ORGANIC
LETTERS

2009
Vol. 11, No. 6
1345−1348

Catalysis in Polysiloxane Gels: Platinum-Catalyzed Hydrosilylation of Polymethylhydrosiloxane Leading to Reusable Catalysts for Reduction of Nitroarenes

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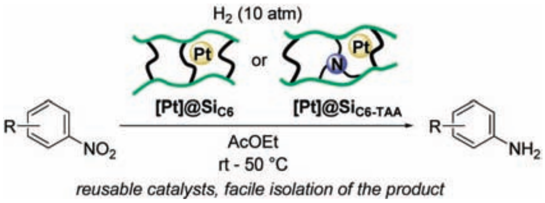
Received January 21, 2009

ABSTRACT



Novel polysiloxane gels, to which platinum species are encapsulated, are prepared by treatment of polymethylhydrosiloxane with alkenes in the presence of Karstedt's catalyst. These gels act as reusable catalysts in the reduction of functionalized nitroarenes with H_2 to the corresponding substituted anilines without leaking the catalyst species.

Heterogeneous transition metal catalysts leading to facile separation of products from reaction mixtures without contamination of metal residues play an important role in environmentally benign chemical processes. The recovery of catalysts that can be reusable and can retain their catalytic activity is ideal.[1] Conventional heterogeneous catalysts are prepared by immobilizing metal particles on surfaces of inorganic materials such as activated carbon, silica, and alumina or by anchoring organometallic species to functionalized organic polymers.[1,2] In contrast, the progress of nanoscience has opened the way for preparing new supports with fine structures such as nanocarbons, organic microcapsules, and membranes, which improve the activity and reusability of heterogeneous catalysts.[3,4]

Cross-linked polydimethylsiloxanes (PDMS) are potentially attractive carrier materials not only because they have good thermal and chemical stabilities but also because diffusion velocity of organic molecules through a siloxane matrix is very fast.[4b,e] Indeed, they have recently been applied

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(3) (a) Kobayashi, S.; Akiyama, R. *Chem. Commun.* **2003**, 449. (b) Yamada, Y. M. A.; Arakawa, T.; Hocke, H.; Uozumi, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 704. (c) Takasaki, M.; Motoyama, Y.; Higashi, K.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *Chem. Asian J.* **2007**, *2*, 1524.

(4) (a) Vankelecom, I. F. J.; Tas, D.; Parton, R. F.; Van de Vyver, V.; Jacobs, P. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1346. (b) Parton, R. F.; Vankelecom, I. F. J.; Tas, D.; Janssen, K. B. M.; Knops-Gerrits, P.-P.; Jacobs, P. A. *J. Mol. Catal. A: Chem.* **1996**, *113*, 283. (c) Wolfson, A.; Janssens, S.; Vankelecom, I.; Geresh, S.; Gottlieb, M.; Herskowitz, M. *Chem. Commun.* **2002**, 388. (d) Mwangi, M. T.; Runge, M. B.; Bowden, N. B. *J. Am. Chem. Soc.* **2006**, *128*, 14434. (e) Runge, M. B.; Mwangi, M. T.; Bowden, N. D. *J. Organomet. Chem.* **2006**, *691*, 5287. (f) Guedes, D. F. C.; Leod, T. C. O.; Gotardo, M. C. A. F.; Schiavon, M. A.; Yoshida, I. V. P.; Ciuffi, K. J.; Assis, M. D. *Appl. Catal., A: Gen.* **2005**, *296*, 120.

10.1021/ol9001366 CCC: $40.75

to the reaction media of molecular catalysts such as BINAP-Ru,[4a,b] salen-Mn,[4a,f] DuPHOS-Rh,[4c] and Grubbs' catalysts.[4d,e] However, methods of entrapping these catalysts in the cross-linked siloxane matrix require further investigation. PDMS has been generally cured in the presence of a cross-linker such as tetrakis(dimethylsiloxy)silane; adsorption of catalytically active species into the resulting cross-linked siloxane matrix allows for the preparation of catalysts immobilized to siloxane gels.

