ELSEVIER

Synthesis and catalytic activity of the transition metal complex catalysts supported on the branched functionalized polysiloxanes grafted on silica

Z.M. Michalska [a,*], Ł. Rogalski [a], K. Rózga-Wijas [b], J. Chojnowski [b], W. Fortuniak [b], M. Ścibiorek [b]

[a] *Institute of Polymers, Technical University of Łódź, 12/16 Stefanowskiego, 90-924 Łódź, Poland*
[b] *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 112 Sienkiewicza, 90-363 Łódź, Poland*

Abstract

Vinyl-functionalized polysiloxanes having different degree of branching, grafted on silica were used as hybrid supports for immobilizing the rhodium and platinum complex catalysts. The attachment of the metal species to the polymer was confirmed by IR and ^{1}H NMR spectroscopy. Both Rh and Pt supported systems effectively catalyzed the hydrosilylation of terminal olefin. The catalyst activity was found to be dependent on the type of a parent complex, the degree of polymer branching and the vinyl ligands content. The stability tests performed during the repeated use of the catalysts indicated a decrease in catalyst activity.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Branched polysiloxanes; Functionalized polysiloxanes; Hybrid supports; Supported catalyst; Rhodium; Platinum; Hydrosilylation; Hexene-1

1. Introduction

Over the past few decades major research efforts have been devoted to the development of a new generation of heterogenized transition metal complex catalysts. This type of catalyst can combine the advantages of easy catalyst recovery, characteristic for a heterogeneous catalyst, with the high activity and selectivity of soluble complexes. The most common method of heterogenizing a metal complex catalysts is to attach them to solid supports. Among a variety of insoluble materials, crosslinked polymers have been most widely used [1]. However, a drawback of crosslinked networks is the nonequivalence of the active sites. Some are buried inside the polymeric structure. This leads to differences in accessibility, local environment, stability, and activity. These disadvantages can be overcome by using a soluble polymer support. Recently, much attention has been focused on dendrimers and dendrimer-like polymers as macromolecular carriers for homogeneous catalysts (for recent reviews, see [2]). They possess a highly branched structure containing functional sites that act as an anchor for the catalytic species [3–8]. The problematic separation of the dendritic catalysts can be overcome by using an ultra filtration technique [9–11] or by attaching the branched units to insoluble crosslinked polymers [12,13] or to silica [6,14].

In the present study we describe our approach to prepare the polymer catalysts by immobilizing the transition metal complexes (TMC) on the branched functionalized polysiloxanes grafted on silica. The degree of branching and the content of the ligands were taken into account when determining the activity of the catalyst in the hydrosilylation of the terminal alkene. The catalyst stabilities after each catalytic cycle have also been reported.

2. Experimental

2.1. Materials

All solvents and reagents were of analytical or chemical grades. Toluene, ethanol, and isopropanol were purified by standard methods. The silane Me_2PhSiH was a commercial sample.

Hydrogen hexachloroplatinate hexahydrate, $H_2PtCl_6\cdot 6H_2O$ was obtained from Aldrich. The metal complexes: $PtCl_2(PhCN)_2$ [15], $Pt(PPh_3)_4$ [16], and $[RhCl(CO)_2]_2$ [17]

---

* Corresponding author. Tel.: +48-42-6313204; fax: +48-42-6362543.
E-mail address: zmich@p.lodz.pl (Z.M. Michalska).

were prepared by published methods. Platinum–divinyl-tetramethyldisiloxane complex [Pt(0) Karstedt catalyst] in xylene (2.1–2.4% of Pt) was from ABCR-Gelest.

Silica gel was from Merck (Kieselgel 60 Å, particle size 0.063–0.2 mm, specific surface area 550 $m^2\,g^{-1}$ (A), Kieselgel 60 Å, particle size 0.2–0.5 mm, specific surface area 550 $m^2\,g^{-1}$ (B), and Kieselgel 100 Å, particle size 0.063–0.2 mm, specific surface area 300 $m^2\,g^{-1}$ (C)).

2.2. General methods

GC analysis was performed with a Hewlett-Packard 5890 II using a 30 m × 0.53 mm non polar capillary column (thin film 1.0 μm) and a thermal conductivity detector equipped with a HP 3396 II integrator. The temperature was set at a rate of 45 °C min^{-1}.

^{1}H NMR spectra were recorded in CD_3Cl on a Brucker MSL 300 or a Brucker AC 200 spectrophotometer using Me_4Si as an internal standard in the temperature range 20 to −40 °C.

IR spectra were recorded on a FTIR Bio-Rad 175 C spectrometer in the range 4000–500 cm^{-1} as film on KBr plate and in the 500–150 cm^{-1} range as film on PE foil. [RhCl(CO)$_2$]$_2$ spectrum was recorded using the diffusion reflection spectrometry.

DSC measurements were performed on a Netzsch DSC 204 differential scanning calorimeter at a heating rate of 10 °C min^{-1} under N_2 atmosphere.

