Structural and Kinetic Study on the Ligand Rearrangement Reaction of 2-Aminomethylpyridine on a Di(μ-acetato)dirhodium(II) Center

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(Received December 3, 1998; CL-980896)

Three new dirhodium(II) complexes, $[Rh_2(\mu\text{-}O_2CCH_3)_2(O_2CCH_3)(amp)_2]ClO_4$ (**1**) (amp = 2-aminomethylpyridine), $[Rh_2(\mu\text{-}O_2CCH_3)_2(amp)_2](ClO_4)_2$ (**2**) and $[Rh_2(\mu\text{-}O_2CCH_3)_2(amp)_2(py)_2](PF_6)_2$ (**3**) were prepared and characterized by X-ray structural analysis except for **2**. The first order rate constant of the conversion of **1** to **2** was $(2.5 \pm 0.1) \times 10^{-4}$ s^{-1} at 75 °C in aqueous solution (I = 0.075 ($LiClO_4$), pH = 6.5).

Substitution rate of the bridging ligands of doubly or quadruply bridged dimetal complexes is significantly different between quadruply metal-metal bonded dimolybdenum(II) and singly bonded dirhodium(II) complexes.[1,2] Information is still rather qualitative, however, and further study is required in order to understand the substitution mechanism of the dimetal centers. Compared with dimolybdenum(II) systems, carboxylate bridged dirhodium(II) complexes are more appropriate for the detailed study because of their substitution inert nature. They are also of practical importance as they have catalytic and antitumor activities.[3-5] Studies on stepwise coordination of multidentate nitrogen donor ligands are useful in understanding the binding process of DNA to the dimer unit. Three main processes, namely, (i) monodentate coordination at the axial positions (*ax*), (ii) axial-to-equatorial chelation (*ax-eq*), and (iii) di-equatorial chelation (*eq-eq*), have been discussed by the isolation of the complexes with varied coordination modes of chelating ligands and qualitative observation of the reaction processes.[2, 6-11] The process (i) is known to be fast with the rate constants in the order of $10^5 - 10^6$ mol^{-1} dm^3 s^{-1}.[12] The process (iii) is considered as a rate-determining step from some qualitative observations. No kinetic study is available so far, however, for the processes (ii) and (iii), and it is clear that kinetic study based on structurally unambiguous intermediate species is required. By using 2 equivalents of 2-aminomethylpyridine (amp) to the dimer, we have isolated both *ax-eq* and *eq-eq* species, $[Rh_2(\mu\text{-}O_2CCH_3)_2(O_2CCH_3)(amp)_2]ClO_4$ (**1**) and $[Rh_2(\mu\text{-}O_2CCH_3)_2(amp)_2](ClO_4)_2$ (**2**), both having two amp ligands. The former is particularly interesting because it contains both *ax-eq* and *eq-eq* chelating amp ligands in the same dimeric unit. We have also isolated $[Rh_2(\mu\text{-}O_2CCH_3)_2(amp)_2(py)_2](PF_6)_2$ (**3**) (py = pyridine) by the reaction of the chloride salt of the cation in **2** with pyridine. Previously, an infinite chain complex, $[Rh_2(O_2CCH_3)_4(amp)]_n$ (*axial*-bridged type), has been reported by the 1:1 reaction in acetonitrile.[13] We wish to report the first kinetic study of the conversion from *ax-eq* to *eq-eq* in aqueous solution based on the isolations and X-ray structural characterization of the complexes containing the two coordination modes (*ax-eq* and *eq-eq*, and two *eq-eq*) of amp.

The new complexes **1** and **2** were prepared by stirring a chlorohoim solution (140 cm^3) containing $Rh_2(\mu\text{-}O_2CCH_3)_4(CH_3OH)_2$ (200 mg, 0.4 mmol) and amp (86 mg, 0.8 mmol) at room temperature for a week. The solution was evaporated and the residue was dissolved into an aqueous solution (10 cm^3) of sodium perchlorate (300 mg, 2.5 mmol). After leaving the solution for several days, the purple crystalline solid (**1**) was formed (111 mg, 40%).[14] The filtrate was allowed to evaporate slowly to give green solid (**2**; 20 mg, 6.5%).[15] Chloride salt of **2** (76 mg, 29%) was prepared by the similar method except for dissolving the residue into aqueous solution (15 ml) of sodium chloride (500 mg, 8.5 mmol). The complex **3** was prepared by stirring an aqueous solution (10 cm^3) containing the chloride salt of **2** (25 mg, 0.04 mmol) and pyridine (49 mg, 0.62 mmol) at room temperature for an hour. Addition of NH_4PF_6 caused the precipitation of pink solid **3** (27 mg, 70%).[16]

