Communications

Synthesis and Reactivity of Hydroxycyclopentadienyl and Aminocyclopentadienyl Ruthenium Alcohol Complexes

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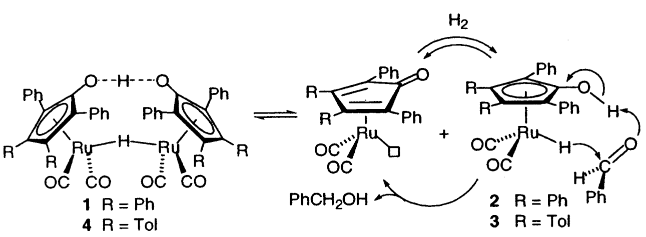
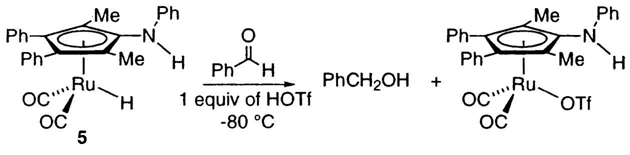
Summary: Cationic aminocyclopentadienyl and hydroxycyclopentadienyl ruthenium alcohol complexes were synthesized from reaction of the corresponding ruthenium chloride with $AgBF_4$ in the presence of an alcohol. Exchange rates of free alcohol with hydroxycyclopentadienyl and aminocyclopentadienyl ruthenium benzyl alcohol complexes were rapid ($t_{1/2} = 5-10$ min) at −47 °C.

Several years ago, Shvo discovered that the diruthenium complex **1** was an efficient ketone hydrogenation catalyst and determined that the active reducing species was the ruthenium hydride **2** (Scheme 1).[1] On the basis of detailed mechanistic studies on the related active reducing agent **3**, including observation of primary deuterium isotope effects for transfer of both OH and RuH, we proposed a mechanism involving concerted transfer of proton and hydride to aldehyde outside the coordination sphere of the metal.[2] Bäckvall has proposed an alternative mechanism involving Cp ring slippage and aldehyde coordination prior to concerted transfer of the hydrogens.[3] In Bäckvall's mechanism, the alcohol is "born" in the coordination sphere of the metal. In our proposed mechanism, an alcohol complex may form reversibly after the rate-determining step. Clearly, information about the kinetic and thermodynamic stability of alcohol complexes is required to fully understand the mechanism of aldehyde reduction. Park's reported isolation of a neutral 2-propanol ruthenium complex piqued our interest. In the course of investigating its properties, we and Bäckvall showed that Park's "alcohol complex" was in fact an amine complex.[4]

Scheme 1



Scheme 2



In an effort to prevent formation of bridging ruthenium hydrides and to develop more active catalysts related to Shvo's complex **1**, we prepared the *N*-phenylamino-substituted cyclopentadienyl complex **5** and found that it reduced benzaldehyde rapidly in the presence of 1 equiv of added acid (Scheme 2).[5,6] Again, the question of alcohol complex involvement arose. Alcohol complexes have been observed as products of some ionic hydrogenations of carbonyl compounds by tungsten, rhenium, and molybdenum hydrides in the presence of a strong acid.[7−9] Other examples of metal alcohol complexes have been reported,[10] but there has been no report of a ruthenium alcohol complex in the reduction of ketones and aldehydes by hydroxycyclopentadienyl ruthenium hydride. Here we report the in situ synthesis of cationic hydroxycyclopentadienyl and

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[1] Blum, Y.; Czarkie, D.; Rahamim, Y.; Shvo, Y. *Organometallics* **1985**, *4*, 1459.

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

[3] Persson, B. A.; Larsson, A. L. E.; Le Ray, M.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1999**, *121*, 1645−1650. Csjernyik, G.; Éll, A. H.; Fadini, L.; Pugin, B.; Bäckvall, J.-E. *J. Org. Chem.* **2002**, *67*, 1657.

[4] Casey, C. P.; Bikzhanova, G. A.; Bäckvall, J.-E.; Johansson, L.; Park, J.; Kim, Y. H. *Organometallics* **2002**, *21*, 1955−1959.

[5] Casey, C. P.; Vos, T. E.; Singer, S. W.; Guzei, I. A. *Organometallics* **2002**, *21*, 5038.

[6] Concurrently, Park made a similar aminocyclopentadienyl ruthenium complex which is a racemization catalyst for dynamic kinetic resolution: Choi, J. H.; Kim, Y. H.; Nam, S. H.; Shin, S. T.; Kim, M.-J.; Park, J. *Angew.* Chem., Int. Ed. **2002**, *41*, 2373.