In the course of our studies on the ruthenium-catalyzed reduction of carboxamides with polymethylhydrosiloxane (PMHS), we discovered that catalytic deoxygenative reduction of carboxamides provided cross-linking of the siloxane chain through Si−O−Si bonds, allowing metals to efficiently encapsulate into the polysiloxane gels that formed.[5a] Further investigation revealed that ruthenium-catalyzed dehydrogenative silylation of diols with PMHS were also effective for production of polysiloxane gels containing ruthenium; notably, these insoluble gels can be used as reusable heterogeneous catalysts for isomerization of alkenes.[5b] To the best of our knowledge, this is the first report on metal-catalyzed cross-linking of PMHS that contributes to production of reusable catalysts immobilized to the polysiloxane gel. These metal-encapsulating polysiloxane gels are easily produced by mixing a catalyst and PMHS with a cross-linker (amides or diols). Thus, a variety of reusable catalysts entrapped in the polysiloxane gels can be prepared by a simple metal-catalyzed cross-linking method.

In this paper, we wish to report the simple synthesis of platinum-encapsulating polysiloxane gels as reusable catalysts for hydrogenation of nitroarenes by treatment of PMHS with 1,5-hexadiene or triallylamine in the presence of Karstedt's catalyst (Figure 1). While previous cross-linking methods were based on Si−O bond formation,[5a,b] a new method formed the gel matrix through Si−C bonding via hydrosilylation. These polysiloxane gels are good catalysts for reducing nitro compounds to their corresponding amines while not affecting the other functional groups in the molecule.[6,7]

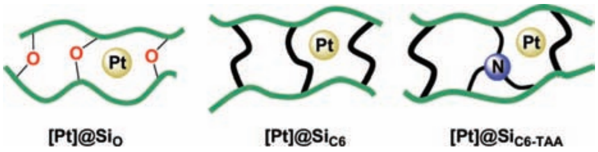
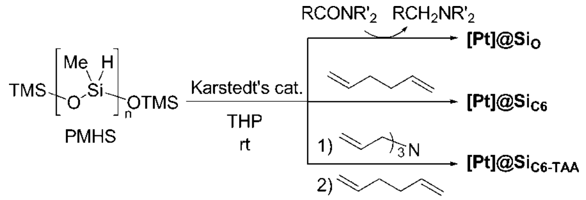


Figure 1. Schematic illustrations of oxygen-bridged [Pt]@Si$_O$, alkyl-bridged [Pt]@Si$_{C6}$, and amine- and alkyl-bridged [Pt]@Si$_{C6\text{-}TAA}$: green chain, siloxane; black chain, alkyl.

Polysiloxane gels containing platinum species ([Pt]@Si) were prepared by the simple method shown in Scheme 1.

Scheme 1. Preparation of [Pt]@Si$_O$, [Pt]@Si$_{C6}$, and [Pt]@Si$_{C6\text{-}TAA}$



[Pt]@Si$_{C6}$ was obtained by the reaction of PMHS [$n = 25.6$ (average)] with 1,5-hexadiene in the presence of $Pt[\{(CH_2{=}CH)Me_2Si\}_2O]_n$ (Karstedt's catalyst: [Pt] = 0.01 mmol) in THP at room temperature for <5 min. The formed wet gel was washed with ether and then dried under reduced pressure to afford [Pt]@Si$_{C6}$ as a pale yellow solid. IR and ^{29}Si NMR analyses revealed that all of the Si−H groups in the gel reacted with 1,5-hexadiene to form the Si−C bonds, and ICP-MS analysis showed almost all (>99.7%) of the charged Pt species was entrapped in the polysiloxane matrix. Introduction of functional groups to the cross-linker leads to the polysiloxane gels with functional groups located in the bridge of the polymethylsiloxane chain. In a typical example, the reaction of PMHS with triallylamine (TAA; 0.05 mmol, 5 equiv to Pt), followed by addition of 1,5-hexadiene at room temperature for 20 min, afforded the modified polysiloxane gel, [Pt]@Si$_{C6\text{-}TAA}$, as an orange solid.[8] NMR analysis revealed that all of triallylamine reacted with the Si−H groups; i.e., 5 equiv of amine moiety to the platinum species was entrapped in the polysiloxane matrix. For comparison in the catalytic performance, the oxygen-bridged [Pt]@Si$_O$ was also prepared by deoxygenative reduction of *N*-benzyl-2-pyrrolidinone with PMHS according to the method reported previously.[9]

The [Pt]@Si catalysts prepared were subjected to the catalytic hydrogenation of *p*-nitroanisole (**1**). The reaction was carried out in an autoclave in the presence of the gels (calculated Pt amounts = 1 mol%; substrate/catalyst mole ratio: $S/C = 100$) in ethyl acetate under H_2 (initial pressure: $P_{H2} = 10$ atm) at room temperature. After the reaction, the mixture was filtered through a membrane under reduced

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(5) (a) Motoyama, Y.; Mitsui, K.; Ishida, T.; Nagashima, H. *J. Am. Chem. Soc.* **2005**, *127*, 13150. (b) Motoyama, Y.; Abe, M.; Kamo, K.; Kosako, Y.; Nagashima, H. *Chem. Commun.* **2008**, 5321.