Metal analysis was performed by a routine procedure. A sample of supported catalyst was heated up to 600 °C and then dissolved in aqua regia and aqueous HF. The resulting solution was diluted and assayed by ICP-OES at the Central Chemical Laboratory of the Polish Geological Institute in Warsaw, Poland.

2.3. Preparation of the hybrid supports by grafting linear and dendritic polysiloxnes on silica

The hybrid supports were prepared by grafting polysiloxanes having different topological structure (linear or highly branched) and varied loadings of the functional vinyl groups on the silica surface [18,19]. Characteristics of the hybrid supports used are presented in Table 1. Full experimental

details are described in [19] but following may serve as examples.

2.3.1. Preparation of the hybrid support G0A

Synthesis was accomplished with a coupling reaction between the living linear polyvinylmethylsiloxane possessing the lithium silanolate group at chain end, and the ≡Si–Cl sites of the functionalized silica.

Synthesis of the living linear poly[vinylmethylsiloxane-co-(grad)-dimethylsiloxane] (G0) was performed by the BuLi initiated anionic living ring opening copolymerization [20,21]. To a reaction vessel containing 11.6 ml of THF, 4.04 g (1.56×10^{-2} mol) of 2,4,6-trivinyl-2,4,6-trimethylcyclotrisiloxane, and 5.99 g (2.55×10^{-2} mol) of 2-vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane were added using vacuum line technique. The system was filled with argon and 1.04 ml of 2.5 M butyllithium solution in *n*-heptane (2.6×10^{-3} mol BuLi) was added. The vessel was maintained at room temperature for 45 min and then polymerization was quenched by adding 12.0 g of silica having 0.21×10^{-3} mol g^{-1} of ≡Si–Cl sites. The suspension was stirred for a further 2 h at room temperature, after which 0.2 ml of chlorotrimethylsilane (TMS) was added to remove unreacted ≡SiOLi groups and the mixture was stirred for another 30 min. The hybrid was removed by suction filtration, washed with toluene, and the excess of TMS was evaporated. It was washed again with toluene and methanol and dried under vacuum (60 °C, 10^{-3} mmHg, 20 h). The amount of vinyl (Vi) ligands in the hybrid G0A was 0.3×10^{-3} mol g^{-1} determined by elemental analysis.

2.3.2. Preparation of the hybrid support G2C

Synthesis of the hybrid support, G2C, was performed in two subsequent hydrosilylation reactions catalyzed by Pt(0) Karstedt catalyst (2.1–2.4 wt.% solution in xylene). In the first reaction vinylated silica reacted with 1,1,3,3-tetramethyldisiloxane to obtain Si–H sites on the silica surface. In the next stage these sites reacted with the vinyl groups of the highly branched dendritic polysiloxanes (G2) prepared by the method described [18,21].

Thus, to a 5 g of Vi-functionalized silica having 1.76×10^{-3} mol g^{-1} Vi groups suspended in 10 ml of dry toluene, 15 mg of Karstedt catalyst, and 3 ml (2.27 g,

Table 1
Characteristics of the hybrid supports [19]

Symbol of hybrid support	Grafted polymer			Hybrid content of functional groups (mmol g^{-1})	
	Topology	M_n	M_w/M_n	Polymer	Silica
G0A	Linear	5000	1.85	1.3	0.3
G1A	Dendritic	7800		1.5	0.4
G2C	Dendritic	140000	1.46	5.4	1.3
G0*C	Linear	2350	2.10	10.6	2.8
G0BPPh$_2$	Linear	2450	1.53	2.8	0.5

G0, G1, G2 denotes the number of the branching degree of the polysiloxane; A, B, C denotes the type of silica used (see Section 2). Polysiloxane G0* was a homopolymer derived from 2,4,6-trivinyl-2,4,6-trimethylcyclotrisiloxane.

18.26 mmol) of 1,1,3,3-tetramethyldisiloxane were added. The mixture was stirred for 96 h at room temperature. The product was filtered, washed with toluene, and dried under vacuum. In the next step silica containing Si–H functions (0.67×10^{-3} mol g^{-1}) was mixed with 10 ml of toluene, 15 mg of Pt(0) catalyst, and 2.5 g of highly branched polysiloxanes containing 5.4×10^{-3} mol g^{-1} vinyl groups. The mixture was stirred for 5 days at room temperature. The hybrid was washed with toluene, filtered, and vacuum dried. It contained 1.30×10^{-3} mol g^{-1} of Vi groups determined by elemental analysis.

2.3.3. Preparation of the PPh₂-functionalized hybrid support G0BPPh₂

See the procedure for the hybrid support G0A. The living poly[2-(diphenylphosphine)ethylmethylsiloxane] was obtained according to the method described in [22]. The content of PPh$_2$ ligands in polymer was 2.8×10^{-3} mol g^{-1} and 0.5×10^{-3} mol g^{-1} in hybrid determined by elemental analysis.

