Synthesis and Structural Studies of Dinuclear Carbonyl Ruthenium(II) Complexes Containing Pyridine-2,6-diyl-2-acetyl-6-methyl Group as an η^2(C,N):η^1(C)-Bridging Ligand

Mayumi Shimizu, Yukio Nakamura,* and Makoto Tadokoro
Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto-3, Sumiyoshi-ku, Osaka 558

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Three new dinuclear ruthenium(II) complexes bridged by a pyridine-2,6-diyl-2-acetyl-6-methyl group were prepared by thermal reaction of 2,6-bis(chloromethyl)pyridine with $[Ru_3(CO)_{12}]$ followed by reactions with methanol and triphenylphosphine, respectively, and the crystal structures of two of them were determined by X-ray analyses.

2,6-Bis(chloromethyl)pyridine (2,6-cmpy), which is potentially bifunctional in oxidative addition reactions, reacts with $[PdL_4]$ (L = PPh_3) to give C,N-bridging dinuclear and C,N,C-bridging tandem tetranuclear complexes, $[\{PdCl[C_5H_3(6\text{-}CH_2Cl)N\text{-}2\text{-}CH_2]L\}_2]$ and $[\{Pd_2Cl_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2]L_2\}_2]$.[1] In contrast, the reaction with $[RhClL_3]$ affords a novel dinuclear complex $[Rh_2Cl_4\{C_5H_3N\text{-}2,6\text{-}(CH_2)_2\}L_2]$, in which the 2,6-dimethylpyridine-α,α'-diyl ligand is C,N-chelated to one rhodium atom and bound to the second one in an η^3-pseudo-1-azaallylic fashion, along with the C,N-chelated mononuclear complexes, *cis*(PP)- and *trans*(PP)-$[RhCl_2\{C_5H_3(6\text{-}CH_2Cl)N\text{-}2\text{-}CH_2\}L_2]$.[2] These results have aroused interest in extending our studies to ruthenium carbonyl clusters that extensive studies have recently been done on their reactivities toward main group donor atoms like O,[3] S,[4] N,[5] and P.[6] We report herein the synthesis and solid-state and solution characterization of dinuclear ruthenium (II) complexes derived from 2,6-cmpy and $[Ru_3(CO)_{12}]$.

$[Ru_3(CO)_{12}]$ (**1**, 0.477 mmol) was allowed to react with an excess of 2,6-cmpy (4.29 mmol) in refluxing toluene for 8 h under nitrogen. The color of the solution changed from wine red to pale yellow, then orange with gradually depositing **2** of the composition of $[Ru_2Cl_2\{C_5H_3N\text{-}2,6\text{-}(CH_2)_2\}(CO)_5]$ (84%). Structurally unknown **2** is insoluble in noncoordinating solvents and precluded its purification and characterization by spectroscopic technique. However, **2** (0.193 mmol) reacted with methanol molecules in refluxing methanol giving a clear solution, from which **3** (62%) was separated out. Both ^1H and ^{13}C NMR spectra of **3** in CD_3CN indicate that (a) CO inserts to one of two Ru-CH_2 σ-bonds; (b) a pyridine-2,6-diyl-2-acetyl-6-methyl group acts as an η^2(C,N):η^1(C)-bridging ligand; and (c) **3** exists in solution as at least two geometrical isomers (ca. 53 : 47) around the metal atoms.[7] The X-ray analysis of single crystals of **3** obtained by recrystallization from MeOH established the solid structure for one isomer of **3** (Figure 1a).[8] The Ru(2) atom attains 6-coordination by cis-*O*-ligation of two methanol molecules along with two terminal carbonyls, one bridging chlorine and one σ-methylene groups.

In order to solubilize, the reaction of **2** with L was examined. A suspension of **2** (0.293 mmol) in benzene was allowed to react with L (0.755 mmol) at 80 °C for 5 h. No color change of the reaction mixture was observed during the reaction. Filtration, washing with ether and recrystallization from $CHCl_3/Et_2O$ gave bis(phosphine) derivative **5** (92 %). In contrast with **3**, ^1H and ^{13}C NMR spectra of **5** in $CDCl_3$ revealed the presence of only one isomer in solution and the coordination of an acyl group, a σ-methylene group, and 2L ligands. Especially the appearance of two singlets in ^{31}P NMR spectrum in $CDCl_3$ suggested that each of the 2L ligands is

