5674 *Organometallics* **2002,** *21,* 5674−5677

Notes

Facile Synthesis of (η^5-Ph_4C_4COH)$(CO)_2$RuCl and Catalytic Oxidation of Alcohols with Chloroform

Hyun Min Jung, Jun Ho Choi, Soon Ok Lee, Yu Hwan Kim, Jung Hye Park, and Jaiwook Park*

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

Received July 1, 2002

*Summary: A hydroxycyclopentadienyl ruthenium chloride, (η^5-Ph_4C_4COH)$(CO)_2$RuCl (**2**), is formed quantitatively by heating the Shvo complex, {[(η^5-Ph_4C_4CO)]$_2$H}-$Ru_2(CO)_4$(μ-H) (**1**), in chloroform containing a stoichiometric amount of ethanol. Alcohols are oxidized by the use of **1** or **2** as the catalyst in chloroform with sodium carbonate. Secondary alcohols and primary diols are oxidized selectively to give ketones and lactones, respectively, in excellent yields.*

The Shvo complex, {[(η^5-Ph_4C_4CO)]$_2$H}$Ru_2(CO)_4$(μ-H) (**1**),[1] has shown intriguing catalytic activities in many hydrogen transfer reactions such as the Tishchenko type disproportionation of aldehydes to esters,[2] the water-gas shift type reduction of aldehydes and ketones,[3] and the Oppenauer type oxidation of secondary alcohols.[4] Furthermore, the Shvo complex has been introduced as a racemization catalyst by Bäckvall for the dynamic kinetic resolution of secondary alcohols,[5] and we have used it in the related asymmetric transformations of ketones and enol acetates into the corresponding chiral acetates.[6]

The transformation of **1** into **2** was observed unexpectedly when a solution of **1** in chloroform was heated.[7] Ethanol contained as a stabilizer was found to be essential for the clean and quantitative transformation (Scheme 1). In contrast to previous reports of **2** as a unstable product in the reaction of (η^4-Ph_4C_4CO)Ru-$(CO)_2(NMe_3)$ with hydrogen chloride gas,[8,9] it is, in fact, a fairly stable solid, and crystals suitable for X-ray diffraction analysis were obtained by recrystallization from a solution of chloroform and hexane. The bond lengths of 1.316(5) and 2.344(5) Å for C(1)−O(1) and Ru(1)−C(1), respectively, are consistent with an η^5-coordination mode of the hydroxycyclopentadienyl ligand in the molecular structure of **2**.[10,11] Another feature of the structure is that the dihedral angle of O(1)−C(1)−Ru(1)−Cl is only 9.8° (Figure 1).

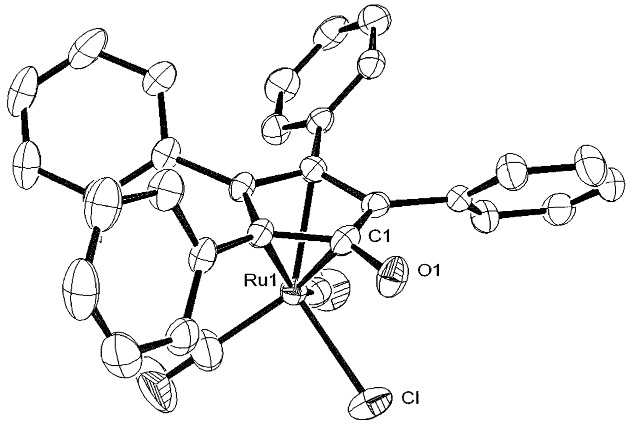
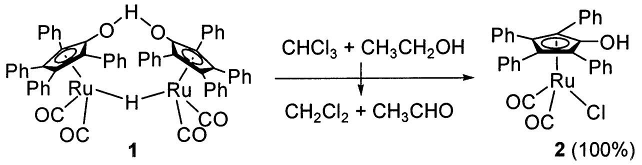


Figure 1. ORTEP drawing (50% probability) of the structure of **2** at 233 K. Selected bond distances (Å): Ru1−C1 = 2.344(4), C1−O1 = 1.316(5), Ru1−Cl = 2.4090(12).

Scheme 1. Transformation of the Shvo Complex 1 to Ruthenium Chloride Complex 2



---

[1] Shvo, Y.; Czarkie, D. *J. Am. Chem. Soc.* **1986**, *108*, 7400.

[2] Menashe, N.; Shvo, Y. *Organometallics* **1991**, *10*, 3885.

[3] Shvo, Y.; Czarkie, D. *J. Organomet. Chem.* **1986**, *315*, C25.