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[9] Bakhmutov, V. I.; Vorontsov, E. V.; Antonov, D. Yu. *Inorg. Chim. Acta* **1998**, *278*, 122.

[10] (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) Field, J. S.; Haines, R. J.; Sundermeyer, J.; Woollam, S. F. *Chem. Commun.* **1990**, 985. (d) Agbossou, S. K.; Smith, W. W.; Gladysz, J. A. *Chem. Ber.* **1990**, *123*, 1293. (e) Sahajpal, A.; Robinson, S. D.; Mazid, M. A.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2119. (f) Sünkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 231.

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Scheme 3

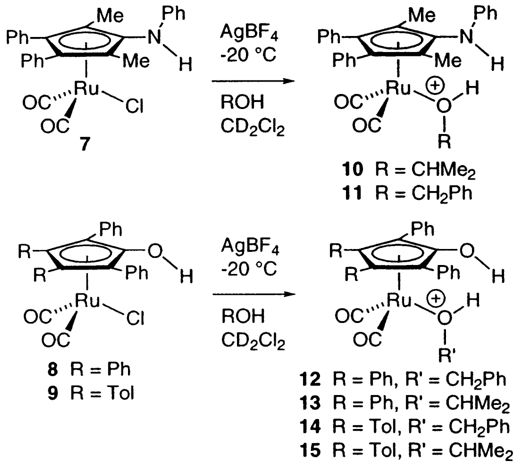


Table 1. NMR of Ruthenium Alcohol Complexes

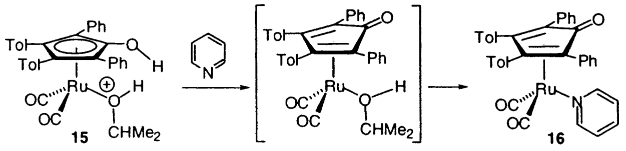
complex	alcohol ligand ^{1}H NMR δ (J_{HH}, Hz)	 ^{13}C NMR δ
10	3.78 (oct, 6.0), HOCH(CH$_3$)$_2$ 5.37 (d, 6.0) HOCH(CH$_3$)$_2$	76.1, HOCH(CH$_3$)$_2$
11	4.76 (d, 4.5), HOCH_2Ph 5.69 (t, 4.5), HOCH$_2$Ph	73.8, HOCH$_2$Ph
12	4.46 (d, 4.5), HOCH_2Ph 5.53 (t, 4.5), HOCH$_2$Ph	74.1, HOCH$_2$Ph
13	3.71 (oct, 6.0), HOCH(CH$_3$)$_2$ 4.44 (d, 6.0), HOCH(CH$_3$)$_2$	78.3, HOCH(CH$_3$)$_2$
14	4.42 (d, 4.5), HOCH_2Ph 5.79 (t, 4.5), HOCH$_2$Ph	74.1, HOCH$_2$Ph
15	3.63 (oct, 6.5), HOCH(CH$_3$)$_2$ 4.32 (d, 6.5), HOCH(CH$_3$)$_2$	78.7, HOCH(CH$_3$)$_2$

cationic aminocyclopentadienyl ruthenium alcohol complexes and the kinetics of alcohol exchange of these complexes.

Aminocyclopentadienyl and hydroxycyclopentadienyl ruthenium 2-propanol and benzyl alcohol complexes were synthesized under mild conditions, starting with the appropriate ruthenium chloride complex and silver tetrafluoroborate in the presence of the alcohol (Scheme 3), and were characterized by NMR at low temperature.

{[2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$CNHPh)]Ru(CO)$_2$(HOCHMe$_2$)}-BF$_4$ (**10**) was synthesized by adding excess AgBF$_4$ to a CD$_2$Cl$_2$ solution of [2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$CNHPh)]Ru-(CO)$_2$Cl (**7**) and 2-propanol in an NMR tube at −20 °C. When the NMR tube was shaken vigorously at −20 °C, AgBF$_4$ never completely dissolved, but a fine new precipitate of AgCl formed and was allowed to settle. ^{1}H and ^{13}C NMR resonances for both free 2-propanol and complex **10** were observed (Table 1). In the ^{1}H NMR spectrum of **10**, exchange of the OH group is slow enough that coupling (J = 6 Hz) is seen to the adjacent CH group.[11] The α-CH proton resonance of the 2-propanol complex **10** (δ 3.78) is shifted to lower frequency than in the free alcohol (δ 4.05), while the α-CH carbon resonance of **10** (δ 76.1) is shifted to higher frequency than in the free alcohol (δ 66.0). Similar changes in chemical shifts of α-CH carbon resonances have been reported for other alcohol complexes.[10] The OH resonance of **10** (δ 5.37) is shifted to higher frequency than in the free alcohol (δ 4.2).[12] Another test to determine if the alcohol is bonded to the organometallic fragment is to determine if the T_1 times are correlated between the alcohol fragment and organometallic fragment and are different from the T_1 times of the free alcohol in solution.[9] T_1 is a measure of the spin−lattice relaxation rate and is dependent on the tumbling rate, which should be faster for free than for complexed 2-propanol.[13] As expected, the T_1 time for the α-CH ^{1}H NMR resonance of **10** (1.0 s) was similar to that for the other proton resonances of **10** (1.0−1.3 s), while the T_1 time for the free alcohol α-CH (3.7 s) was much longer at −10 °C.[14]

