  Bull. Chem. Soc. Jpn., 65, 1411—1414 (1992)

Kinetic Studies on the Terminal Pyridine Exchange Reactions of Some Oxo-Acetate Bridged Trinuclear Ruthenium Complexes. Influence of the Metal Oxidation State and Non-Leaving Terminal Ligand (CO)

Masaaki ABE, Yoichi SASAKI,*,† Akira NAGASAWA,†† and Tasuku ITO*
Department of Chemistry, Faculty of Science, Tohoku University,
Aoba, Aramaki, Aoba-ku, Sendai 980
(Received November 29, 1991)

Substitution reactions of py-d_5 for the terminal pyridines of the three triruthenium complexes, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ (**1**) (Ru_3(III, III, III)), $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3$ (**2**) (Ru_3(II, III, III)), and $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(py)_2$ (**3**) (Ru_3(II, III, III)), have been studied in CD_3CN by following the change in ^1H NMR spectra. The rates are practically independent of [py-d_5] (0.05—1.0 mol dm^{-3}). The first-order rate constants are 3×10^{-5} s^{-1} at 55 °C ($\Delta H^{\ddagger}=123\pm6$ kJ mol^{-1}, $\Delta S^{\ddagger}=+41\pm19$ J K^{-1} mol^{-1}), 5.9×10^{-4} s^{-1} at 50 °C ($\Delta H^{\ddagger}=122\pm14$ kJ mol^{-1}, $\Delta S^{\ddagger}=+69\pm44$ J K^{-1} mol^{-1}), and 3×10^{-5} s^{-1} at 55 °C ($\Delta H^{\ddagger}=126\pm9$ kJ mol^{-1}, $\Delta S^{\ddagger}=+52\pm27$ J K^{-1} mol^{-1}) for **1**, **2**, and **3**, respectively. Rate constants appear to depend on the apparent oxidation state of the metal center. While the three Ru ions in **2** are equivalent and each ion has average oxidation number +2(2/3), Ru ions with coordinated py in **3** are in +3 oxidation state as the +2 oxidation state is localized at carbonyl-Ru ion. A dissociative mechanism is proposed for these reactions on the basis of the absence of [py-d_5]-dependence, the activation parameters, and the comparison of the rate constants with those of the substitution of methanol-d_4 for the terminal water ligands in $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$.

Acetate-bridged trinuclear metal(III) complexes with an oxide ion in the center of the metal triangle, $[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$ (L=neutral monodentate ligands) (Chart 1), are known for various transition metal ions,[1] and are suitable for systematic studies of various properties of polynuclear metal complexes. We are interested in their ligand substitution properties and recently studied the substitution of methanol for the terminal aqua ligands of Ru_3, Rh_3, and mixed $RhRu_2$ complexes (L=H_2O).[2,3] The study revealed that the substitution proceeds 10^2—10^4 times more rapidly than the water exchange reactions of the mononuclear hexaaqua complexes of these metal ions. This is accounted for by the trans labilizing effect of the central oxide ligand. In order to understand the reactivities of these complexes still further, it is important to investigate the influence of various factors controlling the ligand substitution properties. In this paper, we wish to report the study on the effect of the oxidation state, the leaving ligand, and the non-leaving terminal ligand, by the use of the tri(ruthenium) complexes, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ (formal oxidation state of the Ru_3 is (III, III, III)), $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3$ (II, III, III), and $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(py)_2$ (II, III, III) (py=pyridine). The substitution of pyridine-d_5 for the coordinated pyridines has been studied for these complexes by following the change in relative integrated intensities of the ^1H NMR signals of the coordinated and the free pyridines.