Figure 1 shows the structure of the complex cation in **1**.[17] Two amp ligands are not equivalent, one of them occupying *eq-eq* site and the other *ax-eq* site. Such asymmetrical structure involving two didentate nitrogen donor ligands was observed for the first time. Figure 2 shows the structure of the complex cation in **3**,[17] which has approximate C_2 symmetry. Two independent rhodium dimer units are involved in the asymmetric unit. The two axial sites are occupied by the pyridine ligands. The ^1H NMR spectrum of **1** at room temperature in D_2O showed two sets of amp signals and three acetate methyl signals,[14] suggesting that the structure is maintained in aqueous solution at

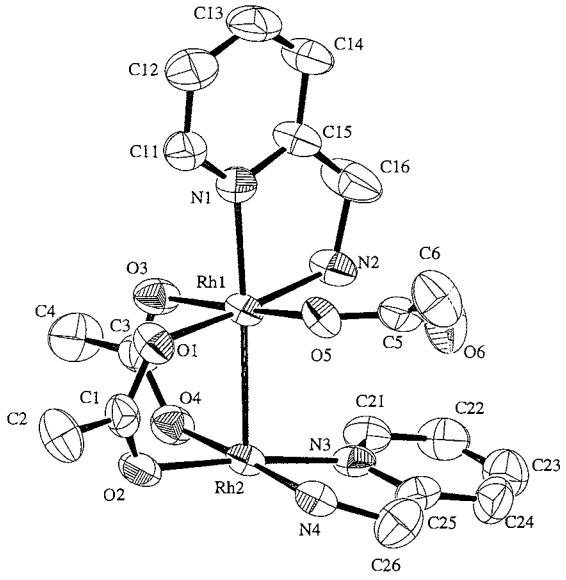

Figure 1. ORTEP drawing of the complex cation in **1**. Selected bond distances (Å) and angles (deg): Rh1-Rh2, 2.5249(9); Rh1-N1, 2.111(6); Rh1-N2, 2.024(6); Rh1-O1, 2.053(5); Rh1-O3, 2.040(5); Rh1-O5, 2.018(5); Rh2-O2, 2.049(5); Rh2-O4, 2.042(5); Rh2-N3, 2.004(6); Rh2-N4, 2.002(6); Rh2-Rh1-N1, 175.9(2).

