

# High surface area polystyrene resin-supported Pt catalysts in room temperature solventless octene hydrosilylation using methyldichlorosilane

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Eight macroporous styrene–divinylbenzene–vinylbenzyl chloride resins have been synthesised by suspension polymerisation. The first four employed toluene as the porogen and the second four *n*-butyl acetate, at a level of 1 : 1 v/v relative to the comonomers. In all cases a high level of divinylbenzene leads to resins with high surface area, ~500 m<sup>2</sup> g<sup>-1</sup>, as determined from a BET treatment of N<sub>2</sub> sorption data. The functional group content of each group of four resins was varied from 5–25%. All resins were aminated to generate benzyltrimethylethylenediamine ligands on the polymer matrix, and then each was loaded with Pt(II) using KPtCl<sub>4</sub>. The analytical data confirmed the formation of ligand PtCl<sub>2</sub> molecular complexes. Each of the resin immobilised Pt complexes has been assessed for catalytic activity in the room temperature, solventless, hydrosilylation of oct-1-ene using methyldichlorosilane, and a comparison made with soluble Speier's catalyst under identical conditions. Though less active than the soluble catalyst the activity of all the polymer catalysts is good, and of practical value, the activity being higher than we have previously reported in the case of supports with lower surface area. Furthermore while Speier's catalyst induces significant levels of oct-1-ene isomerisation, isomerisation in the case of the polymer catalysts is much lower, and indeed can be all but eliminated by appropriate washing. Extensive catalyst leaching and recycling studies have been carried out, with the best catalysts showing retention of useful activity after 10 cycles. Careful control experiments have provided strong circumstantial evidence that the isomerisation that does arise with the polymer catalysts can be attributed to a component of leached soluble Pt species. Overall the most active and stable polymer catalyst has the highest surface area (~550 m<sup>2</sup> g<sup>-1</sup>) of those studied, along with the lowest ligand and Pt contents (each ~0.25 mmol g<sup>-1</sup>). The surface area dependence confirms our earlier view that maximum accessibility to potential metal complex catalytic sites is vital in these systems, and the metal complex loading dependence suggests that generating discrete isolated ligand PtCl<sub>2</sub> species provides optimal use of the loaded Pt.

## Introduction

The hydrosilylation of alkenes is an important industrial process for the production of organosilicon compounds, and is also extremely valuable in laboratory scale synthesis. Many metal complexes are known to be catalysts for the reaction,<sup>1</sup> but the discovery by Speier in 1957 that hexachloroplatinic acid is a very active catalyst, even under ambient conditions,<sup>2</sup> has led to Pt complexes becoming the catalysts of choice for these reactions. Pt-based species are not only useful when alkyl and alkyloxysilanes are employed, but they also have the additional advantage of not being deactivated by chlorosilanes. This versatility, often combined with remarkable turnover frequencies, explains the dominance of these catalysts in industrial processes. Paradoxically, however, these high activities are also associated with potentially high exothermicity in the hydrosilylation reaction which can lead to a rapid temperature rise and the occurrence of a significant level of alkene isomerisation. The internal alkenes that are formed react much more slowly, and so in effect can limit the conversion of alk-1-ene to useful terminally silylated products.

Early studies on the heterogenisation of Pt-based catalysts on both inorganic and polymer supports have been reviewed<sup>3,4</sup> and exploitation of this strategy has continued more recently as well.<sup>5–12</sup> While these various reports have demonstrated active heterogeneous catalysts, data pertaining to the activity and selectivity of these catalysts with prolonged use are rare, particularly with the more experimentally difficult to handle

chlorosilanes, and equally importantly meticulous evaluation of the contribution from leached soluble catalyst has generally been absent.

Recently we made a preliminary disclosure of the remarkable activity, selectivity and stability of some poly(styrene) and poly(methacrylate) resin-supported Pt catalysts synthesised in-house and used under solvent-less conditions at ambient temperature.<sup>13</sup> More detailed studies revealed that gel-type resins were not well suited as supports because of their incompatibility with the components of the reaction, undergoing only poor swelling.<sup>14</sup> Likewise the poly(methacrylate)-based resins produced catalysts which performed more poorly than the comparable polystyrene-based species probably because of the higher polarity of the former. A series of macroporous polystyrene-based resin Pt catalysts with dry state surface areas ranging from 25–200 m<sup>2</sup> g<sup>-1</sup> demonstrated a good correlation between catalyst activity and surface area;<sup>14</sup> while further studies in which the immobilised ligand–Pt mole ratio was adjusted from ~45 : 1 to ~2 : 1 demonstrated that high ligand ratios (designed to minimise Pt leaching) offered no advantage.<sup>15</sup> Typically macroporous resins loaded with ~0.4 mmol Pt g<sup>-1</sup> with a corresponding ligand–Pt ratio of 2 : 1 and a dry state surface area of ~200 m<sup>2</sup> g<sup>-1</sup> were shown to be highly active and stable catalysts capable of being re-cycled up to ~10 times in batch reactions.

Since it is well known that polystyrene-based resins with surface areas well in excess of 200 m<sup>2</sup> g<sup>-1</sup> are readily accessible,<sup>16–18</sup> we felt that further optimisation of our polymer-supported Pt

**Table 1** Surface area of VBC-based resins (PR1–7) suspension polymerised using various porogens

Precursor resin <sup>a</sup>	Porogen	Solubility parameter of porogen (MPa) <sup>1/2</sup>	BET surface area <sup>b</sup> /m <sup>2</sup> g <sup>-1</sup>
PR1	Toluene	18.2	532
PR2	1,2,4-Trichlorobenzene	—	374
PR3	1,2-Dichlorobenzene	20.5	501
PR4	Butyl acetate	17.4	541
PR5	2-Ethylhexanoic acid	—	332
PR6	2-Ethylhexan-1-ol	19.4	343
PR7	<i>m</i> -Xylene	18.0	545

<sup>a</sup> Each resin was produced using a 60 : 25 : 15 vol% mixture of divinylbenzene–vinylbenzyl chloride–ethylstyrene monomers; the volume ratio of monomer–porogen was 1 : 1. <sup>b</sup> 5-point BET surface area analysis.

catalysts might be possible, and we now report on our extended studies of the activity, selectivity and stability of these systems.

## Results and discussion

### Synthesis of high surface area polystyrene-based resins using suspension polymerisation

As a general design criterion it is well documented that high surface area resins can be produced by exploiting a combination of a high level of crosslinker and a porogen with good thermodynamic compatibility with the polymer matrix being synthesised.<sup>16–18</sup> This allows a high conversion to crosslinked polymer to be achieved **before** any phase separation from the porogen occurs. In turn this results in the formation of a mass of microgel particles which become relatively lightly fused, and between which little in-filling of polymer occurs. Typically an even volume balance of comonomers and porogen is required to allow generation of significant pore volume in the product, without producing a structure which is macroscopically fragile. While compositional data for St–DVB resins with these characteristics are fairly well established, this is not the case for functional analogues of these prepared with an additional functional comonomer component. The latter can change significantly the solvation characteristics of the resultant polymer matrix, and hence the conditions for achieving ‘late’ phase separation during the polymerisation. Accordingly therefore a number of control ethylstyrene–divinylbenzene–vinylbenzyl chloride (EtSt–DVB–VBC) resins were synthesised by a standard suspension polymerisation procedure using a fixed comonomer composition of EtSt–DVB–VBC of 25 : 60 : 15 vol% and a fixed comonomer–porogen volume ratio of 1 : 1 with various porogens. The results obtained are summarised with the data in Table 1. Typically excellent yields of beaded product were obtained (>90%), with a broad particle size distribution ~100–700 μm. Despite a common stabilising system, reactor, stirrer *etc.* and polymerisation conditions being used throughout, the actual particle size distribution varied with the nature of the porogen. A larger fraction of smaller beads (<425 μm) was obtained when toluene or xylene was used as the porogen, whereas a large fraction of bigger beads (>425 μm) resulted when *n*-butyl acetate 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 2-ethylhexan-1-ol or 2-ethylhexanoic acid was the porogen. The precise distribution varied with each porogen. This illustrates just how sensitive suspension polymerisations are to all the components used in the polymerisation mixture. For consistency a particle size 212–300 μm was selected for use throughout this work; this provided a good working quantity of quality beads from all suspension polymerisations. The dry state surface area of each resin was determined from a BET treatment of 5-point N<sub>2</sub> sorption data and the results are shown in Table 1. Although the solubility parameters of the porogens examined fall within a relatively narrow range the variation in surface area achieved is quite high. Toluene and *n*-butyl acetate were selected as two chemically contrasting porogens to carry through in the synthesis of a broader range of resins. Both of

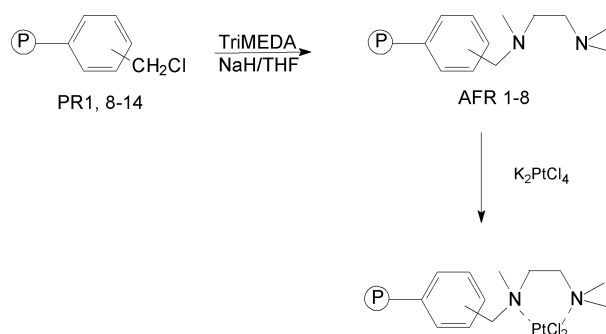
these porogens yielded high quality resins with a surface area >500 m<sup>2</sup> g<sup>-1</sup>. Toluene and *m*-xylene were judged to be chemically very similar porogens.

