Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 45 (2004) 4607–4610

Tetrahedron Letters

Heterogeneous Shvo-type ruthenium catalyst: dehydrogenation of alcohols without hydrogen acceptors

Jun Ho Choi, Namdu Kim, Yong Jun Shin, Jung Hye Park and Jaiwook Park*

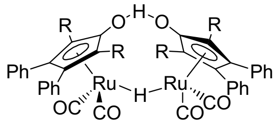
Center for Integrated Molecular System, Department of Chemistry, Division of Molecular and Life Science, Pohang University of Science and Technology (POSTECH), San 31 Hyoja Dong, Pohang 790–784, Republic of Korea

Received 10 March 2004; revised 20 April 2004; accepted 22 April 2004

Abstract—A Shvo-type diruthenium complex is heterogenized by a sol–gel process, which catalyzes the conversion of alcohols to carbonyl compounds and molecular hydrogen without any additive. The heterogeneous catalyst is recoverable by simple filtration, stable in the air, and reusable.

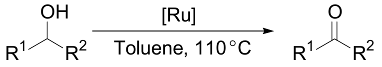
© 2004 Elsevier Ltd. All rights reserved.

The Shvo complex, $[(\eta^5\text{-}Ph_4C_4CO)_2H]Ru_2((CO)_4)(\mu\text{-}H)$ (**1**), is a versatile catalyst.[1] It has been used for many homogeneous hydrogen-transfer reactions such as the disproportionation of aldehydes to esters,[2] the reduction of aldehydes and ketones,[3] the Oppenauer-type oxidation of alcohols and amines,[4,5] and the racemization of alcohols and amines.[6,7] During our study on the dynamic kinetic resolution of alcohols with the catalytic activity for the racemization of alcohols,[6] we recognized that **1** catalyzes also the dehydrogenation of alcohols and found a brief report that describes the catalytic dehydrogenation of 2-octanol and cyclohexanol at 145 °C by a dimeric ruthenium complex, $[(\eta^5\text{-}Ph_4C_4CO)(CO)_2Ru]_2$, which readily converts into **1** in the reaction with alcohols.[8]



1: R = Ph
2: R = Me
3: R = 1-Naphthyl

For practical uses, heterogeneous catalysts are preferable to homogeneous one, thus we planned to synthesize a simple derivative of **1**, which can be easily employed in the sol–gel process to give a recoverable and reusable catalyst. First, we examined the dehydrogenation of 1-phenylethanol with **1**–**3** to see the substituent effect of the pentadienyl ring on the catalytic activity (Scheme 1). Interestingly, **1** having phenyl substituents showed the highest activity; under the conditions of the entry 5 in Table 1, acetophenone was produced in 60% yield by **2** and in 68% by **3**. Then, the efficiency of the



Scheme 1.

Table 1. Dehydrogenation of 1-phenylethanol by **1** in various conditions

Entry	mol %	Concentration (M)	Time (h)	Solvent	Yield (%)[a]
1	4.0	0.1	24	Ethyl acetate	22.8
2	4.0	0.1	24	Benzene	49.5
3	4.0	0.1	24	Heptane	59.7
4	4.0	0.1	9	Octane	98.0
5	4.0	0.1	9	Toluene	89.3
6	2.0	0.1	9	Toluene	81.0
7	1.0	0.1	9	Toluene	65.9
8	8.0	0.1	6	Toluene	94.0
9	4.0	0.5	9	Toluene	95.4

[a] By GC.

Keywords: Silica sol–gel; Diruthenium; Dehydrogenation; Alcohols.

* Corresponding author. Tel.: +82-54-279-2117; fax: +82-54-279-3399; e-mail: pjw@postech.ac.kr

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.04.113

dehydrogenation was optimized with using **1** with varying conditions (Table 1).[9] The reaction rate depended on the reaction temperature; it was almost completed in 9 h in refluxing octane (bp 126 °C) while in refluxing benzene (bp 80 °C) the reaction proceeded in less than 50% even after 24 h, (entry 2 vs entry 4). It was notable that a more concentrated solution led to a higher yield (entry 8 vs entry 9).

