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

X-ray Structure and Reactivity of (η^4-tetraphenylcyclopentadienone)(CO)$_2$Ru(HOCHMe$_2$): Unexpected Stability of the Neutral 2-Propanol−Ruthenium(0) Complex with Respect to *β*-Hydride Elimination

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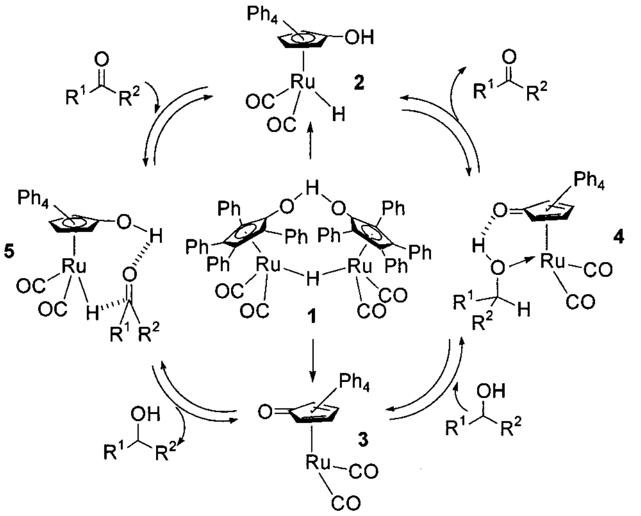
*Summary: A neutral Ru(0)−alcohol complex, (η^4-C_4Ph_4-CO)(CO)$_2$Ru(HOCHMe$_2$) (**7**), was obtained by treating an acetone solution of (η^4-C_4Ph_4CO)Ru(CO)$_3$ (**6**) with aqueous Na_2CO_3 at room temperature, followed by acidification with aqueous NH_4Cl at 0 °C. Complex **7** is stable even at 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-

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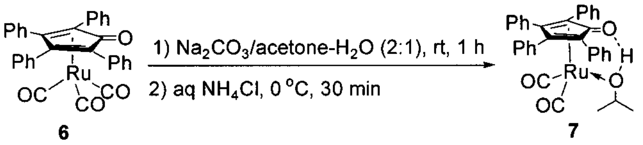
Scheme 2



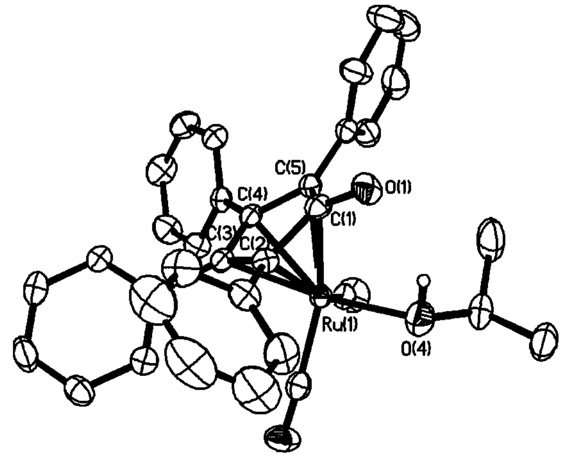
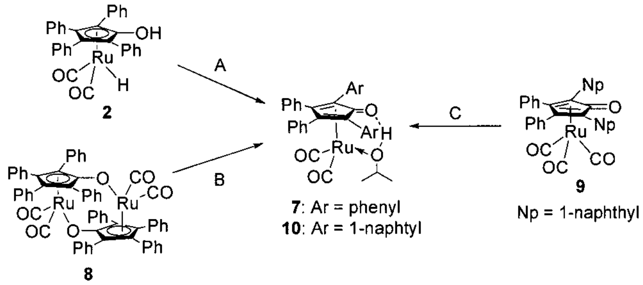


Figure 1. ORTEP drawing (50% probability) of the structure of **7** at 203 K. Selected bond distances (Å): C(1)−C(2) = 1.463(4), C(1)−C(5) = 1.472(4), C(2)−C(3) = 1.447(4), C(3)−C(4) = 1.436(4), C(4)−C(5) = 1.450(4), Ru−C(1) = 2.429(3), Ru−C(2) = 2.239(3), Ru−C(3) = 2.202(3), Ru−C(4) = 2.190(3), Ru−C(5)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

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.

(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 ^{1}H 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

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(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. ^{1}H 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.

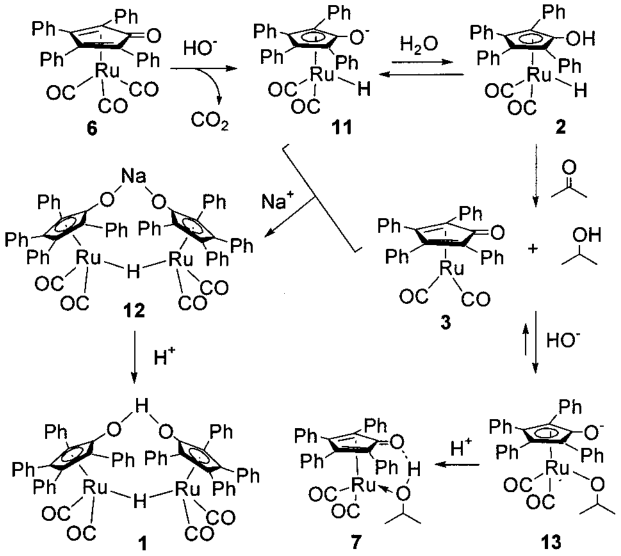
(11) A few alcohol complexes with cationic metal centers are known: (a) Milke, J.; Missling, C.; Sünkel, K.; Beck, W. *J. Organomet. Chem.* **1993**, *445*, 219. (b) Song, J.-S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 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]

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.

Scheme 4



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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.

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(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-bis-(1-naphthyl)-3,4-diphenyl(η^5-C_4CO)]$_2$H}$Ru_2(CO)_4$(μ-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.