2.4. Catalyst preparation

The procedure is exemplified with G0A/Pt(0) catalyst. 0.5 g of the hybrid support G0A having 0.15 mmol of Vi ligands in 3 ml of toluene was treated with a toluene solution of 0.05 mmol (0.0622 g) of Pt(PPh$_3$)$_4$. The mixture was stirred for 2 h and left at room temperature for 24 h. The supported Pt catalyst was separated by filtration, washed with toluene several times, and vacuum dried at 60 °C for 8 h.

In general the metal content was fixed at 0.05 mmol g^{-1} support for Pt catalyst and 0.1 mmol g^{-1} support for Rh catalyst, which was below the metal uptake capacity for the polymer. The metal contents for the supported catalysts are shown in Table 2.

2.5. Catalytic hydrosilylation

Blank hydrosilylation tests with the pure hybrid supports were first performed to ensure that the Pt(0) species that catalyzed the synthesis of the supports were absent.

Reactions were carried out in air in screw top glass vials equipped with teflon-faced silicon rubber septum caps. The typical procedure was as follows. The appropriate mass of supported catalyst with the required level of the metal was introduced to the vial followed by a portion (0.5 ml) of toluene as a solvent, dimethylphenylsilane (0.23 ml, 1.5 mmol) and hexene-1 (0.19 ml, 1.5 mmol) as substrates together with trimethylphenylsilane (0.11 ml) as an internal GC standard. In all experiments the silane to olefin to transition metal molar ratio was $1:1:5 \times 10^{-4}$. The reaction mixture was analyzed at time intervals by gas chromatography. To avoid the presence of readily leached soluble metal species, the progress of the reaction was monitored starting from the second run on. The product was identified by matching retention time with that of an authentic sample.

The catalyst samples were recycled by carefully decanting off reaction supernatant mixture, washing with three portions of solvent, drying under reduced pressure, and recharging the vial with a portion of fresh reaction mixture.

3. Results and discussion

### 3.1. Synthesis and characterization of metal complex catalysts immobilized on hybrid supports

A series of hybrid supports, prepared by grafting to silica, linear and highly branched dendritic polysiloxanes having Vi groups, pendant-to-branches were used for the immobilization of transition metal complex catalysts. These grafted polysiloxanes differ in the branching degree (G0, G1, and G2) and the content of Vi ligands. Characteristics of the hybrid supports and catalysts are shown in Tables 1 and 2.

The supported catalysts were prepared by treating the hybrid matrix with a toluene solution of the appropriate precursor. Thus, the rhodium species were introduced by a bridge splitting reaction between the chloro bridged dicarbonylrhodium dimer and the vinyl-functionalized polysiloxane. Possible mono (**1, 2**) and dinuclear (**3, 4**) products can be formed:
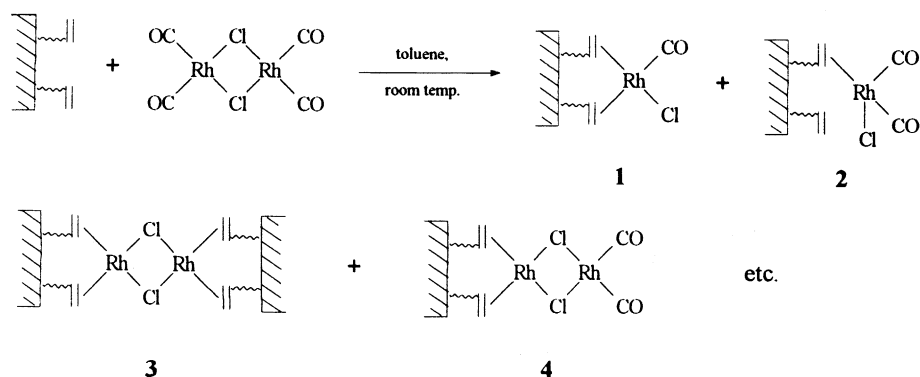
Predominance of one of these structures depends on the concentration and availability of the Vi ligands.

The platinum(II) catalysts were obtained by a ligand displacement in the parent metal complex $PtCl_2(PhCN)_2$ by Vi groups:

5
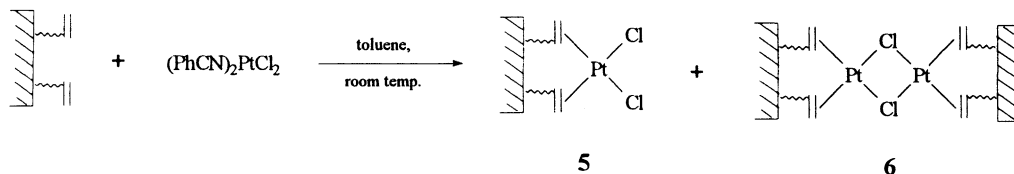
The zerovalent platinum Pt(0) complexes **7** and **8** were derived from chloroplatinic acid hexahydrate by reducing it in isopropanol with addition of $NaHCO_3$ in the presence of an excess of the Vi ligands:

7
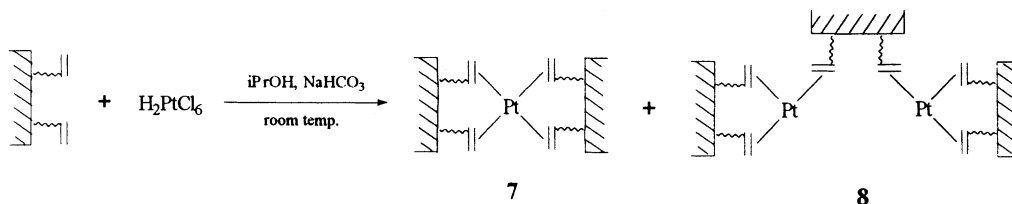
Complexes **7**, **8**, and **9** were also generated from tetrakis(triphenylphosphine)platinum:
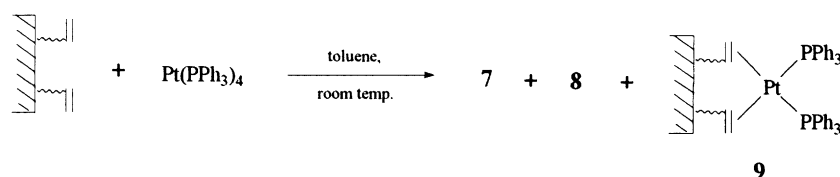
In the latter case the formation of olefin complexes of Pt(0) of the type **7** and **8** was manifested by a rapid disappearance of the yellow colour of $Pt(PPh_3)_4$ solution after the hybrid support was added.

Selected immobilized catalysts have been analyzed by IR, ^1H NMR spectroscopy and thermal analysis. Due to the low polysiloxane loadings on silica and low concentration of the metal species, for these studies the rhodium complexed with pure polysiloxane having a high content of Vi ligands (5.4 mmol Vi g^{-1} polymer, symbol G2) was used to obtain a better detection sensitivity.

3.1.1. IR studies

As an approach to study the process of heterogenizing the metal complex catalyst to the dendritic polysiloxanes the attachment of the rhodium carbonyl dimer $[RhCl(CO)_2]_2$ was explored. The addition to the polysiloxane G2 the solution of $[RhCl(CO)_2]_2$ in CH_2Cl_2 resulted in a rapid rise of the temperature and vigorous evolution of CO. As seen in Fig. 1 the band of the bridging chlorine Cl_b of the parent Rh(I) complex at $279\,cm^{-1}$ (curve I) disappeared and a band attributed to the terminal chlorine Rh–Cl_t at $297\,cm^{-1}$ arose in the spectrum of the rhodium complexed with polymer (curve III). When the polysiloxane with lower content of the vinyl

ligands (1.3 mmol Vi g^{-1} polymer, symbol G0) was used, the IR spectrum of the rhodium–polymer complex showed both bridging and terminal chlorines due to the presence of mono- (**1** and **2**) and dinuclear species (**3** and **4**). However,

6

in both cases the IR spectra (Fig. 2) in the carbonyl region showed two sharp bands at 2079 and $2032\,cm^{-1}$ typical for the Rh *cis*-dicarbonyl moiety. This suggests the predominance of the structure **2** when the hybrid G2 with

