Intriguing Coordination Behaviors of Aquo and Amine Ligands Bound to the Organoruthenium(II) Cation $[Ru(\eta^6\text{-}C_6H_6)(bpop)]^{2+}$ (bpop = 2,2-Bis[4(*R*)-phenyl-1,3-oxazolon-2-yl]propane)

Hideo Asano, Kyoshige Katayama, and Hideo Kurosawa*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received April 17, 1996

There has been increasing interest in basic coordination chemistry[1a−d] and synthetic applications[1e−h] of organoruthenium Lewis acids containing η^5-cyclopentadienyl or η^6-benzene ligands. In this field of chemistry much greater attention has been paid to a class of ligands capable of bonding to Ru through carbon atoms (e.g. alkenes, alkynes, carbenes) than to ligands coordinating through oxygen or nitrogen atoms. We thought that a proper combination of organic ligands (e.g. η^5-C_5H_5, η^6-C_6H_6) and additional inorganic auxiliaries on Ru would provide us a good opportunity to investigate unique coordination behaviors of the oxygen or nitrogen donor ligands which are otherwise not observable. We report here examples of such behavior, namely unusually slow M−O and O−H cleavage processes at coordinated water and diastereoselective exchange of N−H groups of a coordinated amine, which were observable by virtue of the use of the C_2-symmetric bis(oxazoline) auxiliary.[2]

The chloride ligand in $[RuCl((R)\text{-bpop})(C_6H_6)]BF_4$ was readily removed by $AgBF_4$ in the presence of water to give $[Ru(H_2O)((R)\text{-bpop})(C_6H_6)](BF_4)_2$ (**1**) (see Scheme 1) in 77% yield.[3] Complex **1** was characterized by elemental analysis, ^1H NMR and IR spectroscopy, and X-ray diffraction (Figure 1).[4]

In the ^1H NMR spectrum of **1** in CD_2Cl_2 at room temperature, there were observed only one set of the oxazoline ring proton resonances, albeit very broad, and only one resonance for the center methyls of (*R*)-bpop. The resonances of the coordinated water were absent at this temperature. However, peaks of coordinated and free water independently appeared at δ 4.41 and 2.55 ppm, respectively, at −55 °C. Moreover, as the temperature was lowered, each peak of (*R*)-bpop and the methyl peak split into two resonances and became sharper. These splitting patterns at the lower temperatures are consistent with the solid state structure (Figure 1) where there is no C_2 symmetry. A similar temperature dependency was also observed in acetone-d_6. Importantly, coordination of acetone to the ruthenium center could not be observed, and coordinated and free water appeared at δ 6.60 and 3.57 ppm, respectively, at −50 °C.

The variable-temperature NMR features presented above are explained by an interconversion between **A** and **B** (Scheme 2) which may proceed through either associative (bimolecular) H_2O exchange or a dissociative (unimolecular) mechanism involving the C_2-symmetric 16-electron intermediate $[Ru((R)\text{-bpop})(C_6H_6)]^{2+}$. Since the rate in CD_2Cl_2 hardly varied with the amount of water added (from 0.01 to 0.2 M), the interconversion presumably proceeds through the dissociative mechanism. Activation parameters for the interconversion were calculated on the basis of the exchange rates at different coalescence

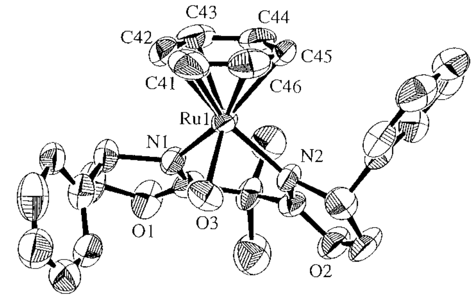
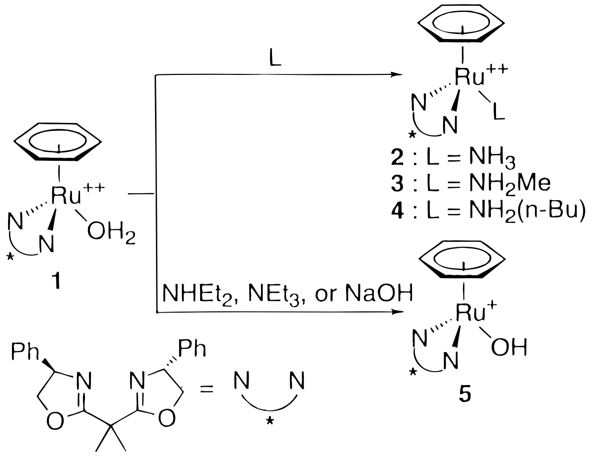
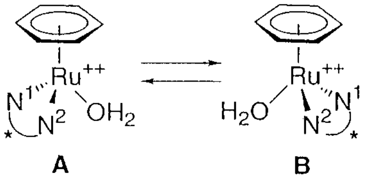


Figure 1. ORTEP drawing of **1**. BF_4 was omitted for clarity. Selected bond lengths (Å): Ru1−N1 = 2.101(10), Ru1−N2 = 2.133(10), Ru1−O3 = 2.161(8), Ru1−C41 = 2.20(2), Ru1−C42 = 2.20(1), Ru1−C43 = 2.21(1), Ru1−C44 = 2.19(1), Ru1−C45 = 2.21(1), Ru1−C46 = 2.28(2).

