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Polymer supported ferrocene derivatives. Catalytic hydrosilylation of olefins by supported palladium and platinum complexes

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Abstract

Platinum and palladium derivatives of polymers functionalized with the ferrocene derivatives 1-ferrocenylethyldimethylamine (**3**), 1,1′-bis(diphenylphosphino)ferrocene (**4**), *N,N*-dimethyl-1-(2-diphenylphosphinoferrocenyl]ethylamine (**5**), and (*S,R*)-**5** are effective catalysts for the hydrosilylation of olefins such as styrene and 1-hexene by trichlorosilane. They can be recycled with no loss of activity. The palladium derivatives catalyze stereoselective α-addition to styrene and the optical yield using (*S,R*)-**5** is 15.2%. The stereoselectivity remains the same but the optical yield drops on recycling. All other reactions studied result in addition to the terminal carbon atom of the olefin. The absence of ligand effects indicates that the platinum derivatives are reduced to catalytically active metal.

The method used for the binding of chiral **5** to the polymer probably results in the induction of chirality at the linking carbon atom, polymer–**C*HOH–(ferrocene derivative).

Introduction

The hydrosilylation of carbon–carbon multiple bonds and carbon–oxygen double bonds, catalyzed homogeneously by transition metal complexes, has been studied extensively for many years [1–4]. In particular, metal derivatives of ligands based on the ferrocene skeleton [5–10] have been used as catalysts and in some cases give higher stereoselectivity than other chiral phosphine transition metal complexes [5].

Polymer supported, "heterogenized", metal catalysts have been employed in many reactions such as hydrosilylation, hydrogenation, and hydroformylation [11–13] but there are few reports on the use of supported chiral metal catalysts in asymmetric synthesis [11–14] and most of this work relates to olefin hydrogenation. The asymmetric hydrosilylation of ketones, eq. 1, is catalyzed by rhodium deriva-

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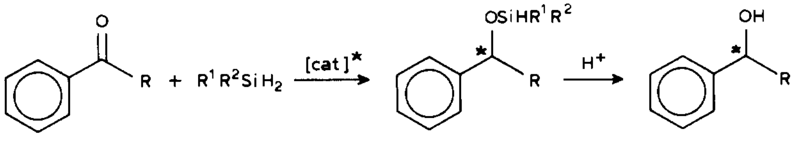
tives of polystyrene containing the optically active di(tertiary phosphine) DIOP [15,16]. In the case of acetophenone (**1**, R = CH_3), optical yields up to 58% are obtained using α-naphthylphenylsilane (**2**, R^1 = Ph, R^2 = α-naphthyl). The same reaction has been studied using chiral rhodium(I) complexes bound to inorganic supports such as silica and glass [17], the optically yields obtained are much lower (0.4–19.7%).



(1)

(1) (2)

The objective of the present work was to study the catalytic hydrosilylation of olefins by palladium and platinum complexes of polymer supported ferrocene derivatives since, to our knowledge, there have been no reports on the use of ferrocene derivatives, either chiral or achiral, to this end.

Experimental

General procedures

Unless otherwise stated all air or moisture sensitive materials were manipulated under a nitrogen atmosphere. Trichlorosilane, styrene and 1-hexene were purchased from Aldrich. The olefins were passed through a neutral alumina column prior to hydrosilylation. Reaction products were identified on the basis of their retention times on 20% SE-30 20M Carbowax columns fitted to a Hewlett Packard Model 5880A gas chromatograph, and by their known ^1H NMR spectra. Optical rotations were recorded in a 1 dm cell using a Perkin–Elmer 141 spectrometer. Microanalyses were performed by Mr. P. Borda of this department and the Canadian Microanalytical Service, Vancouver. Mössbauer spectra were recorded and processed as described previously [18]. Isomer shifts are listed relative to iron foil. The SUPER-COSY NMR experiment was carried out as described for other ferrocene derivatives [19].