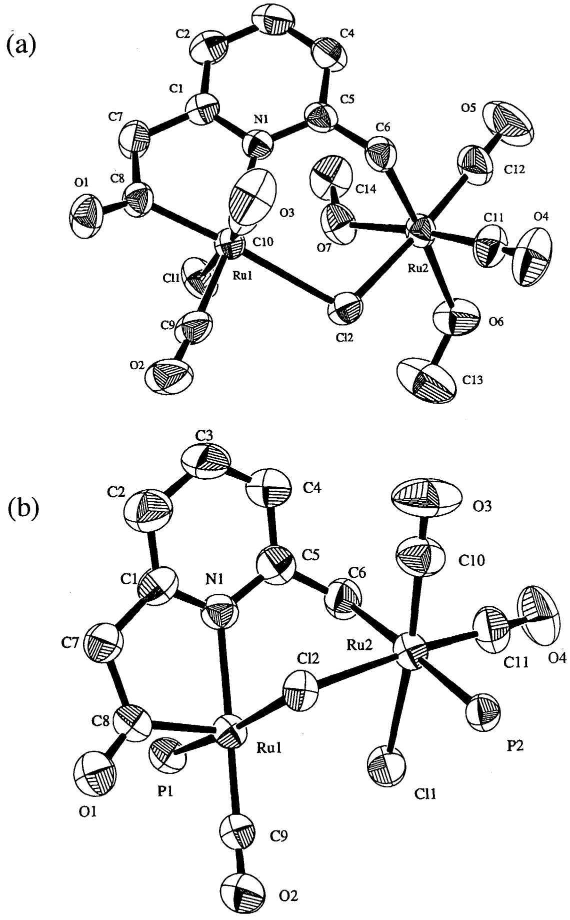
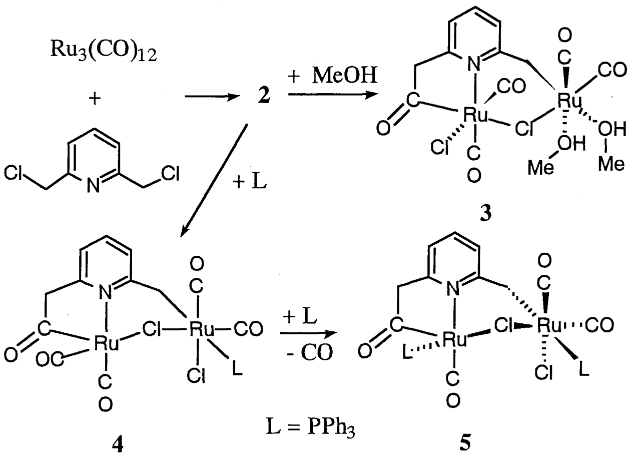


Figure 1. Molecular structures of (a) **3** and (b) **5** with hydrogen and phenyl carbon atoms omitted for clarity. The selected bond distances (Å) and angles (deg) for **3**: Ru1–Cl1, 2.446(1); Ru1–Cl2, 2.623(1); Ru1–N1, 2.153(4); Ru1–C8, 1.987(4); Ru1–C9, 1.878(5); Ru1–C10, 1.861(4); Ru2–Cl2, 2.413(1); Ru2–O6, 2.266(4); Ru2–O7, 2.143(3); Ru2–C6, 2.120(4); Ru2–C11, 1.842(5); Ru2–C12, 1.850(5); O1–C8, 1.216(5); C5–C6, 1.478 (6); Ru1–Cl2–Ru2, 108.29(4); Ru2–C6–C5, 113.3(3); for **5**: Ru1–Cl2, 2.465(2); Ru1–P1, 2.314(2); Ru1–N1, 2.138(6); Ru1–C8, 1.962(7); Ru1–C9, 1.850(8), Ru2–P2, 2.458(2); Ru2–Cl1, 2.420(2); Ru2–Cl2, 2.487(2); Ru2–C6, 2.228(8); Ru2–C10, 1.862(9); Ru2–C11, 1.842(9); O1–C8, 1.240(8); C1–C6, 1.46 (1); Ru1–Cl2–Ru2, 93.49(6), Ru2–C6–C5, 110.8(5).

bonded to the separate metal atoms.[9] Recrystallization from CHCl$_3$/hexane provided single crystals suitable for an X-ray crystallographic analysis, which finally established the exact structure of **5** (Figure 1b).[8] It differs from the structure of **3** in the facts that (a) Ru(1) takes a 5-coordinate, distorted square-pyramidal structure with the apical acyl ligand; (b) Ru(2) is coordinated by two kinds of chlorine atoms, i.e., one terminal and one bridging; (c) there are no bonding interaction between Ru(1) and Cl(1) atoms (Ru(1)···Cl(1) 2.94 Å) and agostic interaction between the Ru(1) atom and a hydrogen atom on an *ortho*-carbon of phenyl ring (Ru(1)···H > 3.30 Å) in contrast to [RuCl$_2$(PPh$_3$)$_3$][10] and [RuHCl(PPh$_3$)$_3$].[11]



During the reaction of **2** with two molecules of L to form **5**, one CO ligand is eliminated. Supposing this elimination occurs during the reaction with the second molecule of L, next we examined the experiment under an atmosphere of CO to suppress its elimination and as a result succeeded in isolating pure **4** as follows. After dissolving **2** (0.195 mmol) in methanol by heating at 65 °C, the CO gas was bubbled through the solution for 1 h, a dichloromethane solution of L (0.194 mmol) was added dropwise, and then the solution was refluxed for 0.5 h under an atmosphere of CO. Filtration of the precipitated product, washing with ether, and recrystallization from CHCl$_3$/Et$_2$O afforded mono(phosphine) derivative **4** (68%). ^{1}H and ^{13}C NMR spectra of **4** in CDCl$_3$ revealed that the first molecule of L is added to the methylene-coordinated ruthenium center without CO substitution, because the methylene proton and carbon signals appear as an ABX spectral pattern and a doublet, respectively, due to coupling with the P atom in addition to geminal coupling.