### Catalyst precursor VBC-resins

Two series of resins were synthesised using toluene and *n*-butyl acetate respectively as porogens employing a comonomer–porogen volume ratio of 1 : 1. Within each series the feed content of VBC was varied from 5 to 25 vol% in order to allow a range of ligand, and hence catalyst, contents to be probed. Table 2 summarises the data for these precursor resins. In all cases there is good correlation between the VBC level used in the polymerisation mixture and the content of –CH<sub>2</sub>Cl functionality in each resin determined from Cl elemental micro-analysis (Table 3). The dry state surface area is >500 m<sup>2</sup> g<sup>-1</sup> for each resin with the biggest area arising with lowest level of –CH<sub>2</sub>Cl functionality in both series of resins. The pores present fall in the micropore to mesopore range (~1–50 nm) with few macropores. There is indeed a suggestion that the surface area varies in an inverse linear fashion with the –CH<sub>2</sub>Cl content, but more data over a broader range of functional group content is really needed to confirm this. This correlation however would imply that both of these porogens become more solvating towards the polymer matrix as the VBC content is reduced. The presence of the –CH<sub>2</sub>Cl functionality in each resin is confirmed by the appearance of a band at 1268 cm<sup>-1</sup> in the FTIR spectra, with the intensity of this varying as expected with the level of VBC used in the preparation of the resins.

### Aminated resins

Benzyltrimethylethylenediamine ligands were introduced onto each resin by reaction of the –CH<sub>2</sub>Cl groups with the sodium salt of trimethylethylenediamine (Scheme 1). The reactions



**Scheme 1** Amination of chloromethylated precursor styrene-based resins and loading of Pt species.

employed a –CH<sub>2</sub>Cl–diamine–NaH mole ratio of 1 : 3 : 3.3 based on the experimentally determined level of –CH<sub>2</sub>Cl in each resin. Reactions were run for 48 h at 60 °C in THF. The ligand content achieved was calculated from the experimentally determined elemental N content (Table 3), and the data are summarised in Table 2 along with an indication of

**Table 2** Composition and properties of VBC-based resins (PR1, 8–14) and corresponding aminated resins (AFR1–8)

VBC resin	Comonomer mixture (vol%) <sup>a</sup>				Porogen (porogen–monomer volume ratio)	–CH <sub>2</sub> Cl Content <sup>b</sup> / mmol g <sup>-1</sup>		BET surface area <sup>c</sup> / m <sup>2</sup> g <sup>-1</sup>	Aminated resin	Diamine content <sup>d</sup> / mmol g <sup>-1</sup>	–CH <sub>2</sub> Cl conversion <sup>e</sup> (%)
	DVB	ESt	St	VBC		Theory	Found <sup>b</sup>				
<b>PR8</b>	60	15	20	5	Toluene (1 : 1)	0.39	0.31	596 (55)	<b>AFR1</b>	0.25	81
<b>PR9</b>	60	15	15	10	Toluene (1 : 1)	0.76	0.73	520 (55)	<b>AFR2</b>	0.36	50
<b>PR10</b>	60	15	10	15	Toluene (1 : 1)	1.13	1.21	519 (55)	<b>AFR3</b>	0.61	45
<b>PR1</b>	60	15	0	25	Toluene (1 : 1)	1.83	1.78	532 (5)	<b>AFR4</b>	1.07	62
<b>PR11</b>	60	15	20	5	Butyl acetate (1 : 1)	0.39	0.45	564 (5)	<b>AFR5</b>	0.18	40
<b>PR12</b>	60	15	15	10	Butyl acetate (1 : 1)	0.76	0.87	539 (5)	<b>AFR6</b>	0.32	37
<b>PR13</b>	60	15	10	15	Butyl acetate (1 : 1)	1.13	1.21	529 (5)	<b>AFR7</b>	0.54	48
<b>PR14</b>	60	15	0	25	Butyl acetate (1 : 1)	1.83	1.78	533 (5)	<b>AFR8</b>	0.89	49

<sup>a</sup> DVB = divinylbenzene, ESt = ethylstyrene, St = styrene, VBC = vinylbenzyl chloride. <sup>b</sup> Calculated from Cl% found. <sup>c</sup> Figure in brackets indicates whether 5-point or 55-point analysis was obtained. <sup>d</sup> Calculated from N% found. <sup>e</sup> Calculated from diamine content of resins.

**Table 3** Elemental microanalytical data for VBC resins (PR1, 8–14) and corresponding aminated resins (AFR1–8)

VBC Resin	%C	%H	%Cl	Aminated resin	%C	%H	%N	%Cl
<b>PR8</b>	90.0	8.0	1.1	<b>AFR1</b>	89.8	7.8	0.7	0.5
<b>PR9</b>	89.0	7.7	2.6	<b>AFR2</b>	88.3	7.7	1.0	1.5
<b>PR10</b>	87.6	7.6	4.3	<b>AFR3</b>	86.6	6.7	1.7	1.9
<b>PR1</b>	85.7	7.2	6.3	<b>AFR4</b>	84.1	8.1	3.0	1.7
<b>PR11</b>	85.5	7.5	1.6	<b>AFR5</b>	89.3	7.7	0.5	1.6
<b>PR12</b>	89.0	7.7	3.1	<b>AFR6</b>	88.6	8.0	0.9	1.6
<b>PR13</b>	87.6	7.5	4.3	<b>AFR7</b>	85.9	7.7	1.5	2.3
<b>PR14</b>	85.4	7.3	6.3	<b>AFR8</b>	83.8	8.0	2.3	2.5

**Table 4** Elemental microanalytical data and ligand–Pt content of catalyst resins (C1–11)

Source resin	Catalyst resin	Microanalytical data (%)				Diamine content <sup>a</sup> / mmol g <sup>-1</sup>	Pt content <sup>b</sup> / mmol g <sup>-1</sup>	Pt loading <sup>c</sup> (%)
		C	H	N	Cl			
<b>AFR1</b>	<b>C1</b> <sup>d</sup>	83.9	7.3	0.7	2.3	0.25	0.25	92
<b>AFR1</b>	<b>C2</b> <sup>d,e</sup>	83.6	7.2	0.6	2.0	0.21	0.27	97
<b>AFR2</b>	<b>C3</b>	77.8	6.9	0.9	3.7	0.32	0.30	94
<b>AFR3</b>	<b>C4</b>	75.6	6.8	1.4	5.3	0.50	0.46	90
<b>AFR4</b>	<b>C5</b>	66.7	6.6	2.2	7.2	0.79	0.73	87
<b>AFR4</b>	<b>C6</b> <sup>e</sup>	66.0	6.5	2.1	7.3	0.75	0.76	91
<b>AFR5</b>	<b>C7</b>	85.1	7.5	0.5	1.6	0.18	0.15	94
<b>AFR6</b>	<b>C8</b>	80.9	7.3	0.8	3.4	0.29	0.27	92
<b>AFR7</b>	<b>C9</b>	75.7	7.2	1.3	4.8	0.46	0.45	94
<b>AFR8</b>	<b>C10</b>	69.9	6.6	2.1	6.4	0.75	0.64	97
<b>PR10</b>	<b>C11</b>	83.4	7.2	—	4.8	0.00	0.18	—

<sup>a</sup> Calculated from N% found. <sup>b</sup> Determined from AAS data for digested resins. <sup>c</sup> Based on original ligand content of aminated source resin. <sup>d</sup> Loaded using ~10 mol% excess of K<sub>2</sub>PtCl<sub>4</sub> relative to ligand, remainder at equimolar with ligand. <sup>e</sup> Loaded using 5 equal portions of K<sub>2</sub>PtCl<sub>4</sub> over extended time period (see Experimental section).

the % conversion of –CH<sub>2</sub>Cl groups. The latter is typically ~40–60% which is comparable with other data in the literature for functional group chemical modification in highly cross-linked macroporous resins. Overall the conversions achieved for the resins prepared with toluene as the porogen are somewhat higher than for the resins derived from *n*-butyl acetate as the porogen. The FTIR spectra of all resins show a significant fall in the intensity of the band at 1268 cm<sup>-1</sup> assigned to the –CH<sub>2</sub>Cl group, and the appearance of shoulders at 2774 and 2813 cm<sup>-1</sup> on the main C–H bands. These were assigned to the tertiary amine groups in the diamine functionality.<sup>19</sup> In all cases the aminated resins displayed good dry state surface area (see later).

#### Pt loaded resins

Each diamine functionalised resin was loaded with Pt by treatment with an aqueous solution of K<sub>2</sub>PtCl<sub>4</sub> employing a ligand–Pt mole ratio of 1 : 1. Minor variations on the method are indicated in Table 4 and in the Experimental section. The ligand content of the derived resin catalysts was calculated from the

experimentally determined N% content and the Pt content from atomic absorption spectrophotometric analysis of solutions of digested catalyst resins. These data are also summarised in Table 4. In each case there is a very good correspondence, close to 1 : 1, between the ligand and the Pt content and this provides good evidence for the formation of well defined diamine PtCl<sub>2</sub> complexes on all the resins. The correspondence of N% with Cl% is however not as good, with the Cl% data being consistently on the high side. The major reason for this is almost certainly the residual Cl content in the aminated resins, arising from incomplete conversion of the –CH<sub>2</sub>Cl groups. When account is taken of this the correspondence of N% with Cl% is much better. Furthermore the variation of Cl% with ligand and Pt content is consistent. Overall therefore for both series of catalysts there is good experimental evidence that the construction of the required Pt complexes on the resins has been successful in all cases.

