# Practical access to the polymer incarcerated platinum (PI Pt) catalyst and its application to hydrogenation

**Yoji Miyazaki, Hiroyuki Hagio and Shū Kobayashi***

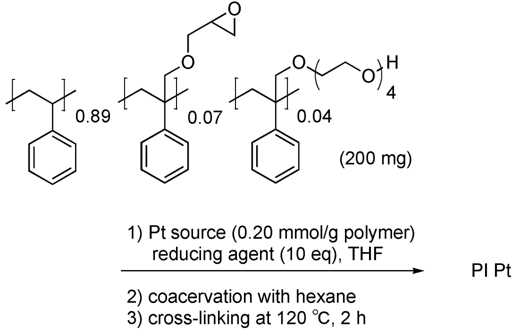
***Received 12th April 2006, Accepted 17th May 2006***
***First published as an Advance Article on the web 31st May 2006***
**DOI: 10.1039/b605288f**

**Polymer incarcerated platinum catalysts (PI Pt) were conveniently prepared from $PtCl_2(COD)$ or $H_2PtCl_6{\cdot}6H_2O$ and styrene copolymers *via* reduction of the Pt sources with triethylamine, coacervation, and cross-linking. The Pt catalysts have been successfully applied to catalytic hydrogenation including saturation of heterocyclic compounds.**

Recently the great importance of polymer supported metal catalysts has been recognized for both academic and industrial use in the aspects of economical and safe use of expensive or toxic metals. In the course of our continuous study to develop highly active polymer-supported metal catalysts,[1] we have already reported the preparation of a polymer incarcerated platinum catalyst (PI Pt), which was prepared from $Pt(PPh_3)_4$ and styrene copolymers.[2] Although this PI Pt effectively catalyzed hydrosilylation of olefins, it did not work well as a catalyst for hydrogenation. The instability of $Pt(PPh_3)_4$ in air also prompted us to invent other versatile and convenient methods to prepare PI Pt from other Pt sources for effective hydrogenation.[3] In this paper, we disclose a new preparation method of PI Pt from platinum salts such as platinum dichloride cyclooctadiene complex, $PtCl_2(COD)$. The application of PI Pt to hydrogenation is also described.

The preparation of PI Pt was first examined using $PtCl_2(COD)$ and styrene copolymers according to our procedure for PI catalysts by using THF and hexane as solvents (Table 1).[1] As reducing agents, hydrogen and hydrazine afforded no immobilized platinum clusters, because the reduction of $PtCl_2(COD)$ was too fast and platinum metal precipitated immediately (Entries 1 and 2). In the case of sodium borohydride, no cross-linking proceeded after the coacervation with hexane (Entry 3). As a reducing agent, silanes were tried next and triethylsilane gave a satisfactory result to afford the desired PI Pt (Entry 5). In this catalyst, the cluster size of Pt was less than 1 nm by transmission electron microscope (TEM) analysis. However, this procedure was not reproducible presumably due to poor solubility of $PtCl_2(COD)$ in THF. In fact, when the solvent was changed to dichloromethane which dissolved $PtCl_2(COD)$ well, PI Pt was obtained reproducibly (Entry 6). The Pt loading value of this PI Pt determined by fluorocene X-ray analysis (XRF) was 0.142 mmol $g^{-1}$. Hydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6{\cdot}6H_2O$) was also found to be a good platinum source of the PI Pt (Entry 7). PI Pt with a higher loading level (0.286 mmol $g^{-1}$) was prepared from $H_2PtCl_6{\cdot}6H_2O$ and triethylsilane by the similar procedure. In this case, THF and hexane were used as solvents and the cluster size of this PI Pt observed by TEM was 2–3 nm.

**Table 1** Preparation of PI Pt from Pt salts and copolymer



| Entry | Pt source | Reducing agent | PI Pt yield/mg | Pt loading/mmol $g^{-1}$ cat (recovery, %) |
|---|---|---|---|---|
| 1 | $PtCl_2(COD)$ | $H_2$ | 0[a] | — |
| 2 | $PtCl_2(COD)$ | $NH_2NH_2$ | 0[a] | — |
| 3 | $PtCl_2(COD)$ | $NaBH_4$ | 0[b] | — |
| 4 | $PtCl_2(COD)$ | $HSi(OEt)_3$ | 218 | Not determined[c] |
| 5[d] | $PtCl_2(COD)$ | $HSiEt_3$ | 162 | 0.193 (78%) |
| 6[e] | $PtCl_2(COD)$ | $HSiEt_3$ | 199[f] | 0.142 (71%) |
| 7 | $H_2PtCl_6{\cdot}6H_2O$ | $HSiEt_3$ | 143[g] | 0.286 (quant.) |