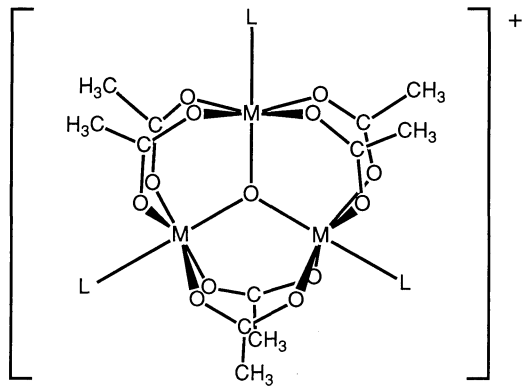

Chart 1. Structure of $[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$.

In relation to this work, we have also studied the ligand substitution properties of the dinuclear ruthenium(III) complexes with μ-oxo-di-μ-acetato-diruthenium(III) core,[4,5] and metal–metal bonded trimolybdenum(IV) and related complexes.[6]

Experimental

Preparation of the Complexes. The trinuclear ruthenium complexes, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]PF_6$, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]\cdot py$, and $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(py)_2$, were prepared by the reported methods,[2,7] and identified by elemental analyses, FAB-MS (m/z=912, 912, and 861, respectively), ^1H and ^{13}C NMR spectra, cyclic voltammograms, and electronic absorption spectra. $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]\cdot py$ was recrystallized from hot pyridine. NMR data for $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(py)_2$ (not reported previously): ^1H NMR in CD_3CN vs. TMS at δ=0, 2.10 (s, 6H, CH_3COO), ca. 2.16 (CH_3COO, overlapped with water signal), 8.13 (t, 4H, py-3,5-H), 8.31 (t, 2H, py-4-H), 9.14 (d, 4H, py-2,6-H); $^{13}C\{^1H\}$ NMR in CD_3CN vs. TMS at δ=0, 30.8 (CH_3COO),

† Present address: Department of Chemistry, Faculty of Science, Hokkaido University, Kita-ku, Sapporo 060.

†† Present address: Department of Chemistry, Faculty of Science, Saitama University, Shimo-okubo, Urawa 338.

126.5 (py C-3), 142.6 (py C-4), 154.4 (py C-5), 212.5 (CH_3COO). $^{13}C\{^1H\}$ NMR data for $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ in CD_3CN: δ=−6.2 (py C-2), 114.8 (CH_3COO), 126.8 (py C-4), 138.3 (py C-3), 199.0 (CH_3COO).

Materials. CD_3CN (99% deuterated, Aldrich) was distilled once before use. C_5D_5N (100%, Aldrich) was used as received.

Kinetic Procedures. The kinetic measurements were carried out by following the change in ^1H NMR spectra with a JEOL GSX-270 FT-NMR spectrometer with a variable temperature controller. Temperature was calibrated within the accuracy of ±0.2 °C using the chemical shift difference between methyl and hydroxyl signals of methanol. The CD_3CN solution containing certain amounts of the complex and py-d_5 was prepared at room temperature and placed in the NMR cell compartment which was thermostated at a desired temperature. In the case of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ py, the solvent was degassed by the freeze-pumping cycle technique, and the reactants were dissolved under nitrogen atmosphere. No appreciable oxidation was found after the NMR measurements as judged from the visible absorption spectra as well as the NMR spectra. The ^1H NMR spectrum was measured at a certain time interval. The rate constants were evaluated from the change in the relative integrated intensity of the py signals.

Results

The change in the ^1H NMR spectra of $[Ru_3(O)(CH_3COO)_6(py)_3]^+$ in CD_3CN was monitored in the presence of py-d_5 (5—10^3 times excess). Signal intensities of the coordinated pyridine decreased, and those of the free pyridine increased simultaneously (Fig. 1). No appreciable change in absorption spectra was observed after the ^1H NMR kinetic measurements. It was concluded that the change in the ^1H NMR spectrum should be caused by the substitution of py-d_5 for the coordinated pyridine.

$$[Ru_3(O)(CH_3COO)_6(py)_3]^+ + 3py\text{-}d_5 \rightarrow [Ru_3(O)(CH_3COO)_6(py\text{-}d_5)_3]^+ + 3py. \quad (1)$$

