ORGANIC LETTERS

2002
Vol. 4, No. 14
2369−2371

$[RuCl_2(p\text{-cymene})]_2$ on Carbon: An Efficient, Selective, Reusable, and Environmentally Versatile Heterogeneous Catalyst

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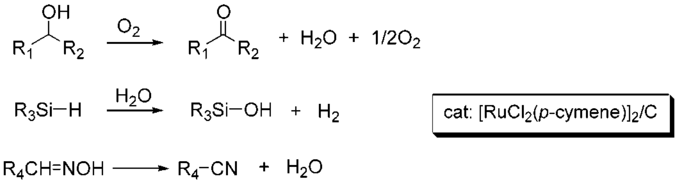
Received April 29, 2002

ABSTRACT



A heterogeneous ruthenium catalyst, easily prepared by adsorption of $[RuCl_2(p\text{-cymene})]_2$ on activated carbon, exhibited a highly efficient and selective catalytic activity in various environmentally attractive transformations such as aerobic oxidation, hydrolytic oxidation, and dehydration processes with excellent recyclability.

Heterogeneous catalysis has been employed as an important chemical technology because of the inherent operational advantages such as ease of handling, separation, and recovery for the reuse of insoluble catalysts.[1] However, certain limitations of heterogeneous catalysis are frequently encountered, such as gradual leaching of transition metals from the solid supports and lower efficiency or selectivity compared to that of homogeneous systems.[2] To improve these properties, a variety of polymer-supported or microencapsulated heterogeneous catalysts have been devised in recent years.[3] During the course of our studies on catalytic reactions,[4] we have found that a dimeric Ru complex, $[RuCl_2(p\text{-cymene})]_2$ (**1**), displays a surprisingly diverse and highly selective catalytic activity in certain transformations such as hydrosilylation of alkynes,[4a] aerobic oxidation of alcohols,[4b,c] hydrolytic oxidation of silanes to silanols,[4d] 1,4-addition of terminal alkynes to conjugated enones,[4e] and dehydration of aldoximes to nitriles.[4f] Given its wide utility as an efficient catalyst in various other reactions,[5] a heterogeneous version of the ruthenium catalyst with practical aspects would be highly desirable. Herein, we describe the preparation of a

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(1) For reviews, see: (a) Smith, K. *Solid Supports and Catalysts in Organic Synthesis*; Ellis Hornood: Chichester, 1992. (b) Keim, W.; Driessen-Hölscher B. In *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; Wiley-VCH: Weinheim, 1997; Vol. 1, p 231. (c) Basset, J. M.; Candy, J. P.; Santini, C. C. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2, p 387.

(2) (a) Blum, J.; Rosenfeld, A.; Polak, N.; Israelson, O.; Schumann, H.; Avnir, D. *J. Mol. Catal*. **1996**, *107*, 217. (b) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1048. (c) Thomas, J. M. *Angew. Chem., Int. Ed*. **1999**, *38*, 3588.

(3) For some selected examples, see: (a) Annis, D. A.; Jacobsen, E. N. *J. Am. Chem. Soc*. **1999**, *121*, 4147. (b) Kobayashi, S.; Endo, M.; Nagayama, S. *J. Am. Chem. Soc*. **1999**, *121*, 11229. (c) Son, S. U.; Lee, S. I.; Chung, Y. K. *Angew. Chem., Int. Ed*. **2000**, *39*, 4158. (d) Yu, X.-Q.; Huang, J.-S.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc*. **2000**, *122*, 5337. (e) Djakovitch, L.; Koehler, K. *J. Am. Chem. Soc*. **2001**, *123*, 5990.

(4) (a) Na, Y.; Chang, S. *Org. Lett*. **2000**, *2*, 1887. (b) Lee, M.; Chang, S. *Tetrahedron Lett*. **2000**, *41*, 7507. (c) Chang, S.; Lee, M.; Ko, S.; Lee, P. H. *Synth. Commun*. **2002**, *32*, 1279. (d) Lee, M.; Ko, S.; Chang, S. *J. Am. Chem. Soc*. **2000**, *122*, 12011. (e) Chang, S.; Na, Y.; Choi, E.; Kim, S. *Org. Lett*. **2001**, *3*, 2089. (f) Yang, S. H.; Chang, S. *Org. Lett*. **2001**, *3*, 4209. (g) Ko, S.; Na, Y.; Chang, S. *J. Am. Chem. Soc*. **2002**, *124*, 750.