Scheme 1



Scheme 2



---

(1) (a) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1. (b) Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761. (c) Bozec, H. L.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163. (d) Bennett, M. A.; Khan, K.; Wenger, E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Chapters 7.8 and 7.9, pp 473−602. (e) Faller, J. W.; Smart, C. J. *Tetrahedron Lett.* **1989**, *30*, 1189. (f) Derien, S.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2551. (g) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259. (h) Chaudret, B. *Bull. Soc. Chim. Fr.* **1995**, *132*, 268.

(2) For related works on $[Ru(H_2O)_3(arene)]^{2+}$ complexes, see: (a) Stebler-Röthlisberger, M.; Hummel, W.; Pittet, P.-A.; Bürgi, H.-B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358. (b) Karlen, T.; Hauser, A.; Ludi, A. *Inorg. Chem.* **1994**, *33*, 2213. (c) Dadci, L.; Elias, H.; Frey, U.; Hörnig, A.; Koelle, U.; Merbach, A. E.; Paulus, H.; Schneider, J. S. *Inorg. Chem.* **1995**, *34*, 306.

(3) $[RuCl((R)\text{-bpop})(C_6H_6)]BF_4$ was prepared in 62% yield from the reaction between (*R*)-bpop and $[RuCl_2(C_6H_6)]_2$ in the presence of $NaBF_4$. For detailed preparation procedures for all complexes, see the Supporting Information.

(4) Crystal data for **1**: $C_{27}H_{30}N_2O_3B_2F_8Ru$, M = 705.22, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 14.261(4) Å, b = 21.156(3) Å, c = 9.688(3) Å, V = 2922.7(9) Å^3, Z = 4, $F(000)$ = 1424, D_c = 1.603 g/cm^3, μ(Mo Kα) = 6.20 cm^{-1}, 389 variables refined with 2852 reflections with $I > 3\sigma(I)$ to R = 0.069, R_w = 0.055.

S0020-1669(96)00410-7 CCC: $12.00

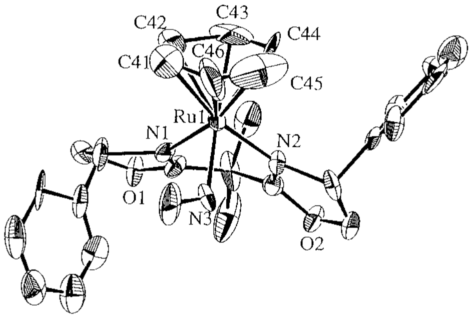


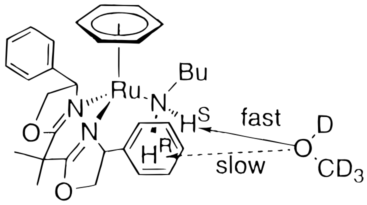
Figure 2. ORTEP drawing of **3**. BF_4 was omitted for clarity. Selected bond lengths (Å): Ru1−N1 = 2.11(2), Ru1−N2 = 2.07(2), Ru1−N3 = 2.16(2), Ru1−C41 = 2.22(3), Ru1−C42 = 2.20(4), Ru1−C43 = 2.22(3), Ru1−C44 = 2.21(4), Ru1−C45 = 2.14(5), Ru1−C46 = 2.12(5).

temperatures determined by using different pairs of resonances undergoing coalescence and different magnetic field instruments.[5] These are $\Delta H^{\ddagger} = 47$ kJ mol^{-1}, $\Delta S^{\ddagger} = -29$ J K^{-1} mol^{-1} in CD_2Cl_2 and $\Delta H^{\ddagger} = 105$ kJ mol^{-1}, $\Delta S^{\ddagger} = 136$ J K^{-1} mol^{-1} in acetone-d_6. The fact that $\Delta H^{\ddagger}$ in acetone-d_6 was larger than that in CD_2Cl_2 is surprising if we assume that acetone could more effectively stabilize the 16-electron intermediate and/or free H_2O than dichloromethane. A more likely explanation would be that acetone molecules are strongly held in the vicinity of the coordinated H_2O via hydrogen bonding in the ground state, with the Ru−O bond being strengthened by such solvation (cf. the nonlabile hydroxide complex described later). In other words, the rate-determining step would involve desolvation prior to the Ru−OH_2 bond cleavage, in agreement with the fact that $\Delta S^{\ddagger}$ in acetone-d_6 was much larger than that in CD_2Cl_2.

