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Reaction of $[Ru_3(CO)_{12}]$ with 2-(chloromethyl)pyridine, syntheses of pyrid-2-ylacetyl ruthenium(II) complexes and crystal structure of $[RuCl(C_5H_4N\text{-}2\text{-}CH_2CO)(CO)(PPh_3)_2]$

Mayumi Shimizu, Yukio Nakamura* and Makoto Tadokoro

Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto-3, Sumiyoshi-ku,
Osaka 558, Japan

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Abstract—The cycloruthenated pyrid-2-ylacetyl complex $[\{RuCl(C_5H_4N\text{-}2\text{-}CH_2CO)(CO)_2\}_2]$ (**1**) was obtained by reaction of $[Ru_3(CO)_{12}]$ with an excess of 2-(chloromethyl)pyridine in refluxing toluene. Subsequent reaction of **1** with two equivalents of triphenylphosphine in refluxing benzene afforded the bis(phosphine) derivative $[RuCl(C_5H_4N\text{-}2\text{-}CH_2CO)(CO)(PPh_3)_2]$ (**2**). X-ray analysis of **2** shows that the complex is monomeric with the ruthenium atom coordinated by ring nitrogen and acyl carbon atoms from the cycloruthenated pyrid-2-ylacetyl group, *cis* chlorine and carbonyl carbon atoms, and *trans* phosphorus atoms, to form a distorted octahedral geometry. Copyright © 1996 Elsevier Science Ltd

Keywords: ruthemium(II) complex; triruthenium dodecacarbonyl; oxidative addition; nitrogen heterocycle; X-ray structure; 2-(chloromethyl)pyridine.

We have previously studied the reactions of 2-(chloromethyl)- and 2,6-bis(chloromethyl)-pyridine (abbreviated as 2-cmpy and 2,6-cmpy, respectively) with low-valent palladium and rhodium complexes. For example, 2-cmpy reacted with $[Pd(PPh_3)_4]$ to give a C,N-bridged dinuclear complex $[\{PdCl(\mu\text{-}C_5H_4N\text{-}2\text{-}CH_2)PPh_3\}_2]$, [1] while 2,6-cmpy gave a tandem tetranuclear complex $[\{Pd_2Cl(\mu\text{-}Cl)[\mu\text{-}C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$ in addition to a dinuclear complex analogous to that mentioned above [2]. In the reaction with $[RhCl(PPh_3)_3]$, 2-cmpy afforded C,N-chelated mononuclear complexes *cis* (PP)- and *trans* (PP)-$[RhCl_2(C_5H_4N\text{-}2\text{-}CH_2)(PPh_3)_2]$, whereas 2,6-cmpy gave the corresponding *cis* (PP) and *trans* (PP) complexes or a novel dinuclear complex $[Rh_2Cl_4\{C_5H_3N\text{-}2,6\text{-}(CH_2)_2\}(PPh_3)_2]$ according to the reactant's mole ratio, 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-aza-allylic fashion [3].

Recently, much attention has been devoted to the reactivities of dodecacarbonyltriruthenium towards N-donor ligands, especially those containing N heterocycles [4]. The reaction of the carbonyl cluster with pyridine gave a cycloruthenated complex $[Ru_3(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{10}]$ [5]. Similar μ-hydrido-triruthenium cluster complexes have been obtained with 2-aminopyridine [6] and pyridine-2-thiol [7]. Although the reactions with other substituted pyridines, like 2-pyridinecarbinol [8], 2-pyridone [6] and 2-(diphenylphosphino)pyridine [9], have been investigated too, no reactions with halo- and halomethyl-substituted pyridines have been described to our knowledge. Here, we report on the products obtained from reaction of $[Ru_3(CO)_{12}]$ with 2-cmpy, followed by reaction with triphenylphosphine.

EXPERIMENTAL

All the reactions were performed under nitrogen, using solvents that were redistilled under argon. The reagent 2-cmpy was freed from its hydrogen chloride

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* Author to whom correspondence should be addressed.

adduct by the action of NEt_3. The carbonyl cluster $[Ru_3(CO)_{12}]$ was purchased from Aldrich Chemical Company Inc. and used without further purification. IR spectra were obtained as Nujol mulls with a JASCO A-702 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Jeol JNM GX-400 instrument at 400 and 100 MHz, respectively. ^{31}P NMR spectra were measured using a Jeol α-400 instrument at 24.2 MHz. Internal TMS (^1H, ^{13}C) and external H_3PO_4 (^{31}P) were used as references. FAB-mass spectra were obtained with a Jeol JMS AX-500 spectrometer in the positive-ion mode using 3-NBA as a matrix, dichloromethane as a solvent and xenon as a bombardment gas.

