3370 *Organometallics* **2001,** *20,* 3370−3372

X-ray Structure and Reactivity of (η^4-tetraphenylcyclopentadienone)$(CO)_2Ru(HOCHMe_2)$: Unexpected Stability of the Neutral 2-Propanol−Ruthenium(0) Complex with Respect to β-Hydride Elimination

Hyun Min Jung, Seung Tae Shin, Yu Hwan Kim, Mahn-Joo Kim,* and
Jaiwook Park*

National Research Laboratory of Chirotechnology, Department of Chemistry, Division of
Molecular and Life Sciences, Pohang University of Science and Technology (POSTECH),
San 31 Hyoja Dong, Pohang 790-784, Republic of Korea

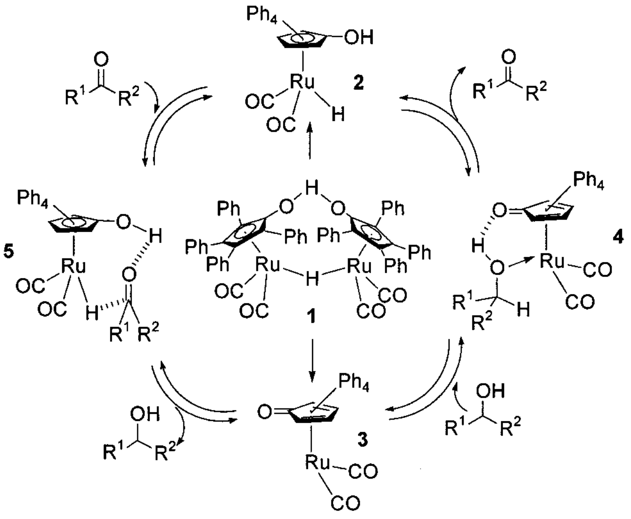
Received April 17, 2001

*Summary: A neutral Ru(0)−alcohol complex, (η^4-C_4Ph_4-CO)$(CO)_2Ru(HOCHMe_2)$ (**7**), was obtained by treating an acetone solution of (η^4-$C_4Ph_4CO)Ru(CO)_3$ (**6**) with aqueous Na_2CO_3 at room temperature, followed by acidification with aqueous NH_4Cl at 0 °C. Complex **7** is stable even at 90 °C in toluene and showed catalytic activities in the transfer hydrogenation of acetophenone in 2-propanol and the racemization of optically active 1-phenylethanol.*

Diruthenium carbonyl cyclopentadienone complex **1**, which is called the Shvo complex, has shown a broad spectrum of catalytic activities with various organic substrates.[1] In particular, its intriguing catalytic activity for hydrogen transfer reactions have been demonstrated in the Tischenko type disproportionation of aldehydes to esters,[1c] hydrogenations and water-gas shift type reductions of aldehydes and ketones,[1e] and Oppenauer type oxidation of secondary alcohols.[1h] Notably, complex **1** catalyzes the transfer hydrogenation of ketones in 2-propanol without the aid of additional base[1f,2] and has been adapted as an effective racemization catalyst for the dynamic kinetic resolution of secondary alcohols using lipases.[3]

It has been proposed that the dissociation of **1** to two monomeric intermediates **2** and **3** is a key step in the reversible hydrogen transfer reactions between alcohols and ketones (Scheme 1).[1f,4] In fact, **2** can be generated by treating **1** with H_2 or formic acid[1a,g] and hydrogenates aldehydes or ketones through transfer of hydride from ruthenium and of a proton from the OH group.[2,5] The alcohol complex **4** has been postulated as a transient intermediate in the reaction of **2** to give the product alcohol and coordinatively unsaturated intermediate **3**. Herein we report the isolation of the unexpectedly stable 2-propanol complex **7**. Also reported is the molecular structure of **7** and its catalytic activity in hydrogen transfer reactions.

Scheme 1



Neutral 2-propanol complex **7** was obtained in 45% yield by treating an acetone solution of **6** with aqueous sodium carbonate at room temperature for 1 h, followed by quenching with aqueous ammonium chloride at 0 °C (Scheme 2).[6] This procedure is almost the same as that reported for the Shvo complex (**1**), except for the acidification temperature.[1e] In fact, **1** was produced exclusively when treatment under basic conditions was prolonged for more than 5 h or when the acidification temperature was higher than 20 °C. Complex **7** was formed to be stable enough to be separated by column chromatography using silica gel. The molecular structure of **7** was elucidated by single-crystal X-ray diffrac-