Preparation of polymer supported ferrocene derivatives and their palladium and platinum complexes

*Polymers-I, -II and -III and -III**

Polymers-I, -II and -III were prepared, respectively from ferrocene derivatives **3**, **4** and **5** by reaction of the appropriate lithium derivatives with aldehyde functionalized cross linked polystyrene [20].

The preparation of the previously unreported chiral version of polymer–III, polymer–III*, is given as an example. (*S*)-*N*,*N*-dimethyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine, (*S*,*R*)-**5** (1.76 g, 4 mmol) was dissolved in anhydrous diethyl ether (50 ml). To this solution n-butyllithium in hexane (2.5 ml, 1.6 *M*, 4 mmol) was added and the mixture was stirred for 2 h before the addition of a mixture of TMED, tetramethylethylenediamine, (0.5 g, 4 mmol) and n-butyllithium in hexane (2.5 ml, 1.6 *M*, 4 mmol). The reaction mixture was left stirring for 2 d, after which 50 ml of THF was added followed by the aldehydic polymer [21] (1.35 g, 4 mmol). The mixture was further stirred for 4 d at 20 ° C. Following hydrolysis with deionized water, the resin was collected on a glass filter and washed successively (3 ×) with water, ethanol, acetone, THF, CH_2Cl_2, hexane and diethyl ether. The resin was dried at 100 ° C under vacuum. Mössbauer δ 0.55, Δ 2.25. Anal. Found: N, 0.40; P, 0.94; Fe, 1.50.

*Pd^{II} derivatives of polymers-I to -III**

The preparation of the new derivative polymer–III*–Pd is given as an example. Polymer–III* (1 g) was added to an acetone solution (30 ml) of $Na_2PdCl_4 \cdot 4\ H_2O$ (0.11 g, 0.3 mmol) with stirring. The mixture was stirred and refluxed for 2 h. The orange brown palladium complex, polymer–III*–Pd, was then filtered off, washed and dried as above. Mössbauer δ 0.57, Δ 2.38. Anal. Found: N, 0.43; Cl, 1.95; P, 0.94; Pd, 2.23%.

*Pt^{II} derivatives of polymers-I to -III**

Polymer–I (1 g) was added to a CH_2Cl_2/H_2O solution (30 ml) of K_2PtCl_4 (0.12 g, 0.3 mmol) with stirring. The mixture was stirred and refluxed for 5 h. The brown black platinum complex, polymer–I–Pt, was then filtered off, washed, and dried as above. Mössbauer δ 0.53, Δ 2.44. Anal. Found: N, 0.84; Cl, 1.25; Pt, 3.81%.

The dark brown platinum complex of polymer–II, –II–Pt, was prepared analogously from polymer–II (1 g) and K_2PtCl_4 (42 mg, 0.1 mmol). Mössbauer not observed. Anal. Found: Cl, 0.20; P, 0.17; Pt, 0.59%.

Similarly dark brown polymer–III–Pt was prepared from polymer–III (0.4 g) and K_2PtCl_4 (42 mg, 0.1 mmol), Mössbauer δ 0.57, Δ 2.29. Anal. Found: N, 0.30; Cl, 0.62; P, 0.64; Pt, 1.99%.

*Reaction of the dilithio derivative of (S,R)-**5** with benzaldehyde. Preparation of **6b** and **7b***

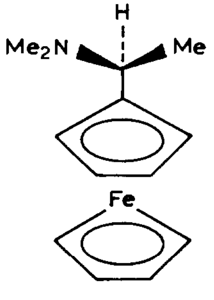
(*R*,*S*)-**5** (enantiomeric purity 85%) (0.88 g, 2 mmol) was dissolved in anhydrous diethyl ether (30 ml). To this solution n-butyllithium in hexane (1.25 ml, 1.6 *M*, 2 mmol) was added and the mixture was stirred for 2 h before the addition of a mixture of TMED (0.25 g, 2 mmol) and n-butyllithium in hexane (1.25 ml, 1.6 *M*, 2 mmol). The reaction mixture was stirred for 2 d, then freshly distilled benzaldehyde (0.21 g, 2 mmol) in hexane (10 ml) was added. The mixture was further stirred for 4 d at room temperature and then hydrolyzed with deionized water. The organic layer was separated and dried ($MgSO_4$). The solution was filtered, the $MgSO_4$ washed with diethyl ether, and the combined organic solution was concentrated to leave a red-brown oil. Chromatography (neutral alumina, diethyl ether eluant) afforded **5** (80%) followed by **6b** and **7b** (~ 20%).