Reaction of $[Ru_3(CO)_{12}]$ *with* 2-cmpy. *Synthesis of* $[\{RuCl(C_5H_4N\text{-}2\text{-}CH_2CO)(CO)_2\}_2]$ (1)

To a suspension of $[Ru_3(CO)_{12}]$ (0.31 g, 0.48 mmol) in toluene (10 cm^3) was added 2-cmpy (7.1 mmol), and the mixture was heated at 110°C for 2 h. A wine-red solution was obtained at 90°C and then a precipitate separated out gradually, which was collected, washed with ether and dried *in vacuo*. Yield 0.40 g (89%). Yellow ochre. IR (cm^{-1}): ν(CO) 2020, 1975, 1952, 1930(sh), 1665. ^1H NMR (CD_3CN): δ 4.14, 3.80 (2H, ABq, $J = 20.5$ Hz, CH_2); Py-ring 7.48 (1H, t, $J = 6.7$ Hz, H^5), 7.56 (1H, d, $J = 7.9$ Hz, H^3), 7.97 (1H, t, $J = 7.3$ Hz, H^4), 8.81 (0.8H, br s, H^6), 9.51 (0.2H, br s. $H^{6'}$). ^{13}C NMR (CD_3CN): δ 63.3 (CH_2); Py-ring 123.7, 124.0 (C^3, C^5), 140.3 (C^4), 150.3 (C^6), 162.6 (C^2). Found: C, 34.3; H, 1.9; N, 4.5: Calc for $C_9H_6ClNO_3Ru$: C, 34.6; H, 1.9; N, 4.5%.

Reaction of **1** *with* PPh_3. *Synthesis of the bis(phosphine) derivative* $[RuCl(C_5H_4N\text{-}2\text{-}CH_2CO)(CO)(PPh_3)_2]$ (2)

A suspension of **1** (0.06 g, 0.20 mmol) in benzene (8 cm^3) containing PPh_3 (0.13 g, 0.55 mmol) was heated at 80°C for 2 h. In a few minutes the suspension turned pink. The crude product was filtered, washed with diethyl ether and dried *in vacuo*. Recrystallization from $CHCl_3/Et_2O$ gave **2** (pink). After drying, the residue was redissolved in dichloromethane and diethyl ether was added to reprecipitate **2** (white). Total yield 97%. The pink and white products were the same based on their NMR data. IR (cm^{-1}): ν(CO) 1928, 1605. ^1H NMR ($CDCl_3$): δ 2.96 (2H, s, CH_2); Py-ring 6.37 (1H, triple d, $J = 7.3$, *ca* 2 Hz, H^5), 6.93 (1H, d, $J = 7.3$ Hz, H^3), 7.36 (1H, triple d, $J = 7.3$, *ca* 2 Hz, H^4), 8.21 (1H, d, $J = 7.3$ Hz, H^6); PPh_3 7.1–7.5. ^{13}C NMR($CDCl_3$): δ 62.1 (CH_2), 120.0 (C^5), 122.7 (C^3), 135.9 (C^4), 152.1 (C^6), 161.2 (C^2); PPh_3 127–135. ^{31}P NMR ($CDCl_3$): δ 32.9. FAB-MS *m*/*z*: 809 (M^+), 774 ($M-Cl^+$), 746 ($M-Cl-CO^+$), 717 ($M-Cl-2CO^+$). Found: C, 65.2; H, 4.4; N. 1.8. Calc. for $C_{44}H_{36}ClNO_2P_2Ru$: C, 65.3; H, 4.5; N, 1.7%.

X-ray crystallography

Pale yellow crystals of $\mathbf{2}\cdot Et_2O$ were obtained by slow evaporation from a chloroform/diethyl ether solution. A crystal of appropriate dimensions, $0.40 \times 0.22 \times 0.15$ mm^3, mounted in a glass capillary was used for data collection at a temperature of 23°C on a Rigaku AFC5R diffractometer with graphite-monochromated Cu-K_α ($\lambda = 1.54178$ Å) radiation and the ω–2θ scan technique. Accurate cell dimensions and crystal orientation matrices were determined by least-squares refinement of 25 reflections ($57.9 < 2\theta < 59.8°$) for complex $\mathbf{2}\cdot Et_2O$. A total of 7041 reflections were collected to a maximum 2θ value of 120.2°; 6710 of them were unique, and of these 4933 were assumed as observed [$I > 3.0\ \sigma\ (I)$], and were used for refinement (506 parameters), converging to $R = 0.037$ and $R_w = 0.048$. For all these structures the data were corrected for Lorenz, polarization, and absorption effects. A decay correction was also applied.