We thought that the derivatives of **1**, which contain hydroxy groups, would be suitable for sol–gel processes to afford robust catalysts.[10] The Shvo-type diruthenium complex **10**, which has two (hydroxylmethyl)phenyl groups, was synthesized from the cyclopetadienone **7** by the procedure reported by Shvo and Menashe[2,11] Meanwhile, **7** was prepared from 4-(phenylethynyl)benzaldehyde (**4**)[12] through a three-step process: (1) protection of the formyl group of **4**; (2) oxidation of the triple bond to give the 1,2-diketone **6**;[13] (3) coupling of **6** and diphenylacetone (Scheme 2).[14] The silica gel entrapping **10** was prepared by the sol–gel process involving a mixture of **10**, tetramethyl orthosilicate, methanol, water and THF. The resulting gel was washed with methanol and dried under vacuum to give **11** as yellow powder entrapping **10** in 77% yield.[15]

The heterogeneous catalyst **11** showed a better activity than **1** in the dehydrogenation of 1-phenylethanol, which was completed in 6 h. The catalyst was recoverable by simple filtration, and reusable several times. Although the activity decreased gradually, over 90% of the original activity was maintained in the fourth use: 1st, 100%; 2nd, 97.4%; 3rd, 96.0%; 4th, 90.5%; 5th, 86.8%. The catalyst **11** was effective for various alcohols (Table 2). Aliphatic alcohols as well as benzylic alcohols were dehydrogenated to the corresponding ketones in high yields. The production of a γ-lactone from 1,2-benzenedimethanol implicates the dehydrogenation of the intermediate hemiacetal. However, the reaction of benzyl alcohol was relatively slow, and produced benzyl benzoate in less than 0.5%. In comparison to the known

Table 2. Dehydrogenation of alcohols with **11**[a]

Entry	Substrate	Time (h)	Yield (%)[b]
1	1-Phenylethanol	6	97
2	1-(4-Chlorophenyl)ethanol	6	97
3	1-(4-Methoxyphenyl)ethanol	6	97
4	1-Cyclohexylethanol	8	97
5	2-Octanol	6	97
6	Cyclohexanol	20	100[c]
7	1,2-Benzenedimethanol	6	96[d]
8	Benzyl alcohol	6	41[e]

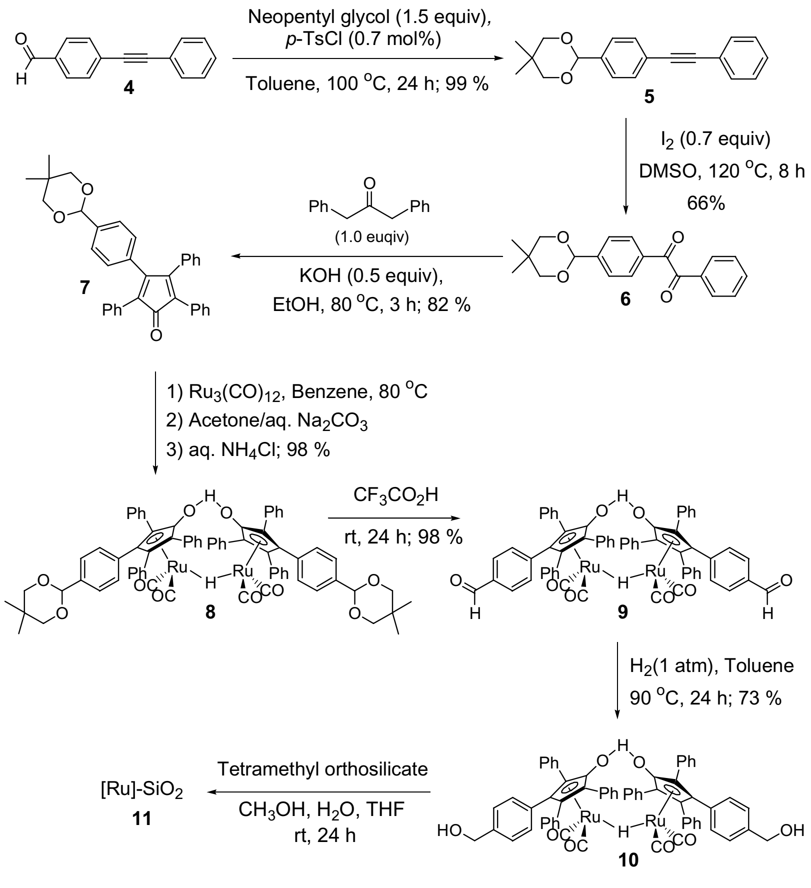
[a] In refluxing toluene (0.1 M) with 4.4 mol% of **11**.