Hydrosilylation of olefins

General procedure. The appropriate amount of the polymer bound metal complex was suspended in the olefin in a Carius tube under N_2. Trichlorosilane was added, the tube was closed with a Teflon valve and the mixture was kept at the appropriate temperature with stirring. After the reaction time the resin was filtered off in air, washed successively (3 ×) with acetone and diethyl ether and dried under vacuum before reuse. The reaction mixture was analyzed by gas chromatography. When necessary the product 1-phenylethyltrichlorosilane was converted to the alcohol 1-phenylethanol using the literature procedure [10].

Results and discussion

Ferrocene and substituted ferrocene derivatives such as the useful ligands **3**, **4**, and **5** [5,7] can be attached to cross-linked polystyrene polymers using the procedures outlined in eqs. 2 and 3 [20]. The aldehydic polymer is easily prepared from the chloromethylated polystyrene (Merrifield resin) by DMSO oxidation [21]. The polymers used in the present investigations were prepared as described in eq. 3. Thus polymer-I was synthesized from the monolithio derivative of **3**, polymer-II from the polylithio derivative of **4** (mainly hetero ring disubstituted and therefore diastereomeric because of planar chirality [22], and polymer-III from the mainly hetero ring dilithio derivative of **5** [22]. In the present investigation the ditlithio derivative of chiral **5**, (S,R)-**5**, was used to prepare polymer-III*. The Mössbauer parameters of the iron doublet observed for polymer-III* (δ 0.55, Δ 2.25) are typical of a ferrocene derivative [23] and compare well with the earlier parameters from polymer III (δ 0.53, Δ 2.37) giving a measure of the reproducibility of the experimental procedures used. This methodology was developed to encourage polymer attachment to the bottom, unsubstituted, ring of **5** (Scheme 1) **6**a. The microanalytical data from the two preparations, from **5** and (S,R)-**5**, also agree well indicating comparable loadings.



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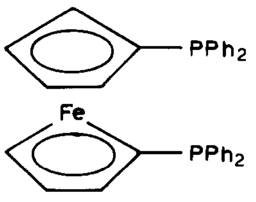

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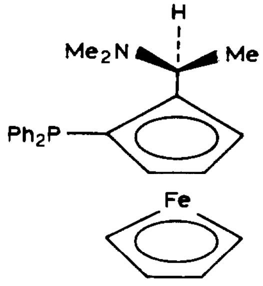

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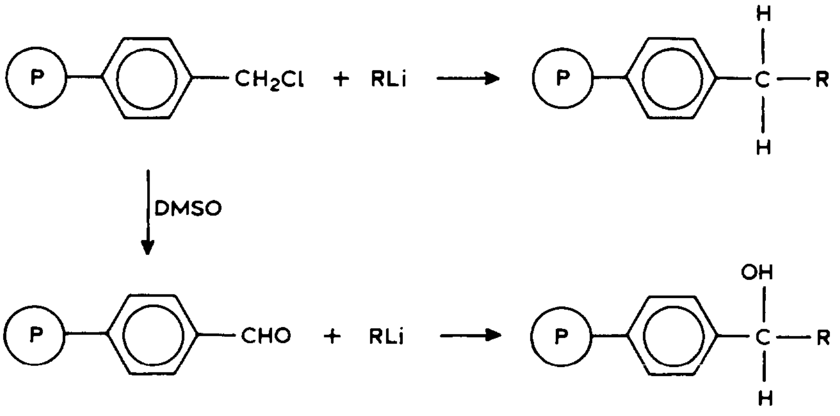

