Immobilization of a Platinum Catalyst Using the Polymer Incarcerated (PI) Method and Application to Catalytic Reactions

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Abstract: Immobilization of a platinum catalyst was carried out on the basis of the polymer incarcerated (PI) method. The PI platinum catalyst thus prepared showed high activity in hydrosilylation, and recovery and reuse of the catalyst were attained without loss of activity. Application of this catalyst to hydrogenation is also reported.

Key words: immobilization, platinum, polymer, hydrosilylation, hydrogenation

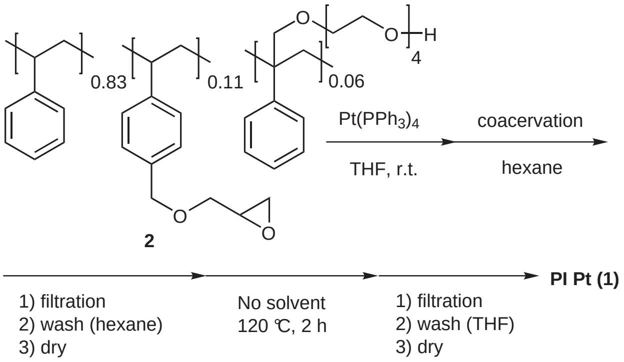

Figure 1 Polymer-incarcerated method

Hydrosilylation of alkenes and alkynes is not only an important industrial process, but also provides very useful synthetic tools in laboratories.[1] While metal catalysts based on Rh and Mn are known in this process,[2,3] Pt complexes are the catalyst of choice since the Speier's pioneering discovery.[4] Indeed, Pt catalysts work well with alkyl and alkoxysilanes as well as chlorosilanes without deactivation. On the other hand, immobilization of Pt catalysts on either inorganic or organic supports have been investigated.[5–7]

Whereas some active heterogeneous Pt catalysts have been developed, their activity and selectivity are often decreased with repeated use, presumably because most Pt catalysts currently used are sensitive to air oxidation. To address this issue, Pt catalysts have been immobilized on polymer-supported phosphines and amines, etc.; however, applicability of these catalysts is limited due to the presence of ligands.[5,7] In the meanwhile, we have recently developed a new method, the polymer incarcerated (PI) method, to immobilize metal catalysts onto polymers.[8] The method is based on microencapsulation[9] and cross-linking. Polymer incarcerated Pd catalyst (PI Pd) was effectively synthesized from $Pd(PPh_3)_4$, and remarkably high activity of PI Pd has been demonstrated. Along this line, we report herein immobilization of Pt onto a polymer using the PI method. Some different properties between PI Pt and PI Pd are also described.

PI Pt (**1**) was prepared from co-polymer **2** and $Pt(PPh_3)_4$ (Figure 1). A solution of **2** and $Pt(PPh_3)_4$ in THF was coacervated by addition of hexane (microencapsulation). The resulting precipitate was washed, dried, and heated (cross-linked) to give PI Pt.

It was revealed by elemental analysis that the P atom remained in PI Pt (P/Pt = 0.88), while it was reported that PI Pd prepared from **2** and $Pd(PPh_3)_4$ contained no phosphine.[8] This difference might be ascribed to higher stability of the Pt-P bonds.[10] SR-MAS ^{31}P NMR analysis[11] suggested that the P atom remained as triphenylphosphine oxide in the PI Pt (**1**).[12] Although it was difficult to remove the P components from PI Pt (**1**) completely, we applied this PI Pt to hydrosilylation.[13] Initially, hydrosilylation of 4-phenyl-1-butene (**3**) with pentamethyldisiloxane (**4**) in several solvents was tested using PI Pt (**1**). Leaching of Pt was measured by fluorocene X-ray (XRF) analysis[14] and Inductively Coupled Plasma (ICP) analysis[15] after separation of the catalyst (Table 1). It was found that leaching of Pt was observed when THF or H_2O was used as the sole solvent, while hexane suppressed the leaching to afford hydrosilylated product **5** in high yield (entries 1–3). However, reactivity was decreased significantly in the second run (entry 2). On the other hand, the reaction in hexane–H_2O (1:2) proceeded quantitatively without leaching of Pt, and the catalyst was recovered by simple filtration quantitatively and could be reused five times without loss of activity (entry 4).

Then, the catalytic activity of PI Pt (**1**) was compared with that of common heterogenous or homogenous catalysts. The effect of additives on reactivity was also investigated (Table 2). The reaction was found to proceed using PI Pt even within 30 minutes (entry 1). Pt on C, which was known to be an effective catalyst for hydrosilylation of alkyne,[16] showed almost the same activity, whereas the reaction did not proceed well when $Pt(PPh_3)_4$[17] was used as a catalyst (entries 2 and 3). In addition, PtO_2, which was recently found to be an effective catalyst for hydrosilylation,[18] gave an inferior result under the conditions (entry 4). While addition of PPh_3 to PI Pt completely suppressed

