Selective addition of hydrosilanes to 1,3-dienes catalyzed by polyamide-supported metal complex catalysts [☆]

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Abstract

Four transition metal complexes [RhCl(CO)$_2$]$_2$, PdCl$_2$(PhCN)$_2$, PtCl$_2$(PhCN)$_2$ and RuCl$_2$(bipy)$_2$ were immobilized on polyamides bearing a pyridine moiety in their repeat units and displaying a relatively uniform distribution of micropores with voids from 1.0 to 3.0 nm. The polymer-supported catalysts were used in the hydrosilylation of isoprene and 2-methyl-1,3-pentadiene with the purpose of investigating the effect of polymer morphology on the catalyst selectivity. The addition of HSiMe$_2$Ph and HSi(EtO)$_3$ to both 1,3-dienes catalyzed by the polymer-supported Rh(I) catalysts was found to proceed highly regioselectively and stereoselectively to give (Z)–(2-methyl-but-en-2-en-1-yl)silanes and (Z)–(2-methyl-pent-2-en-1-yl)silanes as the predominant products (85–95%). The stereochemical assignment of the products was carried out by ^{1}H NMR spectroscopy employing the nuclear Overhauser effect. A similar 1,4-addition of Me$_2$PhSiH to isoprene and 2-methyl-1,3-pentadiene was found to produce Z isomers as the main products for the polymer-supported Pd(II) catalysts. In contrast the same reaction with HSi(EtO)$_3$ proceeded via a 1,2 route with 79–85% selectivity. As a general feature, in all the reactions studied, exception for the hydrosilylations catalyzed by polymer-supported rhodium catalysts, the 1,4 mode of addition prevailed with HSiMe$_2$Ph, but 1,2 addition with HSi(EtO)$_3$. Essentially the same regioselectivity was found for reactions under the homogeneous conditions. These results demonstrated that the microporous structure of the polyamide supports did not exert any particular effect on the regioselective and stereoselective course of the reaction. The explanation was based on a good match of the dimensions of the reaction intermediate to those of the polymer micropores. The constant selectivity of the supported catalysts demonstrated during recycling tests showed that they could be useful for practical application.

Keywords: Rhodium; Platinum; Palladium; Catalysis; Hydrosilylation, Polymer-supported catalysis

1. Introduction

In catalysis involving transition metal complexes supported on polymers it was recognized early that the chemical and physical structure of a polymer matrix can have a large effect on the performance of the catalysts [1]. However, insufficient attention has been paid to making use of favorable specific properties of polymer supports in modelling the activity of a heterogenized catalytic systems.

In recent years we have carried out investigations of the influence of the polymer structure on the catalytic properties of immobilized metal complex catalysts [2–4]. Our investigation has been focused on use of a family of polyamides having a pyridine moiety in their repeat units.

$$n = 2 \div 10$$
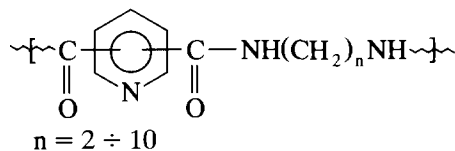
The reason for such a choice was as follows. Firstly, these polymers bear two potential sites for the metal coordination, the pyridine N and carbonyl O which can give to chelation. The use of such bidentate donors usually limits metal leaching. Secondly, they are semicrystalline materials, and their morphology can be modified by changing the polymer crystallinity; thirdly, they show thermal and mechanical stabilities which are much higher than those of styrene copolymers conventionally used as catalyst supports.

[☆] Dedicated to the memory of Zygmunt Lasocki (1922–1993), Professor of Chemistry, Technical University of Łódź, Poland, the distinguished organosilicon chemist, our mentor and best friend. Presented at the 6th International Conference on Polymer-Supported Reactions in Organic Chemistry. June 19–23, 1994, Venice, Italy.

