

Polymethacrylate and polystyrene-based resin-supported Pt catalysts in room temperature, solvent-less, oct-1-ene hydrosilylations using trichlorosilane and methyl-dichlorosilane

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Received 20 October 2000; received in revised form 4 March 2001; accepted 5 March 2001

Abstract

A first group of methacrylate-based resins have been prepared with different amine ligands each co-ordinating Pt(II). Evaluation of each of these as room temperature catalysts in the solvent-less hydrosilylation of oct-1-ene by trichlorosilane has identified a supported ethylene diamine derived ligand as providing the most active and stable Pt catalyst. A second group of methacrylate-based resins and third group of styrene-based resins have also been prepared with a variety of morphologies. Each of these has been chemically modified to introduce the same ethylene diamine derived ligand and subsequently Pt(II) co-ordinated to each of these. Both groups of resin catalysts have been evaluated for activity, selectivity, Pt leaching and recyclability in the hydrosilylation of oct-1-ene by trichlorosilane and methyl-dichlorosilane. Specific samples of resin catalysts have been recycled up to 11 times in successive batch reactions. The styrene-based resins have been shown to be more active than the methacrylate-based ones, almost certainly because as a group they are more hydrophobic. Gel-type morphologies in the support are totally unsuitable and appear to provide severe mass transport limitations. The various macroporous resin based species are very attractive catalysts and the most likely optimum design criteria are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrosilylations; Methyl-dichlorosilane; Trichlorosilane

1. Introduction

The hydrosilylation of alkenes is an important industrial process, but is also extremely valuable in laboratory scale synthesis as well. Many metal complexes are known to be catalysts for the reaction [1], but the discovery by Speier et al. that hexachloroplatinic acid is a very active catalyst, even under ambient

conditions [2], has led to Pt complexes becoming the catalysts of choice for these reactions. Pt-based species are not only useful when alkyl and alkoxy-silanes are employed, but they are also not deactivated by chlorosilanes. This versatility often combined with remarkable turnover frequencies explain the dominance of these catalysts in industrial processes. Paradoxically, however, these high activities, associated also with exothermicity can lead to a rapid temperature rise in alk-1-ene hydrosilylations, and the occurrence of a significant level of alkene isomerisation. The internal alkenes that are formed react much

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more slowly, and so in effect can limit the conversion of alk-1-ene to useful terminally silylated products.

As with many homogeneous catalysts experimental convenience and technological efficiency are improved if the catalyst can be immobilised on a support, yielding a heterogeneous analogue. Providing catalytic efficiency and selectivity are not impaired, the immobilised catalyst offers considerable opportunity to improve processing, and not the least to allow exploitation in rapid robotic combinatorial and parallel syntheses. These adaptations are possible, however, only when optimised immobilised catalysts have been developed.

Early studies on the heterogenisation of Pt-based catalysts on both inorganic and polymer supports have been reviewed (for a summary of work prior to 1985 see [3], for a further summary of work prior to 1992 see [4]). Polystyrene- and polymethacrylate-based resins carrying amino, phosino or nitrile groups have been used to immobilise Pt for alkene hydrosilylation, and the nature of the ligand seemed to have a strong influence on the activity of the catalysts [5]. Polystyrene resins functionalised with thiolmethylene groups [6] and acrylonitrile-containing resins [7] have also been utilised similarly to produce heterogeneous Pt catalysts.

Rh complexes are also potentially useful catalysts, and again immobilised analogues of these have been studied by Michalska and co-workers [8–12]. Polyamide-based supports were shown to influence the ratio of linear to branched adducts [10], and this seems to be related to the microporous structure of these supports.

Recently an immobilised Mn-based catalyst has been reported for alkene hydrosilylations [13]. This system seems useful, but is not active at ambient temperature and the behaviour with chlorosilanes is unclear.

While these various reports have demonstrated active heterogeneous catalysts, data on the activity and selectivity with prolonged use are rare, particularly with the more experimentally difficult chlorosilanes, and equally importantly meticulous evaluation of the contribution from leached soluble catalyst has generally been absent. We recently made a preliminary disclosure of the remarkable activity, selectivity and stability of some polystyrene and polymethacrylate resin-supported Pt catalysts synthesised in-house and

used under solvent-less conditions at ambient temperature [14]. We now report in detail on these systems.

2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA); ethyleneglycol dimethacrylate (EGDMA); trimethylolpropane trimethacrylate (TRIM); styrene; divinylbenzene (DVB) (80% grade balance ethyl styrene); cyclohexanol; propan-2-ol; cyclohexanone; octan-2-one; 2-ethylhexan-1-ol; 2-ethylhexanoic acid; 2-aminoethylpiperazine; 2-aminomethylpyridine; *N,N,N'*-trimethylethylenediamine (TriMEDA); diethylamine; sodium hydride; *n*-BuLi; THF; oct-1-ene; trichlorosilane; methylchlorosilane and hydrogen hexachloroplatinate hexahydrate were all obtained from Aldrich. Dodecanol, toluene and iso-octane were from Merck/BDH; vinylbenzyl chloride (VBC) was from the Dow Chemical Co. and potassium tetrachloroplatinate was from Johnson Matthey.

All materials were used as supplied except THF which, where specified, was dried by refluxing over sodium metal.

Speier's catalyst was made up by dissolving hydrogen hexachloroplatinate in propan-2-ol (dried over molecular sieves) to a concentration of 5 wt.%.

2.2. Synthesis of resins (1) and (4a–n)

All resins were synthesised by suspension polymerisation using procedures reported in detail elsewhere [15]. Resin (1) was prepared from GMA (30 cm³) with EGDMA (20 cm³) with cyclohexanol/dodecanol (50 cm³, 9/1 v/v) as the porogen. Resin (4a–g) are also methacrylate species prepared using the comonomer feeds and porogens (type and level) shown in Table 1. While (4h–n) are styrenic species employing vinyl benzyl chloride as the functional comonomer, and the relevant comonomer feeds and porogens (type and level) are shown in Table 2. In each case beads in the diameter range 212–710 μm were obtained and these were purified by extraction with acetone in a Soxhlet apparatus for 16h followed by vacuum drying (60°C) overnight. Yields were 80–95%. FTIR ν_{\max} (KBr) cm⁻¹: (4a), 1728 (C=O), (4h) 1270 (CH₂Cl).

Table 1
Composition of GMA-based suspension polymerised resins (4a–g)

Resin	EGDMA ^a (vol.%)	TRIM ^a (vol.%)	GMA ^a (vol.%)	Porogen	Porogen:mono- mer (v/v)	Epoxide ^b content (mmol g ⁻¹)
(4a)	2	–	98	–	–	6.9
(4b)	40	–	60	Cyclohexanol/dodecanol (9/1)	1:1	4.2
(4c)	–	50	50	Cyclohexanol/dodecanol (9/1)	2:1	3.5
(4d)	–	50	50	Toluene	2:1	3.5
(4e)	–	50	50	Cyclohexanone	2:1	3.5
(4f)	–	50	50	Octan-2-one	2:1	3.5
(4g)	–	50	50	Octan-2-one	3:1	3.5

^a EGDMA: ethylene glycol dimethacrylate; TRIM: trimethylolpropane trimethacrylate; GMA: glycidyl methacrylate.

^b Nominal values based on GMA in feed.

Table 2
Composition of St/DVB/VBC suspension polymerised resins (4h–n)

Resin	DVB ^a (vol.%)	Est ^a (vol.%)	St ^a (vol.%)	VBC ^a (vol.%)	Porogen	Porogen:mono- mer (v/v)	Cl ^b content (mmol g ⁻¹)
(4h)	52	13	0	35	2-Ethylhexan-1-ol	1.5:1	2.6
(4i)	53	13	0	34	Iso-octane	1:1	2.3
(4j)	53	13	0	34	2-Ethylhexan-1-oic acid	1:1	2.4
(4k)	11	9	60	20	2-Ethylhexan-1-ol	1:1	1.5
(4l)	44	36	0	20	Toluene	1:1	1.5
(4m)	10	2	53	34	2-Ethylhexan-1-oic acid	1:1	2.3
(4n)	16	4	46	34	Iso-octane	1:1	2.2

^a DVB: divinylbenzene isomers; Est: ethylstyrene isomers (in DVB); St: styrene; VBC: vinylbenzyl chloride isomers.

^b Calculated from %Cl found.

Elemental microanalytical data for all the resins are shown in Table 3. The epoxide content of (1) was estimated as 4.0 mmol g⁻¹ from the proportion of GMA in the feed and analogous data for (4a–g) are shown in Table 1. The loading of –CH₂Cl groups in (4h–n) can be estimated more accurately from the experimental percent of Cl data and these figures are shown in Table 2 (Schemes 1 and 2).

Table 3
Elemental microanalytical data for precursor resins (4a–n)

Resin	%C	%H	Resin	%C	%H	%Cl
(4a)	57.9	7.5	(4h)	83.3	7.4	9.3
(4b)	55.7	6.8	(4i)	81.9	6.9	8.2
(4c)	58.0	7.1	(4j)	83.1	7.1	8.6
(4d)	60.2	7.6	(4k)	86.7	7.0	5.3
(4e)	60.3	7.5	(4l)	85.7	7.1	5.3
(4f)	58.0	7.1	(4m)	82.4	6.8	8.3
(4g)	58.8	6.9	(4n)	83.0	7.1	7.9

