Coordination Behavior of Ruthenium(II) Complexes with Alcohol Ligand Tethered to η^6-Arene Donor

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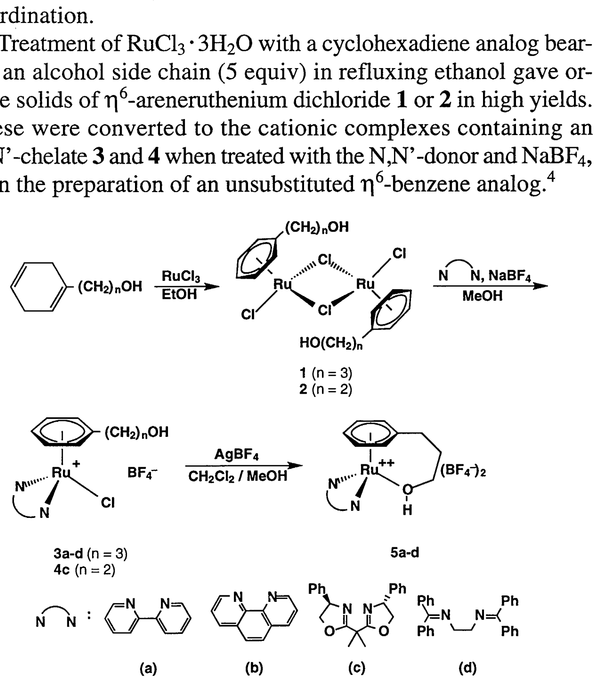
Some ruthenium(II) complexes of an alcohol ligand tethered to η^6-arene group have been prepared. The alcohol-Ru chelate bond of the complexes containing an N,N'-chelate auxiliary was maintained in methanol. The Cl^- ion cleaved the alcohol-Ru bond to give the Ru-Cl bond, while bases (OH^-, RNH_2) abstracted proton of OH bound to Ru affording the alkoxy chelate complex.

In spite of their key role as intermediates in homogeneous catalytic[1] as well as biochemical[2] transformations, alcohol complexes of late transition metals have rarely been subjects of molecular level coordination chemistry. It appears that some unique tactics, e.g. chelate coordination, are required to maintain otherwise unstable metal-alcohol bonds.[3] In addition, these bonds were reported to be susceptible to nucleophiles to result in reversible ligand substitution or deprotonation, with the latter leading to alkoxide formation.[3] It seems important to understand how the course of these transformations is affected by the nature of the nucleophile and the metal, but more works are needed before gaining a general insight into such problem. We report here preparation and structures of several ruthenium(II) complexes of alcohol ligands which are tethered to the η^6-arene group. The present system is particularly well suited for observing unique solution behavior of coordinated alcohols including the first quantitative evaluation of acidity increase of the alcoholic OH hydrogen upon coordination.

Treatment of $RuCl_3 \cdot 3H_2O$ with a cyclohexadiene analog bearing an alcohol side chain (5 equiv) in refluxing ethanol gave orange solids of η^6-areneruthenium dichloride **1** or **2** in high yields. These were converted to the cationic complexes containing an N,N'-chelate **3** and **4** when treated with the N,N'-donor and $NaBF_4$, as in the preparation of an unsubstituted η^6-benzene analog.[4]



Scheme 1.

Reaction of **3** with $AgBF_4$ in CH_2Cl_2 and/or MeOH gave dicationic complexes **5**[5] (Scheme 1). The chelate coordination of the alcohol ligand in **5b** and **5c** was established by X-ray crystallography (Figure 1).[6] The ^1H NMR data of **5c**[7] showing two diastereotopic OCH_2 resonances of the alcohol group at δ 2.18 and 3.55 ($CDCl_3$) are diagnostic for the coordination of the alcohol in solution; *cf.* a single OCH_2 resonance in **3c** (δ 3.50). Treatment of **4c** with $AgBF_4$ gave η^6-arene(oxazoline)ruthenium(II) dication, whose single resonance (δ 3.15) due to OCH_2 protons of the CH_2CH_2OH group suggests non-coordination of alcohol, though the dication thus formed could not be isolated pure.