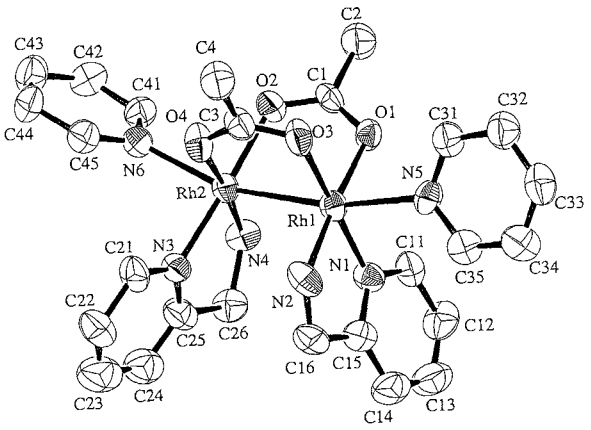

Figure 2. ORTEP drawing of the complex cation in **3**. Selected bond distances (Å) and angles (deg): Rh1-Rh2, 2.587(1); Rh1-N1, 2.001(10); Rh1-N2, 2.053(9); Rh1-O1, 2.067(7); Rh1-O3, 2.077(8); Rh1-N5, 2.281(9); Rh2-N3, 2.013(9); Rh2-N4, 2.071(9); Rh2-O2, 2.062(8); Rh2-O4, 2.048(8); Rh2-N6, 2.247(10); Rh2-RhI-N5, 166.9(3); Rh1-Rh2-N6, 162.7(3) : Rh101-Rh102, 2.585(1); Rh101-N101, 2.013(9); Rh101-N102, 2.059(9); Rh101-O101, 2.053(8); Rh101-O103, 2.057(8); Rh101-N105, 2.28(1); Rh102-N103, 2.023(9); Rh102-N104, 2.055(9); Rh102-O102, 2.044(8); Rh102-O104, 2.041(8); Rh102-N106, 2.233(9); Rh102-Rh101-N105, 165.4(3); Rh101-Rh102-N106, 163.5(2).

room temperature. The axial site of Rh2 may be occupied by a water molecule. The ^{1}H NMR spectrum of **2** at room temperature showed that two amp ligands and two bridging acetates are equivalent, respectively.[15] One of the methylene protons of amp was observed at ca. 2 ppm upfield from that of free amp owing to the ring current influence of the pyridyl ring of the other amp. The ^{1}H NMR spectrum of **3** is similar to that of **2** except for an appearance of axial pyridine signals, suggesting that the C_2 structure of **2** containing the two *eq-eq* amp ligands is maintained in solution. The dimer structure of **2** is further supported by the UV-vis spectrum. The visible absorption band for **1** in aqueous solution is seen at 536 nm, whereas that for **2** at 577 nm. The bands are assigned to the π^* or δ^* (Rh-Rh) $\rightarrow$ σ^* (Rh-Rh) transition.[3-5] It is known that the transition energy depends on the kind of the axial ligands (530-550 nm for nitrogen donors and 580-600 nm for oxygen donors).[3-5] The bands of **1** and **2** were observed at the expected regions for the axial pyridine and water ligands, respectively.

The interconversion of the amp ligand from the *ax-eq* to *eq-eq* coordination mode (conversion of "**1**" to "**2**") was monitored spectrophotometrically in aqueous solution.[18] The first order rate constant was $(2.5 \pm 0.1) \times 10^{-4}$ s^{-1} at 75 °C and activation parameters were $\Delta H^{\ddagger} = 91 \pm 5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -54 \pm 13$ J K^{-1} mol^{-1}.[19] These are the first kinetic data of the substitution of the *eq* site of dirhodium(II) center. Very small rate constant is noted, which may be due to fully occupied δ^* and π^* orbitals that prevent associative attack of the chelating ligands. Activation parameters point to more dissociative character of the rearrangement reaction.[2]

Grant-in Aids for Scientific Research Nos. 10149102 (Priority Area of "Metal-Assembled Complexes") and 10133201 (Priority Area of "The Chemistry of Inter-element Linkage") to YS and KU, respectively, from the Ministry of Education, Science, Sports, and Culture, Japan, are gratefully acknowledged.