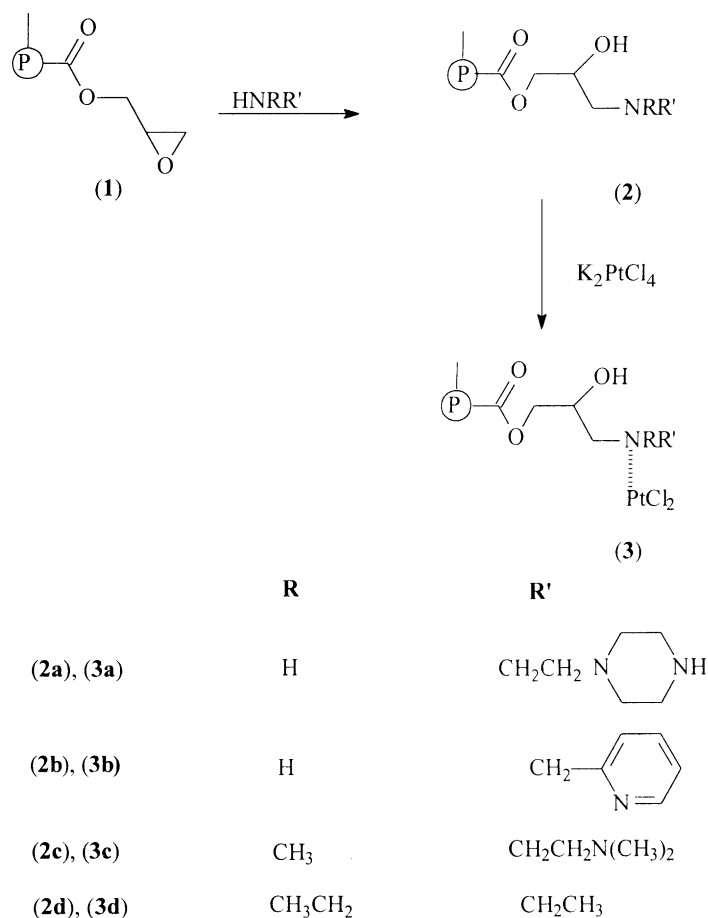
2.3. Synthesis of aminated methacrylate resins (2a–d)

2.3.1. Resin (2a)

1-(2-Aminoethyl)piperazine (10.6 g, 82 mmol) was dissolved in dried and distilled THF (100 cm³) to which resin (1) (10.0 g, 41 mmol epoxide) was added. The mixture was heated to reflux under nitrogen and stirred with an overhead stirrer for 18 h before being filtered, washed with THF, extracted with THF in a Soxhlet apparatus for 16 h and dried in a vacuum oven at 60°C. White beads were recovered (12.0 g). Found: C, 58.1; H, 9.2; N, 5.75. ν_{\max} (KBr) cm⁻¹: 3440, 2953, 2817, 1728, 1636, 1461, 1265, 1162, 750 (Scheme 1).

2.3.2. Resin (2b)

2-Aminomethyl pyridine (4.4 g, 41 mmol) was dissolved in dried and distilled THF (100 cm³) to which resin (1) (5.0 g, 21 mmol epoxide) was added. The



Scheme 1. Synthesis of GMA resin-based catalysts (3a–d).

mixture was heated to reflux under nitrogen and stirred with an overhead stirrer for 24 h before being filtered, washed with THF, extracted with THF in a Soxhlet apparatus for 16 h and dried in a vacuum oven at 60°C. Pale orange beads were recovered (5.9 g). Found: C, 59.4; H, 6.8; N, 4.5; Cl, 1.1. ν_{\max} (KBr) cm^{-1} : 3434, 2992, 2948, 1728, 1596, 1482, 1256, 1155, 759.

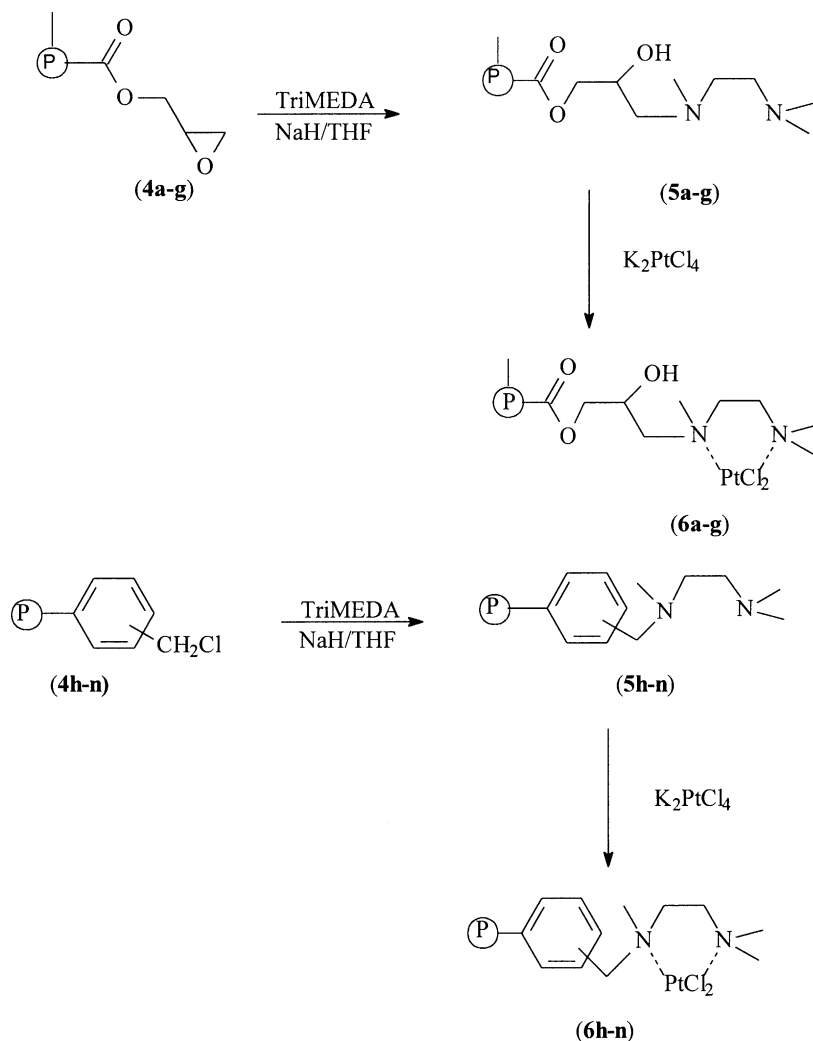
2.3.3. Resin (2c)

N,N,N'-trimethylethylenediamine (8.4 g, 82 mmol) was dissolved in dried and distilled THF (100 cm^3) in a three-necked flask fitted with condenser, overhead stirrer and under dry nitrogen. The solution was cooled at -15°C in an ethylene glycol/dry ice bath before 2.5 M *n*-BuLi (16.4 cm^3) was slowly injected. After 15 min resin (1) (10.0 g, 41 mmol epoxide) was added

to the flask and the contents stirred at -15°C for a further 6 h before being allowed to rise to room temperature overnight. After a total of 24 h reaction, the mixture was quenched in methanol and filtered before extraction with THF in a Soxhlet apparatus (16 h). The resulting beads were dried in a vacuum oven at 60°C. White beads were recovered (7.6 g). Found: C, 55.5; H, 7.0; N, 1.85; Cl, 2.1. ν_{\max} (KBr) cm^{-1} : 3439, 3004, 2985, 1734, 1632, 1485, 1399, 1266, 1160, 756.

2.3.4. Resin (2d)

Resin (1) (5.0 g, 20.5 mmol epoxide), diethylamine (2.1 cm^3 , 41 mmol) and dried, distilled THF (50 cm^3) were charged to a three-necked flask. The reagents were heated to reflux under nitrogen for 24 h before being filtered washed with THF, extracted with THF in



Scheme 2. Synthesis of GMA resin-based catalysts (6a–g) and VBC resin-based catalysts (6h–n).

a Soxhlet apparatus (24 h) and dried in a vacuum oven at 60°C. White beads were recovered (5.6 g). Found: C, 58.4; H, 7.5; N, 1.6; Cl, 1.0. ν_{\max} (KBr) cm^{-1} : 3443, 2971, 2823, 1731, 1633, 1457, 1261, 1154, 771.

2.4. Synthesis of aminated GMA resins (5a–g) and aminated VBC resins (5h–n)

A slightly modified procedure to that used in preparing (2c) was employed here. Typically as in the case of (5a), *N,N,N'*-trimethylethylenediamine (6.5 g, 63 mmol) was added to THF (50 cm^3) in a

cooled (0°C) three-necked flask fitted with condenser and overhead stirrer, under a dry nitrogen atmosphere. Sodium hydride (80% dispersion in oil, 2.1 g, 70 mmol NaH) was washed with dry petroleum ether before being added to the flask. The mixture was then stirred for 15 min. Some gas was observed to evolve. The precursor resin (4a) (5.0 g) was then added and stirring continued for 4 h. The temperature was then raised to 60°C. After 48 h the reaction mixture was quenched in methanol, filtered and the recovered beads washed with THF. The beads were then placed in dilute sodium hydroxide for 1 h before extraction

Table 4

Ligand and Pt loading of resins (5a–n) and (6a–n)

Resin	%N found	Ligand ^a loading (mmol g ⁻¹)	Conversion ^b (%)	Resin	%N found	Ligand ^a loading (mmol g ⁻¹)	Pt ^c loading (mmol g ⁻¹)	Resin type
(5a)	8.0	2.85	41	(6a)	4.75	1.7	1.4	Methacrylate
(5b)	3.5	1.25	30	(6b)	2.7	1.0	0.8	Methacrylate
(5c)	2.9	1.0	33	(6c)	2.25	0.8	0.6	Methacrylate
(5d)	4.2	1.5	43	(6d)	2.6	0.9	0.9	Methacrylate
(5e)	5.0	1.8	51	(6e)	3.2	0.8	1.0	Methacrylate
(5f)	4.15	1.5	42	(6f)	2.4	0.9	0.9	Methacrylate
(5g)	2.8	1.0	28	(6g)	2.25	0.8	0.6	Methacrylate
(5h)	2.7	1.0	40	(6h)	2.2	0.8	0.3	Styrenic
(5i)	2.6	0.9	43	(6i)	2.0	0.7	0.4	Styrenic
(5j)	2.65	0.95	42	(6j)	2.2	0.8	0.5	Styrenic
(5k)	3.0	0.9	62	(6k)	2.5	0.9	0.4	Styrenic
(5l)	1.7	0.6	42	(6l)	1.1	0.4	0.6	Styrenic
(5m)	4.6	1.7	82	(6m)	4.0	1.4	0.5	Styrenic
(5n)	4.4	1.6	80	(6n)	3.7	1.3	0.6	Styrenic

^a Calculated from %N taking 2N atoms per ligand.^b Nominal conversion from epoxide content for (5a–g) and from CH₂Cl content for (5h–n).^c From AAS data from digested resins.

with water (16 h) followed by THF (16 h) in a Soxhlet apparatus. The resulting functionalised beads (5a) were dried in a vacuum oven at 60°C. Typically each sample of beads was recovered with only minor handling losses and the loading of ligand achieved was calculated from the experimentally determined %N. These data are shown in Table 4 (Scheme 2).