8
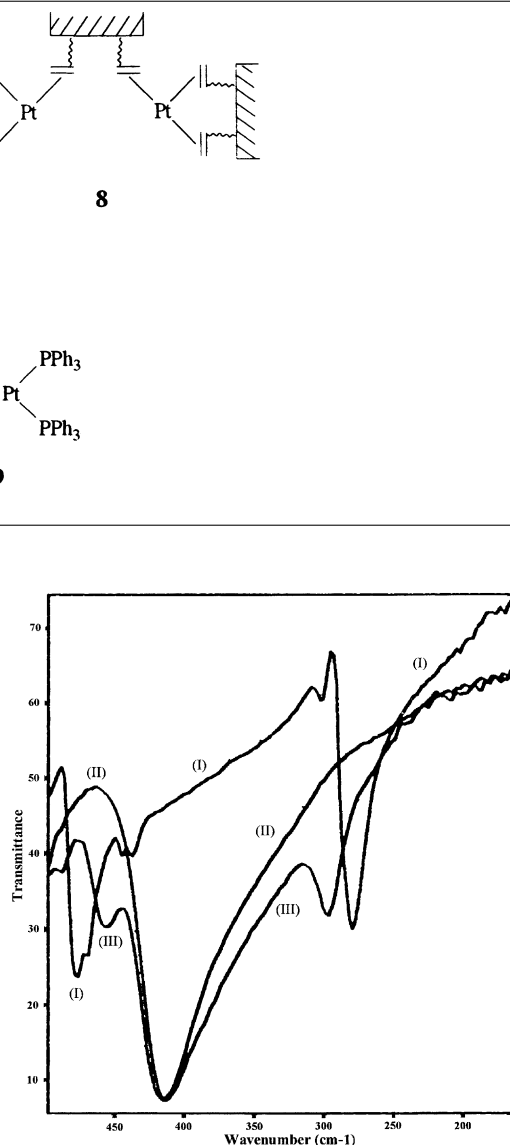

9

Fig. 1. Far infrared spectra: (I) of complex $[RhCl(CO)_2]_2$; (II) of polysiloxane G2; and (III) of G2 complexed with $[RhCl(CO)_2]_2$ (G2/Rh). The sample G2/Rh was prepared by mixing 30 mg of $[RhCl(CO)_2]_2$ dissolved in 0.5 ml of CH_2Cl_2 with 0.11 g of G2.

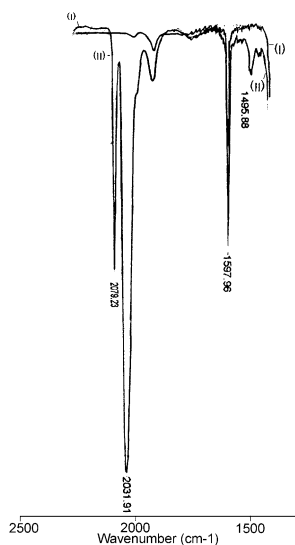Fig. 2. Infrared spectra: (I) of polysiloxane G2; and (II) of G2 complexed with [RhCl(CO)$_2$]$_2$ over the region 2200–1470 cm^{-1}.

high vinyls content was used and majority of the structure **4** for G0 support.

Unfortunately, it was not possible to detect the new metal–alkene band due to being obscured by strong Si–CH$_3$ stretching and C–C bending vibration bands overlapping each other in the range 390–410 cm^{-1}. However, the IR spectrum (Fig. 2) in the region of the vinyl stretching frequencies indicates that along with the band (I) at 1598 cm^{-1} typical for the free vinyls a new band (II) at 1496 cm^{-1} also appeared which can be attributed to the coordinated vinyl ligands.

3.1.2. ^1H NMR studies

The ^1H spectrum of the sample G2/Rh taken at −40 °C shows three characteristic resonances as shown in Fig. 3. A complex multiplet at 5.5–6.2 ppm arises from the free vinyl protons, while the broad two envelopes from 3.4 to 4.8 ppm can be attributed [23] to the coordinated vinyls presumably engaged in the formation of mono- (**2**) and dinuclear (**4**) rhodium complex.

3.1.3. DSC

Differential scanning calorimetry gave us information on the thermal stability of the Pt(0) and Rh(I) complex catalysts
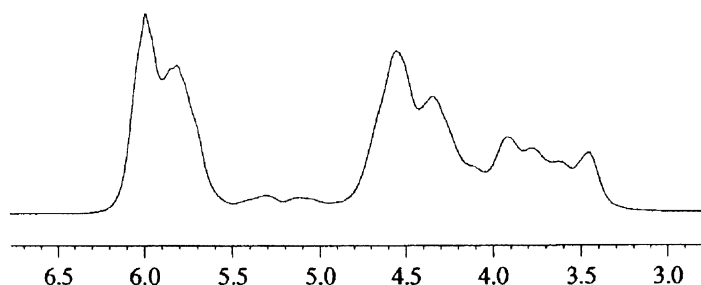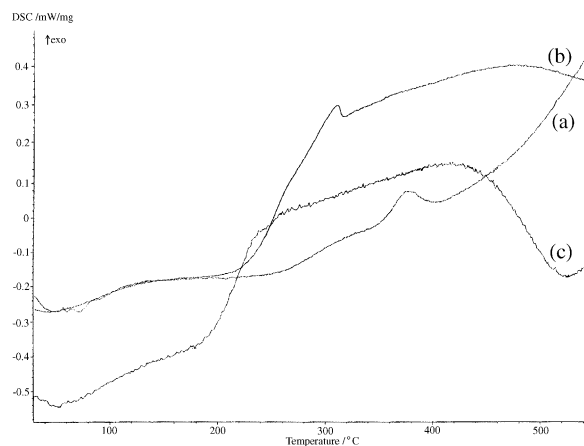

Fig. 4. DSC of the (a) G0A hybrid support; (b) G0A/Pt catalyst; and (c) G0A/Rh catalyst.

immobilized on the hybrid G0A support. Fig. 4 indicates that the introduction of the metal to the polysiloxane decreases its stability. It seems very likely that transition metal catalyses the cleavage of the polysiloxane chains.

3.1.4. Catalyst activity

The catalytic activity of the immobilized complex catalysts was studied in hydrosilylation reaction. The hydrosilylation of carbon–carbon multiple bonds is an important industrial process leading to carbofunctional silanes, versatile intermediates in organic synthesis. Among the variety of catalysts which promote this reaction, particularly platinum but also rhodium species have been the most effective [1,24–26]. There have been many attempts to immobilize soluble transition metal complex catalysts to produce more convenient heterogeneous analogues. Recently, very active polymer-supported Pt [27] and Rh catalysts [28] have been reported for this reaction.