---

[1] (a) Shvo, Y.; Goldberg, I.; Czarkie, D.; Reshef, D.; Stein, Z. *Organometallics* **1997**, *16*, 133. (b) Menashe, N.; Salant, E.; Shvo, Y. *J. Organomet. Chem.* **1996**, *514*, 97. (c) Menashe, N.; Shvo, Y. *Organometallics* **1991**, *10*, 3885. (d) Shvo, Y.; Czarkie, D. *J. Organomet. Chem.* **1989**, *368*, 357. (e) Shvo, Y.; Czarkie, D. *J. Organomet. Chem.* **1986**, *315*, C25. (f) Shvo, Y.; Czarkie, D.; *J. Am. Chem. Soc.* **1986**, *108*, 7400. (g) Blum, Y.; Czarkie, D.; Rahamim, Y.; Shvo, Y. *Organometallics* **1985**, *4*, 1459. (h) Almeida, M. L.; Beller, M.; Wang, G-.Z.; Bäckvall, J-.E. *Chem. Eur. J.* **1996**, *2*, 1533.

[2] Laxmi, Y. R. S.; Bäckvall, J-.E. *Chem. Commun.* **2000**, 611.

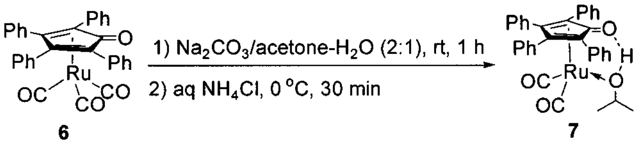
[3] (a) Jung, H. M.; Koh,J. H.; Kim, M-.J.; Park, J. *Org. Lett.* **2000**, *2*, 2487. (b) Kim, M-.J.; Lee, D.; Huh, E. A.; Jung, H. M.; Koh, J. H.; Park, J. *Org. Lett.* **2000**, *2*, 2377. (c) Jung, H. M.; Koh, J. H.; Kim, M-.J.; Park, J. *Org. Lett.* **2000**, *2*, *Org. Lett.* **2000**, *2*, 409 (d) Larsson, A. L. E.; Persson, B. A.; Bäckvall, J.-E. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 121. (e) Persson, B. A.; Larsson, A. L. E.; Ray, M. L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1999**, *121*, 1645. (f) Persson, B. A.; Huerta, F. F.; Bäckvall, J.-E. *J. Org. Chem.* **1999**, *64*, 5237.

[4] Mays, M. J.; Morris, M. J.; Raithby, P. R.; Shvo, Y.; Czarkie, D. *Organometallics* **1989**, *8*, 1162.

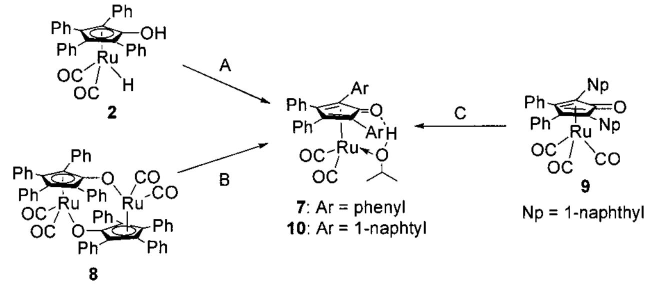
[5] Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090.

10.1021/om0103198 CCC: $20.00

Scheme 2



Scheme 3[a]



[a] Legend: (A) (1) aqueous Na_2CO_3, (2) acetone, (3) aqueous NH_4Cl, 0 °C; (B) (1) Na_2CO_3/acetone−H_2O, (2) 2-propanol, (3) aqueous NH_4Cl, 0 °C; (C) (1) Na_2CO_3/acetone−H_2O, 20 °C; (2) aqueous NH_4Cl, 20 °C.