Scheme 4



The rate of exchange of the (phenylamino)cyclopentadienyl benzyl alcohol complex **11** with 2-propanol was studied by ^{1}H NMR spectroscopy at −47 °C. The rate of exchange was nearly independent of the concentration of 2-propanol, with a first-order rate constant for approach to equilibrium of (1.4 ± 0.5) × 10^{-3} s^{-1} ($t_{1/2}$ = 8 min) at −47 °C. The K_{eq} value for alcohol exchange showed a slight preference for the isopropyl alcohol complex **10**: K_{eq} = [**10**][HOCH$_2$Ph]/[**11**][HOCHMe$_2$] = 2.1 at −47 °C. These kinetic studies establish that unimolecular dissociation of benzyl alcohol from **11** is a rapid process, but the rate of this dissociation is slower than the rate of production of benzyl alcohol from the reaction of protonated **5** with benzaldehyde. Currently, we are examining the reaction of protonated **5** with benzaldehyde to determine if the alcohol is “born” inside or outside of the coordination sphere of the metal.

The rate of exchange of hydroxycyclopentadienyl ruthenium benzyl alcohol complex **12** with 2-propanol at −46 °C was (2.2 ± 0.7) × 10^{-3} s^{-1} ($t_{1/2}$ = 5 min), as determined by ^{1}H NMR spectroscopy. The rates of exchange of **11** and **12** were similar. The equilibrium constant for alcohol exchange showed little dependence on the structure of the alcohol: K_{eq} = [HOCH$_2$Ph][**15**]/[HOCHMe$_2$][**14**] = 1.08 at −10 °C. The rate of alcohol exchange is similar to the rate of formation of benzyl alcohol from reduction of benzaldehyde by hydroxycyclopentadienyl ruthenium hydride **3**.

Initial attempts to prepare a neutral alcohol complex by deprotonation of **15** have been unsuccessful. Reaction of **15** with pyridine at −78 °C led to the formation of the pyridine complex [2,5-Ph$_2$-3,4-Tol$_2$(η^4-C$_4$C=O)]Ru-(CO)$_2$(NC$_5$H$_5$) (**16**) (Scheme 4). We are continuing to pursue the synthesis of neutral alcohol complexes by low-temperature deprotonations using bases that are too

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[11] Coupling between the OH and α-CH hydrogens has been seen for tungsten alcohol complexes.[10b]

[12] Comparable shifts to higher frequency have been observed for other ionic alcohol complexes and have been attributed to hydrogen bonding between the counteranion and the hydroxyl proton.[7a]

[13] (a) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy, A Guide for Chemists*; Oxford University Press: London, 1993. (b) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: London, 1961.

[14] For **11**, the T_1 times were determined at −70 °C. Similar T_1 values were seen for the benzyl protons for the alcohol ligand (0.48 s) and for the other protons of **11** (0.4−0.8 s), and a somewhat longer T_1 time was seen for the free alcohol (0.64 s). The T_1 values were too similar to be conclusive in correlating the alcohol fragment to the organometallic compound by this method.

sterically crowded to complex to ruthenium, so that we can determine the rate of dissociation of alcohols from the neutral complexes.

Since alcohol dissociation from the neutral complexes is anticipated to be substantially faster than from the more electrophilic cationic complexes, it is very likely that alcohol dissociation will be much faster than alcohol production from reduction of aldehydes by hydroxycyclopentadienyl hydride complexes such as **3**. This renders the task of determining whether alcohols are produced inside or outside the coordination sphere of the metal exceedingly difficult.

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Supporting Information Available: Text giving experimental details and characterization data for **10**−**16**, T_1 measurement of **10** and **11**, exchange of 2-propan-d_7-ol with **10**, and exchange of 2-propanol with **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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