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14 **1**: ^{1}H NMR/ppm vs TSP (D_2O, 23 °C). amp signals; aromatic; 8.96(d, 1H), 8.32(d, 1H), 8.02(dd, 1H), 7.91(dd, 1H), 7.62(dd, 1H), 7.54(d, 1H), 7.42(d, 1H), 7.38(dd, 1H), -NH_2; 6.25(br, 1H), 4.94(br, 1H), 4.50(br, 1H), 3.80(br, 1H), -CH_2-; 4.30(m, 1H), 4.01(m, 3H), acetate; 2.26(s, 3H), 2.02(s, 3H), 1.72(s, 3H). UV-vis/nm (ε /dm^{3}mol^{-1}cm^{-1}, in H_2O): 536(220), 311(8700), 274(18300). Anal. Found: C 29.83, H 3.64, N 7.96%. Calcd for $C_{18}H_{25}N_4O_{10}ClRh_2$: C 30.94, H 3.61, N 8.02%.
15 **2**: ^{1}H NMR/ppm vs TSP (D_2O, 23 °C). amp signals; aromatic; 8.57(d, 2H), 7.97(dd, 1H), 7.54(dd, 2H), 7.32(d, 2H), -NH_2; 4.11(br, 2H), -CH_2-; 3.88(d, 2H), 2.0(dd, 2H), acetate; 2.26(s, 6H). UV-vis/nm (ε / dm^{3}mol^{-1}cm^{-1}, in H_2O): 577nm(150), 310(8500), 266(16900). Anal. Found: C 26.22, H 3.16, N 7.56, Cl 9.37%. Calcd for $C_{16}H_{22}N_4O_{12}Cl_2Rh_2$: C 26.00, H 3.00, N 7.58, Cl 9.59%. FAB-MS (M^+): 639
16 **3** : ^{1}H NMR/ppm vs TMS (CD_2Cl_2, 23 °C). amp signals; aromatic: 8.68(d, 2H), 7.95(dd, 1H), 7.70(dd, 2H), 7.19(d, 2H), -NH_2; 3.50(br, 2H), -CH_2-: 3.85(d, 2H), 2.25(d, 2H), pyridine: 8.38(d, 4H), 7.92(dd, 2H), 7.50(dd, 4H), acetate; 2.23(s, 6H). UV-vis/nm (ε / dm^{3}mol^{-1}cm^{-1}, in CD_2Cl_2): 495nm(450), 310(sh), 288(28500). Anal. Found: C 31.60, H 3.26, N 8.50%. Calcd for $C_{26}H_{32}N_6O_4P_2F_{12}Rh_2$: C 31.45, H 3.26, N 8.50%.
17 Crystal data for **1**: formula $C_{18}H_{25}O_{10}N_4ClRh_2$, fw 698.68, monoclinic, space group $P2_1/c$, a = 9.312(3) Å, b = 17.736(6) Å, c = 14.968(3) Å, β = 97.18(2)°, V = 2455(1) Å^3, Z = 4, Dc = 1.890 g cm^{-3}, μ (Mo Kα) = 18.14 cm^{-1}, R = 0.045 (R_w = 0.036) against 3663 reflections ($I \geq 2\sigma(I)$). Crystal data for **3**: formula $C_{26}H_{28}O_4N_6P_2F_{12}Rh_2$, fw 984.29, triclinic, space group $P\bar{1}$, a = 19.103(3) Å, b = 20.390(3) Å, c = 10.428(2) Å, α = 98.35(1)°, β = 104.49(1)°, γ = 108.69(1)°, V = 3611(1) Å^3, Z = 4, Dc = 1.810 g cm^{-3}, μ (Mo Kα) = 11.04 cm^{-1}, R = 0.070 (Rw = 0.098) against 8466 reflections ($I \geq 2\sigma(I)$). Intensity data were collected with a graphite monochromated Mo Kα radiation (λ = 0.71069 Å) on Rigaku AFC5R diffractmeter at 23 °C up to 2θ = 60°(**1**) and 55°(**3**), respectively, and corrected for Lorentz polarization effect. The structures were solved by direct methods (SIR 92) for **1** and Patterson method (DIRDIF 92 PATTY) for **3** , respectively, and all the non-hydrogen atoms were refined anisotropically except for six fluorine atoms in one of hexafluorophosphate anions in **3** with full-matrix least square technique. The axial site of Rh2 for **1** is weakly coordinated by O2 atom of neighboring molecule (2.599(5) Å). Computational work was carried out by Crystallographic Software package in teXsan.
18 Kinetic measurements were carried out at 58 – 80 °C in aqueous solution (pH = 6.5 at 25 °C, I = 0.075 mol dm^{-3} ($LiClO_4$)). Concentration of the complex was 7.3×10^{-4} mol dm^{-3}. Absorbance changes were monitored at 536 and 370 nm. No concentration dependence was observed at 1.9×10^{-4} mol dm^{-3} and 7.3×10^{-4} mol dm^{-3} at 75 °C. The first-order plot gave a good straight line at least up to 80% of the reaction, from the slope of which the first order rate constants were evaluated. The reaction was also monitored by ^{1}H NMR at 80 °C in D_2O. No other species except for **1** and **2** were observed during the reaction.
19 These activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were evaluated from the temperature dependence of the rate constants obtained at 370 nm. The values from the data at 536 nm were $\Delta H^{\ddagger} = 88 \pm 4$ kJ mol^{-1}and $\Delta S^{\ddagger} = -62 \pm 11$ J K^{-1} mol^{-1}, which are in reasonable agreement with the ones in the text.