The rate constant for the exchange reaction was evaluated from the change in relative integrated intensity of the 3,5- and 4-protons of the free (7.33 and 7.74 ppm, respectively) and the coordinated pyridines (6.38 and 6.74 ppm, respectively, at 70 °C)[8] by the use of the McKay type equation (Eq. 2).[10]

$$\ln\{(I_t - I_\infty)/(I_0 - I_\infty)\} = -\{(3m+n)/(3mn)\}Rt + \text{constant}. \quad (2)$$

The m and n are the initial concentration of the complex and py-d_5, respectively. I is equal to $p/(p+q)$ (p and q are the relative integrated intensity of the ^1H NMR signals of the coordinated and the free pyridine, respectively). The plot of the left-hand side of the Eq. 2 against t gave a good straight line (an example is shown in Fig. 2), from the slope of which k_0 ($=R/m$) was evaluated.

The pyridine exchange rate constants for the other two complexes were obtained similarly by analyzing the intensity change of the pyridine 2,6-protons (signal

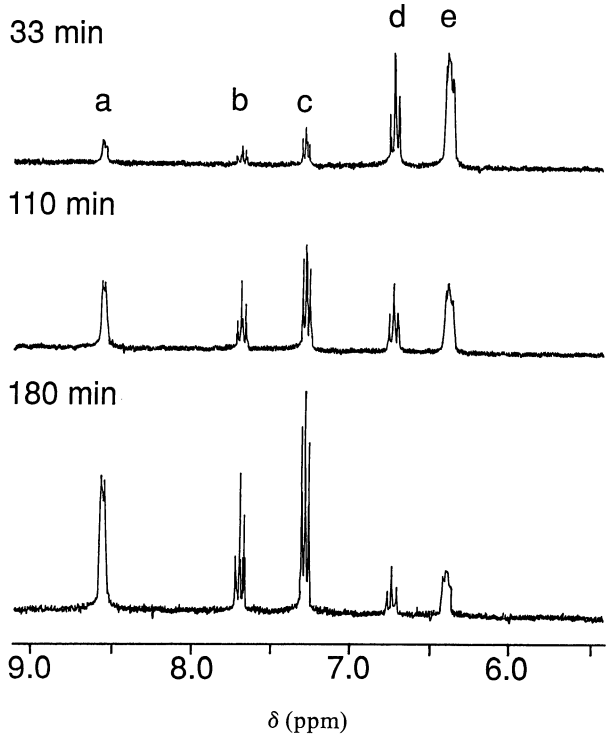

Fig. 1. The change in ^1H NMR spectra in the pyridine signal region of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ in the presence of py-d_5 in CD_3CN at 70 °C (a, free pyridine-2,6-H; b, free pyridine-4-H; c, free pyridine-3,5-H; d, coordinated pyridine-4-H; e, coordinated pyridine-3,5-H).

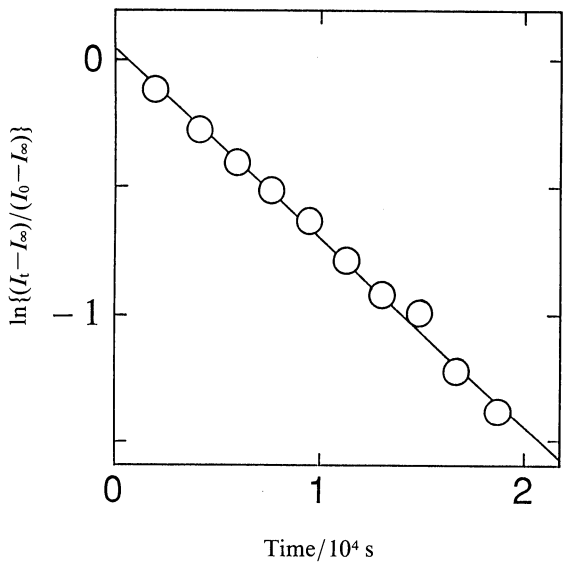

Fig. 2. An example of the first-order plot using Eq. 2 for the reaction of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ with excess py-d_5 (0.78 mol dm^{-3}) in CD_3CN at 70 °C for the relative intensity change of the peaks of pyridine-3,5-H (c and e in Fig. 1).