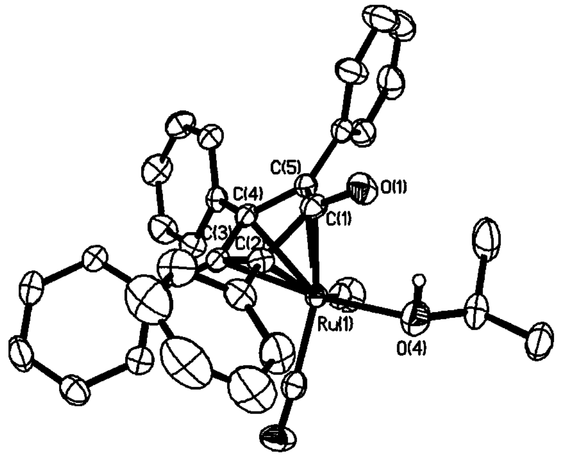


Figure 1. ORTEP drawing (50% probability) of the structure of **7** at 203 K. Selected bond distances (Å): C(1)−C(2) = 1.463(4), C(1)−C(5) = 1.472(4), C(2)−C(3) = 1.447(4), C(3)−C(4) = 1.436(4), C(4)−C(5) = 1.450(4), Ru−C(1) = 2.429(3), Ru−C(2) = 2.239(3), Ru−C(3) = 2.202(3), Ru−C(4) = 2.190(3), Ru−C(5) = 2.257(3), Ru−O(4) = 2.189(2), C(1)−O(1) = 1.259(3). Selected bond angles (deg): C(1)−Ru−O(4) = 82.91(9), O(1)−C(1)−Ru = 126.98(19).

tion analysis and shows the coordination of 2-propanol to the ruthenium through the hydroxyl oxygen (Figure 1).[7] The hydroxyl proton appears to interact with the carbonyl oxygen of the cyclopentadienone ring, but it is not clear whether the interaction is intramolecular or intermolecular in the crystal structure.[8] In comparison to **1**, having an η^5 coordination mode,[1e] **7** exhibits a C(1)−O(1) bond length (1.259 Å) shorter by 0.027 Å and a Ru−C(1) distance (2.429 Å) longer by 0.029 Å. In addition, the Ru−C(1) distance is distinctly longer than those of the other four Ru−ring carbon atom distances (2.190−2.257 Å), suggesting that the cyclopentadienone ring is bonded to the Ru in an η^4 coordination mode.[9]

In contrast to the most known alcohol complexes,[10,11] **7** is thermally stable even at 90 °C in toluene, as indicated by the lack of any detectable change in the ^1H NMR at that temperature over 2 h. However, **7** showed catalytic activity comparable to **1** in the racemization of optically active 1-phenylethanol and in the transfer hydrogenation of acetophenone with 2-propanol. The optical purity of (*S*)-1-phenylethanol (>99% ee, 0.2 M) in toluene was changed to 45% ee (65% ee with 2 mol % of **1**) after heating with 4 mol % of **7** at 70 °C for 5 h, and 1-phenylethanol was obtained in 95% yield (96% yield with 2 mol % of **1**) by heating a solution (0.2 M) of acetophenone in 2-propanol with 4 mol % of **7** at 70 °C for 5 h.

To investigate the mechanism of the formation of **7**, we examined a number of related reactions as shown in Scheme 3. A mixture of **1** and **7** in a 58:42 ratio was obtained from mononuclear hydride complex **2** by sequential treatments with aqueous sodium carbonate, excess acetone at room temperature, and aqueous ammonium chloride at 0 °C. In contrast, only the Shvo complex (**1**) was obtained in the reaction of **2** with acetone at 0 °C. The alcohol complex **7** was also formed along with **1** in a 50:50 ratio upon treatment of an acetone solution of diruthenium complex **8** with aqueous sodium carbonate, followed by adding 2-propanol at room temperature and aqueous ammonium chloride at 0 °C. Interestingly, the naphthyl analogue **10** was prepared from **9** in 51% yield without lowering the acidification temperature to 0 °C.[12,13] This result suggests that the steric hindrance by two naphthyl groups against forming a diruthenium complex analogous to

---

(6) To a solution of **6** (700 mg, 1.23 mmol) in acetone (50 mL) was added a saturated aqueous Na_2CO_3 solution (25 mL) at 20 °C. After it was stirred at 20 °C for 1 h, the reaction mixture was cooled to 0 °C, acidified by adding a saturated aqueous NH_4Cl solution (50 mL), and concentrated under reduced pressure. Then, the resulting residue was extracted with CH_2Cl_2. After CH_2Cl_2 was removed, the crude product was chromatographed on silica gel with CH_2Cl_2/ethyl acetate (6:1) to give **7** (330 mg, 45%) and the Shvo complex (**1**; 305 mg, 46%). Recrystallization of **7** from CH_2Cl_2−hexane afforded air-stable pale yellow crystals. Mp: 166 °C dec. ^1H NMR ($CDCl_3$): δ 7.54 (d, J = 6.96 Hz, 4H), 7.19−7.03 (m, 16H), 2.85 (sept, J = 6.21 Hz, 1H), 2.44 (br s, 1H), 0.95 (d, J = 6.42 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 201.32, 163.19, 132.99, 132.48, 131.95, 130.43, 128.06, 128.01, 126.71, 103.86, 83.59, 51.77, 24.92. IR (KBr, cm^{-1}): ν(CO) 2006 (s), 1949 (s), 1601 (m). MS (FAB, *m/z*): 602 (M^+). Anal. Calcd for $C_{34}H_{28}O_4Ru$: C, 67.87; H, 4.69. Found: C, 67.82; H, 4.68.