#### Surface area analysis

Despite the now considerable literature on polymer-supported

**Table 5** Changes in N<sub>2</sub> sorption BET surface area on amination of VBC resins and loading with PtCl<sub>2</sub>

VBC resins			Aminated resins				Catalyst resins			
Code	VBC content (vol %)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Code	Surface area (m <sup>2</sup> g <sup>-1</sup> )			Code	Surface area (m <sup>2</sup> g <sup>-1</sup> )		
				Expected <sup>a</sup>	Found	Difference <sup>b</sup>		Expected <sup>c</sup>	Found	Difference <sup>b</sup>
PR8	5	596 (55)	AFR1	586	577	-9	C1	538	542	+4
PR8	5	596 (55)	AFR1	586	577	-9	C2	536	527	-9
PR9	10	520 (55)	AFR2	508	490	-18	C3	449	355	-94
PR10	15	519 (55)	AFR3	499	463	-36	C4	405	396	-9
PR1	25	532	AFR4	497	425	-72	C5	351	368	+17
PR1	25	532	AFR4	497	425	-72	C6	348	325	-23
PR11	5	564	AFR5	557	545	-12	C7	523	515	-8
PR12	10	539	AFR6	518	510	-8	C8	473	440	-33
PR13	15	529	AFR7	510	456	-54	C9	401	387	-14
PR14	25	533	AFR8	504	448	-56	C10	370	280	-90
PR10	15	519 (55)	—	—	—	—	C11	494	501	+7

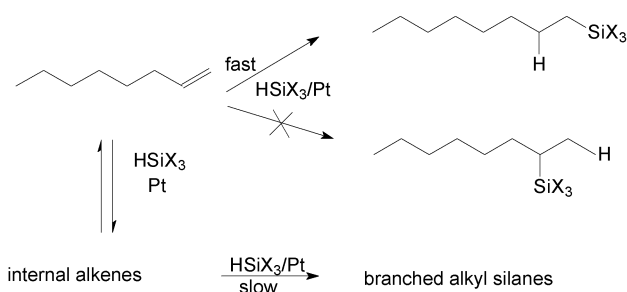
<sup>a</sup> Calculated from experimental data for VBC resin accounting for mass increase on amination. <sup>b</sup> Difference between expected and measured (found) surface area. <sup>c</sup> Calculated from experimental data for aminated resin accounting for mass increase on loading with PtCl<sub>2</sub>. Note: except where otherwise indicated (in brackets) 5-point BET surface area analyses were obtained.

metal complex catalysts there remains a dearth of data on the changes in surface area of resins, if any, that occurs during a sequential chemical modification process. This factor was deemed to be potentially important in the present work, and so the change in surface area of each resin at each step of the catalyst synthesis was monitored carefully. The data for the two series of resins are shown in Table 5. In considering these it is important to realise that chemical modification of a given mass of a resin may change the mass (increase or decrease depending on the chemical change). Computation of surface area from BET treatment of N<sub>2</sub> sorption data yields the surface area per gramme of the resin under analysis, and in evaluating whether the surface area has really changed during the chemical modification process it is vital to account for any mass change arising with the process. In the present case conversion of -CH<sub>2</sub>Cl to ligand and thence to Pt complex causes a progressive mass increase in any given sample of resin and so if no surface area changes occur, the surface areas quoted per gramme of -CH<sub>2</sub>Cl resin, aminated resin and Pt complexed resin should decrease progressively. This is reflected in the data in the surface area 'expected' columns in Table 5. The actual experimentally determined data corresponding to these 'expected' values are listed in the 'found' columns. Clearly in the case of the conversion of -CH<sub>2</sub>Cl resins to aminated resins there is a real and consistent loss of surface area for all the resins examined as indicated in the "difference" column. For the lightly functionalised resins e.g. PR 8 → AFR 1 and PR11 → AFR 5 the loss of surface area is very small, indeed probably within the experimental error of the measurements. For the more heavily functionalised resins the loss of surface area is larger and certainly significant. A possible explanation for this is that minor levels of additional crosslinking might occur in the amination reaction. A bound ligand -N(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>3</sub> could undergo a quaternisation reaction with a nearby -CH<sub>2</sub>Cl group. This complication would be expected to occur with higher probability as the -CH<sub>2</sub>Cl content rises. The analytical data available is not accurate enough to detect such reactions, which almost certainly are not extensive. However, relatively few additional crosslinks might easily give rise to blockage or loss of some (micro) pore structure. The situation with the Pt loading step is less clear. For the series of resins prepared with *n*-butyl acetate as the porogen there seems to be a consistent further drop in surface area (C7-C10) again with evidence that the fall is larger for the more heavily loaded resins. However for the series of resins prepared using toluene as the porogen (C1-C6) the change in surface area is very variable, and indeed in two resins (C1 and C5) there appears to be an increase rather than a decrease. The only realistic explanation for Pt loading causing a

decrease in surface area is the shear bulk of the Pt complex formed. If generated in an appropriate micropore then this could readily cause blockage and effective loss of surface area. Explanations for an increase in surface area, such as Pt complexation inducing local topographic rearrangement of the polymer network, can be advanced, but are more difficult to sustain. Overall, however, though there are clearly real changes in surface area generally involving a loss, these are never more than ~25%, and indeed are usually very much less than this. Hence it is possible to say with some confidence that a precursor resin designed and prepared with a high surface area (say ≥500 m<sup>2</sup> g<sup>-1</sup>) will have this surface area substantially maintained when relatively bulky metal complex catalyst structures are constructed on the polymer matrix, certainly in the case of metal complex loading of ≤25% of polymer segments.

### Octene hydrosilylation chemistry

The hydrosilylation of alkenes such as octene is complicated by the possibility of concurrent alkene isomerisation,<sup>20</sup> and hence hydrosilylation of the *in-situ* formed isomers, and also by the possibility of forming different regio-isomers of the alkylsilane product. In the case of Pt-based catalysts hydrosilylation of terminal alkenes is generally much faster than hydrosilylation of any internal isomers,<sup>21,22</sup> and also the addition reaction is usually very regioselective in terms of yielding the linear alkylsilane product (Scheme 2).

**Scheme 2** Pt catalysed hydrosilylation and isomerisation of oct-1-ene.

### Alkylsilane product

The reaction chosen for study in this work was that of methyl-dichlorosilane with oct-1-ene and it was thought important to confirm the regioselective nature of this particular Pt catalysed reaction as performed by ourselves with our heterogeneous catalysts. Accordingly a number of reaction mixtures from catalyst recycling experiments (see later) were retained and

**Table 6** Relative GC elution times of octene isomers formed during oct-1-ene hydrosilylations

Elution time <sup>a</sup> /min	Octene isomer assignment
-0.04	Unknown A
0.0	Oct-1-ene
+0.01–0.02	<i>trans</i> -Oct-4-ene <sup>b</sup>
+0.03	<i>trans</i> -Oct-3-ene
+0.06	<i>trans</i> -Oct-2-ene
+0.08	Unknown B
+0.11	<i>cis</i> -Oct-2-ene

<sup>a</sup> Relative to that of oct-1-ene. <sup>b</sup> Depending on dilution this isomer sometimes merged with oct-1-ene.

stored under N<sub>2</sub> before analysis by GC and FTIR and NMR spectroscopy. A commercially available sample of 1-octylmethylchlorosilane was analysed in parallel. In all cases GC analysis (see Experimental section) showed the presence of only one product with a retention time identical to that of 1-octylmethylchlorosilane. The reaction mixture from the eighth use of one catalyst was decanted from the polymer-supported Pt complex, and unreacted oct-1-ene any octene isomers and the original nonane GC standard were removed using a Kügel-Röhr distillation apparatus. The residue was analysed by FTIR and NMR spectroscopy yielding the following data. FTIR (cm<sup>-1</sup>) 550, Si–Cl; 1262, CH<sub>3</sub>–Si; 2800–3000, C–H (Note absence of 2200 cm<sup>-1</sup> band due to Si–H). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.51 (m, 2H), 1.35 (m, 10H), 1.13 (m, 2H), 0.90 (m, 3H), 0.78 (t, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 32.60, 32.08, 29.33, 29.32, 22.86, 22.65, 21.88, 14.30, 5.42. In each case the spectral data correlates excellently with the data for a genuine sample of 1-octylmethylchlorosilane.

For completeness the reaction of oct-2-ene with methylchlorosilane catalysed by Speier's catalyst and also by one of the polymer-supported Pt catalysts was examined. The octylsilane product was isolated as described above and shown to be 1-octylmethylchlorosilane. There was no evidence for any silane product from direct hydrosilylation of the oct-2-ene. Hence the slow hydrosilylation that does occur seems to take place *via* the (unfavourable) equilibrium isomerisation of oct-2-ene to oct-1-ene, and this confirms the observations in the literature.<sup>21,22</sup>

### Alkene isomerisation

Since alkene isomerisation can be a very important side reaction in hydrosilylation some effort was made to detect this in our reactions and to identify the isomeric products. There are a total of seven possible isomers of octene: oct-1-ene and the six *cis*–*trans* stereoisomers of oct-2-ene, oct-3-ene and oct-4-ene. Only five of the seven were found to be available from convenient commercial sources *i.e.* oct-1-ene, *cis*-oct-2-ene, *trans*-oct-2-ene, *trans*-oct-3-ene and *trans*-oct-4-ene. GC analysis (see Experimental section) of oct-1-ene reaction mixtures using Speier's catalyst and polymer-supported catalysts, where significant alkene isomerisation occurred, yielded seven peaks in the alkene region with the elution times relative to that of oct-1-ene shown in Table 6. Comparison with the elution behaviour of the available standards allowed the assignment indicated in Table 6, and we assume that unknowns A and B are *cis*-oct-4-ene and *cis*-oct-3-ene, although which is which is not clear. No attempt was made to systematically quantify each of the isomers but it is clear that where isomerisation does arise equilibration occurs along the whole carbon backbone. In all subsequent catalyses the summation of all alkenes other than oct-1-ene was taken as a measure of the level of isomerisation.