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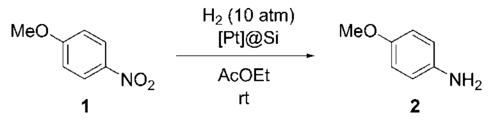
(8) The presence of an amine contributes to slow down the rate of Pt-catalyzed cross-linking of PMHS by 1,5-hexadiene.

(9) Hanada, S.; Motoyama, Y.; Nagashima, H. *Tetrahedron Lett.* **2006**, *47*, 6173.

Table 1. Hydrogenation of Nitroanisole **1** with [Pt]@Si Catalysts[a]

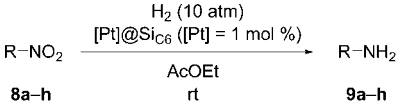


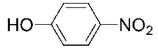
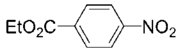
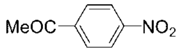
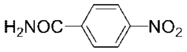
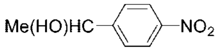
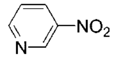
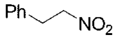
entry	catalyst	*S*/*C*[b]	time (h)	yield (%)
1	[Pt]@Si_O	100	3	<5[c]
2	[Pt]@Si_O	100	24	37[c]
3	[Pt]@Si_{C6}	100	3	>99
4	[Pt]@$Si_{C6\text{-}TAA}$	100	3	99
5[d]	[Pt]@Si_{C6}	900	10	99
6[e]	[Pt]@Si_{C6}	10000	24	99

[a] All reactions were carried out with **1** (1 mmol) and Pt species (1 mol % for **1**) in ethyl acetate (3 mL) at room temperature under H_2 (10 atm). [b] *S*/*C* = mol (**1**)/mol (Pt). [c] Determined by ^{1}H NMR analysis. [d] 9 mmol of **1** and 10 mL of ethyl acetate were used. [e] 10 mmol of **1** and 10 mL of ethyl acetate were used.

pressure. The [Pt]@Si catalysts were recovered as a dry gel on the membrane filter (Teflon; 0.45 μm), and the product was obtained from the filtrate. As shown in Table 1, entries 3 and 4, *p*-aminoanisole (**2**) was obtained in quantitative yields within 3 h using [Pt]@Si_{C6} and [Pt]@$Si_{C6\text{-}TAA}$ as the catalyst; their catalytic activity was higher than that of the oxygen-bridged [Pt]@Si_O (entries 1 and 2). Synthetic utility of [Pt]@Si_{C6} is demonstrated by the following two experiments. First, hydrogenation of **1** (1.378 g, 9.0 mmol) with Pt@Si_{C6} (substrate/catalyst mole ratio: *S*/*C* = 900) at room temperature for 10 h. Separation of the product from the catalyst was carried out by filtration, and removal of the solvent in vacuo afforded **2** as a solid in 99% yield (1.104 g) (entry 5). NMR analysis of **2** showed no contamination of either byproduct or solvent in this stage; its melting point was within a narrow temperature range (57.8−58.3 °C) and identical with the literature,[10] confirming the high purity of the product. Furthermore, no Pt species was detected by ICP-MS. In addition, the turnover number of the present catalyst system reached 10 000, when the reaction was carried out using [Pt]@Si_{C6} ([Pt] = 0.001 mmol) and **1** (1.531 g, 10 mmol) at room temperature for 24 h (entry 6). Next, [Pt]@Si_{C6} recovered from the experiment shown in entry 3 was reusable for catalytic reduction of **1**. The catalyst recovery/reuse cycle (1 mmol scale) was successfully repeated five times in 98−99% yield of **2** in each cycle. ICP-MS analysis of the product obtained in each cycle has shown that the amount of Pt-leaching from the gel was lower than the detection limit.[11]

Table 2. Hydrogenation of Various Nitro Compounds **8a**−**h**[a]

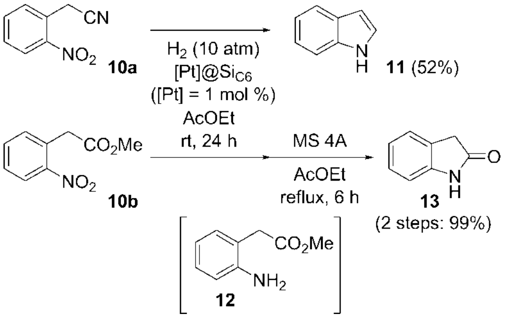


entry	substrate		time (h)	yield (%)
1		**8a**	3	99
2		**8b**	6	>99
3[b]		**8c**	2	>99
4		**8d**	2	99
5[c]		**8e**	3	97
6		**8f**	6	99
7		**8g**	6	99
8[b]		**8h**	30	88