(7) Crystal data for **7**: $C_{34}H_{28}O_4Ru$. M_r = 601.63, light yellow crystal, size 0.25 × 0.30 × 0.40 mm^3, monoclinic, a = 12.09390(10) Å, b = 9.98720(10) Å, c = 23.5615(2) Å, α = 90°, β = 94.4370(10)°, γ = 90°, space group $P2_1/n$, V = 2837.33(4) $Å^3$, Z = 4, T = 203(2) K, d_{calcd} = 1.408 g/cm^3, absorption coefficient 0.589 mm^{-1}, Siemens SMART diffractometer, λ = 0.710 73 Å, scan mode ω (ω-scan width: 1.73−24.13°). 11 160 reflections measured, giving 4450 unique data with $I > 2\sigma(I)$, R = 0.0298, R_w = 0.0837, GOF = 1.123.

(8) Two sites are possible for the location of the hydroxyl proton in the crystal structure. The distance to the carbonyl oxygen is 2.190 Å for an intramolecular hydrogen bonding interaction, while that for an intermolecular one is 1.843 Å.

(9) In comparison to (η^4-C_4Ph_4CO)Ru(CO)$_3$ (Ru(1)−C(1) = 2.53 Å, C(1)−O(1) = 1.22 Å), the structure of **7** has some η^5-coordination character. The hydrogen bonding interaction would be responsible for this character. Blum, Y.; Shvo, Y.; Chodosh, D. F. *Inorg. Chim. Acta* **1985**, *97*, L25.

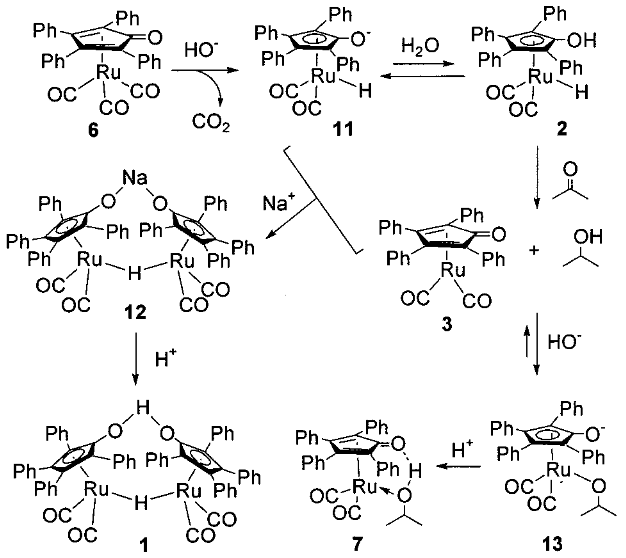
(10) A hydroxybenzyl alcohol complex has been reported to be isolated by recrystallization of the crude product from the reaction of [$RuH_2(CO)(PPh_3)_3$] with salicylaldehyde at the temperature of refluxing toluene: Sahajpal, A.; Robinson, S. D.; Mazid, M. A.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2119.

(11) A few alcohol complexes with cationic metal centers are known: (a) Milke, J.; Missling, C.; Sünkel, K.; Beck, W. *J. Organomet. Chem.* **1993**, *445*, 219. (b) Song, J.-S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1233. (c) Agbossou, S. K.; Smith, W. W.; Gladysz, J. A. *Chem. Ber.* **1990**, *123*, 1293. (d) Field, J. S.; Haines, R. J.; Sundermeyer, J.; Woollam, S. F. *Chem. Commun.* **1990**, 985. (e) Sünkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 231.

12 facilitates the production of alcohol complex **10** at room temperature.

On the basis of the above results, a plausible pathway for the formation of **7** from **6** is outlined in Scheme 4: One of the carbonyl ligands in **6** is replaced with hydride through the reaction with hydroxide to form intermediate **11**, which is in equilibrium with **2**. Complex **2** reacts with acetone to give 2-propanol and **3**. The coupling of **3** and **11** to give **12** competes with the base-induced reaction between **3** and 2-propanol to form the anionic alkoxide complex **13**. Acidifying the mixture of **12** and **13** produces **1** and **7**, respectively. The conversion of **13** to **12** is possible, and extending the reaction time and increasing the temperature favor the formation of **12**.[14]

Scheme 4



In summary, we have isolated the neutral 2-propanol−Ru(0) complex **7** that has been postulated as a transient intermediate in hydrogen transfer reactions catalyzed by the Shvo complex (**1**). Surprisingly, the alcohol complex was found to be thermally stable with respect to dissociation or β-hydride elimination. Despite such stability, **7** shows catalytic activity comparable to that of **1** in hydrogen transfer reactions.