2.5. Loading of Pt to yield catalysts (3a–d) and (6a–n)

The procedure is exemplified with (3a). Aminated resin (2a) (1 g, 1.6 mmol ligand) and potassium tetrachloroplatinate (0.66 g, 1.6 mmol) were weighed into a polyethylene bottle. The resin was wetted with a little THF before the addition of doubly distilled water (60 cm³) to solubilise the Pt salt. The bottle was closed and shaken for 24 h at room temperature. The polymer-supported Pt catalyst (3a) was collected by filtration, washed with water and acetone, and vacuum dried at 60°C for 24 h. The elemental microanalytical data for all the supported Pt catalysts, (3a–d) and (6a–n) are shown in Table 5.

2.6. Pt analyses

A sample of polymer catalyst (50–70 mg) was weighed accurately into either a silica or alumina

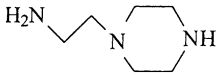
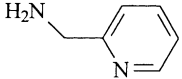
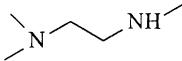

crucible. The lid was fitted and the crucible placed in a muffle furnace. The temperature was raised to 300°C and then increased further at a slow rate (0.3°C min⁻¹ to 600°C). This temperature was maintained for 6 h before the crucible was allowed to cool. Aqua regia (5 cm³) was added to the dark residue at room tem-

Table 5

Microanalytical data for polymer-supported Pt catalysts (3a–d) and (6a–n)

Catalyst	%C	%H	%N	%Cl
(3a)	39.2	5.9	4.1	7.9
(3b)	44.5	5.4	3.2	6.6
(3c)	48.0	6.6	0.9	4.5
(3d)	45.8	6.6	1.3	8.3
(6a)	35.3	5.6	4.8	11.3
(6b)	44.4	6.2	2.7	6.3
(6c)	49.8	6.8	2.3	4.6
(6d)	44.8	6.2	2.6	6.8
(6e)	42.2	5.9	3.2	7.2
(6f)	45.8	6.2	2.4	6.5
(6g)	48.0	6.7	2.3	5.5
(6h)	77.1	7.4	2.2	6.1
(6i)	73.2	6.9	2.0	6.6
(6j)	71.9	6.9	2.2	7.1
(6k)	74.8	7.1	2.5	4.9
(6l)	72.7	6.8	1.1	5.9
(6m)	67.0	7.0	4.0	7.0
(6n)	66.2	6.9	3.7	7.2

Table 6
Ligand and Pt loading of resins (2a–d) and (3a–d)

Resin ^a	HNR ^{1a}	Ligand loading ^b (mmol g ⁻¹)	Epoxide conversion ^c (%)	Resin ^a	Ligand loading ^b (mmol g ⁻¹)	Pt loading ^d (mmol g ⁻¹)
(2a)		1.6	50	(3a)	1.0	0.77
(2b)		1.6	48	(3b)	1.1	0.95
(2c)		0.7	18	(3c)	0.3	0.23
(2d)		1.1	30	(3d)	0.5	0.61

^a See Scheme 1.

^b Calculated from %N.

^c Estimated from original epoxide content of (1) assuming 100% incorporation of GMA monomer and complete retention of epoxide functionality.

^d Calculated from AAS data from digested resin.

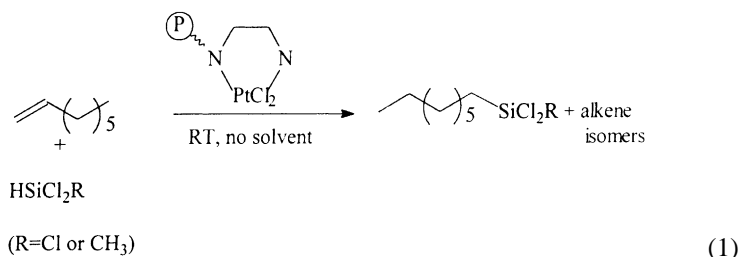
perature and the crucible returned to the furnace and heated to 110°C for 1 h. The resulting clear yellow solution was diluted to 25 cm³ then assayed by ICP AAS.

Data for the ligand and Pt loadings of samples (3a–d) are shown in Table 6 and for (6a–n) in Table 4.

2.7. Catalysed hydrosilylation reactions

The reactions of trichlorosilane and methylchlorosilane with oct-1-ene were both studied (Eq. (1)). Each reaction was carried out in sealed pyrex vials (8 cm³)

in the case of methylchlorosilane) of a freshly prepared reactant mixture containing oct-1-ene (22.4 g, 0.2 mol) and either trichlorosilane (13.5 g, 0.1 mol) or methylchlorosilane (11.5 g, 0.1 mol), together with nonane (10.0 g) as an internal GC standard. The vial was placed on a shaker at room temperature for the duration of the reaction, and the mixture assayed at given times by GC analysis, samples being withdrawn via the teflon-lined septum. Catalyst samples were recycled by carefully decanting off reaction supernatant mixtures and re-charging the vial with a portion of fresh reaction mixture.



the screw top lids being fitted with a teflon-faced silicon septum. The appropriate mass of polymer catalyst (delivering the required level of Pt) was introduced into the vial followed by a portion (4.59 g in the case of the trichlorosilane reactions and 4.39 g

2.8. Analytical methods and instrumentation

Elemental microanalyses were carried out by the Microanalysis Laboratory at the University of Strathclyde. ICP AAS was carried out by the Centre for

Particle Characterisation and Analysis (CPCA) at the University of Paisley, Scotland. N_2 /BET analyses were performed using a Micromeritics ASAP 2000 instrument. Mercury intrusion porosimetry measurements were carried out using a Micromeritics Autopore II 9220. Inverse size exclusion chromatographic (ISEC) [16] measurements were made in the laboratory of Dr. K. Jerabek at the Institute of Chemical Process Fundamentals, Prague, Czech Republic. THF was used as the mobile phase. Solvent uptake was measured by soaking dry polymer samples in solvent for 10 min followed by centrifugation in a sintered tube at 2000 rpm for 1 min. The sample was immediately weighed and the uptake of solvent calculated [17]. GC analyses were carried out on a Carlo Erba mega series HRGC5300 fitted with a 12 m \times 0.32 mm, non-polar capillary column (SGE BPX5) and a flame ionisation detector. FTIR spectra were collected using a Nicolet impact 400D. Ten scans were carried out at a resolution of 4 cm^{-1} for each sample.

3. Results and discussion

3.1. Ligand selection

3.1.1. Synthesis of GMA resin-based catalysts (3a–d)

It was decided to target amine ligands as potentially strong co-ordinators for immobilising Pt(II) and from our previous works with GMA-based resins [18,19] we were aware of the relative ease of introducing amino functions. Accordingly GMA–EGDMA resin (**1**) was prepared with a theoretical epoxide content of $\sim 4 \text{ mmol g}^{-1}$. Cyclohexanol/dodecanol (9/1) was used as a porogen to generate a macroporous morphology that could later be accessed by aqueous solutions (for loading of Pt). Reaction of (**1**) with 2-aminoethylpiperazine, 2-aminomethylpyridine, *N,N,N'*-trimethylethylene diamine (Li salt) and diethylamine prespectively (Scheme 1) yielded the aminated resins (**2a–d**) with good recovery. The level of chemical modification achieved varied from poor to moderate (Table 6) based on the theoretical epoxide content of (**1**). This figure is almost certainly very optimistic, and so the levels of amine incorporated are more satisfactory than implied by the data; these are in particular more than adequate for catalyst generation.

The corresponding experimentally determined ligand and Pt contents of the derived catalysts (**3a–d**) are also shown in Table 6. Resins (**3a–c**) were magnolia coloured, whereas (**3d**) was rather greyish. In simple terms a ligand:Pt ratio of 1:1 might be expected, with perhaps in practice a reduced Pt level arising from inefficient use of all ligand sites. This seems to be the case with (**3a–c**) but with (**3d**) the Pt:ligand ratio is bigger than one. In this case excess Pt may be present as finely dispersed Pt(0) and this may account for the greyish appearance.

3.2. Catalyst activity versus ligand structure

Homogeneous Pt-based species such as Speier's catalyst are known to be highly active in alkene hydrosilylations and the activity of (**3a–d**) was therefore assessed initially in the reaction of oct-1-ene with trichlorosilane (Eq. (1)). A ratio of octene:silane:Pt of 1:1:5 $\times 10^{-4}$ was chosen with reactions carried out at room temperature with no added solvent. To get some measure of whether reactions were truly heterogeneous, or whether leached homogeneous Pt species play a significant role in the catalysis, each reaction was allowed to proceed for 4 h and the yield of octyltrichlorosilane assessed. The reaction supernatant was then decanted from the resin catalyst and the reaction monitored for a further 22 h in the absence of the polymer catalyst. A fresh sample of reactants was also added to the recovered sample of resin catalyst and a second reaction run initiated. The process of catalyst separation after 4 h, with a further reaction period of 22 h in the absence of resin catalyst was repeated. In all three reaction runs were carried with a sample of each catalyst (**3a–d**), the catalyst being present for 4 h, and each reaction run continued for a further 22 h in the absence of resin catalyst. The data obtained are summarised in Table 7. Catalysts (**3a**) and (**3b**) are significantly less active than (**3c**) and (**3d**). With (**3a**) the yield of octyltrichlorosilane rises significantly in all three runs even when the catalyst sample is removed. This suggests a significant contribution from a leached homogeneous Pt species. Leaching from (**3b**) is, however, minimal but the catalyst is not particularly active. Catalyst (**3d**) is overall the most active, but unfortunately yields of octyltrichlorosilane rise significantly even when the catalyst is removed, and a major contribution to the observed activity

Table 7
Preliminary reactions of oct-1-ene with trichlorosilane catalysed by (3a–d)^a

Run	Yield of octyltrichlorosilane (%)							
	(3a) ^b	(3a) ^c	(3b) ^b	(3b) ^c	(3c) ^b	(3c) ^c	(3d) ^b	(3d) ^c
1	3	13	6	7	10	27	17	25
2	3	8	7	8	11	18	14	38
3	2	13	10	9	14	18	22	49

^a Nominal octene:silane:Pt = 1:1:5 × 10⁻⁴ mol in each of three runs of four resin catalysts; room temperature.

^b After 4 h.

^c After further 22h supported catalyst having been removed.

therefore seems to arise from a leached homogeneous Pt species. Catalyst (3c) provides the best overall performance. The activity is better than that of (3a) and (3b) and the contribution from leached Pt species lower than that with (3d). Polymer ligands derived from *N,N,N'*-trimethylethylene diamine were therefore identified for further study.