The isomerisation of a mixture of *cis*- (74.9%) and *trans*-oct-2-ene (24.1%) containing ~1.0% oct-1-ene during hydrosilylation with methylchlorosilane catalysed by both Speier's

catalyst and a polymer-supported Pt catalyst was also investigated. As indicated above the hydrosilylation reaction is slower than with pure oct-1-ene but the product is the same, 1-octylmethylchlorosilane. The ratio of *trans*-oct-2-ene to *cis*-oct-2-ene rises in the reaction mixture indicating that the *cis* isomer undergoes isomerisation more rapidly than the *trans*, presumably because it is able to coordinate more easily to the Pt centre. Interestingly the content of oct-1-ene in the mixture also rises from its starting value (~1.0%) confirming this isomer to be formed in the isomerisation process, subsequently to undergo hydrosilylation to 1-octylmethylchlorosilane.

### Evaluation of catalyst performance in hydrosilylation of oct-1-ene

As in our preliminary studies all reactions were carried out at room temperature in the absence of solvent, although the level of nonane present as an internal GC standard is significant. The standard conditions employed a mole ratio of oct-1-ene–silane–Pt of 2 : 1 : 1 × 10<sup>-3</sup>. The oct-1-ene–silane ratio of 2 : 1 was chosen in some respects to favour isomerisation and to allow any isomerisation reaction to be monitored relatively easily even if 100% conversion of the methylchlorosilane to the octylsilane were to occur.

### Speier's catalyst

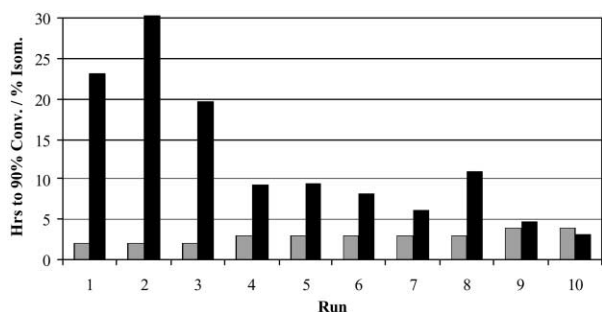
With Speier's catalyst and using the above conditions a short induction period was observed (~2 min) after which the reaction accelerated rapidly with a sharp rise in temperature (to ~90 °C). The conversion to 1-octylmethylchlorosilane reached ~90% (based on the silane feed) in 15 min and ~30% of the original oct-1-ene was found to be isomerised at this time. This confirmed our earlier findings employing this homogeneous catalyst.<sup>13,14</sup> Since ~1 mole equivalent of octenes was present at the end of this reaction it was decided to repeat the reaction under identical conditions and, when all the silane was consumed, to add a second mole equivalent of silane. As before the (first) conversion achieved in only 15 min was >90% with simultaneously ~25% of the original oct-1-ene converted to isomers. On addition of the second mole equivalent of silane the reaction accelerated again with ~55% conversion of methylchlorosilane to the octylsilane in 15 min. This corresponds to a little more than the oct-1-ene content (~50%) of the octenes remaining at the end of the first reaction (**note** 25% of **original** oct-1-ene converted to isomers in the first reaction corresponds to ~50% oct-1-ene and 50% other isomers in the residue of octenes). At the end of the second reaction the proportion of internal octene isomers remaining was ~18% based on the original oct-1-ene feed, indicating that in the second reaction (and presumably in the first as well) some of the internal isomers convert back to oct-1-ene. However, the composition of the residual octene mixture at the end of the second reaction is still ~80% internal alkenes indicating that it is overwhelmingly the existing residual oct-1-ene at the end of the first reaction that undergoes hydrosilylation in the second reaction. Overall therefore the behaviour of Speier's catalyst in our hands is much as expected from the literature and the present catalyst activity and selectivity is consistent with our own earlier data.<sup>13,14</sup>

### Polymer-supported catalysts

Our previous work<sup>13,14</sup> with styrene and methacrylate-based resin supported Pt catalysts showed that gel-type resins are not suitable supports for these solventless alkene hydrosilylations since they do not swell in the reaction media. Styrenic macroporous resin species also proved consistently better than methacrylate derived species probably because the latter are more polar and less compatible with the very hydrophobic components of the reaction mixtures. Of the styrenic

resin-supported catalysts examined, two with a dry state surface area of  $\sim 100 \text{ m}^2 \text{ g}^{-1}$  and a pore volume of  $\sim 1 \text{ ml g}^{-1}$ , with a Pt loading of  $0.5 \text{ mmol g}^{-1}$  and a ligand–Pt ratio of  $\sim 2 : 1$  displayed the best combination of activity, selectivity and stability. Subsequent work demonstrated that higher ligand–Pt ratios provided no advantage in terms of reducing Pt leaching.<sup>15</sup> The design criteria in the present two series of supported catalysts C1–C6 and C7–C10 were therefore: i) to use styrenic-based resins; ii) to employ a high level of crosslinker in resin preparations with two suitable porogens to general high surface area resins; iii) to use a common level of porogen (1 : 1 v/v with comonomers) to generate a common pore volume in the products; iv) to vary the Pt content of catalysts ( $0.25\text{--}0.75 \text{ mmol g}^{-1}$ ) keeping the ligand–Pt ratio at 1 : 1 (See Tables 2, 4 and 5).

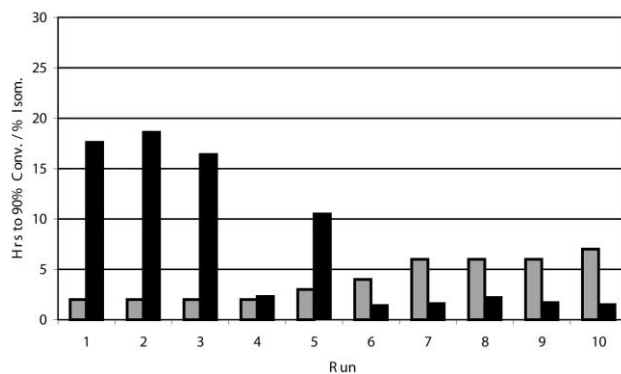
Two series of catalytic experiments were carried out in order to assess the relative activity, selectivity and recyclability of each polymer catalyst. In the first a given sample of each catalyst was used under standard conditions in the room temperature solventless hydrosilylation of oct-1-ene using methyl-dichlorosilane (see Experimental section). At the end of each reaction the catalyst sample was recovered by decantation of the reaction mixture and then re-used in a second catalytic reaction. Each catalyst sample was used in up to 10 successive cycles. Reactions were monitored in real time by GC and the conversion of oct-1-ene to 1-octylmethyl-dichlorosilane calculated. The standard reaction conditions employed an oct-1-ene–silane–Pt mole ratio of  $2 : 1 : 1 \times 10^{-3}$  and the conversion was based on the feed of silane *i.e.* 100% corresponds to 50% conversion of the starting oct-1-ene. At the same time the level of isomerisation of the unused oct-1-ene was also monitored and expressed as a % of the original oct-1-ene feed *i.e.* 50% isomerisation corresponds to all the residual octene being present as internal isomers with 0% oct-1-ene remaining. In order to display in a digestible form the large amount of data generated, the activity of each catalyst has been expressed in terms of the time (h) taken to achieve 90% conversion to 1-octylmethyl-dichlorosilane, and the corresponding % isomerisation quoted at this time. The results in histogram form for catalysts C1–C10 are shown in Figs. 1–10. For comparison similar data for



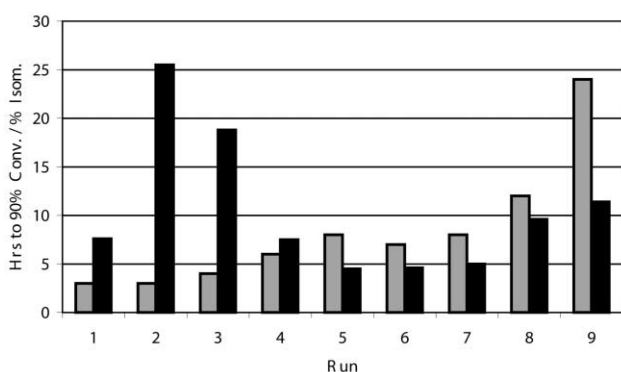
**Fig. 1** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex C1. (Oct-1-ene–silane–Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.

catalyst C11 are shown in Fig. 11 (**note** shift in scale of vertical axis) this control species being loaded with Pt as with the other resins, but possessing no diamine ligand.

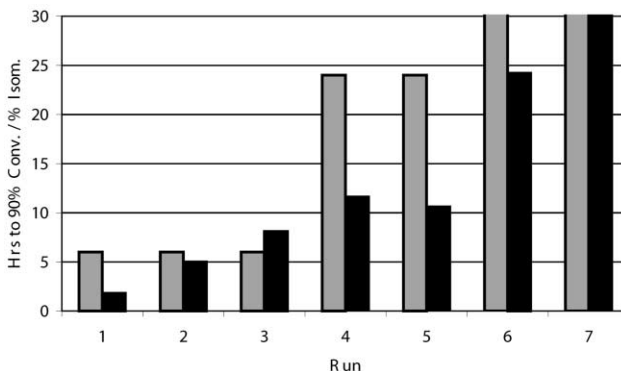
The second series of catalytic experiments was designed primarily to detect and deconvolute any contribution to catalysis from soluble leached Pt species. Again each sample of catalyst was re-used up to 10 times under identical reaction conditions to those previously employed. In each odd numbered experiment (*i.e.* runs 1, 3, 5 *etc.*) the reaction was allowed to run and was monitored by GC until a reasonable conversion ( $\sim 20\text{--}40\%$  if possible) was detected. The reaction mixture was then decanted from the heterogeneous polymer resin catalyst and monitoring of any subsequent additional conversion in the absence of heterogeneous resin catalyst continued for 24 hours.



**Fig. 2** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex C2. (Oct-1-ene–silane–Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.