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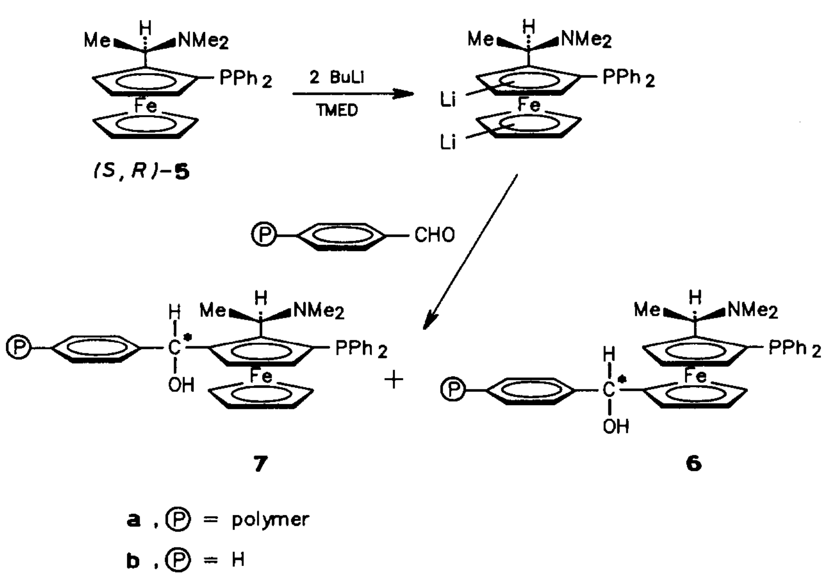


Scheme 1

The reaction of the dilithio derivative of chiral **5** with benzaldehyde was studied as a model for the polymer attachment reaction of eq. 2. This was done in an attempt to establish if the attachment would be primarily at the "bottom" ring as in **6**a (Scheme 1) and to establish if there was any chiral induction in the coupling reaction leading to a chiral polymer–*CH(OH)–(ferrocene derivative) link. The reaction of Scheme 1 was carried out with a sample of (*S*,*R*)-**5** of 85% enantiomeric purity, (as judged by the optical rotation of the amine precursor), under the same conditions used for the polymer coupling reaction. A considerable amount (80%) of **5** was recovered. One other band was isolated following column chromatography. This is probably a mixture of **6b** and **7b** resulting from bottom and top ring substitution, respectively. The most likely position of attachment in the case of **7b** is the one shown, adjacent to the amine substituent [24]. There is no evidence of substitution in both top and bottom rings.

A SUPERCOSY 2-D plot [19,25] of the cyclopentadienyl region of the ^{1}H NMR spectrum of the mixture of **6b** and **7b** is shown in Fig. 1. The off diagonal element indicate the connectivities. A low resolution one-dimensional spectrum is displayed along the chemical shift axis; better spectra were used to interpret the information garnered from the Figure. Even at the resolution shown it is obvious that the truncated peak at ~ 3.8 ppm is associated with a ferrocene derivative with an unsubstituted C_5H_5 ring i.e. **7b**. Simple area measurements reveal that the ratio of **6b** to **7b** is ~ 3/1 confirming that bottom ring reaction, and presumably attachment as in **6a**, predominates.

In order to establish if there is any asymmetric induction at the new asymmetric center produced during the reaction, the –CH(OH)– link, it is necessary to identify peaks in the NMR spectrum associated with particular diastereomers. Compound **6b** has two substituted rings containing four and three protons respectively. If