[b] Isolated yield.

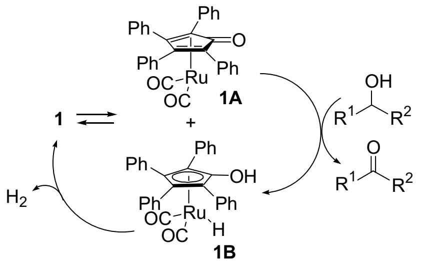
[c] By GC.

[d] The product was 3*H*-isobenzofuran-1-one.

[e] By GC with using biphenyl as the internal standard.



Scheme 2.



Scheme 3.

dehydrogenation catalysts such as $RuH_2(PPh_3)_4$,[16] $IrH_5(^{i}PrP)_2$,[17] $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2P\text{-}t\text{-}Bu_2)_2\}$,[18] $Ru(OCOCF_3)_2(CO)(PPh_3)_2$,[19] $Ru_3(CO)_{12}/PPh_3$,[20] **11** has several advantages: stable in the air and easy to handle; active without additives; active under mild conditions.

A possible pathway for the catalytic dehydrogenation is proposed in Scheme 3: The diruthenium complex **1** is in equilibrium with mononuclear species **1A** and **1B**.[21] An alcohol reacts with the 16-electron species **1A** to give the hydride complex **1B** and the corresponding ketone. Then, **1B** loses molecular hydrogen with being coupled with another **1B** to form **1**.

In summary, we synthesized a heterogeneous version of the versatile Shvo complex through sol–gel process, and demonstrated that it is a recoverable and reusable catalyst for the efficient dehydrogenation of alcohols.

Acknowledgements

This work was supported financially by the Center for Integrated Molecular System, the National Laboratory of Chirotechnology and MOE through the BK21 project.