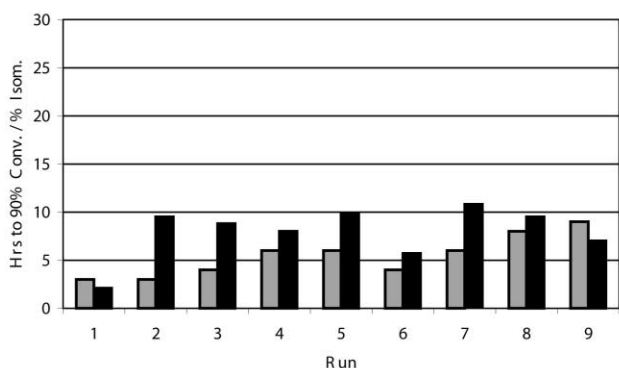
**Fig. 3** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex C3. (Oct-1-ene–silane–Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.



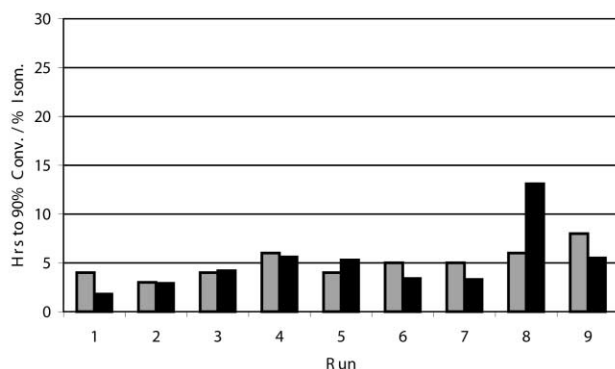
**Fig. 4** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex C4. (Oct-1-ene–silane–Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.

The % isomerisation of residual octene was also calculated at the time the polymer resin catalyst was removed and after 24 h. Again this was expressed as a % of the original oct-1-ene feed. The data for the odd numbered runs using catalyst samples from C1–C10 are shown in Tables 7 and 8. The corresponding even numbered catalyst runs were allowed to proceed in the presence of polymer resin catalyst for 24 h and each mixture was assayed at the end to ensure that reactions were proceeding normally in the presence of heterogeneous polymer catalysts as in the first series of experiments.

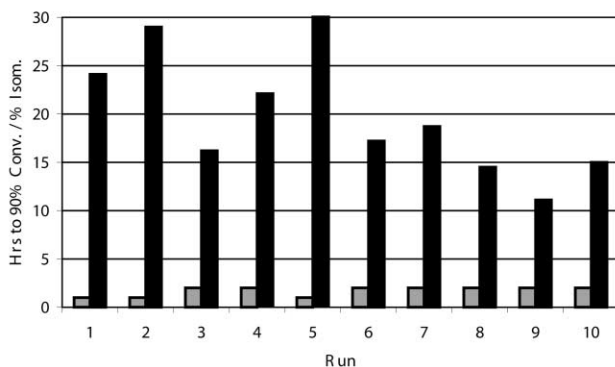
Comparison of the data from the even numbered catalyst runs (not recorded here) in the second series of reactions with those from the first series showed the same activity trends for each catalyst, though the levels of oct-1-ene isomerisation were generally lower. The reason for this (see long-term stability



**Fig. 5** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex **C5**. (Oct-1-ene-silane-Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.



**Fig. 6** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex **C6**. (Oct-1-ene-silane-Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.

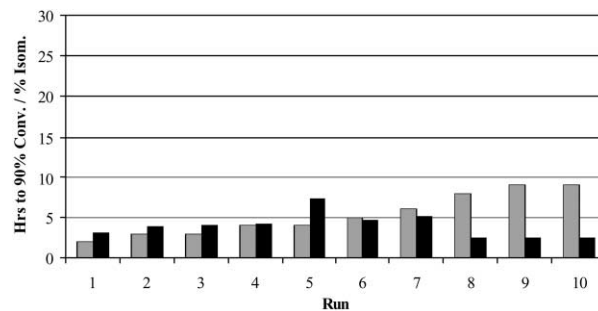


**Fig. 7** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex **C7**. (Oct-1-ene-silane-Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.

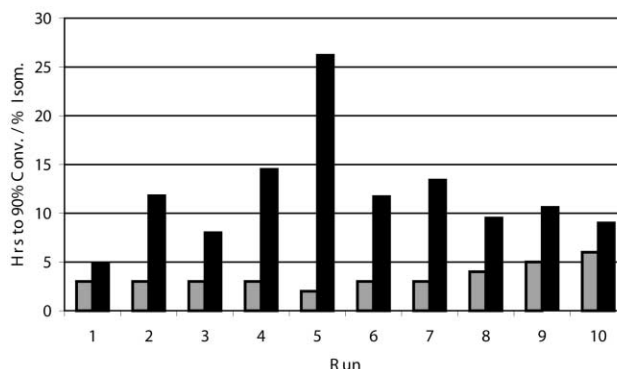
discussion later) is almost certainly the time lapse between the first series of experiments and the second (up to 8 months) during which no special precautions were taken in storing the polymer resin catalysts which were simply kept in air in screw-top sample bottles. Despite this, however, consideration of the results of both series of experiments taken together provides a valuable in-sight into the relative behaviour of the different catalysts.

#### General observations

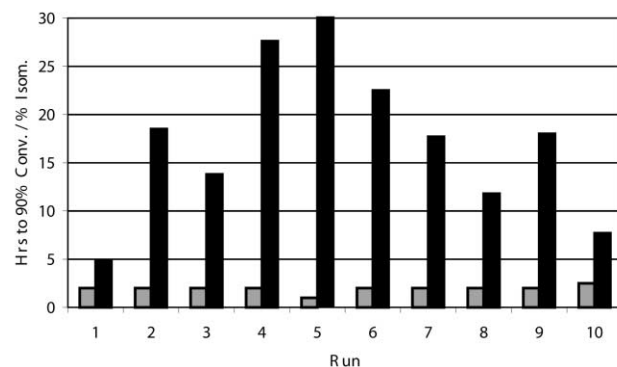
As in our previous work all the polymer-supported catalysts show lower activity than Speier's catalyst. However, the activity is very good, certainly in terms of use on a laboratory scale, and



**Fig. 8** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex **C8**. (Oct-1-ene-silane-Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.



**Fig. 9** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex **C9**. (Oct-1-ene-silane-Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.



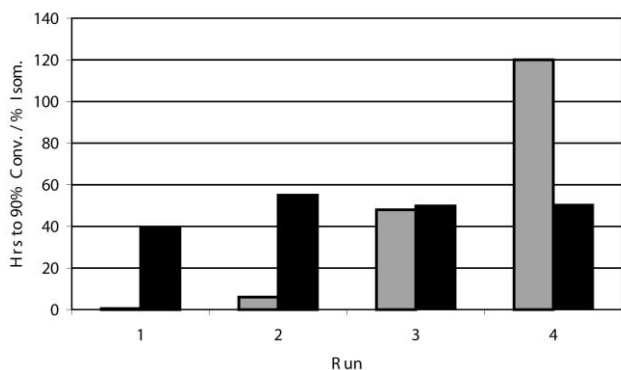
**Fig. 10** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex **C10**. (Oct-1-ene-silane-Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.

potentially on a larger scale as well. Reactions showed no induction period and there was no tendency to exotherm. For many of the polymer catalysts activity was retained during extensive recycling (up to 10 runs) and again this offers considerable benefits, not the least in cost terms, for use on a laboratory scale. The behaviour of catalyst C11 was in marked contrast to the others (C1–C10). The data in Fig. 11 show that while the activity in hydrosilylation is high in run 1 so is the level of oct-1-ene isomerisation. Furthermore the activity falls off dramatically by run 4 with oct-1-ene isomerisation remaining high ~50%. These results suggest that Pt is lost quickly from this resin support and that much of the initially observed catalytic activity arises from Pt species leached into the reaction medium. Since this resin contains no immobilised diamine ligand and this behaviour seems totally reasonable, and demonstrates the vital role the ligand plays in the other resin catalysts in retaining Pt as a discrete molecular complex.

**Table 7** Leaching evaluation of resin catalysts C1–C6 in the reaction of oct-1-ene with methylchlorosilane at room temperature<sup>a</sup>

Resin catalyst	Time	Run 1		Run 3		Run 5		Run 7		Run 9	
		Conv. (%)	Isom. (%)	Conv. (%)	Isom. (%)	Conv. (%)	Isom. (%)	Conv. (%)	Isom. (%)	Conv. (%)	Isom. (%)
C1	0 min	3	0.6	3	0	6	0.7	5	0	0	0.9
	15 min	36	2.6	—	—	—	—	—	—	—	—
	20 min	—	—	39	2.7	30	0.6	—	—	—	—
	35 min	—	—	—	—	—	—	33	0.3	—	—
	90 min	—	—	—	—	—	—	—	—	46	0.6
	24 h <sup>b</sup>	95	39.5	96	40.8	33	1	42	0.4	54	0.7
C2	0 min	2	0	1	0	2	0	0	0	—	—
	20 min	33	0.9	—	—	—	—	—	—	—	—
	25 min	—	—	36	0.9	—	—	—	—	—	—
	35 min	—	—	—	—	20	0.5	17	0.1	—	—
	24 h <sup>b</sup>	89	6.5	50	0.8	26	0.4	13	0.1	—	—
	0 min	—1	0.4	2	0	0	0	—3	0.2	3	0
C3	15 min	21	1.3	—	—	—	—	—	—	—	—
	20 min	—	—	27	1.4	18	0.3	—	—	—	—
	35 min	—	—	—	—	—	—	8	0.2	—	—
	90 min	—	—	—	—	—	—	—	—	6	0
	24 h <sup>b</sup>	70	32	74	32.7	23	0.3	13	0.3	12	0
	0 min	—2	0.4	0	0	—2	0	1	0.4	1	0
C4	15 min	17	0.4	—	—	—	—	—	—	—	—
	20 min	—	—	15	0.5	4	0	—	—	—	—
	35 min	—	—	—	—	—	—	1	0.4	—	—
	90 min	—	—	—	—	—	—	—	—	—2	1.1
	24 h <sup>b</sup>	20	0.4	13	0.5	9	0	7	0.8	4	0
	0 min	—2	0.4	0	0	—1	0.2	2	0.2	1	0.3
C5	15 min	29	0.4	—	—	—	—	—	—	—	—
	20 min	—	—	36	1	29	0.6	—	—	—	—
	35 min	—	—	—	—	—	—	11	0.2	—	—
	90 min	—	—	—	—	—	—	—	—	24	0.8
	24 h <sup>b</sup>	36	2.6	45	10.5	25	0.4	21	0.8	28	0.8
	0 min	0	0.4	0	0	—5	0.2	4	0	—4	1.2
C6	15 min	17	0.4	—	—	—	—	—	—	—	—
	20 min	—	—	34	0	19	0.5	—	—	—	—
	35 min	—	—	—	—	—	—	16	0.2	—	—
	90 min	—	—	—	—	—	—	—	—	22	0.6
	24 h <sup>b</sup>	18	0.4	38	0.8	21	0.5	17	0.2	26	0.6

<sup>a</sup> See Experimental for further details. <sup>b</sup> Analysis of supernatant 24 hours after being decanted from the catalyst.