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In an earlier paper we reported the synthesis, characterization and use of polyamide-supported transition metal complexes in the hydrosilylation of terminal olefins [3]. Details of the close correlation between the catalyst activity and the polymer crystallinity was also described.

In another approach we demonstrated that the selectivity of the polyamide-immobilized Rh(I) catalysts in the hydrosilation of vinyl-type olefins was greatly influenced by the matrix structure [4]. The high selectivity in this reaction towards the formation of linear products was attributed to a favorable distribution of the micropores, whose sizes resulted in the suppression of formation of branched products.

We now report our studies on the hydrosilylation of conjugated dienes with polyamide-immobilized metal complex catalysts. The additions of hydrosilanes to 1,3-dienes catalyzed by various transition metal complexes were extensively studied in the 1970–1980, by many research groups, especially by Lappert and coworkers [5–9], Ojima and coworkers [10–13], Hetflejš and coworkers [14–16], and others [17,18]. However, the use of supported homogeneous catalysts has received less attention, mostly because these systems have often been found to be deactivated during catalytic processes [19,20]. Our aim was to evaluate the usefulness of polyamide-immobilized catalytic systems for these reactions, to look at the effect of a polymer structure on the reaction regioselectivity and stereoselectivity, and to assess the catalyst stability.

2. Experimental details

2.1. Materials

Benzene was dried over and distilled from sodium–benzophenone ketal before use. The dienes were commercial products and were dried over molecular sieves and distilled in an inert atmosphere prior to use. Tri-

ethoxysilanes and dimethylphenylsilanes were prepared as described elsewhere [21]. The catalyst precursor [RhCl(CO)$_2$]$_2$ [22], PdCl$_2$(benzonitrile)$_2$, PtCl$_2$(benzonitrile)$_2$ [23] and Ru(bipy)$_2$Cl$_2$ [24] were prepared by published methods. The polyamide matrices were made from 2,5- and 2,6-pyridine dicarboxylic acid dichlorides and aliphatic diamines, as previously described [3]. Table 1 in Section 3 shows some characteristic properties of the samples used.

2.2. General methods

Analytical gas chromatography (GC) was performed on a Hewlett–Packard 5890 II gas chromatograph equipped with a thermal conductivity detector and 3396 series II integrator, using a 6 ft column of 10% OV-101 on Chromosorb W HP, 100–120 mesh. GC–mass spectroscopy (MS) data were obtained with a Finnigan Mat-Mat 95. Preparative separations were carried out on a high performance liquid chromatography Alltech Adsorbosil C18 column (10 μm packing; 250 mm × 10 mm) with pentane-isopropanol 98.2 v.v at a flow rate of 0.5 cm^3 min^{-1}. ^{1}H NMR spectra were recorded in CDCl$_3$ on a Bruker MSL 300 and/or a Bruker AC 200 spectrometer. Chemical shifts are given downfield from internal tetramethylsilane.

2.3. Catalyst preparation

A typical procedure was as follows. To a known amount of polymer matrix (0.1 g) in a round-bottom flask was added a solution of a known amount of a catalyst precursor in 5 ml of benzene, only in the case of the RuCl$_2$(bipy)$_2$ in a 1:1 CH$_2$Cl$_2$:benzene mixture. The mixture was stirred at room temperature until all the metal complex was taken up by the polymer and the color of the solution had disappeared. The product was then separated, washed with benzene under N$_2$ to remove the metal complex that was not chemically bound and finally dried under vacuum at 50°C for 8 h.

Table 1
Characteristics of selected polyamide matrices

Matrix	Repeat unit	n	Crystallinity (%)	S (m^2 g^{-1})	Porosity in swollen state	T_m (°C)
	~C(O)—C$_6$H$_4$(N)—C(O)—NH(CH$_2$)$_n$NH~					
1		2	17	2.7	0.61	362
2		6	25	3.7	0.45	301
	~C(O)—C$_5$H$_3$N—C(O)—NH(CH$_2$)$_n$NH~					
3		2	10	6.7	0.15	356
4		6	15	1.4	0.09	298

For all supported catalysts the metal content was fixed at 0.1 mM g^{-1}, which was below the metal-uptake capacity for the polymer. Spectroscopic analysis of the filtrates confirmed that all soluble complexes were absorbed by polymer matrices.