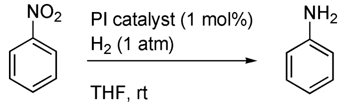
[a] Pt metal precipitated. [b] No cross-linking proceeded. [c] Huge clusters were obtained. [d] Not reproducible. [e] Dichloromethane and methanol were used as solvents. [f] Clusters of less than 1 nm size were observed by TEM analysis. [g] Clusters of 2–3 nm size were observed.

The reactivity of the PI Pt catalysts prepared was tested by hydrogenation of nitrobenzene in THF under atmospheric pressure of hydrogen (Table 2). As expected, with 1 mol% of the PI Pt catalyst prepared from $PtCl_2(COD)$, the reaction completed within 1 hour to give aniline quantitatively and no leaching of Pt from the catalyst was observed by XRF analysis. By contrast, 6 hours were required to finish the same hydrogenation with the PI Pt prepared from $Pt(PPh_3)_4$ and 19% leaching of the platinum was observed. For comparison, PI Pd was also applied to this reaction. Reactivity of the PI Pd was moderate to complete the hydrogenation in 3 hours. It should be noted that the PI Pt from $PtCl_2(COD)$ gave higher activity than the PI Pt prepared from $Pt(PPh_3)_4$. In addition, the PI Pt from $PtCl_2(COD)$ could be reused at least 5 times repeatedly for the reaction without loss of activity and no Pt leaching was observed in each run. It should be also mentioned that the cluster size of the PI Pt did not change after 5 runs.

---

*Graduate School of Pharmaceutical Sciences, The University of Tokyo, Astellas Pharma Inc., Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan E-mail: skobayas@mol.f.u-tokyo.ac.jp; Fax: +81 3 5684 0634; Tel: +81 3 5841 4790*

**Table 2** Hydrogenation of nitrobenzene catalyzed by PI catalysts

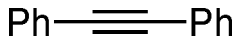
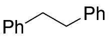
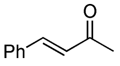
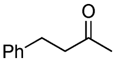
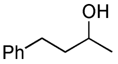
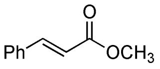
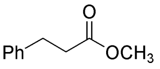
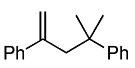
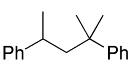
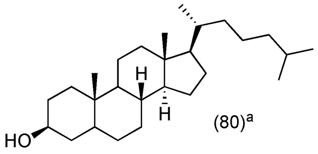
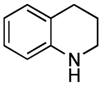


| Entry | Pl catalyst | Time/h | Yield (%) | Leaching (%)[a] |
|---|---|---|---|---|
| 1 | Pl Pt from $PtCl_2(COD)$ | 1 | Quant. | ND[b] |
| 2 | Pl Pt from $Pt(PPh_3)_4$ | 6 | Quant. | 19 |
| 3 | Pl Pd | 3 | Quant. | ND[b] |

[a] Measured by XRF analysis. [b] Not detected (<2%).

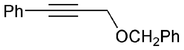
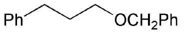
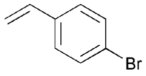
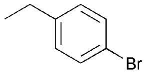
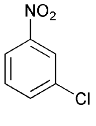
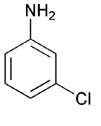
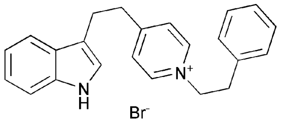
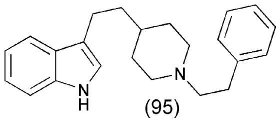
Next the PI Pt catalyst was applied to the hydrogenation of various substrates (Table 3). In most cases, alkenes and alkynes were smoothly hydrogenated with 1 mol% PI Pt prepared from $PtCl_2(COD)$ in THF at room temperature under atmospheric pressure of hydrogen. The sterically hindered C–C double bond of cholesterol was hydrogenated to give cholestanol in 80% yield after 24 hours with 5 mol% PI Pt prepared from $H_2PtCl_6{\cdot}6H_2O$ (Entry 5).[4] In the case of quinoline, 80 hours were required to complete the hydrogenation to afford tetrahydroquinoline in 82% yield (Entry 6). In all cases tested, no leaching of platinum metal was observed by XRF analysis.