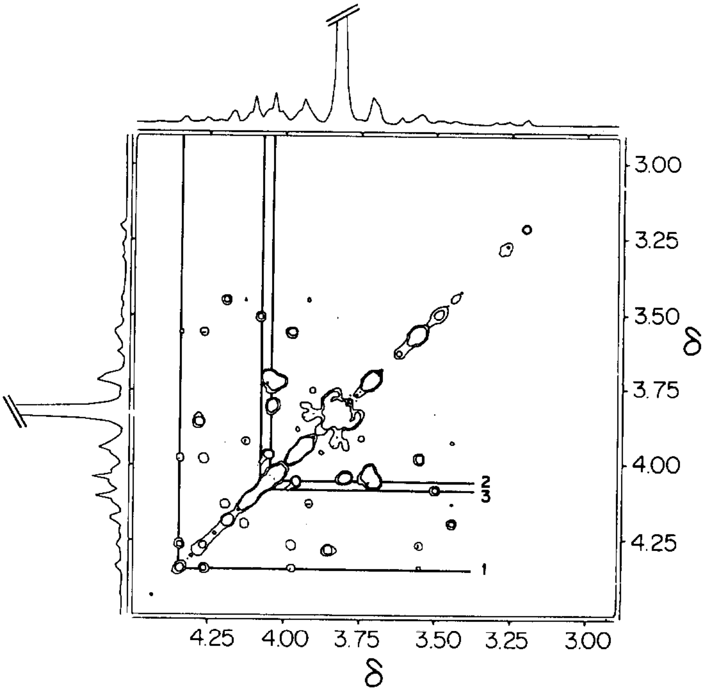


Fig. 1. 400-MHz SUPERCOSY contour plot of the cyclopentadienyl region of the proton NMR spectrum of a mixture of **6** and **7**.

diastereomers are present (a combination of the new asymmetric carbon center with the asymmetric center and plane of chirality of **5**) there should be two sets of signals associated with these protons. The plot of Fig. 1 shows two clear sets of four resonances, lines 1 and 2, which belong to compounds with monosubstituted ferrocenyl groups, i.e. diastereomers of **6b**. Measurement of the high resolution spectrum of the mixture reveals that the area ratio of peaks on lines 1 and 2 is approximately 85/15 which is essentially the same as the optical purity of the starting reagent (*S*,*R*)-**5**. This result shows that the new chiral center in **6b** is produced with ~ 100% induction. Presumably this result is transferable to the polymer bound species **6a**.

In order to establish a similar value for asymmetric induction in the formation of **7b** it is necessary to identify the sets consisting of two and five protons. Unfortunately, although sets of two resonances such as on line 3, Fig. 1, can be distinguished, none of these peaks in the spectra are suitable for area measurement because of spectral over-lap. Not unexpectedly, the peak due to the unsubstituted C_5H_5 ring is unsplit.

An asymmetric induction of ~ 100% has been found for the reaction of the monolithio derivatives of **3** with $PPh(CMe_3)Cl$, however, Ugi and coworkers [26] have reported little induction in the reaction of the same lithio derivative with anisaldehyde. Thus it is difficult to estimate the extent of induction, if any, on producing **7b** and, by extension, **7a**. However, it could be considerable.

The polymer bound ferrocene derivatives all react with K_2PtCl_4 to give dark

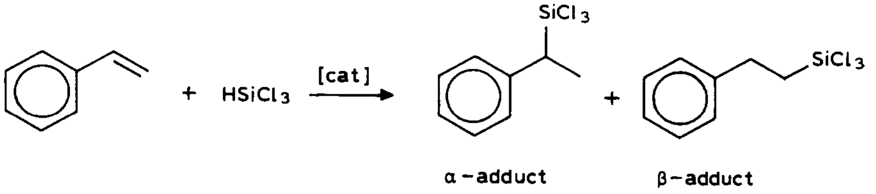
$$\text{Polymer-Y} \xrightarrow[K_2PtCl_4]{Na_2PdCl_4\text{ or}} \text{Polymer-Y-M} \qquad (4)$$