Our test reaction was hydrosilylation of hexene-1 by dimethylphenylsilane

$$Me_2PhSiH + CH_2=CH(CH_2)_3CH_3$$
$$\rightarrow Me_2PhSi(CH_2)_5CH_3$$
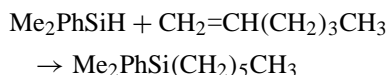
Both the Pt and Rh supported systems exhibited very good hydrosilylation efficiency. The results presented in Table 2 show that the catalyst activity depends on the type of the

Fig. 3. ^1H NMR spectrum of the polysiloxane G2 complexed with [RhCl(CO)$_2$]$_2$ (G2/Rh) in CD$_3$Cl showing free (5.5–6.2 ppm) and Rh-bound vinyls(3.4–4.8 ppm), at −40 °C. The sample G2/Rh was prepared by mixing 30 mg of [RhCl(CO)$_2$]$_2$ dissolved in 0.5 ml of CD$_3$Cl with 0.11 g of G2.
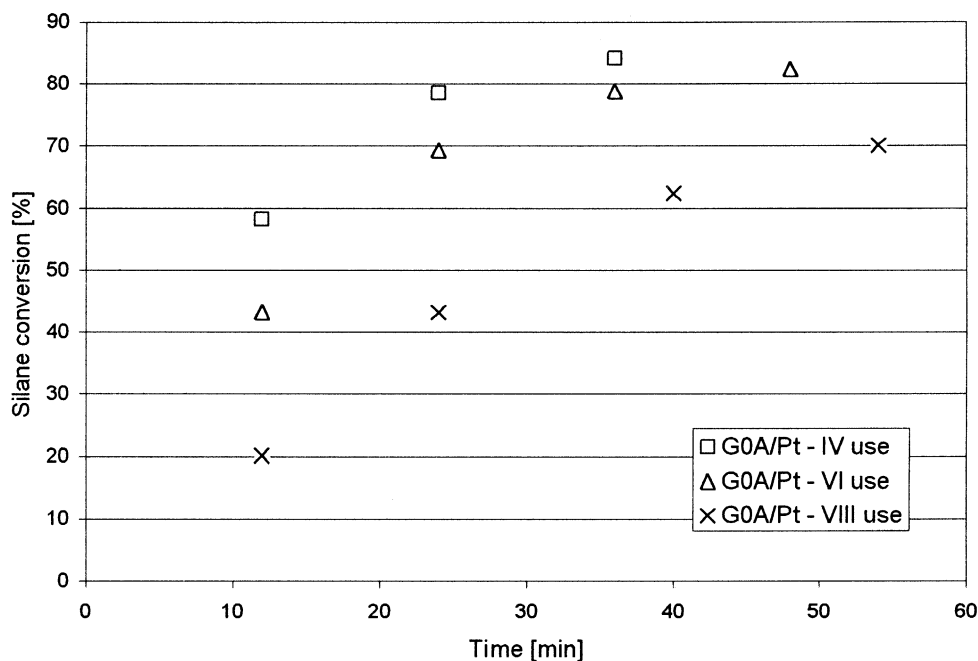
Fig. 5. Hydrosilylation of hexene-1 by Me$_2$PhSiH with the linear G0A/Pt catalyst during the fourth, sixth, and eighth use at 50 °C. For catalyst symbols see Table 2.

catalyst precursor, the branching degree of polymer support and the content of Vi ligands.

Comparison of the silane conversion after 30 min of reaction indicates that the most active system is that derived from zerovalent precursor Pt(PPh$_3$)$_4$. Such a behavior can be ascribed to the presence of highly active species of the structures **7** and **8** being the polymer analogues of Karstedt's

catalyst, which are formed during the immobilization process.