2.4. Catalytic reactions

All the reactions were carried out under nitrogen using freshly distilled dry solvents and liquid reagents. The typical procedure for the hydrosilylation of 1,3-dienes was as follows. In a dried reaction vessel thoroughly flushed with nitrogen was placed the polymer-supported complex (0.002 mmol of metal). Benzene (0.3 ml), the hydrosilane (0.3 mmol) the diene (0.3 mmol) were added successively from via a syringe. The mixture was stirred at room temperature and the progress of the reaction was monitored by GC. Over the range $3 \times 10^{-4} - 7 \times 10^{-3}$ metal-substrate molar ratio the rates were independent of the catalyst concentration.

2.5. Spectroscopic analyses

The reaction products (isoprene–silane adducts) were identified by comparison of GC–MS and ^{1}H NMR spectral data with those for authentic samples and/or those previously reported [7–18]. The NMR data for new products (z isomers) formed from 2-methyl-1,3-pentadiene or isoprene are summarized later in Table 3. The coupling constants for the products from the latter have not been fully determined except for olefinic protons.

Their mass spectrum were as follows.

2.5.1. (Z)-(2-Methylpent-2-en-1-yl)dimethylphenylsilane (Ic)

MS: m/e (relative intensity, %) 246 (M$^+$, 11), 189 (5), 164(12), 163(100), 147(1), 135(9), 133(1), 121(1), 120(3), 119(34), 107(7), 103(1), 91(7), 89(1), 79(10), 77(1), 73(1), 63(6), 62(1), 45(2), 41(1).

2.5.2. (Z)-(2-Methylpent-2-en-1-yl)trietoxysilane (Id)

MS: m/e (relative intensity, %) 232(M$^+$, 12), 165(5), 164(12), 163(100), 147(1), 136(1), 135(11), 133(2), 121(2), 120(4), 119(41), 107(9), 105(1), 103(1), 91(7), 89(2), 79(11), 77(2), 73(2), 63(6), 62(2), 45(4), 41(2).

2.5.3. 2-Methylpent-3-en-1-yldimethylphenylsilane (Vc).

Spectroscopic data for new 1,2-addition products were also found. ^{1}H NMR: δ 0.31 (s, 6H), 0.71–0.78 (m, 2H), 0.89 (m, 3H), 1.50(1H), 1.68 (m, 3H), 4.98–5.05 (m, 2H, vinyl), 7.17–7.23 (m, Ph) ppm. MS: m/e (relative intensity, %): 218(M$^+$, 2), 176(6), 162(1), 161(7), 140(6), 137(4), 136(13), 135(100), 125(4), 122(1), 121(10), 119(3), 109(1), 107(5), 105(6), 93(2),

91(2), 82(2), 79(1), 78(4), 77(1), 69(3), 67(4), 59(2), 56(1), 53(1), 51(1), 44(1), 43(6), 41(6), 39(3).

2.5.4. 2-Methylpent-3-en-1-yltriethoxysilane (Vd)

^{1}H NMR: δ 0.70–0.76(m, 2H), 0.92 (m, 3H), 1.19 (t, 9H), 1.57 (m, 1H), 1.73 (m, 3H), 3.80 (q, 6H), 4.94–5.02 (m, 2H vinyl) ppm. MS:m/e (rel. intensity, %): 246(M$^+$, 8), 175(1), 165(4), 164(11), 163(100), 159(1), 135(11), 133(3), 121(2), 120(3), 119(33), 107(8), 105(1), 103(1), 91(5), 89(1), 83(1), 82(2), 79(9), 77(2), 73(1), 67(1), 63(4), 62(1), 55(2), 45(2), 41(1).