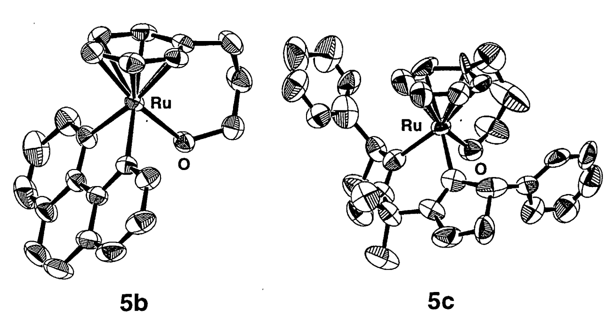
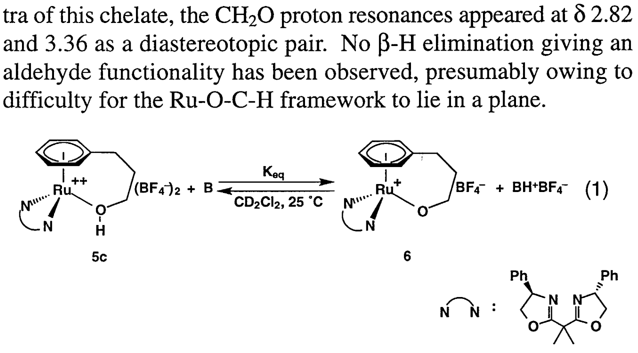


Figure 1. ORTEP drawing of **5b** and **5c** with ellipsoids at 50% probability levels. BF_4 was omitted for clarity.

^1H NMR spectra of **5c** measured in CD_3OD were almost the same as those in $CDCl_3$ or CD_2Cl_2, suggesting that coordination of the pendent alcohol is maintained even in methanol. The analogous coordination of the $CH_2CH_2CH_2OH$ group of **5a**, **5b**, and **5d** in CD_3OD was also assessed by ^1H NMR spectra. Thus, the proton resonances of this group in **1** or **3** bearing the freely rotating C-C bond appeared as a typical $A_2M_2X_2$ spin system, while those in **5a**, **5b**, and **5d** appeared as more complex AA'MM'XX' patterns since the free rotation about the C-C axis is restricted.

Treatment of **5** with 1 equiv of $[PPh_4]Cl$ in CD_2Cl_2 or CD_3OD gave the original chlorides **3** in almost quantitative yields. Of particular note was the reaction of **5c** with NaOH in methanol affording high yield of alkoxide complex **6**.[8] In the ^1H NMR spectra of this chelate, the CH_2O proton resonances appeared at δ 2.82 and 3.36 as a diastereotopic pair. No β-H elimination giving an aldehyde functionality has been observed, presumably owing to difficulty for the Ru-O-C-H framework to lie in a plane.



Addition of amine to a CD_2Cl_2 solution of **5c** resulted in the formation of an equilibrium mixture of **5c** and **6**, the ratio of the two species being dependent on the amount and basicity of the amine. The rate of interconversion between **5c** and **6** was confirmed rapid on the NMR time scale; averaging was observed at 25 ℃ for each pair of resonances due to protons of **5c** and the corresponding protons of **6**. Among these, the averaged position of one of the *meta*-H in η^6-C_6H_5R ring moved from δ 6.80 in **5c** to 5.85 in **6**, when **5c** was titrated with an amine (Figure 2). This allowed us to assess acid-base equilibrium constants expressed by eq. 1; a least-square curve-fitting afforded $K_{eq} = 1.02 \pm 0.13$ for B= $(C_6H_5CH_2)(CH_3)NH$ and 0.43 ± 0.08 for B= $(C_6H_5CH_2)_2NH$, suggesting that in CH_2Cl_2 the acidity of the coordinating alcohol in **5c** is comparable to those of ammonium salts formed from these amines (pK_a in H_2O, ca. 11).[9] Triethylamine was too basic to allow correct estimation of the equilibrium constant.