(Y = I, II, III or III*) (M = Pd or Pt)

colored resins with incorporation of Pt and Cl as judged from the microanalytical data. In the case of polymer–I–Pt (from **3**), the N/Pt ratio is 3/1 indicating that not all nitrogen atoms bind to the metal. A similar excess of NMe_2 groups appears to be present in the Pd^{II} derivatives polymer–I–Pd [20] prepared as in eq. 4. The Pt/Cl ratio of ~ 1/2 is in agreement with a conventional L_2PtCl_2 formulation. This same ratio is found for the other two supported platinum(II) derivatives. The Mössbauer parameters are essentially unchanged in the series polymer–I, polymer–I–Pd, polymer–I–Pt showing that no oxidation of the iron takes place during the metal binding reactions [20,23]. The loading of ligand in polymer–II is low [20] and the Mössbauer spectra of the polymer and its metal derivatives are not useful. The microanalytical data yield a ~ 2/1 ratio for P/Pt indicating a chelate structure as is found for many metal derivatives of this ligand [27,28]. In the case of polymer–III–Pt, the P/Pt ratio is again 2/1 and, as mentioned above, the Pt/Cl ratio is ~ 1/2. These data suggest that the ligand is not using the NMe_2 group to bind to the metal in these materials even though the free ligand **5** is P...N bound in its platinum(II) complexes [6]. This P · · · N mode of binding is also seen in the palladium(II) derivatives of **5** [29] and appear to be maintained to some extent in the polymer supported version, polymer–III*–Pd, since the P/Pd ratio is 1.45/1. A similar ratio was found for polymer–III–Pd [20]. Mössbauer parameters for all derivatives of polymer–III are very little different from those of the polymer.

Hydrosilylation of olefins catalyzed by supported palladium and platinum complexes

Many group VIII metal complexes particularly those of the nickel triad homogeneously catalyze the hydrosilylation of styrene by trichlorosilane, eq. 5. The product is either 1-phenylethyltrichlorosilane (α-adduct) or 2-phenylethyltrichlorosilane (β-adduct) or a mixture of the two [2,3]. Normally palladium(II) derivatives catalyze the formation of predominantly the α-adduct; β-adducts result from reactions catalyzed by other metal derivatives such as platinum(II) and nickel(II) [3].



(5)

In the present investigation, we find that polymer–II–Pd and –III–Pd are active catalysts for the hydrosilylation of styrene (Table 1). As could be anticipated the α-adduct is the major product at 70–90 °C with some β-adduct being formed at lower temperatures. Polymer–I–Pd is less active as a catalyst for the same reaction, although the α/β ratio is still high. Other examples are known [30–32] when palladium derivatives supported on O, N, and CN functionalized polymers show low activity as hydrosilylation catalysts. The present results seem to be in line with

Table 1

Hydrosilylation of styrene by $HSiCl_3$ catalyzed by supported palladium complexes [a]

Run	Complex	Temp. (°C)	Time (h)	Adduct yield (%) [b]	Adduct ratio (α/β) [c]
1	III–Pd	40	48	45	95/5
2	III–Pd	70	48	99	98/2
3	III–Pd	70	24	90	99/1
4	III–Pd	90	48	100	100/0
5	III–Pd	90	24	100	100/0
6	II–Pd	70	48	100	95/5
7	recycle-run 6	70	48	100	96/4
8	recycle-run 7	70	48	100	100/0
9	recycle-run 8	70	48	100	100/0
10	I–Pd	70	48	38	96/4

[a] Olefin, 5 mmol; $HSiCl_3$, 6 mmol; olefin/Pd = 1000. [b] GLC yield based on starting olefin. [c] The ratio of 1-phenylethyltrichlorosilane to 2-phenylethyltrichlorosilane.

the report that phosphine ligands are necessary to produce homogeneous hydrosilylation catalysts from palladium(II) salts [33].

Palladium metal is reported [33] to be inactive as a catalyst for olefin hydrosilylation so presumably reduction to the metal can be eliminated as the origin of the catalytic effect.

In the case of polymer–II–Pd, this catalyst can be used at least five times without loss of activity. It is interesting to note that the regioselectivity of the catalyst actually increases after the first recycling resulting in the formation of the α-adduct exclusively.