[4] (a) Almeida, M. L. S.; Beller, M.; Wang, G.-Z.; Bäckvall, J.-E. *Chem. Eur. J.* **1996**, *2*, 1533. (b) Almeida, M. L. S.; Kočovský, P.; Bäckvall, J.-E. *J. Org. Chem.* **1996**, *61*, 6587.

[5] (a) Larsson, A. L. E.; Persson, B. A.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **1997**, *36*, 121. (b) Persson, B. A.; Larsson, A. L. E.; Ray, M. L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1999**, *121*, 1645.

[6] (a) Jung, H. M.; Koh,J. H.; Kim, M.-J.; Park, J. *Org. Lett.* **2000**, *2*, 2487. (b) Jung, H. M.; Koh, J. H.; Kim, M.-J.; Park, J. *Org. Lett.* **2000**, *2*, 409. (c) Kim, M.-J.; Choi, Y. K.; Choi, M. Y.; Kim, M. J.; Park, J. *J. Org. Chem.* **2001**, *66*, 4736.

[7] An aminocyclopentadienyl ruthenium chloride is formed by heating the corresponding iminocyclopentadiene and $Ru_3(CO)_{12}$ in chloroform: Choi, J. H.; Kim, Y. H.; Nam, S. H.; Shin, S. T.; Kim, M.-J.; Park, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2373.

[8] Our ^{1}H and ^{13}C NMR data for **2** are different from those reported previously: Bailey, N. A.; Jassai, V. S.; Vefghi, R.; White, C. *J. Chem. Soc., Dalton Trans.* **1987**, 2815.

[9] Casey has made another hydroxycyclopentadienyl ruthenium chloride, [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]Ru$(CO)_2$Cl, by bubbling anhydrous HCl through a CH_2Cl_2 solution of {[2,5-Ph_2-3,4-Tol_2(η^5-C_4CO)]-Ru$(CO)_2$}$_2$: Casey, C. P.; Vos, T. E.; Singer, S. W.; Guzei, I. A. *Organometallics* **2002**, *21*, 5038.

[10] In contrast, the corresponding bond lengths are 1.22 and 2.53 Å, respectively, in the structure of (η^4-C_4Ph_4CO)Ru$(CO)_3$, which exhibits a typical η^4 coordination: Blum, Y.; Shvo, Y.; Chodosh, D. F. *Inorg. Chim. Acta* **1985**, *97*, L25.

[11] The iodide analogue of **2** is reported to be formed in the reaction of the Shvo complex with iodomethane or iodine: Schneider, B.; Goldberg, I.; Reshef, D.; Stein, Z.; Shvo, Y. *J. Organomet. Chem.* **1999**, *588*, 92. The iodide analogue also acts as an oxidation catalyst under the conditions of the entry 4 in Table 1, but its reactivity is much lower than that of **2** (44% yield after 48 h).

10.1021/om020516m CCC: $22.00

Scheme 2. Proposed Pathway for the Catalytic Oxidation of Alcohols with Chloroform

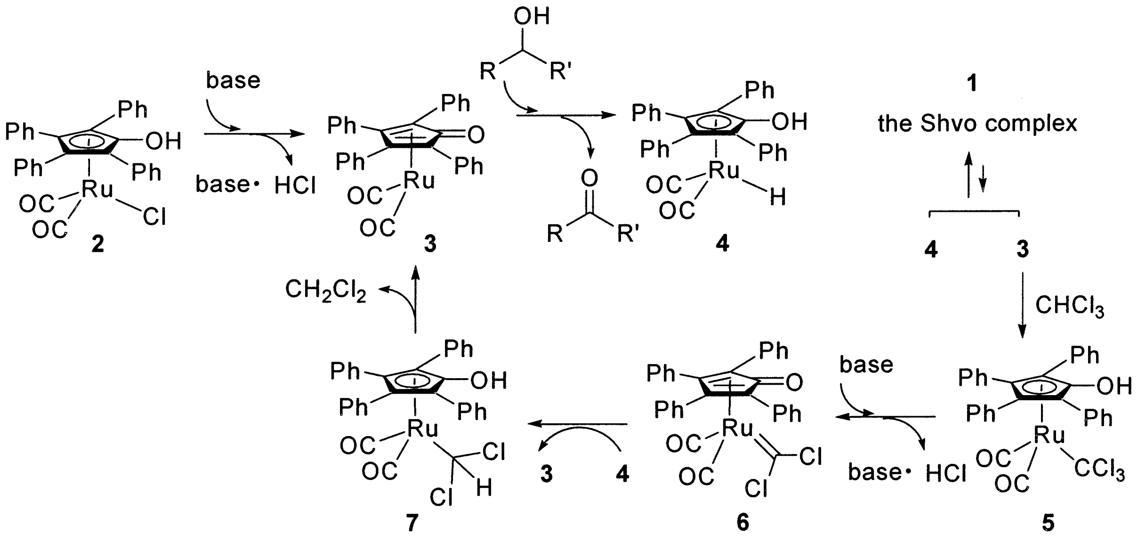


Table 1. Catalytic Oxidation of 1-Phenylethanol to Acetophenone in Chloroform with 2