positions are 9.23 and 9.14 ppm for the $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3$ and $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(py)_2$, respectively, while that of the free pyridine is 8.56 ppm). The rate constants (k_0) are summarized in Table 1. It seems that k_0 decreases slightly with the increase in the py-d_5 concentration. An experiment with $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ (4.9×10^{-3} mol dm^{-3}) and py-d_5 (0.713 mol dm^{-3}) in CD_3CN containing 1.47 mol dm^{-3} of water at 70°C gave a rate constant, 6.4×10^{-5} s^{-1}. It seems that water considerably retards the exchange reaction. We conclude that the small decrease in k_0 with increase in [py-d_5] is likely due to the increase in the concentration of water which was inevitably introduced into the sample solution with py-d_5, and that k_0 is practically independent of [py-d_5]. Activation parameters were evaluated from the temperature dependence of k_0 obtained at similar py-d_5 concentrations, and listed in Table 2. First-order rate constants, $k(=k_0[\text{py-}d_5]^0)$ at 60°C were calculated from the activation parameters, and listed in Table 2 together with the relevant [py-d_5] range.

Table 1. First-Order Rate Constants for the Substitution of Pyridine-d_5 for the Terminal Pyridine in the Trinuclear Ruthenium Complexes in CD_3CN

Complex	Temp	[py-d_5]	k_0
	°C	mol dm^{-3}	10^{-4} s^{-1}
$[Ru_3(O)(CH_3COO)_6(py)_3]^+$	55	0.75	0.3
(7×10^{-3} mol dm^{-3})	60	0.56	0.9
	65	0.60	1.2
	70	0.13	3.0
	70	0.50	2.4
	70	0.78	2.3
	70	1.2	1.9
$Ru_3(O)(CH_3COO)_6(py)_3$	35	0.0024	0.6
(6×10^{-4} mol dm^{-3})	40	0.0050	1.8
	40	0.025	2.0
	40	0.50	1.8
	40	0.83	1.6
	45	0.0043	2.6
	50	0.0050	5.9
$Ru_3(O)(CH_3COO)_6(CO)(py)_2$	55	0.0022	0.3
(1×10^{-3} mol dm^{-3})	60	0.0025	0.5
	65	0.0025	0.9
	70	0.0025	2.1
	70	0.0051	2.6
	70	0.014	2.1
	70	0.025	1.7
	70	0.25	2.1
	70	0.50	2.3
	70	0.71	1.3

Discussion

Meyer and coworkers reported that rapid electron exchange takes place between $[Ru_3(O)(CH_3COO)_6(py)_3]^+$ (oxidation state, (III, III, III)) and its reduced form (oxidation state, (II, III, III)).[11] The second-order rate constant in dichloromethane at 24°C is reported to be 1.1×10^8 M^{-1} s^{-1} (1 M=1 mol dm^{-3}). Thus the electron exchange reaction proceeds significantly more rapidly than the present pyridine exchange reaction. It is possible that the contamination of small amount of the reduced form would catalyze the pyridine exchange of the Ru_3(III, III, III) complex. Table 2 shows that the pyridine exchange of the Ru_3(II, III, III) complex is faster by approximately 40 times than that of the Ru_3(III, III, III) species. Therefore, if the pyridine exchange reaction of the Ru_3(III, III, III) complex occurred exclusively through the contaminated reduced form, at least 2.5% contamination would be required to account for the observation. UV-visible absorption and ^{1}H NMR spectra, however, indicate that the contamination of the reduced form is at most 1%.[12] Although we cannot completely remove the possible contribution from the contaminated reduced form, if any, it would be very small. Thus, it is concluded that the k_0 in Table 1 of the pyridine exchange reaction of the Ru_3(III, III, III) complex must be approximated to the genuine one.