[a] All reactions were carried out with nitro compound **8** (1 mmol) and [Pt]@Si_{C6} ([Pt] = 1 mol % for **8**) in AcOEt (3 mL) at room temperature under H_2 (10 atm). [b] At 50 °C. [c] In THF/EtOH (2:1) at 100 °C.

Reduction of nitrobenzenes with other functional groups also successfully produced their corresponding aniline derivatives in high yields using this method. Typical examples of reactions with [Pt]@Si_{C6} (1 mol % of Pt loading) under H_2 (10 atm) are summarized in Table 2. As shown in entries 2−4, reduction of nitro groups took place without affecting carbonyl groups such as ester, ketone, and amide moieties. No reductive cleavage of the benzylic C−O bond in **8e** and **8g** occurred (entries 5 and 6). The reaction was applicable to reduction of 3-nitropyridine (**8g**) (entry 7). Although reaction of an aliphatic nitro compound with this catalyst system was slow at room temperature, treatment of 2-phenylnitroethane (**8h**) with [Pt]@Si_{C6} at 50 °C for 30 h afforded 2-phenylethylamine (**9h**) in 88% yield (entry 8).

Scheme 2. Synthesis of Indol **11** and Oxindole **13**



Preparation of indole derivatives was also successful (Scheme 2).[12] For example, treatment of *o*-(cyanomethyl)nitrobenzene (**10a**) with [Pt]@Si_{C6} under H_2 (10 atm) resulted in reductive cyclization to afford indole (**11**) in 52% yield. Under the same conditions, *o*-(methoxycarbonyl)methylni-

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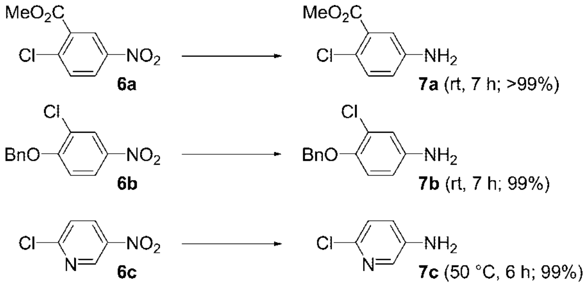
(10) Budavari, S.; O'Neil, M. J.; Smith, A.; Heckelman, P. E. *The Merck Index*, 11th ed.; Merck & Co., Inc.: Rahway, NJ, 1989; p 105.

(11) The calculated Pt amount in the product was <0.3 ppm; see Supporting Information.

trobenzene (**10b**) was converted to a 3:2 mixture of *o*-(methoxycarbonyl)methyl aniline (**12**) and oxindole (**13**), which was then refluxed in ethyl acetate in the presence of 4-Å molecular sieves (MS 4A) to give oxindole **13** in 99% yield.

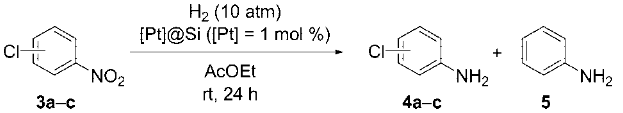
Reduction of chloronitrobenzenes is potentially accompanied by reductive dechlorination.[7] Trisubstituted chloronitrobenzenes (**6a** and **6b**) and chloronitropyridine (**6c**) were hydrogenated in the presence of [Pt]@Si$_{\mathrm{C6}}$ to afford chloroanilines (**7a** and **7b**) and chloroaminopyridine (**7c**), respectively, without the contamination of the byproduct due to the reductive dechlorination (Scheme 3).