2.6. Catalyst recycling

In the recycling tests, when reaction was complete, the catalyst was filtered off from the reaction mixture, washed with 3 × 10 ml of benzene, dried under vacuum and used for the next reaction. Each sample of polymer-supported catalyst was used in this way in up to six runs.
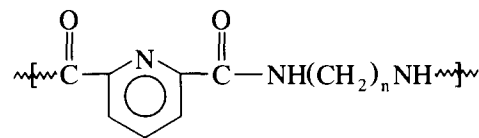
3. Results and discussion

3.1. Polymer-supported complex catalysts

The polymers chosen as supports were derived from the two groups of polyamides containing the 2,5- and 2,6-pyridine moiety in their repeat units and were the same as described in previous studies [3,4].
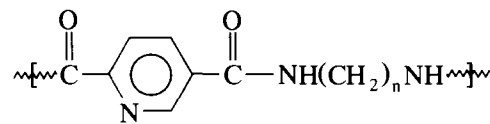
series 2,5-py; n = 2 and 6,

(Support No 1 and 2)

series 2,6-py; n = 2 and 6,

(Support No 3 and 4)

The most important feature of these semicrystalline materials was their microporous structure brought about by polymer crystallinity. Small-angle X-ray scattering (SAXS) measurements indicated that they have a narrow distribution of pores with sizes ranging from 1.0 to 3.0 nm [4]. For the present study, polymer samples having contrasting characteristics, i.e. having lower and higher degrees of crystallinity and in conseqence lower and higher fractions of micropores, were selected. Table 1 shows some characteristic properties of the matrices employed.

Table 2

Hydrosilylation of isoprene and 2-methyl-1,3-pentadiene catalyzed by polyamide-supported Rh(I) complex

Metal or matrix	Silane	Isoprene [a]				2-methyl-1,3-pentadiene [b]				
		Product ratio [c] (%)			Yield [d] (%)	Product ratio [c] (%)				Yield [d] (%)
			(Z)-1,4 addition	1,2 addition			(Z)-1,4 addition	1,2-addition		
Homogeneous	Me$_2$PhSiH	1a	92	6	98	1c	81	15		93
1			91	9	95		88	12		90
2			89	11	91		89	13		89
3			90	10	93		79	11		81
4			90	8	89		83	14		94
Homogeneous	(EtO)$_3$SiH	1b	94	5	94	1d	91	4		91
1			88	9	95		91	2		93
2			95	2	78		90	5		89
3			86	11	90		87	8		82
4			88	9	89		91	5		87

Conditions: silane : diene : Rh molar ratio, 1 : 1 : 3.5 × 10^{-4}.

[a] 30°C, 120 h.

[b] 50°C only for Me$_2$PhSiH, 120 h.

[c] Isomeric ratios derived from GC area.

[d] Based on diene.

The immobilization of the catalyst precursors [RhCl(CO)$_2$]$_2$, PtCl$_2$(PhCN)$_2$, PdCl$_2$(PhCN)$_2$ and RuCl$_2$(bipy)$_2$ was performed by a routine ligand exchange procedure. The mode of coordination for the Rh(I) and Pt(II) complexes in the polymer matrix was established in our earlier investigations by IR spectroscopy [3] and shown to be via the pyridine nitrogen atom (N$_{py}$) with some assistance by bonding through the carbonyl oxygen atom. Studies of the polyamide-bound palladium(II) complex by electron spectroscopy for chemical analysis and IR methods [25] confirmed that coordination to the metal is via N$_{py}$ and O sites.

