Catalysis by Polymer-Bound Rhodium Carbonyl Clusters. Selective Hydrogenation of α,β-Unsaturated Aldehydes to Allylic Alcohols in the Presence of H_2 and CO

Kiyotomi Kaneda[*,†] and Tomoo Mizugaki

Department of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

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Summary: Functionalized polystyrene was prepared by amination of chloromethylated polystyrene with (2-(dimethylamino)ethoxy)ethanol. Using the aminated polystyrene and $Rh_6(CO)_{16}$ in the presence of H_2 and CO, various α,β-unsaturated aldehydes could be chemoselectively hydrogenated to give allylic alcohols in high yields at 30 °C and then the obtained polymer-bound Rh cluster complexes were reusable catalysts for the hydrogenation.

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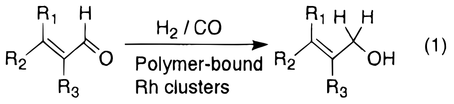
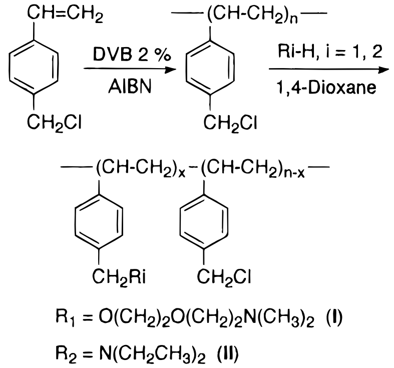
Research in metal cluster catalysis has been stimulated by hopes of finding new and selective reactions catalyzed by the clusters, which is based on multicenter activation through coordination of substrates to metals.[1] We have already reported that a catalyst system of $Rh_6(CO)_{16}$ and *N*,*N*,*N′*,*N′*-tetramethyl-1,3-propanediamine chemoselectively reduced carbonyl functions in α,β-unsaturated aldehydes using a reducing agent of CO and H_2O.[2] Use of molecular hydrogen in place of H_2O also gave high yields of allylic alcohols in the above reduction of α,β-unsaturated aldehydes under an atmosphere of CO. In this paper, we wish to report the highly chemoselective reduction of aldehyde functions catalyzed by aminated polystyrene-bound rhodium cluster complexes in relation to the corresponding homogeneous system under an atmosphere of H_2 and CO (eq 1). Chemoselective reductions of α,β-unsaturated carbonyl compounds to allylic alcohols have been extensively studied because of the high potential utility of allylic alcohols.[3] In the case of catalytic hydrogenations, the olefinic bond in α,β-unsaturated aldehydes and ketones is usually preferentially reduced, but the reverse effect can be observed in a variety of special catalysts.[4]



(1)

Scheme 1. Synthetic Procedures for Functionalized Polymers I and II



Aminated polystyrenes were prepared according to the literature procedure.[5] Bulk polymerization of *p*-(chloromethyl)styrene and divinylbenzene (98/2, w/w) was carried out using AIBN, followed by the amination with (2-(dimethylamino)ethoxy)ethanol (Scheme 1). The amino-substituted polymer **I** (Anal. Found: C, 78.77; H, 9.01; N, 5.70; Cl, <0.03) was obtained, which displayed a 90% degree of amination of chloromethyl moieties. Under conditions similar to those giving the polymer **I**, the amination with diethylamine in place of (2-(dimethylamino)ethoxy)ethanol was carried out to give the polymer **II** (Anal. Found: C, 78.97; H, 8.89; N, 5.13).

Hydrogenation of (*E*,*E*)-5-phenyl-2,4-pentadienal with the above aminated polymer **I** is a typical example. A stainless autoclave containing $Rh_6(CO)_{16}$ (0.010 mmol) and the polymer (**I**, 0.18 mmol of N) was evacuated and flushed three times with CO. A benzene (3.0 mL) solution of (*E*,*E*)-5-phenyl-2,4-pentadienal[6] (1.5 mmol) was added. The reaction mixture was stirred at 30 °C under 10 atm of CO and H_2 (1:1) for 15 h. After a solid polymer was removed, the filtrate was subjected to column chromatography to give 0.227 g of (*E*,*E*)-5-phenyl-2,4-pentadien-1-ol (88%; mp 74−75 °C):[7] ^1H

[†] E-mail: kaneda@cheng.es.osaka-u.ac.jp.