The rate constants and activation parameters of the present reactions are compared with the terminal water substitution reaction (Eq. 3) (Table 2).[3]

$$[Ru_3(O)(CH_3COO)_6(H_2O)_3]^+ + CD_3OD \rightarrow [Ru_3(O)(CH_3COO)_6(CD_3OD)(H_2O)_2]^+ + H_2O. \quad (3)$$

For the Ru_3(III, III, III) complexes, substitution for the terminal water is ca. 10^3 times faster than that for the pyridine ligand. Even the difference in the reaction systems and the solvents is considered, it is still reasonable to conclude that the terminal ligand

Table 2. A Comparison of the Rate Constants of the Substitution of L′ for the Terminal Ligands L in the Trinuclear Ruthenium Complexes $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_{3-n}(CO)_n]^{m+}$

L	L′	n	m	Solvent	k (60°C)[a]	$\Delta H^{\neq}$	$\Delta S^{\neq}$	Ref.
					s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	
H_2O	CD_3OD	0	1	CD_3OD	3.7×10^{-2}	94±10	+9±35	3
py	py-d_5	0	1	CD_3CN	5.0×10^{-5}[b]	123±6	+41±19	e)
py	py-d_5	0	0	CD_3CN	2.1×10^{-3}[c]	122±14	+69±44	e)
py	py-d_5	1	0	CD_3CN	6.3×10^{-5}[d]	126±9	+52±27	e)

a) Calculated from the activation parameters. b) [py-d_5]=0.50—0.78 M (1 M=1 mol dm^{-3}). c) [py-d_5]=0.0024—0.0050 M. d) [py-d_5]=0.0022—0.0025 M. e) This work.

substitution depends strongly on the type of the leaving ligand.

It would be appropriate to discuss on the reaction mechanism at this stage. The present results reinforce the previous conclusion that the terminal ligand substitution reactions of some oxo-centered trinuclear complexes are dissociative[3,6] due to strong trans effect of the oxide ion.[3-6] Independence of the py-d_5 concentration and the significant dependence of the type of leaving ligand are common features to the similar reactions of the metal-metal bonded trimers, $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$ (L=H_2O or pyridine).[6] These features and the strong retardation by water may indicate even the limiting D mechanism with the intermediate of one vacant terminal position. Water molecule would effectively compete with py-d_5 at the vacant terminal position of the intermediate. Assignment of the D mechanism should be reserved, however, until further definite evidence is presented, since ambiguity remains in the interpretation of the activation parameters.

General trend in activation parameters, large $\Delta H^{\neq}$ and positive $\Delta S^{\neq}$ as well as the difference in $\Delta H^{\neq}$ values of the pyridine exchange and the water substitution reactions (Table 2), support highly dissociative nature of these reactions. It was concluded that the divalent state in the Ru_3(II, III, III) complex is delocalized over the three ruthenium ions on the basis of the ESCA and other spectroscopic measurements.[7] Therefore the oxidation state of each ruthenium ion is described as +2(2/3). If the D mechanism operates, $\Delta H^{\neq}$ should be smaller for the Ru_3(II, III, III) as compared with that for the Ru_3(III, III, III) complex. The data of Table 2 do not show such a difference. Expected difference would be small, however, for the two complexes with metal oxidation states of +3 and +2(2/3), and possibly within the uncertainty range of $\Delta H^{\neq}$. It is not possible to extract definite conclusion as to the mechanism of the substitution reactions from the $\Delta H^{\neq}$ values.