Similar studies were carried out using oct-1-ene and methylchlorosilane (Eq. (1)) this time employing an oct-1-ene:silane:Pt ratio of 2:1:1 × 10⁻³. Before monitoring the performance of each catalyst a sample of each was first aged by recycling it four times in reac-

tions without any monitoring. The objective was to try to eliminate any readily leached Pt component from the resins, before assessing the relative activity. In each monitored reaction, resin catalyst was separated after 1 h and the reaction allowed to continue for a further 24 h in the absence of any heterogeneous resin species. The results are shown in Figs. 1 and 2. From the data in Fig. 1 it is clear that resin catalyst (3c) is again the most active, and although some activity is detected in the supernatant liquid from this reaction (Fig. 2) this is not high and almost within experimental error (~5%).

The bidentate ligand derived from immobilisation of *N,N,N'*-trimethylethylenediamine is therefore confirmed as the most promising one for further study.

3.3. Polymer type and catalyst resin morphology

3.3.1. Synthesis of GMA- and VBC-based resins (4a–n)

Two sets of pre-cursor resins were prepared one a methacrylate group derived from GMA and the other a styrenic derived from VBC. Each was prepared using a standard suspension polymerisation methodology with a feed of ~50 g of comonomers. The data in Table 1 shows the composition of the GMA-based

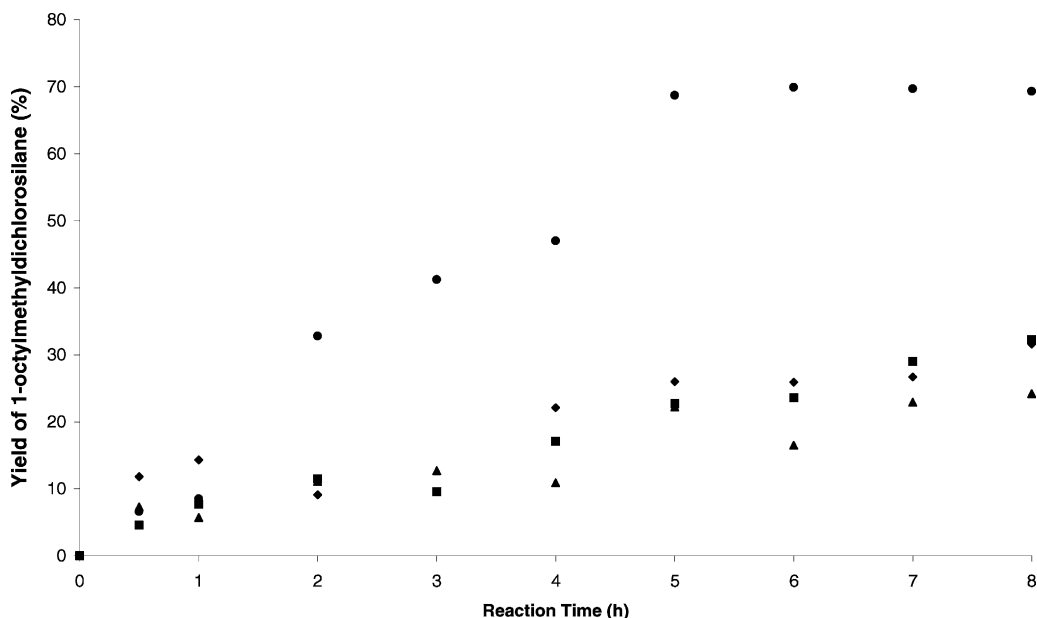


Fig. 1. Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin-supported Pt complexes (oct-1-ene:silane:Pt = 2:1:5 × 10⁻⁴ recycled catalysts fifth use): (3a), (◆); (3b), (■); (3c), (●); (3d), (▲).

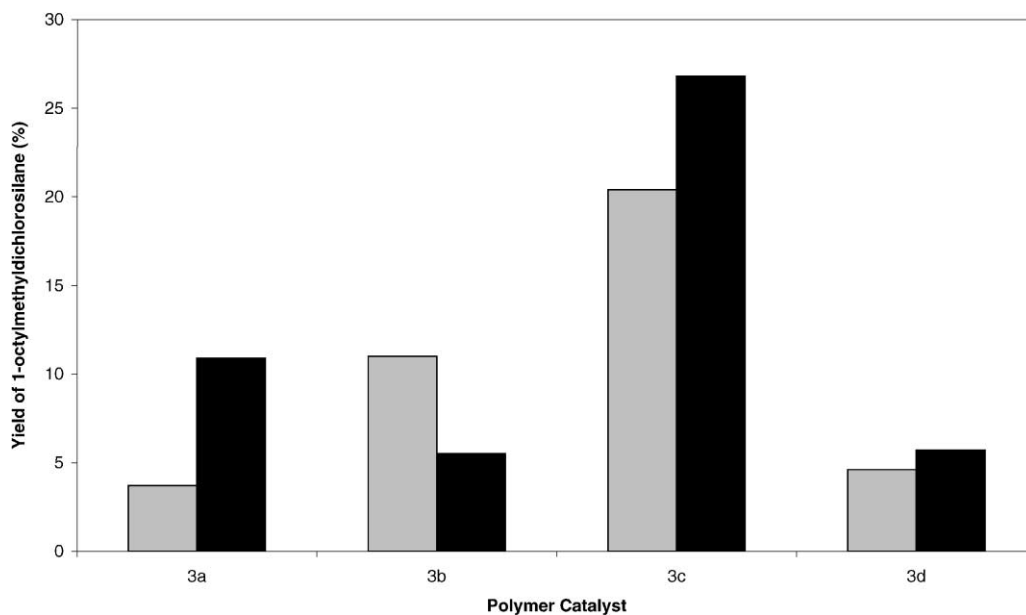


Fig. 2. Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin-supported Pt complexes (**3a–d**) (oct-1-ene:silane:Pt = 2:1:5 × 10⁻⁴). Light bar: yield of 1-octylmethylchlorosilane after 1 h (sixth use of recycled catalyst); dark bar: yield from supernatant after further 24 h in the absence of catalyst.

methacrylate resins and the type and level of porogen employed, while the data in Table 2 give the same information in the case of the VBC styrenic resins.

Resin (**4a**) was targeted as a gel-type resin [20] and indeed this product is clear and glassy in appearance. Its high GMA feed was expected to offer a high ligand and Pt loading. (**4b–g**) were targeted as macroporous species [20]. (**4b–d, f, g**) have an opaque white appearance and indeed superficially appear to be macroporous. However, (**4e**) is glassy and superficially resembles a gel-type species.

The styrenic resins (**4h–n**) were all targeted as macroporous species, and all were produced with thermodynamically poor porogens except (**4l**). The latter has a translucent appearance while the remainder are white and opaque.

3.4. Amination of resins (**4a–n**) to yield (**5a–n**)

The anion of *N,N,N'*-trimethylethylene diamine was generated by treatment of the free amine with NaH, and then it was reacted directly with both the GMA and VBC-based resins. The data in Table 4 show the levels of ligand successfully introduced in

each case. The nominal conversions of the epoxide groups in (**5a–g**) are consistent with previous data published in the literature [18,19]. The values for the styrenic resins (**5h–n**) are consistently higher but are based upon a more realistic, experimentally determined level of CH₂Cl groups in the precursor resins (**4h–n**). In all cases the ligand content is ample to form the basis of heterogeneous catalysts (Scheme 2).

3.5. Pt loading to form resins (**6a–n**)

On loading each resin using a solution of K₂ PtCl₄, off-white catalyst resin particles resulted, except for (**6e**) which was grey and (**6l**) which was brown. In all cases the supernatant solutions were pale orange indicating the presence of residual Pt salt. This is circumstantial evidence that the resins are loaded to their maximum capacity. If the Pt complex structures shown in Scheme 2 are correct the Pt:ligand ratio should be ~1:1 and in most cases it is lower than this indicating the presence of some free ligand (Table 4). The correlation is, however, quite good. Resins (**6e**) and (**6l**) are anomalous in displaying a Pt:ligand ratio >1, and the colour of these two resins may reflect the

presence of excess Pt(0) species. In addition, if the Pt complex structures are as shown in Scheme 2 then the mole ratio Cl:N should be 1:1 and hence the mass ratio 2:1. In practice (Table 5) this correlation is also quite good although there are substantial deviations within the overall picture.

3.6. Surface area and porosity characteristics of catalysts (6a–n) and pre-cursor resins (4a–n)

All the data are summarised in Table 8. With regard to the methacrylate resins (4a–g)/(6a–g) only (4a/6a) were designed as gel-types and indeed all the data confirm this. The Hg intrusion and N₂/BET sorption surface areas are negligible, but perhaps somewhat surprising is the lack of swelling in toluene displayed by (4a). The low value for oct-1-ene is perhaps expected, and suggests that access to the catalytic sites in this species will be impaired. The low surface area of (4e/6e) is also surprising and it seems that the cyclohexanone porogen employed solvates the methacrylate matrix sufficiently well to allow these resins to collapse on drying. This effect has now been quantified in the case of styrene-based materials [21]. Since (4e) does not swell in oct-1-ene, catalyst (6e)

would be expected to perform poorly as well. The remaining methacrylate resins (4b–d, f, g) and corresponding catalysts (6b–d, f, g) all have reasonably good dry state surface areas and imbibe significant levels of oct-1-ene. Likewise the wet-state surface areas determined by ISEC [16] are also adequate as the basis for heterogeneous catalysts.

In the case of the styrenic resins (4h–n) and the corresponding catalysts (6h–n) moderate dry state surface areas are available in all cases. The use of toluene as the porogen in (4l) might have been expected to yield a much higher surface area resin from this thermodynamically good solvent; however, the DVB level used was only 44 vol.% and precedent suggests that a higher crosslink ratio is required to sustain a higher surface area. Overall, however with good imbibition levels for oct-1-ene and good overall porosity the styrenic resins form a good basis for heterogeneous Pt catalysts.