The structure of $\mathbf{2}\cdot Et_2O$ was solved by the heavy-atom Patterson methods (DIRDIF92 PATTY) [10] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on a ΔF map and refined isotropically. The maximum and minimum peaks on the final difference Fourier map, and goodness-of-fit corresponded to 0.41 and -0.42 e$Å^{-3}$, and 1.67, respectively. All calculations were performed using the teXsan [11] crystallographic software package.

Crystal data for $\mathbf{2}\cdot Et_2O$. Formula $= [C_{44}H_{36}ClNO_2P_2Ru][C_4H_{10}O]$, F.W. = 883.37, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.015(4)$, $b = 15.611(3)$, $c = 21.257(3)$ Å, $\beta = 93.15(2)°$, $V = 4312(1)$ $Å^3$, $Z = 4$, $D_{calc.} = 1.360$ g cm^{-3}.

RESULTS AND DISCUSSION

Reactions of $[Ru_3(CO)_{12}]$ with an excess of 2-cmpy in refluxing toluene afforded the cycloruthenated dinuclear complex $[\{RuCl(C_5H_4N\text{-}2\text{-}CH_2CO)(CO)_2\}_2]$ (**1**). Complex **1** is insoluble in non-coordinating solvents, but readily dissolves in CH_3CN, from which the complex could not be recovered as a pure solid. Bridge-splitting reaction and subsequent substitution of the one carbonyl group of **1** with triphenylphosphine in a benzene suspension at 80°C gave the monomeric, organic-soluble bis(phosphine) derivative $[RuCl(C_5H_4N\text{-}2\text{-}CH_2CO)(CO)(PPh_3)_2]$ (**2**). Such a substitution of the carbonyl group with triphenylphosphine has been observed in the complexes $[\{RuCl(phpy)(CO)_2\}_2]$ and $[\{RuCl(bzqn)(CO)_2\}_2]$ (Hphpy = 2-phenylpyridine; Hbzqn = benzol[*h*]quinoline) and is explained by the skeletal conjugation of the cyclometalated organic groups [12]. The ^{31}P NMR spectrum of **2** in $CDCl_3$ shows a sharp singlet, and hence the *trans*-bis(phos-

Table 1. Selected bond lengths (Å), bond angles (°) and torsion angles (°)

Ru(1)—Cl(1)	2.549(1)	Ru(1)—P(1)	2.381(1)
Ru(1)—P(2)	2.400(1)	Ru(1)—N(1)	2.163(3)
Ru(1)—C(7)	2.000(4)	Ru(1)—C(8)	1.847(4)
Cl(1)—Ru(1)—P(1)	87.08(4)	Cl(1)—Ru(1)—P(2)	86.40(4)
Cl(1)—Ru(1)—N(1)	88.82(10)	Cl(1)—Ru(1)—C(8)	101.6(1)
P(1)—Ru(1)—N(1)	91.0(1)	P(1)—Ru(1)—C(7)	94.6(1)
P(1)—Ru(1)—C(8)	89.7(1)	P(2)—Ru(1)—N(1)	89.6(1)
P(2)—Ru(1)—C(7)	92.0(1)	P(2)—Ru(1)—C(8)	90.9(1)
N(1)—Ru(1)—C(7)	81.0(2)	C(7)—Ru(1)—C(8)	88.5(2)
Ru(1)—C(7)—C(6)—C(5)	9.4(5)	O(1)—C(7)—Ru(1)—N(1)	176.8(5)
O(1)—C(7)—C(6)—C(5)	−174.3(4)	C(1)—N(1)—Ru(1)—C(7)	−176.5(4)
C(4)—C(5)—C(6)—C(7)	176.3(5)		

phine) structure can be assigned for **2**. The ^{1}H NMR spectrum of **2** in $CDCl_3$ exhibits a sharp singlet assignable to the CH_2 group, indicating that complex **2** has a symmetrical plane including the pyridyl and cycloruthenated rings. Two geometrical isomers of *trans* (N, CO) and *trans* (N, Cl) are possible for **2**. The IR spectrum of this complex exhibits a comparatively low frequency ν(CO) band. This low stretching frequency of the carbonyl group is known to reflect the structure possessing the carbonyl group *trans* to a nitrogen donor ligand [13,14]. X-ray analysis finally established the exact structure of **2** (Fig. 1). Selected bond lengths, bond angles and torsion angles are listed in Table 1.