When polymer–II–Pd and –III–Pd are recovered after use, their color is lighter. In order to investigate this, polymer–II–Pd was recovered by filtration after a reaction, carefully washed (acetone, diethyl ether) and dried at 100°C under vacuum. The microanalytical data [34*] reveal no significant change apart from an increase in the chlorine content, indicating that there probably is a reaction between the palladium complex and trichlorosilane during the initial catalyzed reaction [33,35], this could be at the –CHOH– link. There is also the possibility of formation of new catalytic species following air exposure during recycling [16]. Either or both of these could account for the progressive lowering of optical yields during recycling experiments, as will be described below.

All three supported platinum complexes are active catalysts for styrene hydrosilylation (Table 2) and in this connection it is important to note that the olefin/metal ratio for the palladium catalyzed reaction in Table 1 is 1000/1, whereas, the ratio used for the reactions in Table 2 is 10,000/1. The products are the β-adducts exclusively, which is a dramatic, but not unexpected [3], demonstration of the effect of changing the central metal in a catalyst, although, as will be discussed below, different species may be involved. The selectivity remains unchanged on recycling the catalyst and it is also unaffected by changing the olefin/silane ratio [2].

The three polymer supported platinum catalysts change color to greenish brown

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* Reference number with asterisk indicates a note in the list of references.

Table 2

Hydrosilylation of styrene by $HSiCl_3$ catalyzed by supported platinum complexes [a]

Run	Complex	Temp. (°C)	Adduct yield (%) [b]	Adduct ratio (α/β) [c]
1	III–Pt	70	97	0/100
2 [d]	III–Pt	70	96	0/100
3	III–Pt	90	100	0/100
4	recycle-run 3	90	95	0/100
5	II–Pt	70	96	0/100
6	I–Pt	70	99	0/100

[a] Olefin, 5 mmol; $HSiCl_3$, 6 mmol; olefin/Pt = 10,000; time, 24 h. [b,c] See footnote in Table 1. [d] Olefin, 10 mmol; $HSiCl_3$, 5 mmol.

after use. Perhaps this is an indication of reduction to metal in each case and could account for the similarity of their catalytic activity (Pt/C is a known hydrosilylation catalyst [36]), however, there is a report which does not support this contention [37].

Asymmetric hydrosilylation of styrene

Kumada and coworkers found that the palladium(II) complex of (*R*,*S*)-**5** is a homogeneous catalyst for the reaction of trichlorosilane with olefins in good optical yield (52%) [10]. Since the same reaction is catalyzed with high regioselectivity by polymer–III–Pd. It was of interest to establish the effectiveness of polymer–III*–Pd in this regard.

The α-adduct from styrene can be converted to 1-phenylethanol using the sequence shown in eq. 6 [10], where MCPBA = *meta*-chloroperbenzoic acid (Table 3). These reactions proceed with retention and the alcohol isolated following the use of polymer–III*–Pd as catalyst is (*R*)-1-phenyl-ethanol with an optical yield of 15.2%. This is less than the 52% obtained in the homogeneous system. The absolute configuration of product, (*R*), is the same as would be anticipated from the results of the homogeneous reaction [10]; however, this is not always the case [17,38].

There is a general observation that lower optical yields are usually found for hydrogenation [12], and hydrosilylation [11,16,17], when heterogenized versions of homogeneous catalysts are used. It is possible that the present results afford another

Table 3

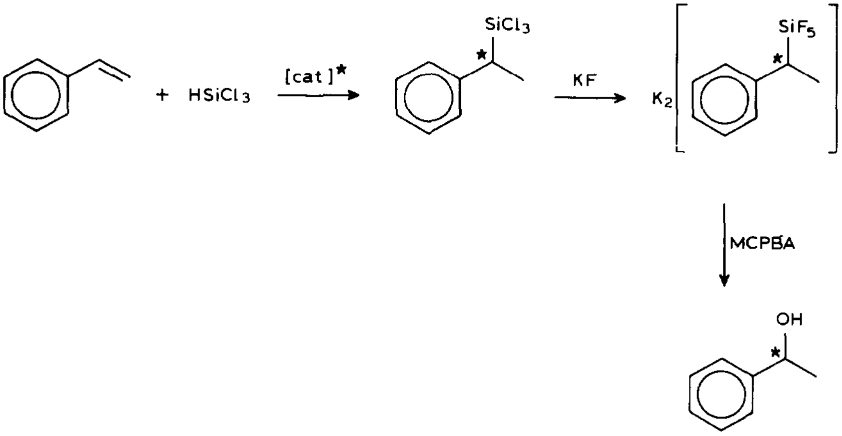
Asymmetric hydrosilylation of styrene by $HSiCl_3$ [a]