**Table 3** Hydrogenation of various substrates catalyzed by PI Pt

| Entry | Substrate | Product (yield, %) |
|---|---|---|
| 1 |  |  (Quant) |
| 2 |  |  (90)[a] |
|  |  |  (10)[a] |
| 3 |  |  (Quant) |
| 4 |  |  (Quant) |
| 5[b] | Cholesterol |  (80)[a] |
| 6 | Quinoline |  (82) |

All reactions were performed at room temperature under atmospheric pressure of hydrogen. In all entries except entry 5, 1 mol% of Pl Pt prepared from $PtCl_2(COD)$ and THF as solvent were used. Reaction time was 1 h for entries 1–4, 24 h for entry 5, and 80 h for entry 6. In all entries, no leaching of Pt was detected by XRF analysis (<2%). [a] The yield was determined by NMR analysis. [b] 5 mol% of Pl Pt prepared from $H_2PtCl_6{\cdot}6H_2O$ and dichloromethane as solvent were used. 20% of starting material was recovered.

**Table 4** Selective hydrogenation catalyzed by PI Pt

| Entry | Substrate | Product (yield, %) |
|---|---|---|
| 1 |  |  (Quant) |
| 2 |  |  (95) |
| 3 |  |  (73) |
| 4[a] |  |  (95) |

In all entries, reaction time was 1 h. In all entries except entry 4, the reactions were performed in THF at room temperature under atmospheric pressure of hydrogen with 1 mol% of Pl Pt prepared from $PtCl_2$ (COD). No leaching of Pt was observed by XRF analysis (< 2%). [a] The reaction was conducted in methanol–THF (1 : 1) under 5 atm pressure of hydrogen with 5 mol% Pl Pt prepared from $H_2PtCl_4{\cdot}6H_2O$.[4] No leaching of Pt was observed by ICP analysis (< 0.06%).

Finally selective reduction with PI Pt catalyst was tried by using multi-functionalized substrates (Table 4). Alkene, alkyne and nitro groups were hydrogenated selectively in the presence of *O*-benzyl or aromatic halogen substituents (Entries 1 to 3). Hydrogenation of the pyridine ring is a characteristic transformation by platinum catalysts.[5] As shown in Entry 4, hydrogenation of the pyridinium salt successfully proceeded in the presence of indole and benzene rings to give the analgesic compound[6] in 95% yield with 5 mol% PI Pt prepared from $H_2PtCl_6{\cdot}6H_2O$ under 5 atm pressure of hydrogen.[4] In this reaction, no leaching of Pt was detected by ICP analysis which detection limit was 0.06%.

In summary, a practical method to prepare a PI Pt catalyst has been developed by using $PtCl_2(COD)$ or $H_2PtCl_6{\cdot}6H_2O$ as a Pt source and triethylsilane as a reductant. This catalyst was successfully applied to hydrogenation of various substrates. Further study to synthesize biologically active compounds and to prepare chemical libraries for drug discovery research with this catalyst is now in progress.

## Preparation of the copolymer

The copolymer was prepared according to the literature.[1f]

The molar ratio of the components was determined by $^1H$ NMR analysis (x : y : z = 89 : 7 : 4). $M_w$: 23189, $M_n$: 8258, $M_w/M_n = 2.81$ (gel permeation chromatography analysis).

## Preparation of the PI Pt from $PtCl_2(COD)$

To a stirred solution of the copolymer (1.00 g) and triethylsilane (0.32 $cm^3$, 2.0 mmol) in dichloromethane (10 $cm^3$) was added dropwise $PtCl_2(COD)$ (75 mg, 0.20 mmol) in dichloromethane (10 $cm^3$) at 40 °C. The mixture was stirred at this temperature for 3 h, and then methanol (150 $cm^3$) was slowly added for coacervation. The resulting mixture was left at room temperature overnight and the supernatant liquid was removed by decantation. The residual dark brown solid was heated at 120 °C for 2 h, washed with THF, and dried *in vacuo* to afford PI Pt (996 mg). Pt loading amount was 0.142 mmol $g^{-1}$ determined by XRF after decomposition of the catalyst with sulfuric acid and nitric acid at 180 °C for 2 h. The loading yield of Pt was 71%.