3.7. Oct-1-ene hydrosilylation by trichlorosilane

3.7.1. Speier's catalyst

A preliminary reaction of oct-1-ene with trichlorosilane and 1×10^{-3} mol Pt as Speier's catalyst, initially at room temperature, gave rise to a very rapid exother-

Table 8
Porosity characteristics of Pt loaded resins (6a–n) and their precursor resins (4a–n)^a

Resin	Hg intrusion porosimetry data			Liquid uptake data (cm ³ g ⁻¹)			Resin	Surface area (m ² g ⁻¹) ^b	
	Surface area, A (m ² g ⁻¹)	Intrusion volume (cm ³ g ⁻¹)	Average pore diameter (Å)	CH ₃ OH	Toluene	Oct-1-ene		N ₂ /BET	ISEC ^c
(4a)	–	–	Very low	0.05	0.04	0.02	(6a)	0.1	NR ^d
(4b)	190	0.58	123	0.75	0.88	0.47	(6b)	82	82
(4c)	218	1.23	226	1.46	1.82	1.10	(6c)	128	142
(4d)	220	1.11	201	1.36	1.69	0.97	(6d)	113	NR
(4e)	–	–	Very low	0.41	0.04	0.05	(6e)	0.1	NR
(4f)	194	1.28	264	1.68	1.91	1.30	(6f)	119	91
(4g)	35	0.80	924	2.32	2.38	1.80	(6g)	107	118
(4h)	132	1.53	464	1.26	1.40	1.12	(6h)	44	NR
(4i)	184	1.09	236	0.86	1.00	0.82	(6i)	100	64
(4j)	221	1.16	210	1.00	1.02	0.83	(6j)	108	77
(4k)	39	1.23	1270	1.72	2.34	1.64	(6k)	25	46
(4l)	154	0.27	71	0.50	0.69	0.36	(6l)	184	NR
(4m)	110	1.58	576	1.35	1.25	0.84	(6m)	33	NR
(4n)	165	0.84	205	0.75	1.92	0.95	(6n)	48	NR

^a See Section 2 for procedures.

^b From $4 \times$ intrusion volume per area.

^c Inverse size exclusion chromatography.

^d Not recorded.

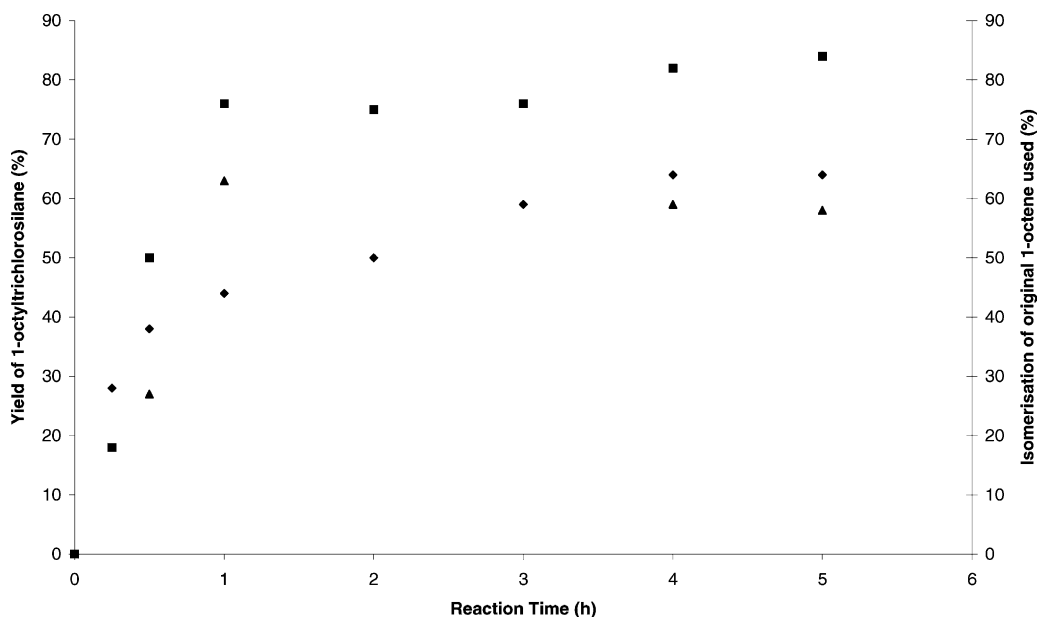


Fig. 3. Hydrosilylation of oct-1-ene by trichlorosilane catalysed by homogeneous Speier's catalyst initially at room temperature (oct-1-ene:silane = 2:1); (■) yield of 1-octyltrichlorosilane for $Pt = 1 \times 10^{-3}$; (▲) level of oct-1-ene isomerisation for $Pt = 1 \times 10^{-3}$; (◆) yield of 1-octyltrichlorosilane for $Pt = 1 \times 10^{-4}$.

mic reaction and a rapid temperature rise. To allow better temperature control and better monitoring of the appearance of octyltrichlorosilane and any alkene isomerisation by-products the reaction was repeated with an oct-1-ene:silane:Pt ratio of 2:1:1 × 10⁻⁴. GC analysis of the product showed selective production of octyltrichlorosilane (Eq. (1)), i.e. no branched silane product, along with some isomerised alkenes. Fig. 3 shows the conversion data. Although the reaction was allowed to run for 5 h in fact the consumption of trichlorosilane and conversion to octyltrichlorosilane reached ~75% in only 1 h (quoted yield of octyltrichlorosilane is based on conversion of initial trichlorosilane, and initial oct-1-ene:silane was 2:1). Thereafter the reaction rate slowed considerably. Simultaneously all the remaining alkene was isomerised to internal alkenes corresponding to ~63% of the starting oct-1-ene (an oct-1-ene:silane ratio of 2:1 was employed deliberately to favour any isomerisation side-reaction). It seems therefore that the productive conversion to octyltrichlorosilane slows dramatically as the remaining oct-1-ene is fully isomerised to internal alkenes, which are known to be less reactive. Interestingly the yield of octyltrichlorosilane does

however rise slowly after 1 h and the percent of isomerised alkene slowly fall presumably reflecting the isomerisation equilibrium involving a low level of oct-1-ene. The latter is slowly but continually bled off as linear hydrosilylated product.

3.8. Methacrylate resin catalysts (6a–g) and styrenic resin catalysts (6h–n)

Since the preliminary experiments using methacrylate resin catalysts (3a–d) indicated that leaching of Pt species is always a possibility, all catalysts (6a–n) were first aged by recycling samples through reactions four times before any monitoring of catalytic activity and selectivity. The conversion data obtained on run 5 for the methacrylate resin catalysts (6a–g) are shown in Fig. 4. The oct-1-ene:silane:Pt ratio is 2:1:1 × 10⁻³ and the reactions were run at room temperature. Analogous data for the aged styrenic resin catalysts (6h–n) also in run 5 appear in Fig. 5. The analytical GC curves also allowed the level of oct-1-ene isomerisation to be monitored and generally this was far lower than with Speier's catalyst. For all the methacrylate resin catalysts alkene isomerism at 8 h was <4%. For

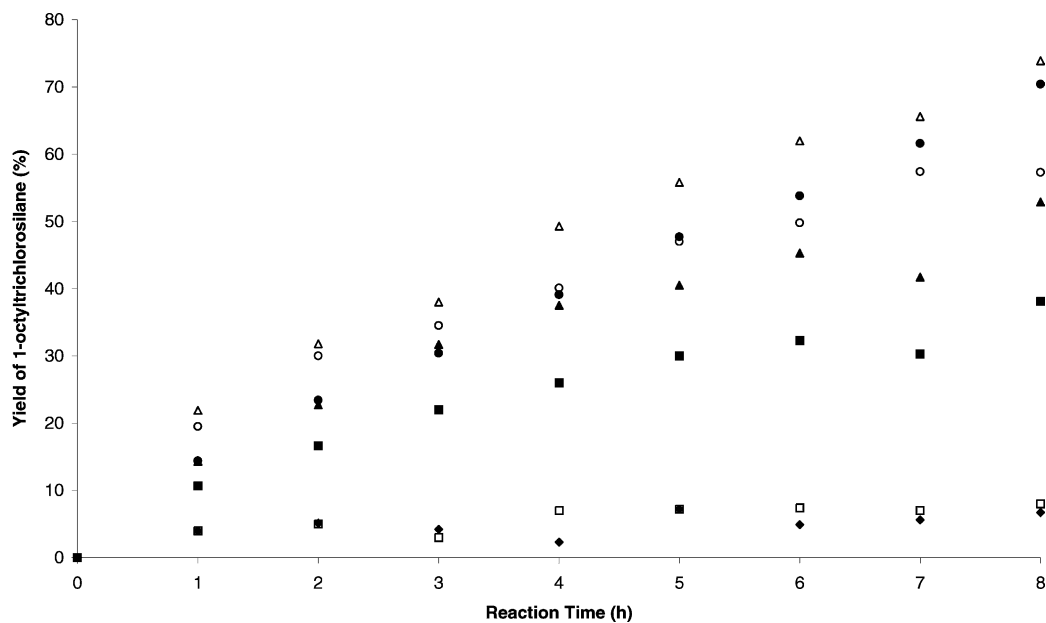


Fig. 4. Room temperature hydrosilylation of oct-1-ene by trichlorosilane catalysed by resin-supported Pt complexes (oct-1-ene:silane:Pt = 2:1:1 $\times 10^{-3}$, recycled catalysts fifth use): (6a), (◆); (6b), (■); (6c), (▲); (6d), (●); (6e), (□); (6f), (△); (6g), (○).