**Fig. 11** Room temperature hydrosilylation of oct-1-ene by methylchlorosilane catalysed by resin supported Pt complex **C11**. (Oct-1-ene–silane–Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene.

### Leaching behaviour

Considering the data for catalyst C1 in Table 7, in runs 1 and 3 hydrosilylation of oct-1-ene continues significantly over 24 h after the polymer catalyst is removed and the % isomerisation observed is simultaneously high, ~40%. In runs 5, 7 and 9 however hydrosilylation essentially stops when the heterogeneous catalyst is removed, and at the same time the level of isomerisation drops dramatically to ~1%. These results suggest that Pt leaching is significant in runs 1–3 (potentially also in run 4) and that thereafter leaching is minimal or absent. The data also provides powerful circumstantial evidence that it is leached soluble Pt species that are largely responsible for catalysing oct-1-ene isomerisation, and that the tightly bound heterogeneous

Pt complexes are active selectively in hydrosilylation. The picture for catalyst C2 is similar, while for C3 the level of leaching seems lower. In contrast the data for C4–C6 suggest that these resin catalysts leach very little Pt, or at least active Pt species. In these experiments therefore catalyst C6 is the best performer along with C5. These resins have the highest Pt loading (~0.75 mmol g<sup>-1</sup>) and a corresponding content of diamine ligand. Interestingly these species are identical except for the method of loading Pt. C5 was loaded in one-step, whereas C6 was loaded in 5 steps but using the same total quantity of Pt. It seems that the latter method produces a more uniform distribution of Pt complex and overall better immobilisation of the Pt. C1 and C2 are also identical species except for the same variation of method of loading. While Pt leaching is evident from both of these, C2, loaded in multiple steps seems somewhat better than C1.

The results using catalysts C7–C10 show similar trends (Table 8), although the rather variable data for C10 spoils the quality of the correlation. Why this is so is unclear. However, C7 clearly shows evidence of leaching active Pt species in runs 1–3, while C8 and C9 display low or negligible leaching.

These results must be borne in mind when considering the more extensive catalyst activity and selectivity data generated in the first series of experiments.

### Catalyst activity and selectivity in extensive recycling

**Catalysts C1–C6.** Very rewardingly the extensive catalyst recycling data for resin catalysts C1–C6 correlate well with the experimental data from the leaching studies. Catalysts C1–C3 show good activity over 10 cycles, and in the case of C1 the particularly impressive performance is retained throughout. All



**Table 8** Leaching evaluation of resin catalysts C7–C10 in the reaction of oct-1-ene with methylchlorosilane at room temperature<sup>a</sup>

Catalyst	Time	Run 1		Run 3		Run 5		Run 7		Run 9	
		Conv. (%)	Isom. (%)	Conv. (%)	Isom. (%)	Conv. (%)	Isom. (%)	Conv. (%)	Isom. (%)	Conv. (%)	Isom. (%)
C7	0 min	0	0	3	0	3	0.5	2	0.4	4	0
	20 min	49	0.8	—	—	—	—	—	—	—	—
	25 min	—	—	41	2.2	—	—	—	—	—	—
	45 min	—	—	—	—	59	1.1	—	—	—	—
	1 h	51 <sup>c</sup>	2.2 <sup>c</sup>	—	—	—	—	69	3.1	55	0.7
	2 h	—	—	—	—	—	—	—	—	—	—
	24 h <sup>b</sup>	79	10.6	96	24.8	80	5.2	87	13.4	60	0.7
C8	0 min	3	0	2	0.4	2	0.5	0	0.2	2	0
	20 min	29	0.2	—	—	—	—	—	—	—	—
	25 min	—	—	6	0.6	—	—	—	—	—	—
	1 h	—	—	—	—	28	0.4	—	—	—	—
	90 min	—	—	—	—	—	—	4	0.7	—	—
	2 h	—	—	—	—	—	—	—	—	41	0
	24 h <sup>b</sup>	33	1.3	8	0.6	7	0.5	11	0.9	5	0
C9	0 min	3	0	0	0	1	0.6	0	0.5	2	0
	25 min	—	—	24	0.7	—	—	—	—	—	—
	28 min	33	0.8	—	—	—	—	—	—	—	—
	1 h	—	—	—	—	35	0.5	—	—	—	—
	90 min	—	—	—	—	—	—	27	0.5	—	—
	2 h	—	—	—	—	—	—	—	—	20	0
	24 h <sup>b</sup>	39	0.8	40	3.4	42	2.4	45	2.3	24	0
C10	0 min	0	1.2	0	0.6	6	0.2	1	0.9	3	0
	25 min	—	—	43	0.8	—	—	—	—	—	—
	28 min	56	0.9	—	—	—	—	—	—	—	—
	45 min	—	—	—	—	57	1.1	—	—	—	—
	1 h	—	—	—	—	—	—	58	1.8	49	0.8
	24 h <sup>b</sup>	60	0.9	85	21.3	70	2.9	90	15	54	0

<sup>a</sup> See Experimental for further details. <sup>b</sup> Analysis of supernatant 24 hours after being decanted from the catalyst. <sup>c</sup> Analysis carried out as beads were noticed in the supernatant – beads removed thereafter.

three catalysts also show a significant level of isomerisation in runs 1–3 and thereafter isomerisation declines considerably. Clearly therefore in runs 1–3 catalysis arises primarily from immobilised Pt complexes but there is a contribution from leached soluble Pt species. Catalysts C1 and C2 were loaded originally with a 20 mol% excess of Pt relative to polymer ligand, and this may well have contributed to the early leaching with these two species. Beyond run 4, however, the evidence is that catalysis is overwhelmingly *via* the polymer supported Pt complexes. Catalyst C4 (Fig. 4) is again very active initially but beyond run 5 the activity falls dramatically. It is not clear why this is so but it may be associated with the onset of accessibility problems. The performances of C5 and C6 (Fig. 5 and 6) are very similar which is not surprising since they differ only in the method of loading the Pt. They are a little less active than C1 but nevertheless the activity is good and is maintained over 9 runs, with a low level of isomerisation. Overall however, C1 is the most active and long-lived of the C1–C6 catalyst series, and performs consistently better than our previous best polymer-supported species.<sup>14</sup> It has significantly higher surface area than the latter (~550 *versus* 100 m<sup>2</sup> g<sup>-1</sup>) and indeed has the highest surface area of the C1–C6 series. This result confirms our hypothesis<sup>15</sup> that surface area is a particularly important parameter in determining the activity of polymer-supported catalysts in these solventless reactions. Catalyst C1 also has the lowest Pt loading of the C1–C6 series (0.25 mmol g<sup>-1</sup>) which suggests that generating discrete isolated ligand PtCl<sub>2</sub> species is important in optimising the use of loaded Pt. However we have shown previously<sup>15</sup> that catalyst activity declines when the Pt loading becomes too low (~0.03 mmol g<sup>-1</sup>), at least in the case of a resin with modest surface area (~100 m<sup>2</sup> g<sup>-1</sup>). Clearly therefore resin surface area and Pt loading are both important, and in the latter context it remains unclear what proportion of the Pt complexes are actually active in catalysis. Some indirect evidence relevant to this was gleaned from additional experiments with catalysts C1 and C4. A sample of each of these was finely crushed in a mortar and pestle, and then used repeatedly in

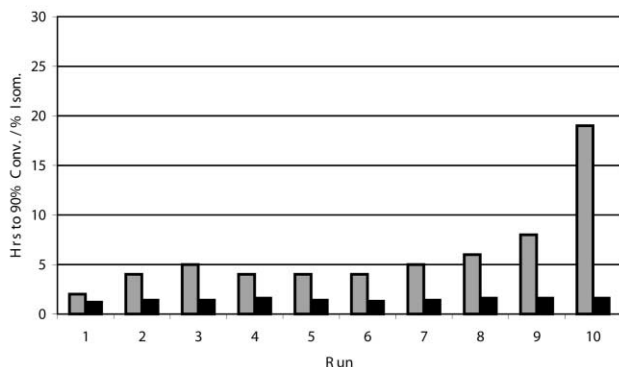
hydrosilylation reactions. With both catalysts the activity was higher than when the beaded form was used, ~100% conversion being reached typically in 30 min. With C1 the level of isomerisation was ~15%, whereas with C4 it was ~5%. With both crushed catalysts the reaction mixtures warmed a little when the catalyst was contacted, but the exotherm was by no means as severe as that with Speier's catalyst. The balance between hydrosilylation and isomerisation for each crushed catalyst sample is similar to that seen with the corresponding intact beaded samples and it seems therefore that crushing does expose catalyst sites previously inaccessible, but does not for example increase significantly the level of Pt leaching.