entry	**2** (mol %)	Na_2CO_3 (equiv)	concn (M)	T (°C)[a]	t (h)	yield (%)[b]
1	4	0	0.10	90	12	5.0
2	2	0.6	0.10	90	24	58.2
3	4	1.5	0.10	90	1.5	99.7
4	2	1.5	0.10	90	5	99.5
5	2	1.5	0.05	90	5	98.5
6	0.2	1.5	1.0	90	12	99.9
7	2	1.5	0.25[c]	90	18	99.5
8	2	1.5	0.10	60	24	98.5
9	2	1.5	0.10	40	5	6.8
10	2	1.5	0.10	25	5	5.3

[a] Heating-bath temperature. [b] Determined by gas chromatography. [c] Toluene was employed as solvent with 3 equiv of $CHCl_3$.

Fomally, **2** is an adduct of hydrogen chloride and a 16-electron species, (η^4- $Ph_4C_4CO)Ru(CO)_2$, which is known as an active hydrogen acceptor in the catalytic reactions involving the Shvo complex.[12] Thus, we anticipated that a proper base would abstract hydrogen chloride from **2** and generate the hydrogen acceptor that can oxidize alcohols. In fact, acetophenone was obtained from 1-phenylethanol in 91% yield in the initial attempt using 3 equiv of triethylamine and 4 mol % of **2** in boiling chloroform within 24 h. More interestingly, replacement of triethylamine with sodium carbonate led to the completion of the oxidation within 5 h to give acetophenone quantitatively despite decreasing the amount of **2** to 2.0 mol %. Table 1 shows the effects of reaction conditions on the oxidation of 1-phenylethanol: The use of base is crucial for the catalytic oxidation. Only 5% of the substrate is oxidized in 12 h without base (entry 1), and more than 1 equiv of Na_2CO_3 is needed to complete the oxidation (entry 2). The reaction rate increases when the amount of the catalyst is increased but is still effective with 0.2 mol % of **2** (entry 6). The concentration of the substrate little affects the efficiency of the catalytic oxidation in the range of 0.05−1.0 M (entries 5 and 6). The use of chloroform as a solvent is optional and can be minimized by employing another solvent (entry 7). The reaction rate slows down with decreasing reaction temperature but is reasonable still at 60 °C (entries 8−10).

Dichloromethane and the Shvo complex (**1**) were observed in the ^1H and ^{13}C NMR spectra of the reaction mixture.[13] On the basis of this observation, a plausible pathway for the catalytic oxidation is proposed in Scheme 2: the coordinatively unsaturated species **3** is generated from **2** by the removal of hydrogen chloride with the aid of base. An alcohol is dehydrogenated to the corresponding carbonyl compound by **3**, which simultaneously transforms to ruthenium hydride **4**. The oxidizing species **3** is regenerated from **4** in the reduction of dichlorocarbene intermediate **6** to give the dichloromethyl complex **7**.[14,15] Dichloromethane is liberated from **7**, producing **3**. The carbene complex **6** is formed through the reaction of **3** with chloroform followed by the dehydrochlorination of the resulting intermediate **5** with the aid of base. Meanwhile, **3** and **4** are in equilibrium with **1** in the reaction mixture.[16] In fact, **1** was recovered in more than 95% yield and showed a catalytic activity similar to that of **2** for the oxidation of alcohols.

The scope of our catalyst system is illustrated by the highly selective oxidation of nonactivated aliphatic alcohols as well as activated benzylic alcohols in excellent yields with the use of **1** or **2** (Table 2): all the secondary alcohols are transformed into the corresponding ketones selectively and almost quantitatively. The benzylic alcohol with an electron-donating substituent at the benzene ring reacts faster than that with an electron-withdrawing substituent (entries 1−3). An

---

(12) Csjernyik, G.; Éll, A. H.; Fadini, L.; Pugin, B.; Bäckvall, J.-E. *J. Org. Chem.* **2002**, *67*, 1657 and references therein.