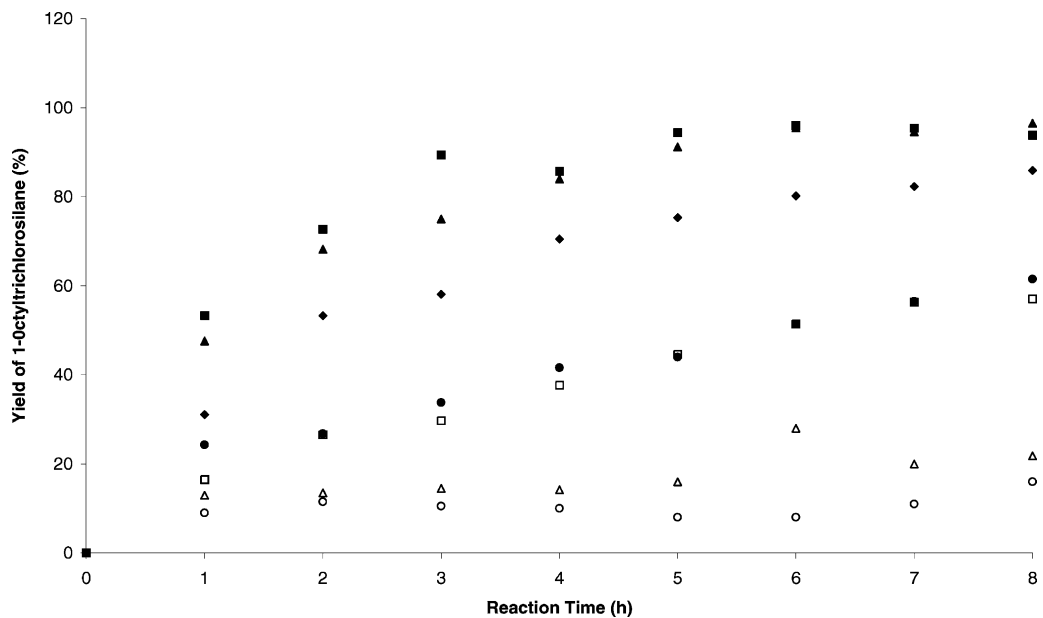


Fig. 5. Room temperature hydrosilylation of oct-1-ene by trichlorosilane catalysed by resin-supported Pt complexes (oct-1-ene:silane:Pt = 2:1:1 $\times 10^{-3}$, recycled catalysts fifth use): (6h), (◆); (6i), (■); (6j), (▲); (6k), (●); (6l), (□); (6m), (△); (6n), (○).

the styrenic resin catalyst (6h) alkene isomerisation was ~27% at 8 h, but <8% for all other styrenic resin species. The former high value is difficult to rationalise, and is certainly not representative of these heterogeneous resin catalysts.

Clearly the resin-supported catalysts are not as active as Speier's catalyst under comparable conditions but they are very active, bearing in mind the data in Figs. 4 and 5 refer to the fifth use of each particular sample of catalyst. This demonstrates remarkable ability to recover and recycle these species. Generally the resins show no induction period, very low levels of oct-1-ene isomerisation, and no uncontrollable exothermicity.

As before in order to assess any contribution to catalysis from leached homogeneous Pt species each resin catalyst was used in a sixth run under conditions identical to those used earlier. The yield of octyltrichlorosilane was recorded after 1 h, then the supernatant reaction mixtures were decanted from the resin catalysts and the level of octyltrichlorosilane assessed again 24 h later in the absence of any discrete heterogeneous catalyst. The data are recorded in Figs. 6 and 7. Interestingly the results are variable. As

a group the methacrylate resin catalysts (6a–g) confirm their somewhat lower activity than the styrenic species (6h–n), but also there is evidence of more leaching with the former group. With the styrenic resin catalysts, though, for example, (6h) and (6k) show evidence of significant leaching, the remainder appear to be essentially stable, or to leach catalytically inactive Pt species. Resins (6i) and (6j) in particular show extremely attractive properties with the highest activity, low leaching and considerable stability on recycling.

3.9. Oct-1-ene hydrosilylation by methylchlorosilane

3.9.1. Speier's catalyst

Using an oct-1-ene:silane:Pt ratio of 2:1:1 × 10⁻³ the yield of octylmethylchlorosilane (based on conversion of methylchlorosilane) was ~95% in 30 min, but was accompanied by ~16% alkene isomerisation (initial octene:silane = 2 : 1). Using a 10-fold lower level of Pt (i.e. 2:1:1 × 10⁻⁴) gave a much slower reaction reflecting the lower reactivity of methylchlorosilane relative to trichlorosilane.

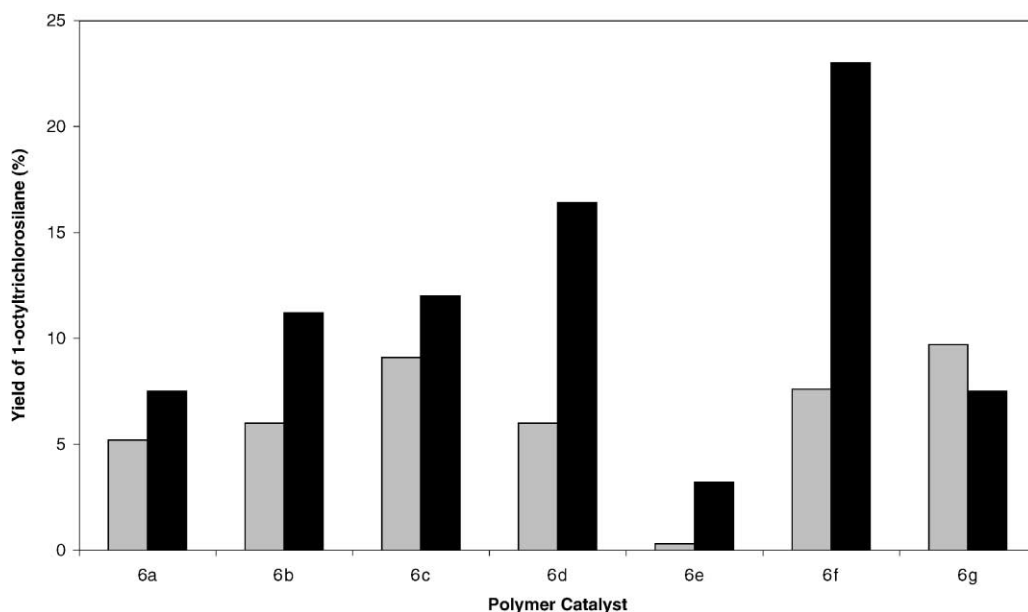


Fig. 6. Room temperature hydrosilylation of oct-1-ene by trichlorosilane catalysed by resin-supported Pt complexes (6a–g) (oct-1-ene:silane:Pt = 2:1:1 × 10⁻³ sixth use of catalyst samples). Light bar: yield of 1-octyltrichlorosilane after 1 h; dark bar: yield from supernatant after further 24 h in the absence of catalyst.

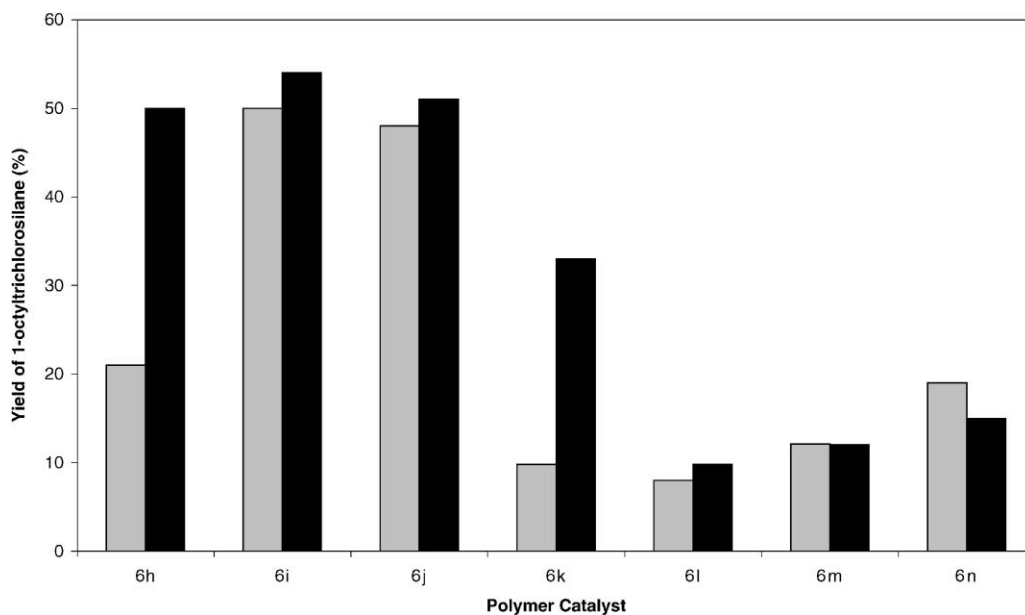


Fig. 7. Room temperature hydrosilylation of oct-1-ene by trichlorosilane catalysed by resin-supported Pt complexes (**6h–n**) (oct-1-ene:silane:Pt = 2:1:1 × 10⁻³, sixth use of catalyst samples). Light bar: yield of 1-octyltrichlorosilane after 1 h; dark bar: yield from supernatant after further 24 h in the absence of catalyst.

3.10. Methacrylate resin catalysts (**6a–g**) and styrenic resin catalysts (**6h–n**)

As before samples of all the resin catalysts were aged by recycling through reactions four times before any monitoring of activity and selectivity. Reactions were performed at room temperature using an oct-1-ene:silane:Pt ratio of 2:1:1 × 10⁻³. The conversion data for the methacrylate resins (**6a–g**) in run 5 are shown in Fig. 8 and those for the styrenic resins (**6h–n**) in Fig. 9. Again as before run 6 for each resin catalyst was analysed after 1 h, the reaction supernatants decanted from the catalyst resins, and the reactions allowed to run for a further 24 h in the absence of any discrete heterogeneous catalyst, and then analysed again. The data are shown in Figs. 10 and 11.

Though the resin catalysts are not as active as Speier's catalyst, even in run 5 some remain highly active. Furthermore, the level of oct-1-ene isomerisation is always <5%. The difference between the methacrylate-based resin catalysts (**6a–g**) and the styrenic species (**6h–n**) is somewhat less with this silane, but the best catalyst species are again (**6i**) and (**6j**). In all cases the level of leaching of active

Pt species is very low. With all resin catalysts the increase in yield of octylmethyldichlorosilane after 24 h following resin catalyst removal is often within the analytical error.

3.11. Long-term use of catalysts

Some of the resin catalysts described are sufficiently active, selective and stable to be considered for exploitation in a continuous process. Unfortunately to set-up such an experimental system is not straightforward because of the noxious nature of the chlorosilanes. However, to give further evidence that use in a continuous reactor was worth pursuing, all of the samples of resin catalysts were used in five additional cycles of the methyldichlorosilane reaction and conversion curves for run 10 are shown in Figs. 12 and 13. As before run 11 was interrupted after 1 h, the catalyst removed, and the reactions left for a further 24 h. The data obtained are shown in Figs. 14 and 15.