10.1021/ol0260977 CCC: $22.00

supported ruthenium catalyst **1** and its versatile uses for some environmentally attractive reactions.

The heterogeneous catalyst was readily prepared by the treatment of $[RuCl_2(p\text{-cymene})]_2$ (**1**) with activated carbon (KB, 100 mesh) in benzene.[6] The adsorbed amounts of ruthenium was determined by elemental analysis to be in the range of 2.15−2.65 wt % to C.[7] Although the Ru complex **1** was also easily adsorbed on other types of carbon to a similar extent,[8] supported catalysts thus obtained showed lower activities in the examined reactions compared to that adsorbed on the charcoal KB (100 mesh). A transmission electron microscopy (TEM) image of **1** immobilized on the activated carbon (KB, 100 mesh) shown in Figure 1 reveals that ruthenium atoms are not uniformly distributed in the carbon atoms.[9]

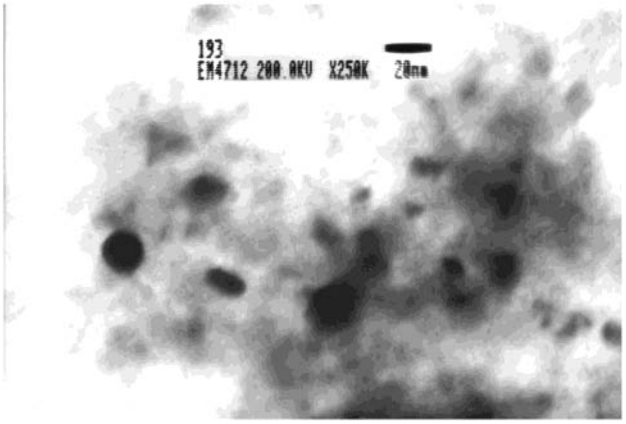
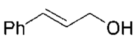
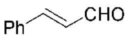
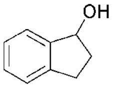
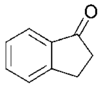
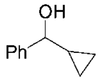
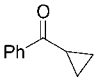
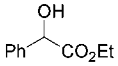
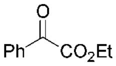
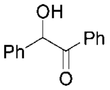
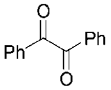


Figure 1. Transmission electron microscopy (TEM) of **1**/C.

On the basis of our earlier reports on the aerobic oxidation of alcohols by the soluble catalyst $[RuCl_2(p\text{-cymene})]_2$ (**1**),[4b,c] we first examined the catalytic activity of **1**/C thus prepared for the aerobic oxidation. Using the heterogeneous catalyst **1**/C (2.2 wt %), various substrates such as benzylic, allylic, and α-carbonyl alcohols (6.5 mol % of ruthenium atom)[10] were readily oxidized under 1 atm of O_2 to the corresponding carbonyl compounds in high yields in the presence of Cs_2CO_3 (5 mol %) (Table 1).

Table 1. Catalytic Aerobic Oxidation of Various Alcoholic Substrates[a]

entry	alcohol	t/h	product	yield (%)[b]
1	$PhCH_2OH$	3	PhCHO	92
2		6		80
3		6		80
4		9		96
5		7		95
6		1		93

[a] A solution of alcohol (1.0 mmol) in toluene (4 mL) was heated to 110 °C in the presence of **1**/C (2.2 wt %, 300 mg) and Cs_2CO_3 (5 mol %) under 1 atm of O_2. [b] Isolated yield after column chromatography.