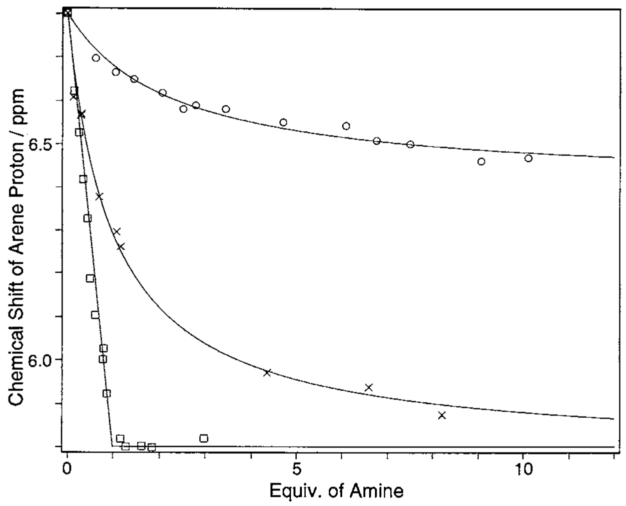
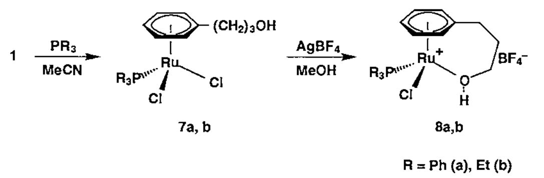


Figure 2. Variation of chemical shift of *meta*-H in η^6-C_6H_5R ring as a function of equivalent of amine added to **5c**; triethylamine(□), benzylmethylamine(×), and dibenzylamine(○).



Scheme 2.

The complex **1** was converted to PR_3 adducts **7** in high yields by addition of PR_3 (1 equiv) in acetonitrile. Removal of Cl ligand in **7** with $AgBF_4$ in methanol gave crystalline solids **8** in moderate yields. The diastereotopic CH_2O proton resonances of **8** in CD_2Cl_2 again suggest chelate coordination of the alcoholic oxygen.[10] Treatment of **8** with base afforded yet uncharacterizable products. Further studies are in progress to elucidate their structures as well as to delineate roles of the new alcohol and alkoxy complexes obtained here in Ru-mediated organic transformations.

References and Notes

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5 Complexes **5**, **6** and **8** gave satisfactory elemental analyses.

6 The Ru-O length (2.145(3) Å in **5b**, 2.11(2) Å in **5c**) is comparable to that of $[C_6H_6Ru(bisoxazoline)(H_2O)]^{2+}$ (2.161(8) Å).[4] Crystal data for **5b**: $C_{21}H_{20}N_2OB_2F_8Ru$, M= 591.08, triclinic, space group $P\bar{1}$(#2), a= 10.002(2) Å, b= 11.714(2) Å, c= 9.722(2) Å, α= 92.03(2)° , β= 92.77(2)° , γ= 79.37(2)° , V= 1117.7(4) Å³, Z= 2, F(000)= 588, Dc= 1.756 g/cm³, μ(Mo Kα)= 7.86 cm⁻¹, 316 variables refined with 4874 reflections with $I > 3\sigma(I)$ to R= 0.043, Rw= 0.064. Crystal data for **5c**•$(H_2O)_2$: $C_{30}H_{38}N_2O_5B_2F_8Ru$, M= 781.32, monoclinic, space group $P2_1$(#4), a= 9.304(1) Å, b= 19.063(2) Å, c= 10.485(2) Å, β= 110.17(1)° , V= 1745.6(4) Å³, Z= 2, F(000)= 796, Dc= 1.486 g/cm³, μ(Mo Kα)= 5.31 cm⁻¹, 479 variables refined with 2563 reflections with $I > 3\sigma(I)$ to R= 0.099, Rw= 0.124.

7 H-H COSY spectra established assignments of protons in η^6-C_6H_5R and the oxazoline ligands.

8 No well characterizable products could be obtained from **5a** or **5b** and base; **5d** and $(C_6H_5CH_2)(CH_3)NH$ in CD_2Cl_2 gave ^1H NMR spectra suggestive of formation of the alkoxide, though not isolable.

9 The pK_a values of free alcohols are around 16; W. Reeve, C. M. Erikson, and P. F. Aluotto, *Can. J. Chem.*, **57**, 2747 (1979).

10 Notice δ(CH_2O) at 3.35 (m) and 3.78 (m) for **8a** and 3.48 (m) and 3.92 (m) for **8b**, which can be compared with that at 3.79 (t) for **7a** and 3.83 (t) for **7b**, respectively.