While it is clear that in run 10 (Figs. 12 and 13) some of the resin catalysts have become exhausted, some remain sufficiently active to be of practical interest. Likewise in run 11 (Figs. 14 and 15) the activity

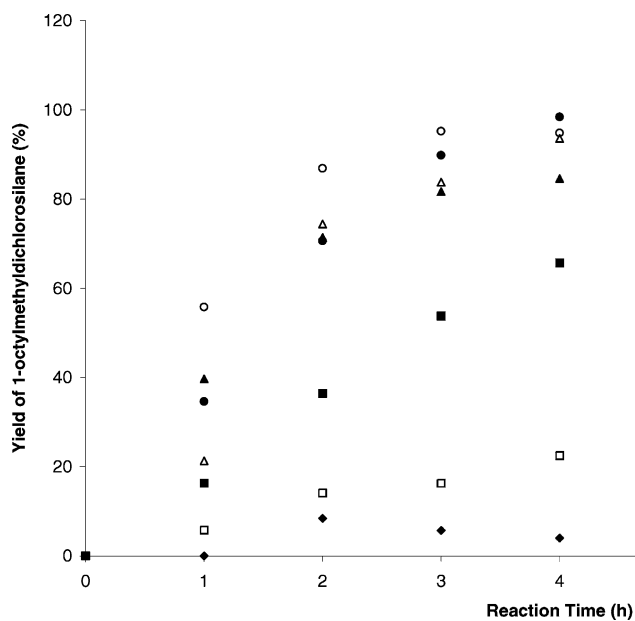


Fig. 8. Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin-supported Pt complexes (**6a–g**) (oct-1-ene:silane:Pt = 2:1:1 $\times 10^{-3}$, recycled catalysts fifth use: (**6a**), (◆); (**6b**), (■); (**6c**), (▲); (**6d**), (●); (**6e**), (□); (**6f**), (△); (**6g**), (○).

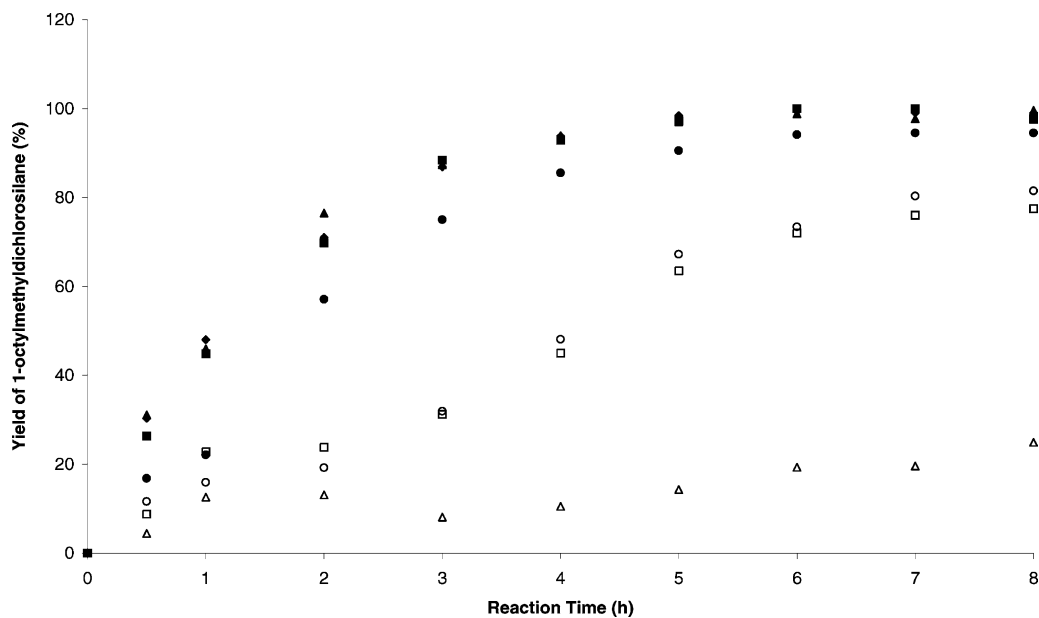


Fig. 9. Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin-supported Pt complexes (**6h–n**) (oct-1-ene:silane:Pt = 2:1:1 $\times 10^{-3}$, recycled catalysts fifth use: (**6h**), (◆); (**6i**), (■); (**6j**), (▲); (**6k**), (●); (**6l**), (□); (**6m**), (△); (**6n**), (○).

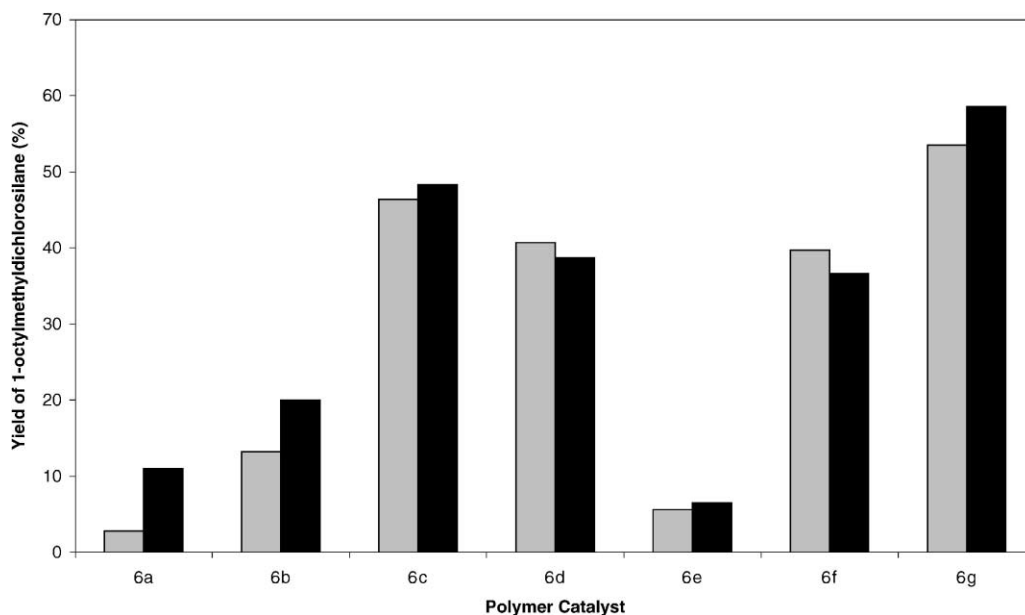


Fig. 10. Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin-supported Pt complexes (**6a–g**) (oct-1-ene:silane:Pt = 2:1:1 $\times 10^{-3}$, sixth use of catalyst samples). Light bar: yield of 1-octylmethylchlorosilane after 1 h; dark bar: yield from supernatant after further 24 h in the absence of catalyst.

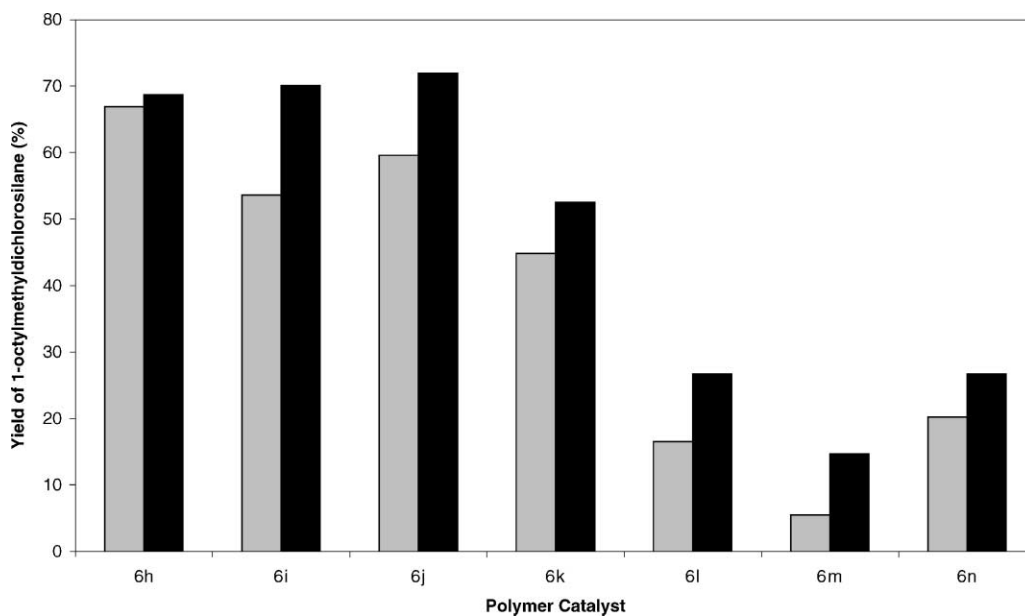


Fig. 11. Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin-supported Pt complexes (**6h–n**) (oct-1-ene:silane:Pt = 2:1:1 $\times 10^{-3}$, sixth use of catalyst samples). Light bar: yield of 1-octylmethylchlorosilane after 1 h; dark bar: yield from supernatants after further 24 h in the absence of catalyst.

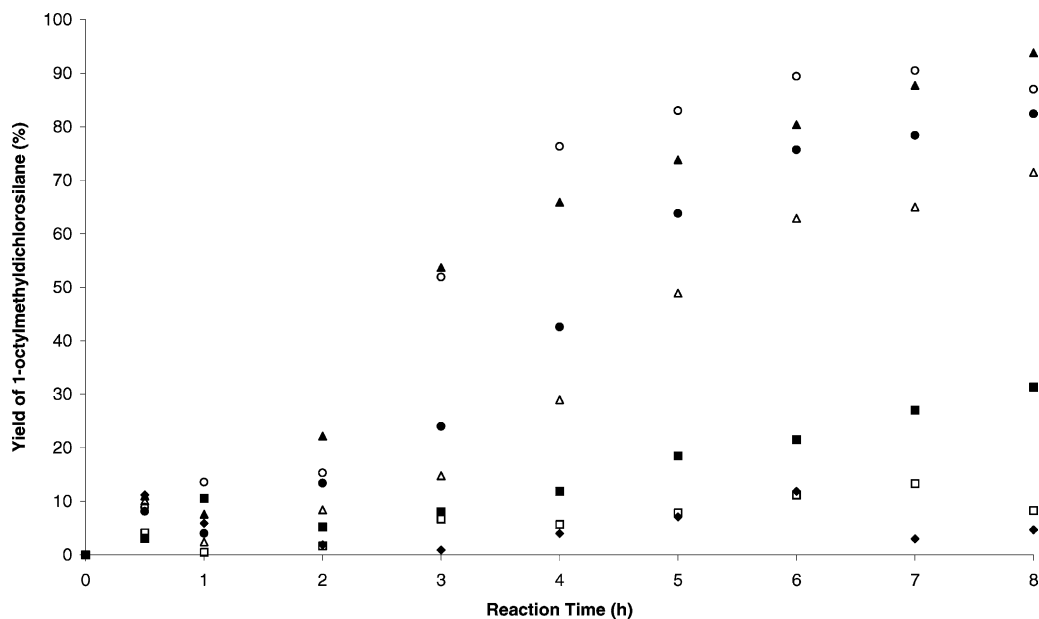


Fig. 12. Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin-supported Pt complexes (oct-1-ene:silane:Pt = 2:1:1 $\times 10^{-3}$, tenth use of catalyst samples): (6a), (◆); (6b), (■); (6c), (▲); (6d), (●); (6e), (□); (6f), (△); (6g), (○).