Scheme 3. Nitro-Selective Reduction of Trisubstituted Benzene Derivatives **6a**, **6b**, and Chloronitropyridine **6c** with [Pt]@Si$_{\mathrm{C6}}$



Reduction of disubstituted chloronitrobenzenes is more problematic for selective reduction of the nitro group without contamination of the reductive dechlorination products.[7,13] Amines are known as a catalyst poison in heterogeneous hydrogenation; addition of certain amines to the catalytic hydrogenation often retards the reaction rate but sometimes suppresses possible side reactions.[7] The amino groups in [Pt]@Si$_{\mathrm{C6\text{-}TAA}}$ actually contributed to suppression of the reductive dechlorination of chloronitrobenzenes (Table 3). Reduction of *p*-chloronitrobenzene (**3a**) with [Pt]@Si$_{\mathrm{O}}$ at room temperature for 24 h afforded a 3:1 mixture of *p*-chloroaniline (**4a**) and aniline (**5**) (entry 1). In contrast, conversion of **3a** with [Pt]@Si$_{\mathrm{C6}}$ reached over 98% within 3 h, and the **4a**/**5** ratio was improved to 60:1 (entry 2). Complete suppression of the reductive dechlorination was accomplished with [Pt]@Si$_{\mathrm{C6\text{-}TAA}}$, but the reaction required a longer reaction time (24 h) than that with [Pt]@Si$_{\mathrm{C6}}$ (entry 3). Both *meta*- and *ortho*-chloronitrobenzenes were also converted to the corresponding chloroanilines with 100% selectivity (entries 4 and 5).

Table 3. Hydrogenation of Chloronitrobenzenes **3a−c** with [Pt]@Si Catalysts[a]



entry	substrate	catalyst	**4** (%)	**5** (%)
1	**3a**: X = *p*-Cl	[Pt]@Si$_{\mathrm{O}}$	63.0[b]	22.5[b]
2[c]	**3a**: X = *p*-Cl	[Pt]@Si$_{\mathrm{C6}}$	96.8[b]	1.6[b]
3	**3a**: X = *p*-Cl	[Pt]@Si$_{\mathrm{C6\text{-}TAA}}$	>99	ND[d]
4	**3b**: X = *m*-Cl	[Pt]@Si$_{\mathrm{C6\text{-}TAA}}$	>99	ND[d]
5	**3c**: X = *o*-Cl	[Pt]@Si$_{\mathrm{C6\text{-}TAA}}$	>99	ND[d]

[a] All reactions were carried out with **3a−c** (1 mmol) and [Pt] species (1 mol % for **3**) in AcOEt (3 mL) at room temperature for 24 h under H_2 (10 atm). [b] Determined by GLC analysis. [c] For 3 h. [d] ND = not detected.

In summary, we successfully synthesized polysiloxane gels containing Pt species, [Pt]@Si$_{\mathrm{C6}}$ and [Pt]@Si$_{\mathrm{C6\text{-}TAA}}$, by a simple method of mixing commercially available Karstedt's catalyst and PMHS with either 1,5-hexadiene or triallylamine. These gels act as recyclable heterogeneous catalysts for reduction of various nitro compounds to their corresponding amines with other functional groups remaining intact. Further studies are actively investigating appropriate cross-linkers and catalysts for designing polysiloxane gels as suitable reaction media used in a variety of metal-catalyzed reactions.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Detailed experimental procedures, characterization data, and copies of NMR spectra of the gels, substrates, and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Humphrey, G. R.; Kuethe, J. T. *Chem. Rev.* **2006**, *106*, 2875.

(13) Other catalyst systems: Cp_2TiCl_2/Sm system: (a) Huang, Y.; Liao, P.; Zhang, Y.; Wang, Y. *Synth. Commun.* **1997**, *27*, 1059. Pt/C in $ScCO_2$: (b) Ichikawa, S.; Tada, M.; Iwasawa, Y.; Ikariya, T. *Chem. Commun.* **2005**, 924. Pt/C in ionic liquid: (c) Xu, D.-Q.; Hu, Z.-Y.; Li, W.-W.; Luo, S.-P.; Xu, Z.-Y. *J. Mol. Catal. A: Chem.* **2005**, *235*, 137. $Pd(OAc)_2$−hydrosilanes: (d) Rahaim, R. J., Jr.; Maleczka, R. E., Jr. *Org. Lett.* **2005**, *7*, 5087. Au/TiO_2: (e) Corma, A.; Serna, P. *Science* **2006**, *313*, 332. $Mo(CO)_6$/DBU under microwave irradiation: (f) Spencer, J.; Anjum, N.; Patel, H.; Rathnam, R. P.; Verma, J. *Synlett* **2007**, 2557. Pd catalyst on basic nanocrystalline magnesium oxide [NAP-Mg-Pd(0)]: (g) Kantam, M. L.; Chakravarti, R.; Pal, U.; Sreedhar, B.; Bhargava, S. *Adv. Synth. Catal.* **2008**, *350*, 822. (h) Cu/HCO_2NH_4: (i) Saha, A.; Ranu, B. *J. Org. Chem.* **2008**, *73*, 6867.