3.2. Catalytic reactions

3.2.1. Selectivity studies

Addition of hydrosilanes HSiMe$_2$Ph and HSi(OEt)$_3$ to isoprene and 2-methyl-1,3-pentadiene catalyzed by the metal complexes immobilized on the polyamide(py) were, with one exception (see footnote b in Table 2), carried out in benzene at room temperature. No attempts were made to optimize the reaction conditions in order to achieve high yields of products. Soluble complexes were used for reference. Identification of the products, including the stereochemical assignment, was per-

Table 3

^{1}H NMR spectra of (Z-)2-methylbut-2-en-1-ylsilanes (Ia and Ib) and (Z-)2-methylpent-2-en-1-ylsilanes (Ic and Id) obtained with polyamide-supported Rh(I) catalysts

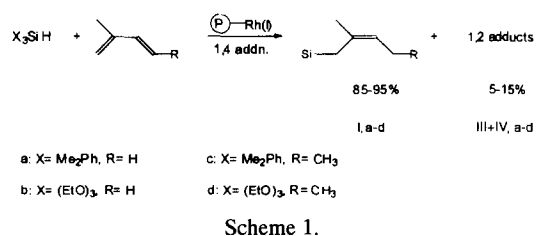| Isomer	Silyl group	Proton	δ (ppm)	J (Hz)	Reference	Isomer	Silyl group	Proton	δ (ppm)	J (Hz)
Ia	Me$_2$PhSi	a	1.76	$^4J_{a,b} = 1.40$	[11–13]	Ic [a]	Me$_2$PhSi	a	2.11	$^4J_{a,b} = 1.46$
		b	1.60	$^4J_{b,c} = 0.94$				b	1.96	$^4J_{b,c} = 1.22$
		c	5.12	$^3J_{c,d} = 6.70$				c	5.38	$^3J_{c,d} = 6.80$
		d	1.45					d	2.38	$^3J_{d,e} = 5.75$
								e	1.27	
Ib [b]	(EtO)$_3$Si	a	1.56	$^4J_{a,b} = 1.47$	[7,9,16,17]	Id [c]	(EtO)$_3$Si	a	1.53	$^4J_{a,b} = 1.30$
		b	1.73	$^4J_{b,c} = 1.34$				b	1.71	$^4J_{b,c} = 1.17$
		c	5.12	$^3J_{c,d} = 6.70$				c	4.99	$^3J_{c,d} = 6.80$
		d	1.53					d	1.95	$^3J_{d,e} = 7.55$
								e	0.89	

[a] Obtained by homodecoupling technique.

[b] 11% NOE, increase in the integral of the signal of the H^c proton by irraddiating CH$_3$^{b} protons.

[c] 14% NOE increase in the integral of the signal of the H^c proton by irradiating CH$_3$^{b} protons.

formed by GC–MS and ^{1}H NMR spectroscopy. The results of the addition reactions are summarized in Tables 2–4.

In general, the mode of the addition depends upon the nature of both the hydrosilane and the catalyst [26,27]. As Table 2 shows, hydrosilylation of isoprene by $HSiMe_2Ph$ and $HSi(OEt)_3$ catalyzed by the polymer-immobilized rhodium(I) complex occurred mainly via the 1,4 route very similar much like that catalyzed by the parent complex $[RhCl(CO)_2]_2$ and other soluble Rh(I) catalysts as reported earlier [7,11,13,14,16]. The reaction proceeded highly regioselectively to give 2-methyl-2-butenylsilanes (Ia and Ib) exclusively with high yields (85–95%) as the predominant products (Table 2 and Scheme 1). The stereochemistry of the adducts was established from the ^{1}H NMR spectra by use of the nuclear Overhauser effect (NOE); upon irradiation of the methyl protons H^b an 11% increase in the integral of the signal from the H^c proton was observed (see Table 3), and so the z-stereochemistry was assigned to of the adducts obtained by use of

X_3SiH + [structure] → (P)—Rh(I) 1,4 addn. → Si—[structure]-R + 1,2 adducts

85-95%   5-15%

I, a-d   III+IV, a-d

a: X= Me_2Ph, R= H   c: X= Me_2Ph, R= CH_3
b: X= (EtO)_3, R= H   d: X= (EtO)_3, R= CH_3