**Catalysts C7–C10.** The results for the second series of polymer catalysts, C7–C10, did not correlate as well with the data from the leaching studies as did the first series. Why this is so is not clear. Use of *n*-butyl acetate instead of toluene as the progen in synthesising the precursor resins would be expected to change the finer detail of the pore structure of the resins, but the dry state surface areas of the derived catalysts C7–C10 (Table 5) fall within a similar range to those of C1–C6, and so it is difficult to believe that this is a major factor. The poor correlation between the leaching studies and the recycling experiments almost certainly arises in part because of the 8 months storage time between the two series of experiments but why should the correlation be poorer for C7–C10 than for C1–C6? In the recycling experiments C7 is characterised by a high hydrosilylation activity (Fig. 7) but also a consistently high level of isomerisation. C8 on the other hand shows good catalytic activity which falls off a little beyond run 6, accompanied by a consistently low level of leaching (Fig. 8). C9 and C10 are very similar with good activity maintained over 10 cycles but in each case accompanied by significant levels of isomerisation, which appears to grow to a maximum at run 5 and thereafter decline again (Figs. 9, 10). Relative to the results of the leaching behaviour studies the biggest difference is in the level of isomerisation detected which in the leaching studies is consistently

low. A possible rationalisation lies in the mechanism of the deactivation which arises when the catalysts are stored without protection from the air.

### Long-term catalyst stability

Catalyst C10 was reassessed in extensive recycling tests 17 months after its synthesis and 14 months after the first extensive recycling tests (Fig. 10). The results are shown in Fig. 12. Two



**Fig. 12** Room temperature hydrosilylation of oct-1-ene by methyl-dichlorosilane catalysed by resin supported Pt complex **C10**. (Oct-1-ene–silane–Pt = 2 : 1 :  $1 \times 10^{-3}$ ). Left-hand bar = time to achieve 90% conversion; right hand bar = % isomerisation of alkene. Reassessment of recycling behaviour 14 months later than earlier assessment (Fig. 10).

major differences are clear. Firstly the activity in hydrosilylation is reduced a little and in particular falls off progressively with recycling. Perhaps more remarkably, however, the level of isomerisation is very low and remains so through all cycles. Overall this behaviour is more consistent with the results of the leaching experiments (Table 8) than with the data from the first recycling experiments (Fig. 10). Significantly the leaching experiments were also carried out 8 months later than the first recycling experiments. A very similar pattern of results was obtained when catalyst C7 was re-subjected to recycling experiments again, and then likewise with catalysts C5 and C9 (data not shown).

It is fairly clear therefore that storing the polymer-supported Pt catalysts (in air) in simple screw top sample bottles is not sufficiently adequate to maintain the catalysts in their original state. Most likely oxidation to PtO<sub>2</sub> occurs fairly readily, and interestingly one can speculate that PtO<sub>2</sub> formation might be faster with unbound or weakly bound Pt located on or near the resin surface. If we hypothesise further that oct-1-ene isomerisation occurs primarily *via* leached soluble Pt species, and that the most easily leached species are those located on or near the resin surface, then clearly selective oxidation of these species on storage in contact with air will reduce the isomerisation activity of the polymer catalyst. Intriguingly therefore the selectivity towards hydrosilylation of polymer bound Pt catalysts might well be improved by deliberate oxidation of surface located species. Alternatively if the original state of these catalysts needs preserving during long-term storage then the presence of a suitable inert (*e.g.* N<sub>2</sub>) or reducing atmosphere would be advisable.

### Catalyst washing experiments

In an attempt to confirm the picture that some weakly bound Pt is rapidly lost from polymer-supported species and that this component is largely responsible for much of the isomerisation observed a number of careful catalyst washing experiments were carried out using species C1. Firstly C1 was used under identical conditions to those in the earlier recycling experiments and the conversion to 1-octylmethylchlorosilane was >90% within 2 h with the level of isomerisation being ~13%. The

activity is therefore similar to that in the earlier experiments (Fig. 1) though the isomerisation is a little lower (the catalyst having been stored for some months – see previous section). The catalyst was then recovered and washed with three successive mixtures of oct-1-ene and *n*-nonane for 20, 10 and 13 h respectively, the composition and quantity of each wash mixture being the same as in a catalytic run (**but** with no silane present). Wash mixtures 2 and 3 each then received the appropriate quantity of methyl-dichlorosilane used in a normal reaction and the solutions monitored for any catalytic activity. Solution 2 showed a conversion to 1-octylmethylchlorosilane of ~90% in 4 h with a level of isomerisation of ~50%. The data for solution 3 were ~50% conversion in 4 h and ~23% isomerisation. Clearly therefore these wash solutions contain sufficient Pt to show reasonable hydrosilylation activity, and certainly good isomerisation activity. The washed sample of C1 was then used in a second reaction under standard conditions yielding ~90% conversion in 2 h with ~4% isomerisation. The washing procedure therefore leaves C1 as active in hydrosilylation as previously, but reduces the isomerisation very significantly (see Fig. 1). This tends to confirm therefore that the easily leached Pt in early runs contributes in a significant manner to the observed isomerisation.

A second washing experiment was also performed using C1. Firstly a catalyst sample was used under standard conditions and the conversion was 100% after 3 h with ~16% isomerisation. The catalyst sample was then recovered by decantation and washed for 5 min with each of 10 batches of oct-1-ene–*n*-nonane. The catalyst sample was then used in a second reaction under standard conditions and the conversion was >90% and isomerisation ~2% after 2 h. Thus the washing procedure almost eliminates isomerisation completely. Each of the wash solutions was also assayed for activity by addition of the appropriate amount of methyl-dichlorosilane. All proved to be active and though there was some variation in the data wash solution 1 gave ~100% conversion after 24 h with ~50% isomerisation, and these fell to ~50% conversion and ~20% isomerisation after 24 h with wash solution 10. These results therefore confirm those from the longer washing experiments and show that the isomerisation observed in the early runs with polymer-supported catalysts such as C1 arises mainly from reaction involving leached soluble Pt species. Washing tends to eliminate this component and at the same time reduces isomerisation with the polymer catalysts to very low levels.

### Conclusions

Polystyrene resins prepared with vinylbenzyl chloride comonomer and designed to be permanently porous with a high dry state surface area (~500 m<sup>2</sup> g<sup>-1</sup>) are readily aminated and yield good supports for Pt(II) chloro complexes. The so-formed polymer-supported Pt complexes are highly active and selective heterogeneous catalysts in the room temperature, solventless hydrosilylation of oct-1-ene using methyl-dichlorosilane. Though the hydrosilylation activity is lower than that of soluble Speier's catalyst, the activity is high, and certainly high enough to be a practical value in the laboratory, and potentially on a large scale. The polymer-supported catalysts can be easily recovered and re-used up to 10 times with useful activity. They also show a very much reduced tendency to isomerise oct-1-ene during hydrosilylation and so are significantly more selective than Speier's catalyst under the conditions employed. Careful control washing experiments have shown that the isomerisation that does arise with the polymer catalysts seems to derive primarily from Pt species leached from the support, and that isomerisation can be almost eliminated by appropriate washing. Polymer catalysts stored in contact with air in simple screw top sample bottles for many months remain active but the activity is reduced somewhat; most remarkably however such storage reduces considerably the isomerisation activity of the catalysts

most likely as a result of oxidation of weakly surface bound Pt to PtO<sub>2</sub> which effectively eliminates leachable active Pt species.

The catalyst displaying the optimum balance of activity, selectivity and recycling stability is C1. This has a surface area of ~550 m<sup>2</sup> g<sup>-1</sup>, a Pt loading of ~0.25 mmol g<sup>-1</sup>, a ligand–Pt ratio of ~1 : 1 and it outperforms those polymer catalysts of lower surface area that we have reported earlier.<sup>14,15</sup> We believe that we are now close to achieving the optimum combination of physical and chemical parameters in these polymer-supported systems. There remains, however, methodologies for pushing the surface area of resins beyond even the figure of ~550 m<sup>2</sup> g<sup>-1</sup>, and we are currently exploring this possibility.

## Experimental

### Materials

Styrene was supplied by Fisher Scientific and vinylbenzyl chloride (VBC) was secured from the Dow Chemical Company as a mixture of *para*- and *meta*-isomers in a ratio of 44% : 56%. Divinylbenzene (DVB) was supplied as 80% technical grade by Aldrich, again as a mixture of isomers (28% *para*- : 72% *meta*-), with the bulk of the remaining 20% being ethylvinylbenzene. The isomer ratios applicable to the VBC and DVB were determined *via* gas chromatography. Boric acid was supplied by BDH, Cellosize (QP4400L) by Hythe Chemicals. Xanthan Gum I (90/GV/233) by Kelco International and AIBN by BDH. Toluene was from BDH, *m*-xylene, *n*-butyl acetate, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 2-ethylhexanoic acid and 2-ethylhexan-1-ol were from Aldrich.

*n*-Nonane was supplied by Lancaster Chemicals, oct-1-ene was obtained from Avocado Research Chemicals Ltd., oct-2-ene was supplied by Lancaster Synthesis as a mixture of *cis*- and *trans*-isomers in a ratio of 74.9% : 24.1%, along with 1.0% oct-1-ene (determined *via* gas chromatography), and *trans*-oct-2-ene, *trans*-oct-3-ene and *trans*-oct-4-ene were from Aldrich. Methylchlorosilane was from Aldrich and 1-octylmethyl-dichlorosilane from Fluorochem.