References and notes

1. (a) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. *J. Am. Chem. Soc.* **1986**, *108*, 7400–7402; (b) Jung, H. M.; Shin, S. T.; Kim, Y. H.; Kim, M.-J.; Park, J. *Organometallics* **2001**, *20*, 3370–3372; (c) Jung, H. M.; Choi, J. H.; Lee, S. O.; Kim, Y. H.; Park, J. H.; Park, J. *Organometallics* **2002**, *21*, 5674–5677.
2. Menashe, N.; Shvo, Y. *Organometallics* **1991**, *10*, 3885–3891.
3. Shvo, Y.; Czarkie, D. *J. Organomet. Chem.* **1986**, *315*, C25–C28.
4. (a) Almeida, M. L. S.; Beller, M.; Wang, G.-Z.; Bäckvall, J.-E. *Chem. Eur. J.* **1996**, *2*, 1533–1536; (b) Almeida, M. L. S.; Kočovský, P.; Bäckvall, J.-E. *J. Org. Chem.* **1996**, *61*, 6587–6590; (c) Csjernyik, G.; Éll, A. H.; Fadini, L.; Pugin, B.; Bäckvall, J.-E. *J. Org. Chem.* **2002**, *67*, 1657–1662.
5. Éll, A. H.; Samec, J. S. M.; Brasse, C.; Bäckvall, J.-E. *Chem. Commun.* **2002**, 1144–1145.
6. (a) Larsson, A. L. E.; Persson, B. A.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **1997**, *36*, 1122–1211; (b) Persson, B. A.; Larsson, A. L. E.; Ray, M. L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1999**, *121*, 1645–1650; (c) Kim, M.-J.; Ahn, Y.; Park, J. *Curr. Opin. Biotechnol.* **2002**, *13*, 578–587; (d) Pàmies, O.; Bäckvall, J.-E. *Chem. Rev.* **2003**, *103*, 3247–3261.
7. Pàmies, O.; Éll, A. H.; Samec, J. S. M.; Hermanns, N.; Bäckvall, J.-E. *Tetrahedron Lett.* **2002**, *43*, 4699–4702.
8. Blum, Y.; Shvo, Y. *J. Organomet. Chem.* **1985**, *282*, C7–C10.
9. *A typical procedure for dehydrogenation*: In a 50 mL flask equipped with a grease-free high vacuum stopcock, **1** (8.6 mg, 0.0080 mmol) and 1-phenylethanol (0.20 mmol) were mixed with dry toluene (2 mL) under Ar atmosphere. The mixture was heated to reflux. The reaction was checked by GC.
10. (a) Zehl, G.; Bischoff, S.; Mizukami, F.; Isutzu, H.; Bartoszek, M.; Jancke, H.; Lücke, B.; Maeda, K. *J. Mater. Chem.* **1995**, *5*, 1893–1897; (b) Lu, Z.; Lindner, E.; Mayer, H. A. *Chem. Rev.* **2002**, *102*, 3543–3578; (c) Kawano, S.; Tamaru, S.; Fujita, N.; Shinkai, S. *Chem. Eur. J.* **2004**, *10*, 343–351.
11. Compound **5**: yield: 99%; mp: 115 °C; ^{1}H NMR ($CDCl_3$) δ 7.46–7.57 (m, 6H), 7.30–7.37 (m, 3H), 5.39 (s, 1H), 3.78 (d, $J = 11.2$ Hz, 2H), 3.65 (d, $J = 10.7$ Hz, 2H), 1.29 (s, 3H), 0.80 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 138.6, 131.8, 131.8, 128.8, 128.5, 126.4, 124.0, 123.4, 101.5, 89.9, 89.5, 77.8, 30.5, 23.3, 22.1; MS (EI): *m/z*: 292.14 (M^+); Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.25; H, 6.81.
    Compound **6**: yield: 66%; mp: 95.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.92–8.0 (m, 4H), 7.63–7.67 (m, 3H), 7.47–7.53 (m, 2H), 5.44 (s, 1H), 3.78 (d, $J = 11.1$ Hz, 2H), 3.66 (d, $J = 11.0$ Hz, 2H), 1.27 (s, 3H), 0.81 (s, 3H); ^{13}C NMR δ 194.7, 194.6, 145.3, 135.1, 133.4, 133.2, 130.2, 130.1, 129.2, 127.1, 100.7, 77.9, 30.5, 23.2, 22.1; FT-IR (KBr) 1667 cm^{-1}; MS (EI): *m/z*: 324.15 (M^+); Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 74.02; H, 6.13.
    Compound **7**: yield: 82%; mp: 200–202 °C; ^{1}H NMR δ 7.10–7.36 (m, 15H), 6.88–6.98 (m, 4H), 5.33 (s, 1H), 3.76 (d, $J = 11.2$ Hz, 2H), 3.63 (d, $J = 10.7$ Hz, 2H), 1.28 (s, 3H), 0.79 (s, 3H); ^{13}C NMR δ 200.5, 154.7, 154.0, 238.8, 133.7, 133.2, 130.9, 130.8, 129.7, 129.5, 128.7, 128.3, 128.2, 127.7, 127.6, 126.1, 125.9, 125.6, 101.8, 77.9, 23.3, 22.1, FT-IR (KBr) 1707 cm^{-1}; MS (EI): *m/z*: 498.31 (M^+); Anal. Calcd for $C_{35}H_{30}O_3$: C, 84.31; H, 6.06. Found: C, 84.11; H, 6.24.
    Compound **8**: yield: 98%; mp: 143 °C; ^{1}H NMR ($CDCl_3$) δ 6.90–7.50 (m, 38H), 5.21 (s, 2H), 3.68 (d, $J = 10.9$ Hz, 4H), 3.54 (d, $J = 11.1$ Hz, 4H), 1.22 (s, 6H), 0.75 (s, 6H), −18.43 (s, 1H); ^{13}C NMR δ 201.0, 200.9, 200.8, 200.7, 154.6, 138.1, 132.2, 132.1, 131.4, 131.3, 131.3, 131.2, 130.7, 130.6, 130.4, 130.4, 130.3, 128.1, 128.0, 127.8, 127.0, 125.6, 103.5, 103.1, 103.0, 101.6, 88.1, 88.1, 88.0, 87.9, 77.7, 30.4, 23.2, 22.0; FT-IR (KBr) 2030, 2005, 1977 cm^{-1}; MS (FAB): *m/z*: 1314.16 ($M^{+}+1$); Anal. Calcd for $C_{74}H_{62}O_{10}Ru_2$: C, 67.67; H, 4.76. Found: C, 67.65; H, 4.83.
    Compound **9**: yield: 98%; mp: 139.5 °C (dec); ^{1}H NMR ($CDCl_3$) δ 9.85 (s, 2H), 7.49–7.56 (m, 4H), 6.93–7.22 (m, 34 H), −18.37 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 200.8, 200.9, 200.6, 200.5, 191.6, 154.8, 137.7, 135.7, 132.8, 132.1, 131.2, 130.2, 130.0, 129.9, 129.0, 128.5, 128.2, 128.0, 127.4, 127.2, 104.4, 104.3, 101.9, 101.7, 88.7, 88.5, 87.8, 87.6; FT-IR (KBr) 2035, 2007, 1978 cm^{-1}; MS (FAB): *m/z*: 1142.17 ($M^{+}+1$); Anal. Calcd for $C_{64}H_{42}O_8Ru_2$:C, 67.36; H, 3.71. Found: C, 67.35; H, 3.73.
    Compound **10**: yield: 73%; mp: 83 °C; ^{1}H NMR ($CDCl_3$) δ 7.20–6.90 (m, 38 H), 4.48 (s, 4H), −18.39 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 201.0, 154.5, 140.7, 132.3, 132.2, 132.1, 131.4, 131.3, 131.2, 131.1, 130.8, 130.4, 130.0, 128.1, 128.0,