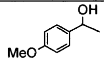
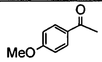
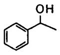
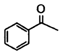
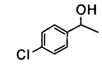
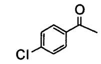
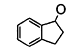
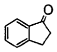
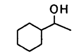
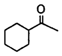
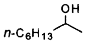
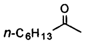
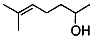
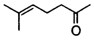
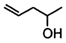
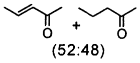
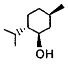
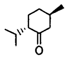
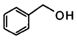
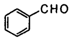
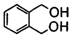
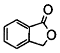
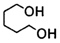
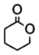
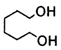
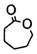
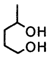
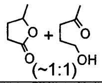
(13) $CDHCl_2$ was formed in the reaction of 1-phenylethanol with $CDCl_3$ in 89% of acetophenone. The amount of $CDHCl_2$ was estimated by measuring the intensity of the peaks at 5.28 ppm (t, $J_{HD} = 0.96$ Hz) in the ^1H NMR spectrum. The characteristic peak for the hydride of **1** was observed at −18.3 ppm.

(14) The suggestion of dichlorocarbene complex **6** as an intermediate is supported by the previous examples that show generation of metal dichlorocarbene complexes from the activation of chloroform as isolable compounds as well as reactive intermediates: (a) Park, J. H.; Koh, J. H.; Park, J. *Organometallics* **2001**, *20*, 1892. (b) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 3846 and references therein.

(15) In a separate experiment, a radical scavenger 2,4,6-trimethylphenol did not inhibit the catalytic oxidation of 1-phenylethanol.

(16) (a) Mays, M. J.; Morris, M. J.; Raithby, P. R.; Shvo, Y.; Czarkie, D. *Organometallics* **1989**, *8*, 1162. (b) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090.

Table 2. Catalytic Oxidation of Various Alcohols[a]

Entry	Substrate	Product	*t* [h]	Yield [%][b,c]
1			6	99 (100)[d]
2			8	98 (100)[d]
3			10	96 (98)[d]
4			10	99 (100)
5			10	98 (100)
6			8	99 (100)
7			12	99 (100)
8		 (52:48)	8	(100)[e]
9			18	96 (98)
10			20	87 (100)[f,g]
11	n-$C_8H_{17}OH$	n-$C_7H_{15}CHO$	20	39 (90)[f,h]
12			20	99 (100)[e]
13			24	99 (100)[e]
14			20	99 (100)[e]
15			36	90 (100)[e,i]
16		 (~1:1)	8	(100)[e,j]

[a] Perfomed with an alcohol (1.0 mmol), **2** (2.0 mol %), Na_2CO_3 (1.5 equiv), and degassed $CHCl_3$ (8 mL) in a closed vessel heated to 90 °C. [b] The ^{1}H NMR data of the products are identical with those reported previously. [c] The isolated yield of the product. The percent conversion of the substrate is given in parentheses. [d] The percent conversions of 1-(*p*-methoxyphenyl)ethanol, 1-phenylethanol, and 1-(*p*-chlorophenyl)ethanol are 97, 75, and 65, respectively, after 4 h. [e] The Shvo complex (1.0 mol %) was used instead of **2**. [f] 16 mL of $CHCl_3$ and 4 mol % of **2** were used. [g] Benzyl benzoate was isolated in 8% yield. [h] The yield of octanal was estimated by ^{1}H NMR. [i] 16 mL of $CHCl_3$ was used. [j] 5-Methyldihydrofuran-2-one, 5-hydroxypentan-2-one, 4-oxopentyl 4-oxopentanoate, and 4-oxopentanal were observed in the mole ratio of 42:37:16:5 by ^{1}H NMR.

olefinic group remote from the hydroxy group remains intact under the oxidation conditions (entry 7). However, a mixture of 2-pentanone and pent-3-en-2-one is obtained from the reaction of pent-4-en-2-ol through the migration of the carbon−carbon double bond (entry 8). (−)-Menthol is successfully transformed to (−)-menthone in high yield (entry 9) while maintaining the stereochemistry at the 2-position. The catalytic system is less effective for the transformation of primary alcohols to aldehydes because of the competitive formation of esters (entries 10 and 11).[2] Octyl octanoate (51% yield) is the major product in the dehydrogenation of 1-octanol, although benzaldehyde is obtained from benzyl alcohol in good yield by decreasing the concentration. Notably, however, lactones of five- to seven-membered rings are produced selectively from the corresponding primary diols in high yields (entries 12−15). Meanwhile, a complex mixture is obtained in the reaction of pentane-1,4-diol as an example of unsymmetrical diols. 5-Methyldihydrofuran-2-one and 5-hydroxypentan-2-one are observed as the major products by ^{1}H NMR (entry 16).