Likewise in reactions using the soluble catalyst **1**, over-oxidized side products such as carboxylic acids or esters were not observed under the heterogeneous conditions. The solid-supported catalyst (**1**/C) was recovered quantitatively by a simple filtration, and the filtered catalyst along with the replenished Cs_2CO_3 (3 mol % each run) could be reused for the next cycles with minimal loss of activity up to nine cycles (Table 2).[11] It should be noted that leaching of Ru metal from the solid support was almost negligible over the recycles. For example, when **1**/C of 2.2 wt % Ru to C was employed as an initial catalyst in the aerobic oxidation, the Ru content on C was determined to be 1.5 wt % after nine

Table 2. Reusability of a Heterogeneous Catalyst **1**/C for the Aerobic Oxidation of 4-Bromobenzyl Alcohol[a]

	run								
	1	2	3	4	5	6	7	8	9
time (h)	6	7	8	8	8	8	8	8	9
yield (%)[c]	89	92	97	92	94	89	93	85	81

[a] A solution of alcohol (1.0 mmol) in toluene (3.3 mL) was reacted under 1 atm of O_2 in the presence of **1**/C (initially 2.2 wt %, 300 mg) at 110 °C. [b] Additional amounts of Cs_2CO_3 (3 mol %) were added in each cycle from the second run. [c] Indicates isolated yield after chromatography.

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(5) For some recent examples, see: (a) Karlsson, U.; Wang, G.-Z.; Bäckvall, J.-E. *J. Org. Chem.* **1994**, *59*, 1196. (b) Gendre, P. L.; Offenbecher, M.; Bruneau, C.; Dixneuf, P. H. *Tetrahedron: Asymmetry* **1998**, *9*, 2279. (d) Lee, D.; Huh, E. A.; Kim, M.-J.; Jung, H. M.; Koh, J. H.; Park, J. *Org. Lett.* **2000**, *2*, 2377. (e) Trost, B. M.; Doherty, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 3801. (f) Iwasa, S.; Takezawa, F.; Tuchiya, Y.; Nishiyama, H. *Chem. Commun.* **2001**, 59.

(6) **Procedure for Preparation of Supported Catalyst 1/C.** To a stirred suspension of charcoal (KB, 100 mesh, surface area 1500 m^2/g, 1.25 g) in benzene (37 mL) was added the ruthenium complex **1** (250 mg), and the mixture was stirred for 14 h at room temperature. The mixture was filtered and washed with DMF, methanol, and hot benzene, and the filtered solid was dried under vacuum at 50−60 °C for 24 h.

(7) The adsorbed amounts of Ru on C were lower when other solvents were used (e.g., 0.6 wt % to C prepared in CH_3CN, 1.4 wt % in CH_2Cl_2, 1.2 wt % in 1,4-dioxane, and 2.1 wt % in THF).

(8) Recently, a supported catalyst of $RuCl_2(PPh_3)_3$/C was prepared and used for the oxidative cleavage of vicinal diols; see: Takezawa, E.; Sakaguchi, S.; Ishii, Y. *Org. Lett.* **1999**, *1*, 713.

(9) Although further studies have to be carried out to elucidate what type of interactions the adsorbed ruthenium maintains, it is assumed that the cleaved ruthenium monomer replaces cymene ligand with a solvent that was observed by ^1H NMR of filtrate after the adsorption procedure.

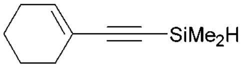
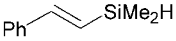
(10) It is based on the elemental analysis of the prepared solid-supported complex.

cycles. To demonstrate whether the observed catalysis is heterogeneous, the catalyst was filtered off after ca. 50% conversion at the same temperature of the reaction and the filtrate was then allowed to react at 110 °C. No further reaction proceeded from the filtrate even in the presence of additional cesium salt, demonstrating that the present system is heterogeneous.[12]

The hydrolytic oxidation of organosilanes with the heterogeneous ruthenium catalyst turned out also to be highly efficient and selective for the formation of silanols (Table 3).[4d] Using **1**/C as a catalyst (9.8 mol % of ruthenium atom), conversion of silanes to silanols proceeded smoothly at room temperature upon addition of excess water (4 equiv) in CH_3CN. Under the heterogeneous conditions, silanols were obtained in high yields with only negligible formation of disiloxanes (<5%, entries 1−5). Recovery and reuse of the heterogeneous catalyst in the hydrolytic oxidation was readily achieved, as demonstrated in the reaction of diphenylmethylsilane in THF, although the reaction times were longer over the cycles (entries 6−10). Of special note is that the conversion of silanes to silanols is highly practical judged from the reusability of the heterogeneous catalyst as well as the use of water as an environmentally benign oxidant.