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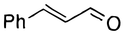
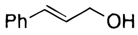
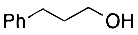
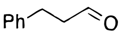
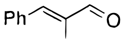
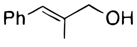
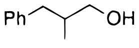
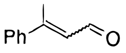
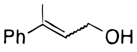
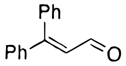
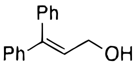
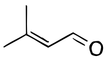
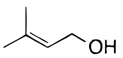
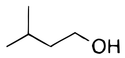
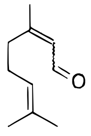
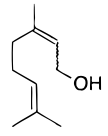
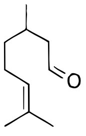
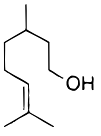
Table 1. Hydrogenation of α,β-Unsaturated Aldehydes Using Rh Carbonyl Cluster Catalysts in the Presence of H_2 and CO[a]

Run	Substrate	Conv. (%)	Products Selectivity[b] (%) 1		2		3	
1		100		96 (85)[c]				4
2[d]	reuse 1	100		94				6
3[d]	reuse 2	98		82		2		16
4[e]		45		77		14		9
5		100		94 (80)[c]				6
6	 (E/Z=0.38)	100	 (E/Z=0.38)	~100				
7		99		~100 (97)[c]				
8		100		91				9
9		97		87		4		9
10[e]	(E/Z=2.01)	34	(E/Z=2.01)	84		16		0

[a] Conditions and definitions: Substrate, 1.5 mmol; $Rh_6(CO)_{16}$, 0.010 mmol; benzene, 3.0 mL; polymer (**I**, 40 mg (0.18 mmol of N); $P_{H_2/CO}$ = 10 (1:1) atm; 30 °C; 15 h. 1, Unsaturated alcohol; 2, saturated aldehyde; 3, saturated alcohol. [b] Selectivity = $i/\Sigma i$ (i = yields of 1, 2, and 3). Quantitative analyses of reaction products were performed by GC. [c] Values in parentheses are isolated yields. In the isolation of products, the reaction scale was 3-fold under $P_{H_2/CO}$ = 12 (1:1) atm and use of column chromatography on alumina with a 1:10 mixture of ethyl acetate and *n*-hexane gave pure reduction products. [d] The spent catalyst was recharged. [e] For the homogeneous system: benzene, 3.0 mL; Et_3N, 0.18 mmol.

NMR (270 MHz, $CDCl_3$) δ 4.18 (d, J = 4.95 Hz, 2H), 5.90 (tt, J = 15.34 Hz, 1H), 6.49 (d, J = 15.83 Hz, 2H), 6.72 (dd, J = 10.14 and 15.7 Hz, 1H), 7.12–7.35 (m, 5H); IR 3350, 3000, 1445, 1380, and 995 cm^{-1}. The IR spectrum of the obtained polymer showed the formation of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_{12}(CO)_{30}]^{2-}$ anions as main species together with a small amount of $[Rh_6(CO)_{15}H]^-$ (2075 w (sh), 2066 m, 2035 s, 2000 m (sh), 1992 s (br), 1967 s (br), 1817 w (sh), 1803 w (sh), 1769 s (br), 1763 s (sh), 1717 w (br) cm^{-1}; Nujol mull).[8,9]

Homogeneous hydrogenations of 3-phenyl-2-propenal (cinnamaldehyde) using $Rh_6(CO)_{16}$ and triethylamine in various solvents were carried out in the presence of a reducing agent of H_2 and CO (3:1, 4 atm). Use of THF gave a high yield of cinnamyl alcohol, while methanol, benzene, toluene, and cyclohexane were poor solvents, respectively. In our scrutiny of additives, we found triethylamine to be excellent for this selective hydrogenation. Therefore, we think that amino and ether functions are important elements for attaining high chemoselectivity for the hydrogenation using the $Rh_6(CO)_{16}$ catalyst. A functionalized polystyrene having both amino and ether functions **I** was prepared by a reaction of (chloromethyl)polystyrene with (2-(dimethylamino)ethoxy)ethanol (*vide supra*). Use of the polymer **I** led to high yields of cinnamyl alcohol even in hydrocarbon solvents; *e.g.* cyclohexane gave 83% yield, while hydrogenation with the polymer **II** resulted in a 40% yield of cinnamyl alcohol.[10]

Heterogeneous hydrogenations of various α,β-unsaturated aldehydes using the polymer **I** in place of amines were carried out under conditions similar to those for the above homogeneous system. The results are shown