Scheme 1.

the polymer-supported Rh(I) catalyst, as was found earlier for soluble Rh(I) complexes [7,11,13,16,17]. Similar 1,4 addition was found in the hydrosilylation of 2-methyl-1,3-pentadiene with $HSi(OEt)_3$ (Table 2 and Scheme 1). The reaction gave mainly 2-methyl-2-pentenylsilane (Id) with a high selectivity (about 90%). Use of the NOE procedure involving irradiation of the methyl protons H^b resulted in a 14% enhancement of the integral of the signal from the vinyl proton H^c. This indicated that the adducts were the Z isomers. In contrast, in the hydrosilylation of 2-methyl-1,3-pentadiene

Table 4

Addition of hydrosilanes to isoprene and 2-methyl-1,3-pentadiene catalyzed by the free (homogeneous) polyamide-supported metal complex catalysts

Diene Catalyst metal or matrix	Silane	Isoprene						2-methyl-1,3-pentadiene	
		I + II	1,4 addition		1,2 addition		III + IV	Product ratio	
			I	II	III	IV		1,4 addition Ic and Id (Z + E)	1,2 addition Vc and Vd (Z + E)
Palladium(II)									
Homogeneous	Me_2PhSiH	67	41	26	34	0	34	96	4
1		100	97	3	0	0	0		
2		94	73	21	7	0	7		
3								95	5
4								85	15
Homogeneous	(EtO)_3SiH	31	10	21	58	11	69	30	70
1		18	15	3	57	25	82		
2		22	17	5	42	36	78		
3								26	74
4								25	75
Platinum(II)									
Homogeneous	Me_2PhSiH	92	11	81	5	3	8	61	39
1		90	17	73	2	8	10		
2		92	5	87	5	3	8		
3								62	38
4								90	10
Homogeneous	(EtO)_3SiH	5	0	5	6	89	95	29	71
1		30	25	5	42	28	70		
2		18	11	7	39	45	84		
3								16	84
4								14	86
Ruthenium(II)									
Homogeneous	Me_2PhSiH	81	9	72	6	13	19	90	10
1		100	10	90	0	0	1	51	49
2		81	8	73	7	12	19	65	35
Homogeneous	(EtO)_3SiH	25	11	14	35	40	75	17	83
1		11	5	9	34	52	86	15	85
2		28	28	0	10	62	72	19	81

Conditions: silane : diene : metal molar ratio, $1 : 1 : 3.5 \times 10^{-4}$; 30°C; 120 h.
Isomeric ratio derived from GC areas.

Table 5

Addition of hydrosilanes to 2-methyl-1,3-pentadiene catalyzed by free (homogeneous) and polyamide-supported metal complex catalysts

Catalyst metal or matrix	Silane	Product ratio	
		1,4-addition Ic and Id (Z + E)	1,2-addition Vc and Vd (Z + E)
Palladium(II)			
Homogeneous	Me$_2$PhSiH	96	4
3		95	5
4		85	15
Homogeneous	(EtO)$_3$SiH	30	70
3		26	74
4		25	75
Platinum(II)			
Homogeneous	Me$_2$PhSiH	61	39
3		62	38
4		90	10
Homogeneous	(EtO)$_3$SiH	29	71
3		16	84
4		14	86
Ruthenium(II)			
Homogeneous	Me$_2$PhSiH	90	10
1		51	49
2		65	35
Homogeneous	(EtO)$_3$SiH	17	83
1		15	85
2		19	81

Conditions: silane:diene:Rh molar ratio, $1:1:3.5\times10^{-4}$; 30°C; 120 h.

with HSiMe$_2$Ph in the presence of the Rh(I) catalyst was less stereoselective. The ^{1}H NMR analysis with the use of a homodecoupling technique, revealed that the adduct Ic was a 1:1 mixture of Z and E isomers.