Although the comparison of the rate constants at a single temperature should be made with caution, it leads to some meaningful conclusions for the present three reaction systems which have similar $\Delta H^{\neq}$ values. The Ru–N(py) bond in the Ru_3(III, III, III) complex is stronger from the electrostatic view point so that the observed difference in the rate constants of the two tris(py) complexes is accounted for. The carbonyl complex has (II, III, III)-oxidation state, but the substitution rate is close to the Ru_3(III, III, III) complex rather than that of the tris(py) Ru_3(II, III, III) complex. It is possible that the divalent state in the carbonyl complex is localized at the ruthenium ion with coordinated CO and other two ruthenium ions where the pyridine exchange reaction takes place are essentially trivalent. Following considerations may support this view. Various properties such as electronic absorption spectrum and redox potentials of the carbonyl complex are significantly different from those of the tris(py) Ru_3(II, III, III) complex. While the tris(py) Ru_3(II, III, III) complex shows broad absorption peaks at 895 and 390 nm, the carbonyl complex has distinct peak at 585 nm without significant absorption towards the longer wave length region. Single absorption peak in the visible region is also observed for some mixed metal complexes, $Ru^{III}_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3$ ($M=Ni^{II}$, Zn^{II}, etc),[13] and appears to represent the $Ru^{III}_2(\mu\text{-}O)$ moiety. One electron oxidation and reduction potentials of the carbonyl complex are closer to those of the mixed-metal complexes[13] rather than the tris(pyridine)triruthenium complex.

This work was supported by a Grant-in-Aid for Scientific Research No. 02245106 on Priority Area of "Molecular Approaches to Non-equilibrium Processes in Solutions" and a Grant-in-Aid for Scientific Research No. 01430009 from the Ministry of Education, Science and Culture.

References

1) R. D. Cannon and R. P. White, *Prog. Inorg. Chem.*, **36**, 195 (1988), and references therein.

2) Y. Sasaki, A. Tokiwa, and T. Ito, *J. Am. Chem. Soc.*, **109**, 6341 (1987).

3) Y. Sasaki, A. Tokiwa, A. Nagasawa, and T. Ito, *Inorg. Chem.*, to be submitted for publication.

4) Y. Sasaki, M. Suzuki, A. Nagasawa, A. Tokiwa, M. Ebihara, T. Yamaguchi, C. Kabuto, T. Ochi, and T. Ito, *Inorg. Chem.*, **30**, 4903 (1991).

5) T. Ochi, Y. Sasaki, T. Yamaguchi, and T. Ito, *Chem. Lett.*, **1991**, 2019.

6) K. Nakata, A. Nagasawa, N. Soyama, Y. Sasaki, and T. Ito, *Inorg. Chem.*, **30**, 1575 (1991).

7) J. A. Baumann, D. J. Salmon, S. T. Wilson, T. J. Meyer, and W. E. Hatfield, *Inorg. Chem.*, **17**, 3342 (1978).

8) The ^{1}H NMR signals of the paramagnetic $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ are subject to the temperature dependence:[9] (CH_3COO, py-2,6-H, py-3,5-H, py-4-H) signals (in ppm) are (4.76, 0.51, 5.94, 6.62) at 30°C, (4.66, 0.83, 6.06, 6.65) at 40°C, (4.56, 1.12, 6.17, 6.68) at 50°C, (4.48, 1.40, 6.27, 6.71) at 60°C, and (4.40, 1.66, 6.38, 6.74) at 70°C.

9) Temperature dependence of the magnetic susceptibility: H. Kobayashi, N. Uryu, A. Tokiwa, T. Yamaguchi, Y. Sasaki, and T. Ito, *Bull. Chem. Soc. Jpn.*, **65**, 198 (1992).

10) H. A. C. McKay, *Nature* (*London*), **142**, 997 (1938).

11) J. L. Walsh, J. A. Baumann, and T. J. Meyer, *Inorg. Chem.*, **19**, 2145 (1980).

12) Since the corresponding ^{1}H NMR signal positions of the two Ru_3 complexes, $[Ru_3(O)(CH_3COO)_6(py)_3]^+$ and $Ru_3(O)(CH_3COO)_6(py)_3$, are appreciably different, amount of the reduced form can be evaluated from the signal shift after the reaction.

13) A. Ohto, Y. Sasaki, and T. Ito, 40th National Conference on Coordination Chemistry, Kanazawa, October 1990, Abstr., 2AP26.