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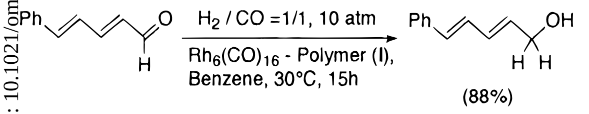
[8] IR assignments: $[Rh_{12}(CO)_{30}]^{2-}$, 2075, 2035, 2000, 1803, 1769 cm^{-1}; $[Rh_6(CO)_{15}]^{2-}$, 1992, 1967, 1817, 1763, 1717 cm^{-1}; $[Rh_6(CO)_{15}H]^-$, 2066 cm^{-1}. These assignments are based on comparison of IR data with those in: (a) Kaneda, K.; Takemoto, T.; Kitaoka, K.; Imanaka, T. *Organometallics* **1991**, *10*, 846. (b) Martinengo, S. Personal communication. (c) Chini, P.; Martinengo, S. *Inorg. Chim. Acta* **1969**, *3*, 299. Adsorption bands at about 2020 s, 1995 m, and 1780 cm^{-1} for $[Rh_6(CO)_{15}H]^-$ were overlapped by strong adsorption bands at 2035, 2000, and 1769 cm^{-1} due to $[Rh_{12}(CO)_{30}]^{2-}$.

[9] Extraction of Rh clusters from the greenish brown polymer using a THF solution of NBu_4Cl was carried out under an N_2 atmosphere. The IR spectrum of the reddish brown solution showed adsorption bands at 2046 s, 2015 s, 1869 m, and 1839 m (sh) cm^{-1} due to the formation of $[Rh_5(CO)_{15}]^-$. For reference data for $[Rh_5(CO)_{15}]^-$ (2046 s, 2015 s, 1868 m, 1838 ms cm^{-1}), see: (a) Fumagalli, A.; Koetzle, T. F.; Takusagawa, F.; Chini, P.; Martinengo, S.; Heaton, B. T. *J. Am. Chem. Soc.* **1980**, *102*, 1740. (b) Chini, P.; Martinengo, S. *Inorg. Chim. Acta* **1969**, *3*, 21. (c) Kawi, S.; Gates, B. C. *Inorg. Chem.* **1994**, *33*, 503.

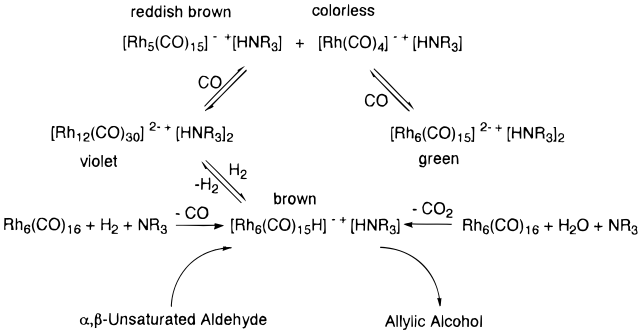
[10] In the case of the heterogeneous reaction, THF is not an excellent solvent: after the reduction in a THF solvent, the filtrate of the reaction mixture was reddish brown, which shows elution of Rh complexes from the aminated polymer. Detailed results of the homogeneous catalysis are given in the Supporting Information.

in Table 1 together with the corresponding homogeneous ones (runs 4 and 10). It should be noted that the polymer-bound Rh complex has a higher catalytic activity for the hydrogenation than the corresponding homogeneous Rh system (runs 1 vs 4 and 9 vs 10). In the cases of methyl-substituted cinnamaldehydes, 2-methyl-3-phenyl-2-propenal gave a 94% yield of 2-methyl-3-phenyl-2-propen-1-ol, accompanied by a small amount of 2-methyl-3-phenylpropanol, and a carbonyl function was exclusively reduced to afford 3-phenyl-2-buten-1-ol from 3-phenyl-2-butenal. The hydrogenation of 3,3-diphenyl-2-propenal also occurred chemoselectively to give 3,3-diphenyl-2-propen-1-ol as the sole product. Further, the aliphatic α,*β*-unsaturated aldehydes 3-methyl-2-butenal and citral gave rise to the corresponding allylic alcohols in high yields. The isolated olefinic function in citral remained intact under the reaction conditions.[11] Hydrogenation of citral containing two geometrical isomers ($E/Z = 2.01$) proceeded with high retention of olefinic configuration (runs 9 and 10). A similar stereospecificity could be observed in 3-phenyl-2-butenal (run 6). This high chemoselectivity could be observed also in the hydrogenation of a diene system; (*E*,*E*)-5-phenyl-2,4-pentadienal gave (*E*,*E*)-5-phenyl-2,4-pentadien-1-ol in high yield (eq 2). Notably, the reaction of allylic alcohols as starting materials, *e.g.* cinnamyl alcohol and geraniol, resulted in quantitative recovery of the alcohols. This shows that both hydrogenation and isomerization of allylic alcohols do not occur under the above reaction conditions.[12]