Acknowledgment. We are grateful for financial support by MOST through the NRL program 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 **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0103198

---

(12) A solution of $Ru_3(CO)_{12}$ (281 mg, 0.44 mmol) and 2,5-bis(1-naphthyl)-3,4-diphenylcyclopentadienone (640 mg, 1.32 mmol) in benzene (120 mL) was heated to reflux for 48 h under an argon atmosphere. After it was cooled to room temperature, the reaction mixture was concentrated and purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate to give a yellow solid (744 mg, 84%). Recrystallization from CH_2Cl_2/hexane afforded **9** as pale yellow crystals. Mp: 202 °C dec. ^1H NMR ($CDCl_3$): δ 7.93−7.82 (m, 6H), 7.50−7.40 (m, 8H), 7.02−6.83 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 194.63, 176.07, 134.60, 134.04, 132.88, 131.47, 130.22, 129.65, 129.11, 128.93, 128.07, 126.91, 126.20, 125.90, 109.25, 86.82. IR (KBr, cm^{-1}): ν(CO) 2081 (s), 2023 (s), 2006 (s), 1654 (m). Anal. Calcd for $C_{40}H_{24}O_4Ru$: C, 71.74; H, 3.61. Found: C, 71.51; H, 3.93.

(13) According to a procedure similar to that for **7** except for acidification at room temperature, **10** (206 mg, 51%) and a Shvo-type diruthenium complex (130 mg, 35%) were obtained from **9** (390 mg, 0.58 mmol). **10**: mp 180 °C dec; ^1H NMR ($CDCl_3$) δ 8.26 (d, J = 8.43 Hz, 2H), 7.83−7.76 (m, 4H), 7.55−7.34 (m, 8H), 6.94−6.80 (m, 10H), 3.27 (sept, J = 6.36 Hz, 1H), 2.51 (br s, 1H), 1.32 (d, J = 6.39 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 201.28, 165.01, 132.62, 131.83, 131.01, 129.13, 128.82, 127.97, 127.70, 126.75, 126.68, 126.23, 125.63, 103.97, 88.09, 52.47, 25.82; IR (KBr, cm^{-1}) ν(CO) 2001 (s), 1939 (s), 1608 (m); MS (FAB, *m/z*) 702 (M^+). Anal. Calcd for $C_{42}H_{32}O_4Ru$: C, 71.88; H, 4.60. Found: C, 71.65; H, 4.52. Shvo-type diruthenium complex, $\{[2,5\text{-bis-}(1\text{-naphthyl})\text{-}3,4\text{-diphenyl}(\eta^5\text{-}C_4CO)]_2H\}Ru_2(CO)_4(\mu\text{-}H)$: mp 198 °C dec; ^1H NMR ($CDCl_3$) δ 11.92 (br s, 1H), 7.84−7.55 (m, 14H), 7.35−7.24 (m, 12H), 6.96−6.82 (m, 22H), −18.95 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 201.66, 157.26, 135.55, 133.68, 132.98, 131.02, 129.04, 128.61, 128.34, 127.80, 127.32, 126.53, 125.97, 125.82, 125.45, 105.00, 90.47; IR (KBr, cm^{-1}) ν(CO) 2032 (s), 2004 (m), 1975 (s), 1961 (m), 1542 (w); MS (FAB, *m/z*) 1287 ($M^+ + 1$). Anal. Calcd for $C_{78}H_{50}O_6Ru_2$: C, 72.88; H, 3.92. Found: C, 73.04; H, 4.15.

(14) Complex **12** was precipitated almost quantitatively upon concentrating the reaction mixture before acidifying with aqueous ammonium chloride. The precipitate was filtered, washed with water, and recrystallized from CH_2Cl_2 and hexane to give orange crystals. Mp: 184 °C dec. ^1H NMR ($CDCl_3$): δ 7.16−6.93 (m, 40H), −16.19 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 202.38, 133.59, 132.40, 132.22, 132.28, 128.29, 127.78, 126.91, 101.29, 82. IR (KBr, cm^{-1}): ν(CO) 2011 (s), 1980 (m), 1950 (s), 1935 (m), 1613 (br m). MS (FAB, *m/z*): 1108 (M^+). Anal. Calcd for $C_{62}H_{43}NaO_7Ru_2$: C, 66.18; H, 3.85. Found: C, 65.90; H, 3.61.