The addition of HSiMe$_2$Ph to isoprene and 2-methyl-1,3-pentadiene with polymer-supported Pd(II) catalysts gave high yields of the isomers Z Ia and Ic (80–95% (Table 4)), whose stereochemistry was confirmed as usual by ^{1}H NMR analysis. However, the corresponding reaction with HSi(OEt)$_3$ involved the 1,2 mode of addition.

It was a general feature that in hydrosilylation of isoprene and 2-methyl-1,3-pentadiene catalyzed by polymer-immobilized Pd(II), Pt(II) and Ru(II) complexes, 1,4 regioselectivity was observed when HSiMe$_2$Ph was used but the 1,2 pattern predominated with HSi(OEt)$_3$ (Table 4 and Schemes 2 and 3).
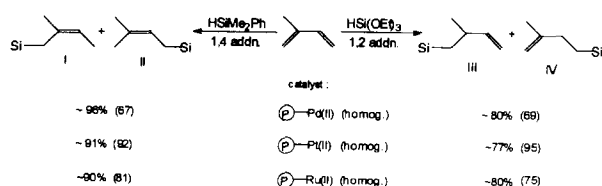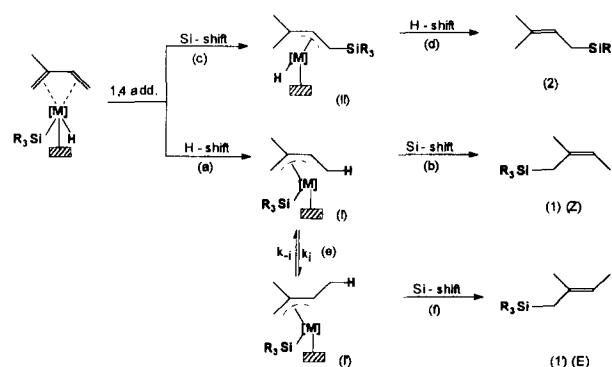

Scheme 2.
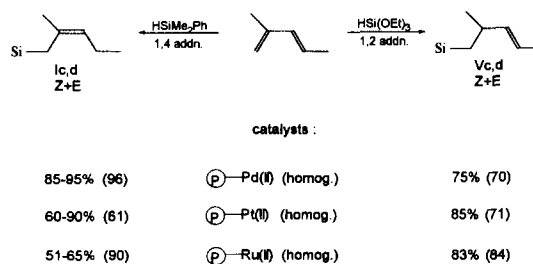
Scheme 3.

Comparison of the hydrosilylation of 2-methyl-1,3-pentadiene with that of isoprene indicated that the extent of regioselectivity in both reactions in the homogeneous and heterogeneous systems are much the same.

These results clearly demonstrate that the microporous structure of the polyamide matrices does not exert any significant effect on the regioselective and stereoselective outcomes of the reaction compared with that for the homogeneous systems. The only distinctive polymer influences observed were the higher rates of the reactions with the catalysts attached to supports with a lower degree of crystallinity. For example, in the hydrosilylation of isopropene by HSiMe$_2$Ph, the turn-over frequencies at 30°C were 5.96 s^{-1} and 4.65 s^{-1} for Rh(I)–3 and Rh(I)–4 respectively. This observation is in agreement with our earlier findings [3] and can be attributed to the better accessibility of the active sites located in less crystalline regions.

3.2.2. Reaction mechanism

To account for the absence of an influence of the structure of the studied polyamides on the selectivity of hydrosilylation of 1,3-dienes it seems necessary to discuss the reaction mechanism and morphology parameters on a nanoscale level.

In view of the observed regioselectivity and stereoselectivity it was apparent that the mechanism of the hydrosilylation of the 1,3-dienes catalyzed by polyamide-supported transition metal complexes is similar that accepted for the homogeneous catalysts. Therefore the mechanism proposed by Ojima et al. [13] (Scheme

Scheme 4.