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7 **3**: ^{1}H NMR (CD$_3$CN) (major isomer) δ 3.72, 4.66 (AB$_q$, *J* = 20.1 Hz, 2H), 7.14 (d, *J* = 6.7 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.9 Hz, 1H), (minor isomer) δ 2.79, 3.18 (AB$_q$, *J* = 9,2 Hz, 2H), 3.69, 4.59 (AB$_q$, *J* = 19.5 Hz, 2H), 7.12 (d, *J* = 5.5 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (CD$_3$CN) (major isomer) δ 17.2, 63.8, 121.7, 123.4, 138.9, 162.2, 175.5, 194.7, 195.8, 196.7, 198.0, (minor isomer) δ 20.1, 63.6, 121.7, 139.3, 162.2, 176.0, 195.1, 195.8, 196.7, 198.2. IR (ν(CO)) 1630, 1970, 2050 cm^{-1}. Anal. Found: C, 28.98; H, 2.51; N, 2.52%. Calcd for $C_{14}H_{15}Cl_2NO_7Ru_2$: C, 28.88; H, 2.60; N, 2.40%.

8 Crystal data for **3**: $C_{14}H_{15}Cl_2NO_7Ru_2$, *FW*=582.32, monoclinic, space group $P2_1$(No. 4), a = 9.771(1), b = 9.183(2), c = 11.7297(9) Å, β = 108.317(7) °, Z = 2, V = 999.1(2) Å^3, D*calc* = 1.936 g/cm^3, Mo-Kα, λ = 0.71069 Å, R = 0.022 and Rw = 0.031, 2902 reflections (I > 3σ(I)). All the hydrogen atoms were located on a ΔF map and refined isotropically; for **5**: $C_{47}H_{37}Cl_2NO_4P_2Ru_2$, *FW* = 1014.81, monoclinic, space group *C*2/c (No. 15), a = 19.265(4), b = 9.279(3), c = 48.814(3) Å, β = 102.03(1)°, Z = 8, V = 8947(3) Å^3, D*calc* = 1.506 g/cm^3, Cu-Kα, λ = 1.54178 Å, R = 0.049 and Rw = 0.087, 5134 reflections (I > 3σ(I)). The solvent hexane molecules were located in difference Fourier synthesis, but disorder in the molecule was not resolved for thermal vibrations.

9 **4**: ^{1}H NMR(CDCl$_3$) δ 3.60, 3.93 (ABX, *J* = 9.7, *J*$_{PH}$ = 7.9, 9.5 Hz, 2H), 3.76, 3.98 (AB$_q$, *J* = 19.5 Hz, 2H), 6.92 (d, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), omitted for PPh$_3$; ^{13}C NMR (CDCl$_3$) δ 26.3 (d, *J* = 63 Hz), 62.7, 116.1, 121.2 (d, *J* = 2.7 Hz), 138.9, 158.6, 173.6 (d, *J* = 4.4 Hz), 173.6 (d, *J* = 4.4 Hz), 193.4, 193.6, 195.6 (d, *J* = 5.9 Hz), 196.2 (d, *J* = 7.3 Hz); ^{31}P NMR (CDCl$_3$) δ from H$_3$PO$_4$ 19.4. IR (ν(C=O)) 1675, 1950sh, 1975, 2029, 2050 cm^{-1}. FAB MS m/z 780 (M$^+$). Anal. Found: C, 45.54; H, 2.80; N, 1.83%. Calcd for $C_{30}H_{22}Cl_2NO_5P\ Ru_2$: C, 46.16; H, 2.84; N, 1.79%.

5: ^{1}H NMR (CDCl$_3$) δ 2.96, 3.34 (AB$_q$, *J* = 19.5 Hz, 2H), 3.25, 3.27 (ABX, *J* = 9.0, *J*$_{PH}$ = 13.0 Hz, 2H), 6.52 (d, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), omitted for PPh$_3$; ^{13}C NMR (CDCl$_3$) δ = 24.9 (d, *J*$_{PC}$ = 64.6 Hz), 60.0, 115.2, 119.8, 137.4, 158.8, 171.6, (d, *J*$_{PC}$ = 4.4 Hz), 196.2 (d, *J* = 11.8 Hz), 196.3, 201.4 (d, *J* = 19.1 Hz); ^{31}P NMR (CDCl$_3$) δ 17.23, 51.96; IR (ν (C=O)) 1630, 1970, 2040 cm^{-1}. FAB MS m/z 1015 (M$^+$). Anal. Found: C, 54.53; H, 3.41; N, 1.38%. Calcd for $C_{47}H_{37}Cl_2\ NO_4P_2Ru_2$: C, 55.63; H, 3.67; N, 1.38%.

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