Table 3. Crystallographic Data for 2

formula	$C_{31}H_{21}ClO_3Ru$
mol wt	578.00
space group	$P2_1/n$
a, Å	11.7387(3)
b, Å	8.1410(2)
c, Å	27.1190(7)
α, deg	90
β, deg	101.5400(10)
γ, deg	90
V, Å^3	2539.23(11)
Z	4
d_{calcd}, g cm^{-3}	1.512
radiation (λ, Å)	0.710 73
F(000)	1168
μ, mm^{-1}	0.754
T, K	233(2)
scan mode	ω
no. of measd rflns	10162
no. of indep rflns	4057
refinement mothod	full-matrix least-squares on F_2
goodness of fit on F^2	1.171
final R indices ($I > 2\sigma(I)$)	R1 = 0.0467, wR2 = 0.1243
R indices (all data)	R1 = 0.0621, wR2 = 0.1379

In summary, we have found the clean transformation of the Shvo complex (**1**) into the hydroxycyclopentadienyl ruthenium chloride **2**. A simple and efficient method for the catalytic oxidation of alcohols has been demonstrated with the use of **1** or **2** as the catalyst, chloroform as the stoichiometric oxidant, and sodium carbonate as the acceptor of hydrogen chloride.

Experimental Section

All manipulations except workup and purification were carried out under an atmosphere of argon with the use of standard Schlenk techniques. The Shvo complex was prepared according to the literature procedures.[2] If not otherwise stated, all NMR spectra were recorded on a Bruker AM 300 or DPX 300 instrument. Chemical shifts are given in δ (ppm) downfield from tetramethylsilane as an internal standard. IR spectra were taken for KBr pellets. Mass spectral analysis was recorded on a JEOL JMS-AM505WA instrument and is reported in units of mass to charge (*m*/*e*). Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by the Center for Biofunctional Molecules at Pohang University of Science and Technology.

(η^5-Ph_4C_4COH)Ru(CO)$_2$Cl (2). In a 50 mL flask equipped with a grease-free high-vacuum stopcock, **1** (200 mg, 0.184 mmol) was dissolved in degassed HPLC grade chloroform (9.0 mL), containing ethanol as the stabilizer, under argon. After the flask was closed, the solution was stirred at 90 °C for 7 h. A pale yellow solid (213 mg, 100% yield) was obtained after the solvent was removed under high vacuum. Mp: 152 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.44−6.81 (m, 20H), 5.50 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 197.7, 139.8, 132.2, 131.9, 129.5, 129.12, 129.07, 128.4, 128.1, 100.3, 89.6. IR (KBr, cm^{-1}): ν(CO) 2033 (s), 1983 (s). MS (FAB, *m*/*z*): 578 (M$^+$). Anal. Calcd for $C_{31}H_{21}O_3ClRu$: C, 64.42; H, 3.66. Found: C, 64.13; H, 3.83.

X-ray Crystallography of (η^5-Ph_4C_4COH)Ru(CO)$_2$Cl. A suitable crystal coated with Paratone was mounted on a Siemens SMART diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation source and a CCD detector. Data collection was performed with a detector distance of 6 cm. The raw data collected were processed to produce conventional intensity data by the program SAINT. The intensity data were corrected for Lorentz and polarization effects. The structure was solved by a combination of Patterson and difference Fourier methods provided by the program package SHELXTL. All the non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and included in the final cycle of refinement. Crystallographic data of **2** are summarized in Table 3.

Representative Procedure for the Oxidation of Alcohols. In a 100 mL flask equipped with a grease-free high-vacuum stopcock, **2** (12 mg, 0.021 mmol), Na_2CO_3 (159 mg, 1.50 mmol), and 1-phenylethanol (121 μL, 1.00 mmol) were mixed with degassed HPLC grade $CHCl_3$ (8 mL). After the flask was closed, the mixture was stirred at 90 °C for 8 h. The reaction mixture was filtered through Celite, and the filtrate was concentrated and chromatographed on a silica gel column to give acetophenone (118 mg, 98% yield).

Acknowledgment. We are grateful for the financial support by MOST through the National Research Laboratory of Chirotechnology and by KOSEF through the Center for Integrated Molecular System. H.M.J. is grateful for his postdoctoral fellowship through the Brain Korea 21 Project in 2001 by the Korean Ministry of Education.

Supporting Information Available: Structural diagrams with full atom labeling and tables of bond distances, angles, anisotropic parameters, and atomic coordinates for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020516M