Addition of ammonia, methylamine, and butylamine to the solution of **1** in CD_2Cl_2 produced amine complexes **2**−**4** (Scheme 1) which were characterized by elemental analysis and ^{1}H NMR spectroscopy. (Methylamine)ruthenium complex **3** was also characterized by X-ray diffraction (Figure 2).[6] In the solid state, the methyl group of the coordinated amine is directed away from two nitrogen atoms of (*R*)-bpop and slightly tilted toward the nearby phenyl group of (*R*)-bpop.

In contrast to the Ru−O bond of **1**, the Ru−N bonds of **2**−**4** are rigid in solution on the NMR time scale. The two N-hydrogens are diastereotopic. It is very remarkable that these two protons not only were observed to be nonequivalent but also underwent exchange with deuteriums in CD_3OD solution with greatly different rates. Thus, we observed the amine hydrogens of **4** at δ 3.07 and 2.07 ppm in CD_3OD, which underwent deuterium exchange, with the rate constants being 1.0×10^{-5} and 1.3×10^{-6} s^{-1} at 25 °C, respectively.[7] The fact that the higher field hydrogen underwent the slower exchange can be understood in terms of steric effects deduced from Figure 2. That is, the pro-*R* hydrogen (Scheme 3) to which we assign the peak at δ 2.07 ppm is subject to a ring current effect from the nearby phenyl group of (*R*)-bpop and at the same time the approach of the methanol oxygen to this hydrogen is retarded.

Scheme 3



As can be seen in Figure 2, one phenyl group of (*R*)-bpop is located in close proximity to the coordination site, so (*R*)-bpop and benzene create a narrow coordination site. In agreement with this, addition of secondary and tertiary amines such as diethylamine and triethylamine to the CD_2Cl_2 solution of **1** did not result in Ru−N bond formation but produced hydroxoruthenium complex **5**[8] (Scheme 1) which was also obtained from the reaction of **1** and sodium hydroxide. The ^{1}H NMR spectra of **5** in acetone-d_6 showed no fluxional aspects up to 55 °C. Addition of less than 1 equiv of a secondary or tertiary amine to a solution of **1** gave a mixture of the aqua and hydroxo complexes, and interestingly ^{1}H NMR resonances of both were separately detected at room temperature. This indicates the slow interconversion between **1** and **5** on the NMR time scale, representing another rare example of the slow proton transfer between the coordinated H_2O and OH ligands.[9]

Application of these complexes and their analogs to molecular recognition and asymmetric synthesis is now under way.

Acknowledgment. Partial support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan is acknowledged. Thanks are also expressed to the Analytical Center, Faculty of Engineering, Osaka University, for access to NMR facilities.

Supporting Information Available: Text giving preparative procedures, analytical data for products, and the exchange rates in Scheme 2, additional structural diagrams, and listings of crystallographic details, atomic coordinates, anisotropic displacement parameters, and bond lengths and angles (18 pages). Ordering information is given on any current masthead page.

IC960410H

---

(5) The exchange rates, *k*, were calculated by the following equation, $k = \pi(\nu_0(\Delta\delta))/2^{1/2}$, where ν_0 is the instrument frequency and $\Delta\delta$ is the difference in chemical shifts for the coalescing pair of peaks. See the Supporting Information.

(6) Crystal data for **3**: $C_{28}H_{33}N_3O_2B_2F_8Ru$, $M = 718.26$, monoclinic, space group $P2_1$ (No. 4), $a = 9.164(4)$ Å, $b = 15.660(2)$ Å, $c = 11.094(3)$ Å, $\beta = 110.76(3)°$, $V = 1488.8(8)$ Å^3, $Z = 2$, $F(000) = 728$, $D_c = 1.602$ g/cm^3, μ(Mo Kα) = 6.09 cm^{-1}, 397 variables refined with 1842 reflections with $I > 3\sigma(I)$ to $R = 0.085$, $R_w = 0.100$.

(7) Complex **4** began to decompose after about 8 days under the following conditions: [**4**] = 0.0132 M, [CD_3OD] = 24.6 M.

(8) Attempts to isolate analytically pure **5** failed. ^{1}H NMR (CD_2Cl_2, 270 MHz): δ 1.11 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$), 4.10 (dd, *J* = 4.7, 9.2 Hz, 1H), 4.20 (br, 1H, O*H*), 4.31 (dd, *J* = 4.0, 8.2 Hz, 1H), 4.63 (dd, *J* = 6.2, 9.2 Hz, 1H), 4.95 (dd, *J* = 4.7, 6.2 Hz, 1H), 4.95 (dd, *J* = 8.2, 9.8 Hz, 1H), 5.25 (s, 6H, C_6*H*$_6$), 5.82 (dd, *J* = 4.0, 9.8 Hz, 1H), 7.33−7.50 (m, 10H, 2 × Ph).

(9) (a) Carroll, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1992**, *114*, 8744. (b) Kramarz, K. W.; Norton, J. R. *Prog. Inorg. Chem.* **1994**, *42*, 1. (c) La, T.; Miskelly, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 3613.