It can be also seen from the Table 2 that in all cases the activity of the Pt and Rh supported catalysts decreased along with increasing degree of branching and increasing content of Vi ligands. It is very likely that an excess of vinyl ligands facilitates formation of the less active dinuclear
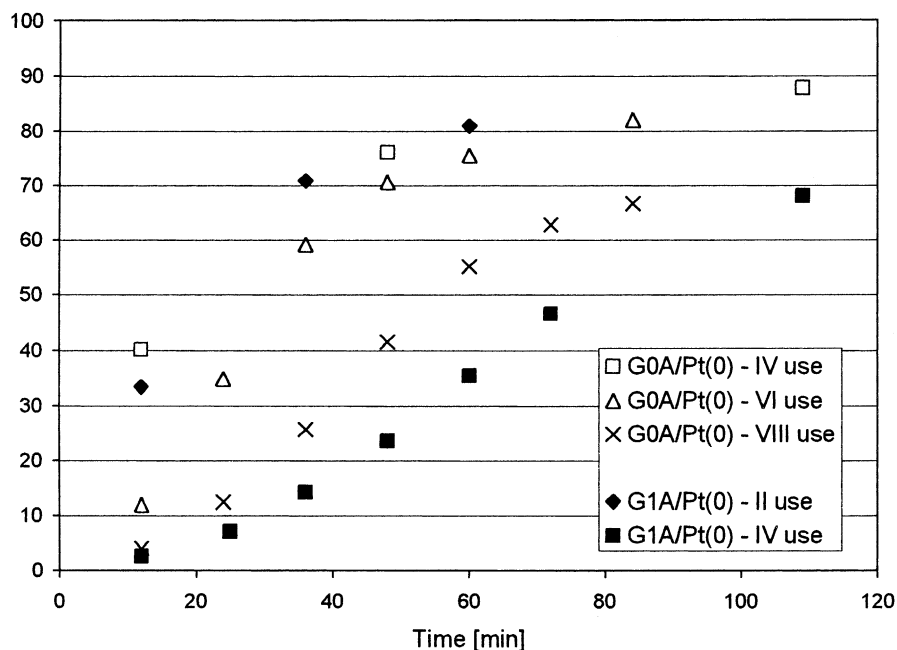

Fig. 6. Hydrosilylation of hexene-1 by dimethylphenylsilane with linear G0A/Pt(0) and dendritic G1A/Pt(0) catalysts over eight and four repeated runs, respectively, at 50 °C. For catalyst symbols see Table 2.

Table 2

Hydrosilylation of hexene-1 with dimethylphenylsilane using platinum and rhodium catalysts immobilized on hybrid supports in toluene at 40 °C

Symbol of hybrid supported catalyst	Catalyst precursor	Metal (Pt or Rh) content (%)	Silane conversion after 30 min (%)		
			II use	III use	IV use
G0A/Pt(0)		0.9	87	77	
G1A/Pt(0)	Pt(PPh$_3$)$_4$	0.8	66	49	
G2C/Pt(0)		0.9	78	57	
G0A/Pt		0.8	57	53	
G1A/Pt	H$_2$PtCl$_6$	1.0	48	33	
G0A/Pt(II)		0.7	49	31	
G1A/Pt(II)	Pt(PhCN)$_2$Cl$_2$	0.8	38	24	
G1A/Rh		0.9	61	37	
G0A/Rh		0.7	44	29	
G2C/Rh	[RhCl(CO)$_2$]$_2$	1.0	40	25	
G0*C/Rh		1.0	33	20	
G0BPPh$_2$/Rh		0.9	49	46	43

Conditions: silane (1.5 mmol), alkene (1.5 mmol), polymer catalyst (1×10^{-3} mmol of Rh or Pt) in toluene (0.5 cm^3).

complexes of the structures **3** and **6** when the Rh(I) and Pt(II) complexes are used as catalyst precursors. The high concentration of Vi ligands can also saturate the coordination sphere of the metal centre which makes the substrate addition more difficult. It is also possible that when the branched polysiloxanes with crowded structures are used as supports, catalytic sites might be blocked. Their availability might be limited by the excluded volume effect as the sites are located throughout the polymer structure.

3.1.5. Catalyst stability

Stability of the supported platinum(0) catalysts was studied over eight repeated catalytic runs. Data presented in Figs. 5 and 6 indicate a decrease in the initial reaction rates after each catalytic cycle due to the metal leaching from the support. The AAS analysis of the eight times recycled catalyst G0A/Pt showed a 50% loss of Pt loading. However, as can be seen from these figures despite this decrease, at longer reaction times the final conversion of silane was not significantly affected by the Pt loss in the catalyst. It indicates that Pt content still remained at the safe level to catalyze reaction. A similar 40% decrerase of the Rh content in the polymer catalyst we have also found in the hydrosilylation of phenylacetylene after nine catalytic cycles [29] and have not observed any significant deterioration in catalyst activity and selectivity.

To limit the metal leaching and improve catalyst stability we replaced the Vi groups with the better donor phosphine ligands. The prelininary results (Table 2) showed that the Rh catalyst supported on the phosphine containing hybrid G0BPPh$_2$ demonstrated fairly stable activity on recycling. We checked the supernatant solutions after third and fourth run of the catalyst G0BPPh$_2$/Rh to see whether the homogeneous active species are present in the reaction mixture and contribute in catalysis. Following the procedure applied by Sherrington [30] we found rather low hydrosilylation activity for the supernatants; i.e. 12% and 10% yield of reaction product after third and fourth catalyst use after 1 h at 40 °C.

The catalytic systems immobilized on phosphine functionalized polysiloxanes grafted on silica are currently the subject of our further investigation in hydrogenation of carbon–carbon multiple bonds.