4) can be adopted for the polymer-supported complex catalysts. It involves the formation of π-allylic intermediate **I** and/or **II** of the type proposed for most diene reactions [26,27], which leads to 1,4 head *Z* adducts (**1**) and/or 1,4 tail adducts (**2**).

If the intermediate **I** is sufficiently stable and undergoes isomerization (route e) at a comparable rate with that of the silicon shift (route b), then a 1 : 1 mixture of isomers *Z* and *E* is observed. Such an outcome was found in the hydrosilylation of 2-methyl-1,3-pentadiene by $HSiMe_2Ph$ catalyzed by the polymer-supported Rh(I) complex.

On the contrary, the polymeric supports and polymer-attached catalysts are porous materials containing relatively uniform distribution of pores, mostly in the range from 1.0 to 3.0 nm. If no effect of the polymer is observed, it is because the steric requirements for the formation of the cisoid structure of the π-allylic intermediate are small (less than 1 nm) and match the dimensions of the micropores. Simple computer modelling calculations confirmed such a possibility.

3.2.3. Catalyst recycling

The highest selectivity was found for the supported rhodium catalysts, and so, these were chosen for stability studies. Two separate samples of the Rh(I) catalyst supported on matrices **3** and **4** (2,6-py series) were tested for repeated use in the hydrosilylation of isoprene by Me_2PhSiH and Fig. 1 shows the results obtained. Except for the usually observed initial small drop in the yields of the (*Z*)-1,4 product (**Ia**), the activity and selectivity of the polymer catalysts remained essentially constant within experimental error over six catalytic cycles. Such a performance could form the basis for using the immobilized systems, particularly the rhodium-based systems, giving a high selectivity, as potent catalysts in the synthesis of useful silicon coupling agents.
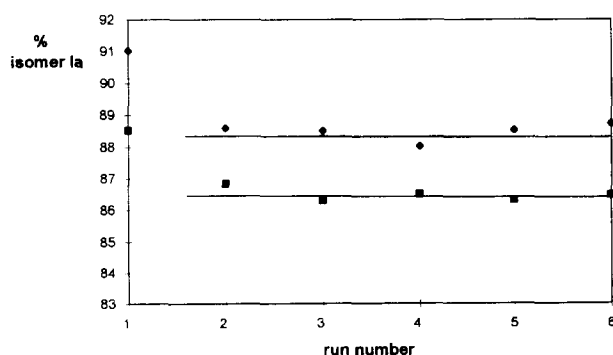

Fig. 1. Stability of the polyamide (2,6-py series)-bound catalysts Rh–3 (◆) and Rh–4 (■) during recycling tests (hydrosilylation of isoprene by Me_2PhSiH).

4. Conclusions

The investigations have shown that the microporous structure of the polyamides used as catalyst supports did not affect the regiochemistry and stereochemistry of the addition of silanes to the 1,3-dienes although the opposite effect might have been expected. The absence of any effect was ascribed to a good match between the dimensions of the reaction intermediate and those of the polymer micropores.

From our present and earlier previous studies we conclude that polyamides of the type employed are useful materials for immobilization of transition metal complex catalysts. Depending on the type of reaction involved and the polymer structure the same polymer matrix can give rise to different effects as follows.

(i) In the hydrosilylation of the vinyl-type olefins, it can improve the catalyst chemoselectivity by serving as a molecular sieve and by preventing formation of the branched products [4].

(ii) In hydrosilylation of linear olefins, it can induce considerable changes in the activity of the immobilized catalysts [3].

(iii) As in the present case, it can preserve the regiospecificity and stereospecificity of a parent homogeneous catalyst by providing, the correct approach of the reactants to the active sites.

Furthermore, a very high stability of the polymer-supported catalysts such as that demonstrated for the supported Rh(I) catalysts during the recycling tests, suggests that they can be useful for prolonged use in the synthesis of functional organosilicon compounds.

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