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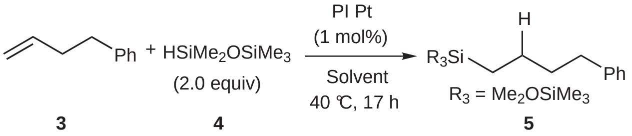
Table 1 Effect of Solvents

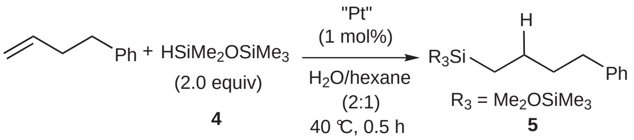


		Yield (%)[a] leaching (%)				
Entry	Solvent	First	Second	Third	Fourth	Fifth
1	THF	Quant. (27.4)	–	–	–	–
2	Hexane	90 (nd)[b]	42 (nd)	49 (nd)	–	–
3	H_2O	95 (nd)	99 (9.7)	99 (2.3)	–	–
4	H_2O–hexane (2:1)	Quant. (nd)	Quant. (nd)	Quant. (nd)	Quant. (nd)	Quant. (nd)

[a] Determined by ^1H NMR analysis using durene as an internal standard.

[b] Measured by XRF analysis; nd = not detected (<2.6%).

Table 2 Comparison of Catalytic Activity



Entry	'Pt'	Additive (1 mol%)	Yield (%)[a] leaching (%)
1	PI Pt	–	99 (nd)[b]
2	Pt/C	–	99
3	$Pt(PPh_3)_4$	–	7
4	PtO_2	–	87
5	PI Pt	PPh_3	0
6	PI Pt	$Ph_3P=O$	Quant.

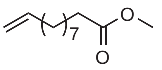
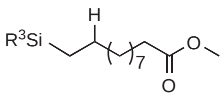
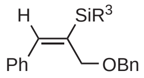
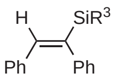
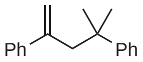
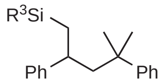
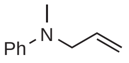
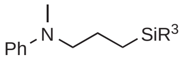
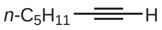
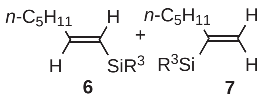
[a] Determined by ^1H NMR analysis using durene as an internal standard.

[b] Measured by XRF analysis; nd = not detected (<2.6%).

the reaction, triphenylphosphine oxide ($Ph_3P=O$) did not affect the reactivity (entries 5 and 6). These results also support that the P atom in PI Pt (**1**) remains as $Ph_3P=O$.

Next, we surveyed the substrate scope of PI Pt (**1**)-catalyzed hydrosilylation (Table 3). The reactions proceeded smoothly to afford the desired products in good to high yields in the presence of ester, ether, and amine functionalities (entries 1, 2 and 5). It is noteworthy that the reaction was successfully carried out even with an alkenylamine, though hydrosilylation of aminated alkenes is generally thought to be difficult.[18,19] The hydrosilylation of a symmetrical, internal alkyne gave only the *cis*-isomer in high yield,[20] while reactions of terminal alkynes afforded a mixture of two regioisomers, β-adduct **6** and α-adduct **7** (entries 3 and 6).[21] A sterically hindered alkene also worked well (entry 4). In all cases, no leaching of Pt was detected by XRF and ICP analyses,[14,15] and PI Pt (**1**) could be recovered quantitatively and reused.

Table 3 Hydrosilylation of Several Substrates Using PI Pt (**1**)[a]

Entry	Substrate	Time (h)	Product	Yield (%)[b]
1		3		90
2		17		Quant.
3[c]		1		Quant.
4		17		81
5		17		83[e]
6[c,d]		16		82

[a] All reactions were carried out with pentamethyldisiloxane (2 equiv) using 1 mol% of **1** (the loading level of platinum = 0.768 mmol/g) in hexane–H_2O (2:1) under Ar at 40 °C. The leaching of platinum was measured by XRF and ICP analyses. No peaks of the platinum were detected in all entries.

[b] Determined by ^1H NMR analysis using durene as an internal standard.

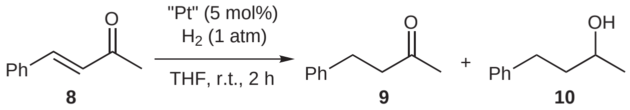
[c] Triethoxysilane (2 equiv) was used.

[d] Ratio of **6**:**7** = 83:17.

[e] Isolated yield.

PI Pt (**1**) was then applied to hydrogenation. Hydrogenation of benzalacetone (**8**) was conducted smoothly to afford reduced products **9** and **10** in high yield, and recovery and reuse of the catalyst were attained without loss of activity even after the fifth use (Table 4). No leaching of Pt was detected by XRF analysis in all runs (entry 1). While Pt/C gave a better yield in the 1st run than PI Pt (**1**), $Pt(PPh_3)_4$ was completely ineffective (entries 2 and 3).