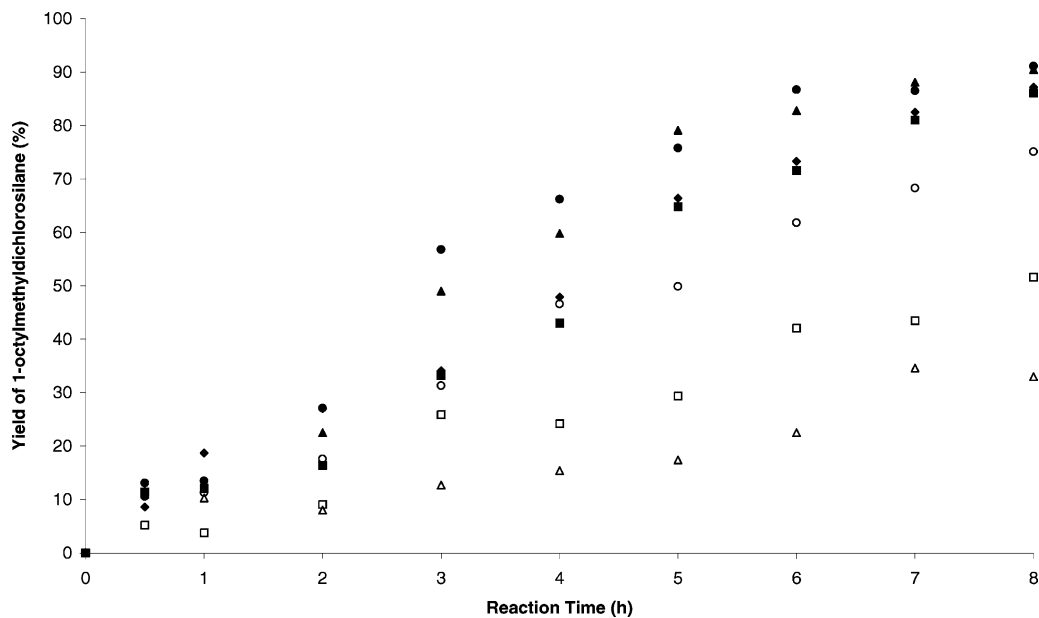


Fig. 13. Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin-supported Pt complexes (oct-1-ene:silane:Pt = 2:1:1 $\times 10^{-3}$, tenth use of catalyst samples): (6h), (◆); (6i), (■); (6j), (▲); (6k), (●); (6l), (□); (6m), (△); (6n), (○).

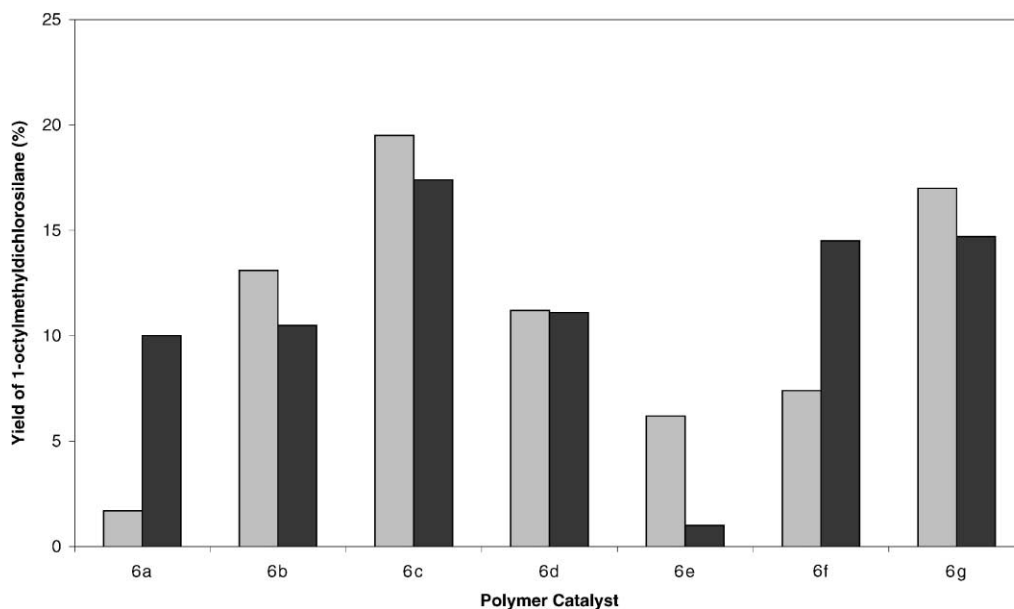


Fig. 14. Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin-supported Pt complexes (**6a–g**) (oct-1-ene:silane:Pt = 2:1:1 $\times 10^{-3}$, eleventh use of catalyst samples). Light bar: yield of 1-octylmethylchlorosilane after 1h; dark bar: yield from supernatant after further 24h in the absence of catalyst.

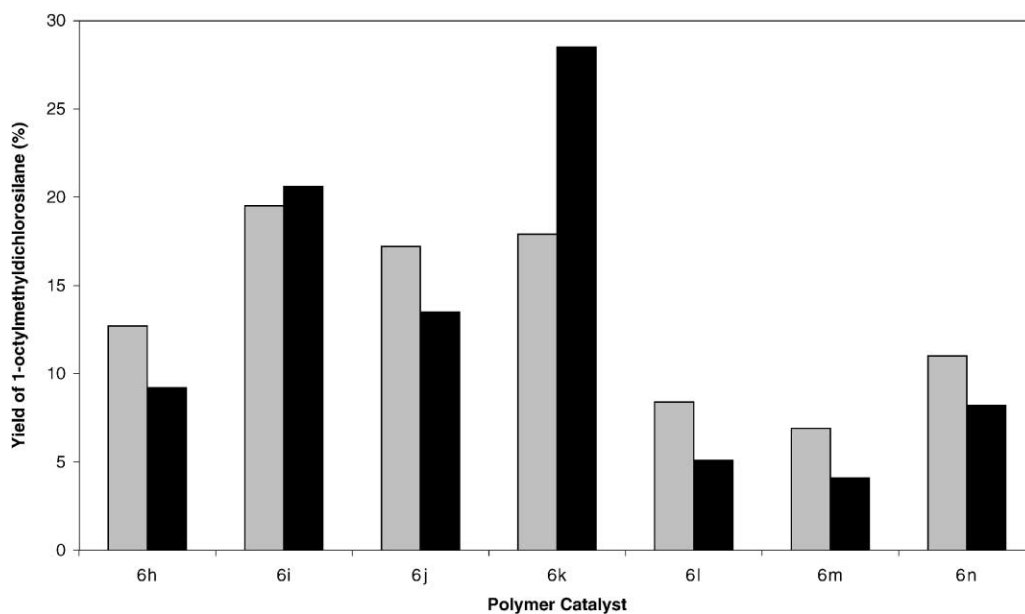


Fig. 15. Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin-supported Pt complexes (**6h–n**) (oct-1-ene:silane:Pt = 2:1:1 $\times 10^{-3}$, eleventh use of catalyst samples). Light bar: yield of 1-octylmethylchlorosilane after 1h; dark bar: yield from supernatant after further 24h in the absence of catalyst.

remains significant in some cases and generally there is little evidence for any leached active Pt species. Since it proved experimentally to be very difficult to work up, purify and extract supernatant solutions, and indeed recycled resins, no quantitative evaluation of residual Pt loading on extensively recycled resins was possible. It is important to realise therefore that unambiguous comparison of absolute catalytic activity and, e.g. turnover number cannot be made.

Overall, however it seems that examination of some of these resin catalysts in a continuous reactor is well worthy of pursuing.

3.12. Optimum resin catalyst design — future work

As a group the styrenic resin catalysts performed consistently better than the methacrylate resin catalysts. Since the variation in morphology is not significantly different between the groups the key factor here seems to be the relative polarity. The methacrylate resins are more polar than the styrenics and these hydrosilylations involve rather hydrophobic reactants. The up-take of oct-1-ene by the two groups (Table 8) is not particularly different, but the imbibition of the silanes (not measured because of experimental difficulties) could well show a significant differential.

The gel-type methacrylate resin catalyst (**6a**) displayed very poor catalytic activity and indeed a very low level of alkene isomerisation. This suggests as anticipated earlier that gel-type morphologies are totally unsuitable as catalyst supports in these reactions. Resin catalyst (**6e**) also was very poor, and though the precursor resin was prepared with a porogen, the porosity data suggest that it has a collapsed structure and is almost a gel-type. Almost certainly mass transfer limitation of the reactants means access to the catalytic sites in these two resins is severely impaired.

Drawing other general conclusions regarding optimum resin morphology from the data on the remaining resins is difficult because there is some run-to-run variation, and variation between the results for the two silanes studied. However, styrenic resins (**6i**) and (**6j**) perform consistently well and these are indeed the styrene-based species with the highest surface areas. Definitive conclusions cannot be drawn, however, because ligand and Pt loadings

also vary. However, in extending this work it looks most favourable to focus on styrenic resins and to examine more carefully the effect of a systematic increase in surface area with parallel studies involving progressive variation of ligand, loading, and ligand:Pt ratio. The species described to date already hold good prospect for exploitation as clean, recyclable laboratory-scale alkene hydrosilylation catalysts.

Acknowledgements

R.D. and S.J.T. acknowledge the receipt of studentships from Dow Corning. The gift of vinylbenzyl chloride from the Dow Chemical Co. is appreciated. The gathering and interpretation of ISEC data by Dr. K. Jerabek, Institute of Chemical Process Fundamentals, Prague, Czech Republic is warmly acknowledged. Likewise the supply of ICP AAS data from Dr. G. Wiltshire, University of Paisley, Paisley, UK.

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