(2)

Scheme 2. Interconversion of Rh Carbonyl Clusters under the Reaction Conditions



In the case of a reducing agent consisting of CO and H_2O, a hydride–metal species is formed by attack of hydroxyl anion at the carbonyl moiety on Rh clusters, followed by decarboxylation.[13] We think that similar hydride species can be generated also from the heterolytic splitting reaction of molecular hydrogen with $Rh_6(CO)_{16}$ in the presence of the amines.[14] In a separate experiment, reaction of the polymer **I** with $Rh_6(CO)_{16}$ under an atmosphere of H_2 and CO was carried out at 30 °C for 15 h. The IR spectrum of the isolated polymer-bound metal complex showed the formation of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_{12}(CO)_{30}]^{2-}$ as major species with a small amount of $[Rh_6(CO)_{15}H]^-$ (Scheme 2). On exposure to air, the $[Rh_6(CO)_{15}H]^-$ and $[Rh_6(CO)_{15}]^{2-}$ species were gradually converted into $[Rh_{12}(CO)_{30}]^{2-}$ species with a color change from greenish brown to violet through reddish brown. The color change of polymer-bound Rh complexes and the IR spectra suggest the formation of the reddish brown $[Rh_5(CO)_{15}]^-$ anion as an intermediate. A reverse process from the Rh_{12} species to the Rh_6–H species might be achieved during the above hydrogenation of α,*β*-unsaturated aldehydes; a spent polymeric complex containing the $[Rh_{12}(CO)_{30}]^{2-}$ species could be reused for hydrogenation of cinnamaldehyde without appreciable loss of the catalytic activity (run 2) and the polymer after hydrogenation was again greenish brown, which contained the above Rh_6 and Rh_{12} species.

In conclusion, polymer-bound Rh cluster complexes obtained from treatment of a functionalized polystyrene having 2-(dimethylamino)ethoxy moieties with $Rh_6(CO)_{16}$ can catalyze the chemoselective hydrogenations of α,*β*-unsaturated aldehydes to allylic alcohols in high yields. The active species in the above reactions is a $[Rh_6(CO)_{15}H]^-$ anion, which forms ion pairs with ammonium cation in the polymer. Using the multifunctional polymer ligands, it becomes possible not only to reuse the hydrogenation catalyst but also to enhance its activity and selectivity.[15]

Supporting Information Available: Table 2, giving data for the homogeneous hydrogenation of cinnamaldehyde using $Rh_6(CO)_{16}$ (1 page). Ordering information is given on any current masthead page.

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(11) 1-Octene as a common oelfin was not reduced under the above conditions. In the case of α,*β*-unsaturated aldehydes, reduction of olefinic functions might not occur by 1,2-addition of metal–hydride to olefinic carbons but by 1,4-addition.

(12) Isomerization of allylic alcohols to saturated aldehydes easily occurred in the presence of metal catalysts; see: Süss-Fink, G.; Meister, J. In *Advances in Organometallic Chemistry*; Stone, E. G., West, R., Eds.; Academic Press: San Diego, CA, 1993; Vol. 35, p 107.

(13) (a) Heaton, B. T.; Strona, L.; Martinengo, S.; Strumolo, D.; Goodfellow, R. J.; Sadler, I. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1499. (b) Dufour, P.; Huang, L.; Choplin, A.; Sanchez-Delgado, S. G.; Theolier, A.; Basset, J. M. *J. Organomet. Chem.* **1988**, *354*, 243.

(14) (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (c) Collmann, J. P.; Hegedus, L. S. *Prnciples and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 319.

(15) Books and review on polymer-bound metal complex catalysts: (a) Gates, B. C. *Catalytic Chemistry*; Wiley: New York, 1992. (b) Sheats, J. E., Carraher, C. E., Jr., Pittman, C. E., Jr., Zeldin, M., Currell, B., Eds. *Inorganic and Metal-Containing Polymeric Materials*; Plenum Press: New York, 1990. (c) Bergbreiter, D. E. *CHEMTECH* **1987**, *17*, 686.

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