectivity. The *E*-selectivity can be improved by a solvent such as acetonitrile which brings about a further decrease in the electron density on the rhodium species.

Our experiments have shown that the morphology of the polymer supports in these reactions seems to have a lower impact on the reaction selectivity as compared with the influence of the chemical structure of the support.

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