Potassium tetrachloroplatinate was supplied by Johnson Matthey and hexachloroplatinic acid was from Aldrich, as was *N,N,N'*-trimethylethylenediamine. NaH (60%) stabilised in mineral oil and isopropanol (propan-2-ol) (HPLC) grade were from Aldrich. Cyclohexane, THF, acetone, dichloromethane and methanol were all bench reagents. THF was distilled from sodium–benzophenone. Cyclohexane, isopropanol, *n*-nonane and oct-1-ene were dried over molecular sieves.

### Synthesis of precursor resins PR1–PR14

These were all synthesised *via* suspension polymerisation using a procedure already reported in detail elsewhere.<sup>23</sup> The aqueous stabiliser system was based on a mixture of Cellulose, Xanthan gum and boric acid. The organic phase (100 cm<sup>3</sup>) comprised comonomers (50 cm<sup>3</sup>) and porogen (50 cm<sup>3</sup>) as indicated in Tables 1 and 2. AIBN (1% wt) was used as initiator and the polymerisations were carried out at 80 °C for 5 h while stirring at 600 rpm. Resin beads (typically 85–95%) were recovered by filtration and were washed copiously with water and acetone. The air dried resin was separated into various size fractions and that fraction in the range 212–300 μm was selected and exhausted extracted with acetone in a Soxhlet for 24 h before being vacuum dried at 40 °C for 24 h. VBC-containing products displayed a band at 1268 cm<sup>-1</sup> in the FTIR spectrum assigned to the –CH<sub>2</sub>Cl group. Elemental microanalytical data are summarised in Table 3.

### Amination of VBC resins

Initially the appropriate amount of *N,N,N'*-trimethylethylenediamine (TrMEDA) was charged into a cooled (0 °C) three-necked round-bottomed flask (100 cm<sup>3</sup>), fitted with a

condenser, containing dry THF (50 cm<sup>3</sup>). Under dry N<sub>2</sub>, the required amount of NaH was added and the mixture stirred for 15 min using an overhead stirrer. The appropriate precursor resin beads (4.0 or 5.0 g) were then added and the temperature raised to 60 °C. The mixture was then left stirring for 48 h, at this temperature, under N<sub>2</sub> gas. The quantities of TrMEDA and NaH used were such that a 1 : 3 : 3.3 molar ratio of resin benzyl chloride functionality : TrMEDA : NaH was present in the reaction mixture. The benzyl chloride contents of the precursor resins are shown in Table 2. The reaction was quenched in methanol (150 cm<sup>3</sup>), filtered and the beads washed with THF. The beads were then placed in dilute NaOH (2 M) for 1 h, with constant stirring, before extraction in a Soxhlet apparatus with water (24 h), and then THF (24 h) before vacuum drying. The FTIR spectra indicated a reduction in intensity of the CH<sub>2</sub>Cl band at 1268 cm<sup>-1</sup>, and the appearance of shoulders at 2774 and 2813 cm<sup>-1</sup> on the main CH bands assigned to the tertiary amine groups. The corresponding elemental microanalytical data are shown in Table 3.

### Loading of Pt to yield catalysts C1–C10 (Scheme 1)

Each aminated resin (2.0 g) was first wetted with THF (5 cm<sup>3</sup>) before being placed in a poly(ethylene) bottle along with the appropriate amount of potassium tetrachloroplatinate dissolved in doubly distilled water (200 cm<sup>3</sup>). The quantity of the platinate used was stoichiometrically equivalent to the diamine content of the aminated resin (AFR1–8) used, and was calculated from the values detailed in Table 2. The bottle was closed and the resulting mixture was shaken for 24 h at room temperature. The polymer-supported catalyst produced was collected by filtration, washed with water (doubly distilled) and acetone, and vacuum dried at 40 °C for 24 h. The elemental microanalytical data for all the supported catalysts (C1–10) are shown in Table 4.

In the case of catalysts C2 and C6 the method of loading of Pt was modified. The total amount of platinate used was calculated as before but the feed solution was divided into 5 equal portions and each portion added to the resin over an extended period of time. Successive portions were added when the solution cleared after the addition of the previous portion. Since control precursor resin PR10 contained no ligand a typical quantity of platinate was used in the loading procedure *i.e.* 0.498 g (1.20 mmol) for 2.0 g of resin. The experimental details were otherwise as before.

### Platinum analysis

A sample of polymer catalyst (~100 mg) was weighed accurately into either a silica or alumina crucible. The crucible, without its lid, was then placed in a muffle furnace and the temperature raised to 300 °C at a rate of 2.0 °C min<sup>-1</sup>. The temperature was then raised further, at a slower rate (0.5 °C min<sup>-1</sup>), until it reached 600 °C. This temperature was maintained for 6 h before the crucible was allowed to cool. Aqua regia (5 cm<sup>3</sup>) was added to the dark residue, at room temperature, and the crucible (with its lid fitted) returned to the furnace and heated to 110 °C where it was held for 1 h. The resulting clear yellow solution was diluted to 25 cm<sup>3</sup> then assayed by ICP AAS.

Polymer resin catalysts were also subjected to elemental microanalysis and the results of this and the Pt analysis are summarised in Table 4.

### Homogeneous hydrosilylation reactions

Homogeneously catalysed hydrosilylations using *Speier's* catalyst (Scheme 2) were carried out in 8 cm<sup>3</sup> Pyrex vials which were equipped with tight fitting screw caps. The reaction mixtures consisted of methylchlorosilane (1.15 g, 10 mmol), *n*-nonane (1.0 g, 7.8 mmol) and oct-1-ene (and occasionally oct-2-ene) (2.24 g, 20 mmol). The *n*-nonane was used as the internal

reference for GC analysis. The appropriate amount of catalyst was added at time zero corresponding to the desired silane–Pt molar ratio of 1 :  $1 \times 10^{-3}$ . A 5% w/w  $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$  in isopropanol catalyst was used. The vial was then shaken using a Stuart Scientific shaker and the mixture was left to react under ambient conditions. The reaction was followed by gas chromatography.

### Heterogeneous hydrosilylation reactions

These were carried out essentially as described for the homogeneous reactions although in this case the appropriate amount of the resin catalyst corresponding to a molar ratio of silane–Pt of 1 :  $1 \times 10^{-3}$  was weighed initially into the vial. The reaction mixture was then added at time zero and the above procedure followed.

### Catalyst recycling reactions

In these experiments the performance of a sample of each catalyst C1–C10 was evaluated in up to 10 back-to-back catalytic reactions. After each run was complete the supernatant liquid phase was carefully decanted from the reaction vial, taking care that all of the resin catalyst beads remained behind in the vial. The sample of catalyst was then recycled by adding a fresh reaction mixture. The quantities of materials were standardised as described above and each reaction was monitored by GC.

### Catalyst leaching reactions

Initially, a fresh reaction mixture and catalyst resin were added to a reaction vial (as detailed above) and then shaken for a previously decided length of time, this being long enough for an intermediate conversion to be achieved. At this point the reaction mixture was sampled for analysis in order to assess the progress of the reaction. The supernatant (liquid phase) was then decanted into a second vial, taking care that no resin catalyst beads were also removed. The second vial was then shaken for 24 h before being analysed to check whether further conversion had occurred. Simultaneously, over the same 24 h period, the original vial containing the heterogeneous catalyst (along with a fresh reaction mixture) was also put through another catalysis cycle. This whole procedure was then repeated until each catalyst sample had catalysed either eight or ten different hydrosilylations.

### Control reactions

In those recycling experiments using crushed resin catalysts it was necessary to centrifuge reaction mixtures (3000 rpm, 30 min) to effect separation of the catalyst particles.

In those recycling experiments where the catalyst resin beads were washed between successive runs two procedures were employed. In the first, recovered catalyst from decantation of the previous reaction mixture was washed successively with three oct-1-ene–nonane mixtures of the same composition and volume as those used in a reaction. The wash solutions were left in contact with catalyst for 20, 10 and 13 hours respectively. Again separation was by decantation. In the second method recovered catalyst was washed successively with ten oct-1-ene–nonane mixtures as above each for 5 min only.

### 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.  $\text{N}_2$  BET analyses were performed using a Micromeritics ASAP 2000 instrument. FTIR spectra were collected using a Nicolet

Impact 400D instrument using 10 scans at a resolution of  $4 \text{ cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses were recorded using a 400 MHz Bruker DPX-400 spectrometer.

GC analysis of each hydrosilylation reaction was carried out using initially a Fisons DP 1701 ( $30 \times 0.32 \times 0.25$ ) silica capillary column and later a Chrompack CP-SIL 19CB ( $30 \times 0.32 \times 0.25$ ) silica capillary column. These were mounted on a Carlo Erba HRGC 5300 Mega Series instrument fitted with a flame ionisation detector. Hydrogen was used as the mobile phase and *n*-nonane was used as an internal reference standard. Samples were prepared for injection by dripping one drop of the appropriate reaction mixture into  $1 \text{ cm}^3$  of cyclohexane and  $0.2 \mu\text{l}$  of this mixture was injected and analysis run using a two minute temperature program [ $60 \text{ }^\circ\text{C}$  (1 min)  $\rightarrow$   $100 \text{ }^\circ\text{C}$  (at  $40 \text{ }^\circ\text{C min}^{-1}$ )]. It was necessary to calibrate the GC instrument at regular intervals to maintain accuracy.

Confirmation of the identity of the hydrosilylation product was also carried out *via* GC analysis. Samples were prepared for injection by dripping one drop of the appropriate spent reaction mixture into  $1 \text{ cm}^3$  of cyclohexane;  $0.5 \mu\text{m}$  of this mixture was then injected and analyses run using a ten minute temperature program [ $50 \text{ }^\circ\text{C}$  (1 min)  $\rightarrow$   $200 \text{ }^\circ\text{C}$  (at  $25 \text{ }^\circ\text{C min}^{-1}$ ; maintained for 3 min)].

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