Table 4 Hydrogenation of Benzalacetone Using PI Pt (**1**)[a]

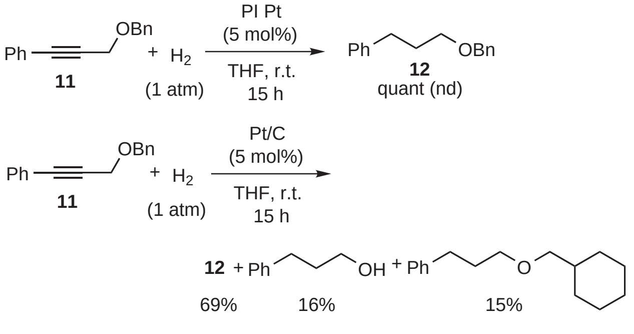


Entry	'Pt'	Yield (%)[b] (Ratio of **9**:**10**) First	Second	Third	Fourth	Fifth
1	PI Pt	84 (95:5)	Quant. (95:5)	Quant. (94:6)	Quant. (94:6)	Quant. (94:6)
2	Pt/C	Quant.	–	–	–	–
3	$Pt(PPh_3)_4$	0	–	–	–	–

[a] All reactions were carried out using 5 mol% of **1** (the loading level of platinum = 0.768 mmol/g) in THF under atmospheric H_2 pressure at r.t. The leaching of Platinum was measured by XRF and ICP analysis. No peaks of the platinum were detected in all entries.

[b] Determined by ^1H NMR analysis using durene as an internal standard.

Selective hydrogenation of the C-C triple bond of benzyloxyalkyne **11** was achieved by using PI Pt to give **12** quantitatively (Scheme 1), whereas Pt/C gave several byproducts. It is noteworthy that cleavage of the benzyl group of **11** did not proceed at all, while other Pt and Pd catalysts generally catalyze debenzylation.



Scheme 1 Selective hydrogenation using PI Pt (**1**)

In summary, we have demonstrated that Pt catalysts could be immobilized by using the PI method. The catalyst showed high catalytic activity not only in hydrosilylation but also in hydrogenation. It is noted that the catalyst can be recovered quantitatively and reused without leaching of Pt. Further investigations to develop new immobilization methods as well as to apply this catalyst to other reactions are now in progress.

Synthesis of PI Pt (1)

Copolymer (**2**, 2.00 g) was dissolved in THF (40 mL) at r.t., and to this solution was added tetrakis(triphenylphosphine)platinum(0) [$Pt(PPh_3)_4$, 3.4 g] as a core. The mixture was stirred for 12 h at that temperature, and hexane (80 mL) was slowly added to the mixture at r.t. Coacervates were found to envelope the core dispersed in the medium. The mixture was left to stand at r.t. for 12 h, and the catalyst capsules were then washed with hexane several times and dried at r.t. for 3 h. Next, the catalyst capsules were heated with stirring at 120 °C for 2 h to cross-link the polymer chain. The cross-linked catalyst was then washed with THF several times and dried under vaccum at r.t. for 24 h to give polymer incarcerated platinum (PI Pt 1, 2.6 g, 0.768 mmol/g of platinum metal was loaded).

Typical Procedure for the Hydrosilylation of 3 (Table 2, Entry 1)

PI Pt (**1**, 6.5 mg, 0.005 mmol), 4-phenyl-1-butene (75.1 μL, 0.50 mmol) and pentamethyldisiloxane (196 μL, 1.0 mmol) were combined in hexane–H_2O (1:2) co-solvent (3 mL) under argon atmosphere. The mixture was stirred for 30 min at 40 °C. The catalyst was filtered and washed with THF, and the solvents of the filtrate were removed under reduced pressure. The yield of hydrosilylated product **5** was estimated by ^1H NMR analysis using 1,2,4,5-tetramethylbenzene as an internal standard. Recovered PI Pt (**1**) was dried under reduced pressure and reused. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.24–7.08$ (m, 5 H), 2.55 (t, $J = 7.8$ Hz, 1 H), 1.59 (apparent quint, $J = 7.7$ Hz, 2 H), 1.30–1.23 (m, 2 H), 0.01 (s, 9 H), 0.00 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 142.9$, 128.4, 128.2, 125.5, 35.7, 35.2, 23.0, 18.2, 2.0, 0.4.

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(12) (a) $^{31}P\{^{1}H\}$ NMR analysis data (ppm): PI Pt (**1**) ($CDCl_3$, SR-MAS): δ = 28.8 (s) [solid PPh_3 (δ = –8.4) was used as an external standard]. Confer: $O{=}PPh_3$ ($CDCl_3$): δ = 29.3; PPh_3 ($CDCl_3$): δ = –4.7. (b) For platinum–phosphine complexes, see: Sen, A.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 1073. (c) $Pt(PPh_3)_4$ (toluene-d_8): δ = 9.2; $Pt(PPh_3)_3$ (toluene-d_8): δ = 49.9; $Pt(PPh_3)_2(O_2)$ (toluene-d_8): δ = 16.4.

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(15) The lower detection limit is 0.4 ppm.

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(21) The reaction using pentamethyldisiloxane gave the hydrosilylation product in 69% yield (**6**:**7** = 85:15), while diethoxymethylsilane also gave a similar result (60% yield, **6**:**7** = 85:15).