Table 3. Hydrolytic Oxidation of Organosilanes to Silanols[a]

$$R_3SiH + H_2O \xrightarrow[\text{solvent, RT}]{2.2\text{wt\% } \mathbf{1}/C} R_3Si{-}OH$$

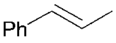
entry	silane	t/min	yield (%)[b]
1	$PhMe_2SiH$	10	87
2	$Ph{-}C{\equiv}C{-}SiMe_2H$	20	77
3		90	91
4		15	82
5	Ph_2MeSiH (cycle 1)	60	96
6	(cycle 2)	60	98
7	(cycle 3)	180	97
8	(cycle 4)	120	92
9	(cycle 5)	180	92
10	(cycle 6)	180	83

[a] Silane (1.0 mmol) was reacted with water (4 equiv) in the presence of **1**/C (450 mg) in a solvent (10 mL, CH_3CN in entries 1−4 and THF in entries 5−10) at room temperature. [b] Isolated yield.

Catalytic conversion of aldoximes to the corresponding nitriles was another example of the successful application of the solid **1**/C catalyst (Table 4). Various aldoximes were readily dehydrated under the heterogeneous conditions (4.4 mol % of ruthenium atom) at 80 °C in CH_3CN to afford the corresponding nitriles in high yields (entries 1−5) with similar efficiency compared to that of the reaction of the homogeneous conditions.[4f] Recovery and reuse of **1**/C catalyst was examined in the dehydration of 4-bromobenzaldoxime under the same conditions (entries 6−10). The efficiency of the heterogeneous catalyst on the dehydration was maintained up to four runs in this case, and then it took slightly longer to get a complete conversion.

Table 4. Catalytic Dehydration of Various Aldoximes to Nitriles[a]

$$RCH{=}NOH \xrightarrow[CH_3CN,\ 80\ ^{o}C]{\mathbf{1}/C,\ MS\ 4A} R{-}CN + H_2O$$

entry	R	time	yield (%)[b]
1	Cyclohexyl	15 min	85
2	$(4\text{-}MeO)C_6H_4$	20 min	93
3	$(4\text{-}HO)C_6H_4$	20 min	94
4	2-thienyl	15 min	93
5		15 min	91
6	$(4\text{-}Br)C_6H_4$ (cycle 1)	30 min	84
7[c]	(cycle 2)	1 h	88
8[c]	(cycle 3)	2 h	93
9[c]	(cycle 4)	2 h	90

[a] A solution of aldoxime (0.5 mmol) in CH_3CN (5 mL) was heated to 80 °C in the presence of **1**/C (200 mg) and molecular sieves 4 Å (2 wt equiv to aldoxime). [b] Isolated yield. [c] No additional molecular sieves were added during the recycles.

In conclusion, a heterogeneous ruthenium catalyst has been readily prepared by a simple adsorption of $[RuCl_2(p\text{-cymene})]_2$ on active charcoal, and its utility has been demonstrated in some environmentally attractive reactions of the aerobic oxidation of alcohols, hydrolytic oxidation of silanes, and dehydration of aldoximes with high efficiency, selectivity, and reusability.

Acknowledgment. We thank the Center for Molecular Design and Synthesis (CMDS) at KAIST for this work. E.C. is a recipient of a fellowship of Research Institute for Basic Science at Ewha Womans University.

OL0260977

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(11) Addition of fresh Cs_2CO_3 in certain amounts (2−3 mol %) in each cycle was important to maintain the catalytic activity of the filtered **1**/C high. For example, catalytic activity of the recycled **1**/C was lost gradually after the second cycle when fresh Cs_2CO_3 was not replenished.

(12) For references, see: (a) Arends, I. W. C. E.; Sheldon, R. A.; Wallau, M.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1144. (b) Sheldon, R. A.; Wallau,; Arends, I. W. C. E.; Schuchardt, U. *Acc. Chem. Res*. **1998**, *31*, 485.