127.9, 127.0, 126.2, 103.6, 103.5, 103.4, 103.4, 88.2, 88.1, 88.0, 87.9, 64.8; FT-IR (KBr) 2034, 2006, 1976 cm^{-1}; MS (FAB): *m*/*z*: 1146.76 (M^{+}+1); Anal. Calcd for $C_{64}H_{46}O_8Ru_2$:C, 67.12; H, 4.05. Found: C, 67.36; H, 4.04.

12. De La Rosa, M. A.; Velarde, E.; Guzman, A. *Synth. Commun.* **1990**, *20*, 2059–2064.
13. Yusybov, M. S.; Filimonov, V. D. *Synthesis* **1991**, 131–132.
14. (a) Neckers, D. C.; Hauck, G. *J. Org. Chem.* **1983**, *48*, 4691–4695; (b) Jutzi, P.; Siemeling, U.; Müller, A.; Bögge, H. *Organometallics* **1989**, *8*, 1744–1750.
15. The silica sol–gel process for **11**: A mixture of **1** (50 mg), tetramethyl orthosilicate (3.5 mL), degassed methanol (2.5 mL), degassed water (2.5 mL) and degassed THF (5.0 mL) in 50 mL flask equipped with a grease-free high vacuum stopcock was stirred at room temperature for 24 h under Ar and then it was stand aside for 24 h at room temperature, which yielded homogeneous sol–gel. After removing volatiles under vacuum, the resulting yellow solid was washed with methanol and dried under vacuum to afford **11** (1.639 g); 0.362 wt% Ru by Induced Coupled Plasma (ICP) analysis.
16. Mrahashi, S.; Naota, T.; Ito, K.; Maeda, Y.; Yaki, H. *Tetrahedron Lett.* **1981**, *22*, 5327–5330.
17. Lin, Y.; Ma, D.; Lu, X. *Tetrahedron Lett.* **1987**, *28*, 3115–3118.
18. Morales-Morales, D.; Redon, R.; Wanf, Z.; Lee, D. W.; Yung, C.; Magnuson, K.; Jensen, C. M. *Can. J. Chem.* **2001**, *79*, 823–829.
19. Ligthart, G. B. W. L.; Meijer, R. H.; Donners, M. P. J.; Meuldijk, J.; Vekemans, J. A. J. M.; Hulshof, L. A. *Tetrahedron Lett.* **2003**, *44*, 1507–1509.
20. Meijer, R. H.; Ligthart, G. B. W. L.; Meuldijk, J.; Vekemans, J. A. J. M.; Hulshof, L. A.; Mills, A. M.; Kooijman, H.; Spek, A. L. *Tetrahedron* **2004**, *60*, 1065–1072.
21. (a) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090–1100; (b) Samec, J. S. M.; Bäckvall, J.-E. *Chem. Eur. J.* **2002**, *8*, 2955–2961.