## Typical procedure for hydrogenation catalyzed by the PI Pt

Nitrobenzene (131 mg, 1.07 mmol) was dissolved in THF (5 $cm^3$) and hydrogenated with PI Pt (75 mg, 0.0107 mmol Pt, 1 mol%) at room temperature under atmospheric pressure of hydrogen. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the PI Pt was recovered (69 mg, 92%).[7] The filtrate was concentrated *in vacuo* and Pt leaching was measured by XRF. The crude product was purified by silica gel column chromatography eluted with chloroform–methanol–25% aqueous ammonia = 190 : 9 : 1 to give aniline as colorless oil (99 mg, quant.).[8]

## Acknowledgements

This work was partially supported by Grant-in-Aid for Scientific Research from the Japan Society of the Promotion of Sciences (JSPS).

## Notes and references

1 (*a*) R. Akiyama and S. Kobayashi, *J. Am. Chem. Soc.*, 2003, **125**, 3412; (*b*) K. Okamoto, R. Akiyama and S. Kobayashi, *J. Org. Chem.*, 2004, **69**, 2871; (*c*) K. Okamoto, R. Akiyama and S. Kobayashi, *Org. Lett.*, 2004, **6**, 1987; (*d*) R. Nishio, M. Sugiura and S. Kobayashi, *Org. Lett.*, 2005, **7**, 4831; (*e*) H. Hagio, M. Sugiura and S. Kobayashi, *Org. Lett.*, 2006, **8**, 375; (*f*) K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida and S. Kobayashi, *J. Am. Chem. Soc.*, 2005, **127**, 2125.

2 H. Hagio, M. Sugiura and S. Kobayashi, *Synlett*, 2005, 813.

3 Recently hydrogenation using polymer supported platinum catalyst has been reported. See: (*a*) X.-X. Han, R.-X. Zhou, G.-H. Lai, B.-H. Yue and X.-M. Zheng, *React. Kinet. Catal. Lett.*, 2004, **81**, 41; (*b*) J. Aumo, J. Lilja, P. Maki-Arvela, T. Salmi, M. Sundell, H. Vanio and D. Y. Murzin, *Catal. Lett.*, 2002, **84**, 219; (*c*) Z. M. Michalska, B. Ostaszewski, J. Zientarska and J. M. Rynkowski, *J. Mol. Catal. A: Chem.*, 2002, **185**, 279; (*d*) L. M. Bronstein, D. M. Cherynylshov, I. O. Volkov, M. G. Ezernitskaya, P. M. Valetsky, V. G. Matveeva and E. M. Sulman, *J. Catal.*, 2000, **196**, 302; (*e*) C. Lange, D. D. Caro, A. Gamez, S. Storck, J. S. Bradley and W. F. Maier, *Langmuir*, 1999, **15**, 5333; (*f*) Z. Yu, S. Liao, Y. Xu, B. Yang and D. Yu, *J. Mol. Catal. A: Chem.*, 1997, **120**, 247; (*g*) D. G. Duff, T. Mallat, M. Schneider and A. Baiker, *Appl. Catal. A*, 1995, **133**, 133; (*h*) E. Tronconi, C. Crisafulli, S. Galvagno, A. Donato, G. Neri and R. Pietropaolo, *Ind. Eng. Chem. Res.*, 1990, **29**, 1766; (*i*) H. C. Clark, C. A. Fyfe, P. J. Hayes, I. McMahon, J. A. Davies and R. E. Wasylishen, *J. Organomet. Chem.*, 1987, **322**, 393.

4 With a less amount of PI Pt or with PI Pt prepared from $PtCl_2(COD)$, the yield of the desired compounds was not satisfactory.

5 (*a*) P. N. Rylander, in *Catalytic Hydrogenation over Platinum Metals*, Academic Press, New York, 1967; (*b*) R. L. Augustine, in *Catalytic Hydrogenation*, Marcel Dekker Inc., New York, 1965.

6 A. P. Gray and H. Kraus, *J. Org. Chem.*, 1961, **26**, 3368.

7 Due to handling problems, a small amount of the used PI Pt was not recovered.

8 The crude product after filtration and concentration was almost pure. Purification was not necessarily required.