The structure is monomeric and has a distorted octahedral geometry. The ruthenium atom is coordinated by the N, C (acyl), C (carbonyl) and Cl atoms in an equatorial plane and the two axially situated phosphorus atoms. The pyrid-2-ylacetyl group is cycloruthenated and constitutes a five-membered ring with the ruthenium atom. The pyridyl and cycloruthenated rings are almost coplanar to one another.

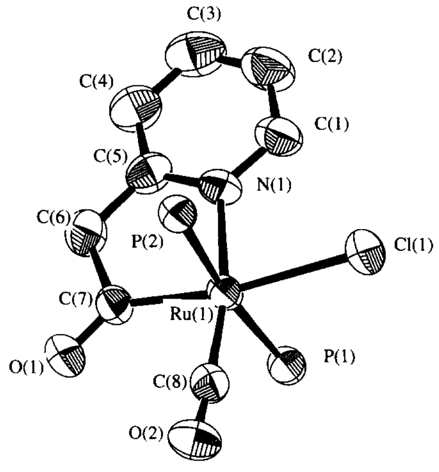
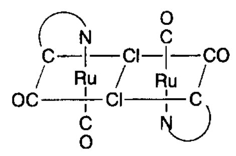


Fig. 1. The crystal structure of **2** with hydrogen and phenyl carbon atoms omitted for clarity. The solvent of crystallization is also omitted.

As is to be expected from the above discussion, the carbonyl group is situated in the position *trans* to the ring nitrogen atom. The bite angle (N(1)—Ru(1)—C(7)) is relatively small and as a result the angle Cl(1)—Ru(1)—C(8) is spread out. Other bond lengths and angles are generally normal. Complex **2** (pink) is photosensitive and turns white gradually when irradiated with the sunlight. It cannot be ruled out that the *trans* (N, CO) to *trans* (N, Cl) isomerization is responsible for this colour change.

The IR spectrum of **1** shows two strong bands in the terminal carbonyl region suggesting a *cis* arrangement of the two carbonyl groups coordinated to each ruthenium atom in the dinuclear complex [12]. The spectrum also shows an additional ν(CO) band at 1665 cm^{-1} indicating the presence of a CH_2CO group formed by cycloruthenation of the pyrid-2-ylmethyl group followed by CO insertion. The presence of the cycloruthenated pyrid-2-ylacetyl group is also shown by the ^{1}H and ^{13}C NMR spectra of **1** in CD_3CN. In addition to these facts and the consideration mentioned above for the structure of complex **2**, the appearance of the two separate signals (approximately 1 : 4 in intensity) which can be assigned to the H^6 pyridyl ring proton, suggests the coexistence of the two kinds of isomers (**I** and **II**) coming from different arrangements of the other ligands around the metal. Only a few examples of the cyclometalated pyrid-2-ylacetyl complexes have been described to our knowledge: $[PdCl(C_5H_4N\text{-}2\text{-}CH_2CO)(PPh_3)]$ [1a], $[Mn(C_5H_4N\text{-}2\text{-}CH_2CO)(CO)_4]$ [15] and $[Mo(C_5H_4N\text{-}2\text{-}CH_2CO)(\eta^5\text{—}C_5H_5)(CO)_2]$ [15]. All these complexes, as well as **2**, have a symmetrical plane



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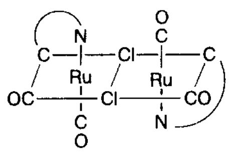

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including the cycloruthenated ring, and hence the methylene protons appeared as a singlet, while those of complex **1** appear as an AB quartet, indicating that the structure of **1** is unsymmetrical about the cycloruthenated ring. The tendency for metal carbonyl anions to form a cyclic derivation on reaction with 2-cmpy is directly related to the tendency for the derivatives formed from the same metal carbonyl anions and acyl halides to undergo decarbonylation on heating or irradiation [15]. Both of these tendencies are thought to be directly related to the strength of the M—CO bond in these compounds [16].

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