References

[1] F.R. Hartley, Supported Metal Complexes—A New Generation of Catalyst, D. Reidel Publishing Co., Dordrecht, Germany, 1985.
[2] (a) J.-P. Majoral, A.-M. Caminade, Chem. Rev. 99 (1999) 845;
(b) G.R. Newkome, E. He, C.N. Moorfield, Chem. Rev. 99 (1999) 1689;
(c) G.E. Oosterom, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Angew. Chem. Int. Ed. 40 (2001) 1828;
(d) D. Astruc, F. Chardac, Chem. Rev. 101 (2001) 2991.
[3] G. van Koten, J.T.B.H. Jastrzebski, J. Mol. Catal. A. Chem. 146 (1999) 317.
[4] M.T. Reetz, G. Lobmer, R. Schwickardi, Angew. Chem. Int. Ed. 36 (1997) 1526.
[5] M.T. Reetz, D. Giebel, Angew. Chem. Int. Ed. 39 (2000) 2498.
[6] S.C. Bourque, F. Maltais, W.-J. Xiao, O. Tardif, H. Alper, P. Arya, L.E. Mauzer, J. Am. Chem. Soc. 121 (1999) 3035.
[7] L. Ropartz, D.F. Foster, R.E. Morris, A.M.Z. Slavin, D.J. Cole-Hamilton, J. Chem. Soc. Dalton Trans. (2002) 1997.
[8] L. Ropartz, D.F. Foster, R.E. Morris, A.M.Z. Slavin, D.J. Cole-Hamilton, J. Chem. Soc. Dalton Trans. (2002) 4323.
[9] N. Brinkmann, G. Giebel, G. Lohmer, M.T. Reetz, U. Kragl, J. Catal. 183 (1999) 163.
[10] D. de Groot, E. Eggeling, J.C. de Wilde, H. Kooijman, R.J. van Haaren, A.W. van der Made, A.L. Spek, D. Vogt, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. (1999) 1623.

[11] N.J. Hovestad, E.B. Eggeling, H.J. Heidbüchel, J.T.B.H. Jastrzebski, U. Kragl, W. Keim, D. Vogt, G. van Koten, Angew. Chem. Int. Ed. 38 (1999) 1655.

[12] P.B. Rheiner, H. Sellner, D. Seebach, Helv. Chim. Acta 80 (1997) 2027.

[13] H. Sellner, D. Seebach, Angew. Chem. Int. Ed. 38 (1999) 1918.

[14] S.C. Bourque, H. Alper, L.E. Manzer, P. Arya, J. Am. Chem. Soc. 122 (2000) 956.

[15] F.R. Hartley, The Chemistry of Platinum and Palladium, Applied Science, London, 1973, p.462.

[16] R. Ugo, F. Cariati, G. La Monica, Inorg. Synth. XI (1968) 105.

[17] J.A. Cleverty, Inorg. Synth. VIII (1966) 211.

[18] J. Chojnowski, M. Cypryk, W. Fortuniak, K. Kaźmierski, K. Rózga-Wijas, M. Ścibiorek, in: S.J.Clarson, J. Fitzgerald, M.J. Owen, S.D. Smith, M.E. Van Dyke (Eds.), Synthesis and Properties of Silicones and Silicone-modified Materials, ACS Washington DC, 2003, p.12 (Chapter 2).

[19] K. Rózga-Wijas, J. Chojnowski, W. Fortuniak, M. Ścibiorek, Z.M. Michalska, Ł. Rogalski, J. Mater. Chem. (accepted for publication 2003, DOI: 10,1039/B304134D).

[20] J. Chojnowski, M. Cypryk, W. Fortuniak, K. Rózga-Wijas, M. Ścibiorek, Polymer 43 (2002) 1995.

[21] J. Chojnowski, M. Cypryk, W. Fortuniak, M. Ścibiorek, K. Rózga-Wijas, Macromolecules 36 (2003) 3890.

[22] J. Chojnowski, K. Rózga-Wijas, J. Inorg. Organomet. Polym. 2 (1992) 297.

[23] L.N. Lewis, J. Stein, R.E. Colborn, Y. Gao, J. Dong, J. Organomet. Chem. 521 (1996) 221.

[24] B. Marciniec, Comprehensive Handbook on Hydrosilylation, Pergamon Press, Oxford, 1992.

[25] I. Ojima, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organosilicon Compounds, Willey, New York, 1989, p. 1479.

[26] I. Ojima, Z. Li, J. Zhu, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organosilicon Compounds, Wiley, 1998, pp. 1687–1792.

[27] R. Drake, R. Dunn, D.C. Sherrington, S.J. Thompson, J. Chem. Soc., Chem. Commun. (2000) 1931.

[28] Z.M. Michalska, K. Strzelec, J. Mol. Catal. A. Chem. 177 (2001) 89.

[29] Z.M. Michalska, K. Strzelec, J.W. Sobczak, J. Mol. Catal. 156 (2000) 91.

[30] R. Drake, R. Dunn, D.C. Sherrington, S.J. Thompson, J. Mol. Catal. A. Chem. 177 (2001) 49.