Run	Complex	Adduct yield (%) [b]	Ratio adduct (α/β)	Optical yield (%) [c]
I	III*–Pd	100	100/0	15.2 (*R*)
2	recycle-run 1	100	100/0	8.5 (*R*)
3	recycle-run 2	100	100/0	8.0 (*R*)

[a] Styrene, 25 mmol; $HSiCl_3$, 30 mmol; styrene/Pd = 1000; Temp. 70°C; time, 48 h. [b] GLC yield based on starting olefin. [c] Optical yields are calculated with respect to optically pure 1-phenylethanol, $[\alpha]_D$ $-52.5°$ (c 2.27, CH_2Cl_2), U. Nagar, T. Shishido, R. Chiba and H. Mitsushashi, Tetrahedron, 21 (1965) 1701. Configuration is given in brackets.

example of the generality. However, there are at least three other possible rationalizations. Firstly, it is possible that the metal in polymer–III*–Pd is not always P · · · N bound (see above) so a reduction in optical yield might be anticipated on the basis that chelating asymmetric ligands are more effective in producing higher optical yields. Secondly, the results of the NMR experiments described above indicate the presence of an asymmetric center in the link to the polymer; this could affect the optical yield [39] (indeed the –CHOH– group could even be involved in binding the metal). Thirdly, the ligand is bound to the polymer primarily as in 6a but probably some 7a is present. This again reduces the similarity between the homogeneous and supported catalysts.

On recycling polymer–III*–Pd (Table 3) the same regioselectivity is found but the stereoselectivity diminishes. This provides further evidence for catalyst modification during recycling as discussed above. The results do indicate that the ligand plays an important part in the catalytic cycle and hence reduction of the complex to metal during the reaction seems unlikely.



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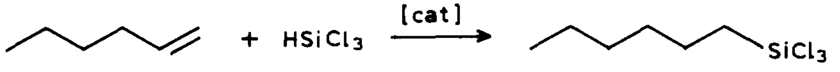
Hydrosilylation of 1-hexene

All six catalysts, polymer–Y–M, catalyze the hydrosilylation of the unactivated olefin, 1-hexene (Table 4). As is usually found, 1-trichlorosilylhexane, the terminal adduct, is the only product, eq. 7, under the same conditions as developed for the hydrosilylation of styrene, eq. 5.

Again the palladium complexes are less active than their platinum counterparts. The uniform reactivity of the latter derivatives, however, again suggests that platinum metal may be involved.



(7)

In summary palladium and platinum complexes of polymer supported ferrocene derivatives are effective catalyst precursors for the hydrosilylation of olefins by trichlorosilane. The catalysts can be easily separated from the reaction mixture by simple filtration and can be reused without loss of activity. In the case of the platinum based polymers it is likely that platinum metal is the actual catalyst. The

Table 4

Hydrosilylation of 1-hexene by $HSiCl_3$ [a]

Run	Complex	Olefin/M	Product yield (%) [b]
1	III–Pd	1,000	15
2	II–Pd	1,000	26
3	I–Pd	1,000	0
4	III–Pt	10,000	95
5	II–Pt	10,000	95
6	I–Pt	10,000	94

[a] Olefin, 5 mmol; $HSiCl_3$, 6 mmol; time 24 h; Temp. 70 ° C. [b] GLC yield of 1-trichlorosilylhexane based on starting olefin.

pronounced effect of the attached ligand in the palladium based catalysts, indicates that free metal is not involved in these cases.

Acknowledgements

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