

A Kinetic Study on Ligand Substitution Reaction of *N*-Cyclohexyl-2-pyrrolidone for Triphenylphosphine in Trichlorooxorhenium(V) Complex

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The crystal structure of the $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ (PPh_3 = triphenylphosphine and NCP = *N*-cyclohexyl-2-pyrrolidone) complex was determined by a single-crystal X-ray diffraction method. It was found that NCP coordinates to the *trans*-position of the oxo group, $\text{Re} = \text{O}$, and that the Re(V) center is in a distorted octahedral geometry. The equilibrium reaction of $\text{ReOCl}_3(\text{PPh}_3)_2 + \text{NCP} \leftrightarrow \text{ReOCl}_3(\text{PPh}_3)(\text{NCP}) + \text{PPh}_3$ was examined, and its equilibrium constant was determined as 0.33 ± 0.1 in CH_2Cl_2 at 25 °C. Kinetic studies were carried out for the forward and backward reactions, and revealed that the rate determining steps for the both reactions are dissociation of the coordinated ligand from the Re center. Taking into account of geometrical isomers of the $\text{ReOCl}_3(\text{PPh}_3)_2$ complex, a reaction mechanism was proposed.

1. Introduction

The wide use of $^{99\text{m}}\text{Tc}$ as diagnostic agents and the recent development of ^{186}Re and ^{188}Re radiopharmaceuticals have promoted studies for Tc and Re coordination chemistries.^{1,2} It is known that ^{186}Re and ^{188}Re decay by β -ray emission as well as γ -ray emission. Therefore, ^{186}Re and ^{188}Re compounds should be used as diagnostic and therapeutic medicines.³ From this point of view, a number of Re complexes have been synthesized.⁴ In syntheses, $\text{ReOCl}_3(\text{PPh}_3)_2$ (PPh_3 = triphenylphosphine) is often used as a starting material.^{5,6} Its molecular structure in solid state has been reported as a *mer-trans* geometry.⁷ However, it is also subjected that this kind of Re complexes have geometrical isomers, *i.e.* *mer-cis* and *fac-cis*.⁸ The ligand substitution behavior of this complex is not well understood so far. We have previously found out that *N*-cyclohexyl-2-pyrrolidone (NCP) is a preferable ligand for metal-oxo ions such as the uranyl ion.⁹⁻¹¹ Crystallographic studies of uranyl complexes have clarified that NCP coordinates through amide O atom to the uranyl ion. It was also found that donicity of NCP is comparable to *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide.¹¹ It is often observed that Re(V) complexes prefer soft donor atoms. Therefore, it would be interesting to compare the reactivity of O-donor and S-donor ligands. We have selected tetramethylthiourea (TMTU) as a S-donor ligand representative. In this study, we have examined the substitution reactions of NCP or TMTU (Figure 1) for PPh_3 in the $\text{ReOCl}_3(\text{PPh}_3)_2$ complex.

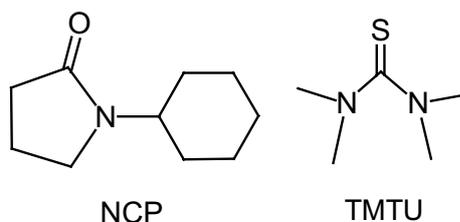


Figure 1. Chemical formulas of NCP and TMTU.

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2. Experimental

Materials and Instruments: All chemicals used in this study were of reagent grade and used without further purification. The $\text{ReOCl}_3(\text{PPh}_3)_2$ complex was synthesized by using the literature method.¹² The equilibrium reaction and kinetic studies were performed in dehydrated CH_2Cl_2 by using an UV-vis spectrophotometer (Shimadzu UV-3150). NMR spectra were measured by a Jeol GXR 270 NMR spectrometer.

Synthesis and X-ray diffraction of $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$: A green crystalline complex of $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ was synthesized by mixing $\text{ReOCl}_3(\text{PPh}_3)_2$ with NCP and grown in the mixture with diethyl ether. The molecular structure was determined by an X-ray diffraction method. Intensity measurements were carried out on a Rigaku RAXIS RAPID diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$). Crystal data collection and final refinement parameters are summarized in Table 1. The structures were solved by a heavy-atom Patterson method, and expanded using Fourier techniques. The non-hydrogen atoms were refined using anisotropic temperature factors. Hydrogen atoms were introduced at calculated positions using

TABLE 1: Crystallographic Data of $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ Complex

| | |
|-------------------------------|--|
| Empirical formula | $\text{C}_{28}\text{H}_{32}\text{NO}_2\text{PCl}_3\text{Re}$ |
| Formula weight | 738.11 |
| Crystal system | monoclinic |
| Space group | $\text{P}2_1/\text{c}$ |
| <i>a</i> (Å) | 13.2336(8) |
| <i>b</i> (Å) | 10.228(1) |
| <i>c</i> (Å) | 20.752(2) |
| β (°) | 95.487(4) |
| <i>V</i> (Å ³) | 2796.0(4) |
| <i>Z</i> | 4 |
| Temperature (K) | 113 ± 1 |
| Residuals: R_1^a , wR_2^b | 0.020, 0.051 |
| Goodness of fit | 1.04 |

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)} \right\}^{1/2}$$

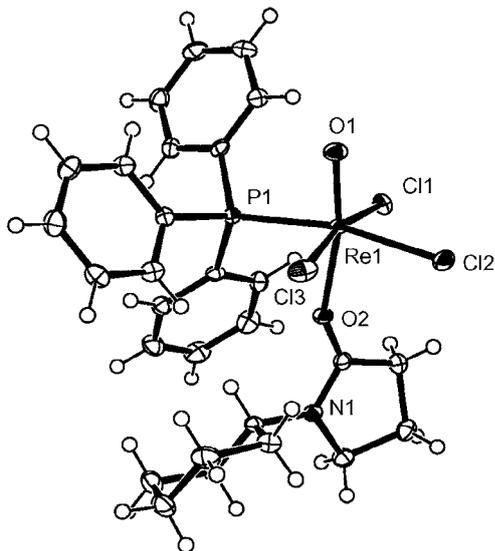


Figure 2. Molecular structure of $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ complex.

the riding model. All calculations were performed using the Crystal Structure crystallographic software package.¹³

3. Results and Discussion

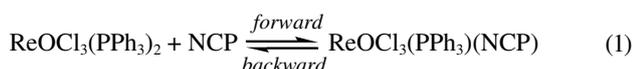
Molecular structure of $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$: The obtained molecular structure of $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ is shown in Figure 2 and selected bond lengths and angles are listed in Table 2. It was found that NCP coordinates to the Re(V) center on the *trans*-position of Re-O1 bond, and Re(V) center is in a distorted octahedral geometry.¹⁴ The geometry around Re(V) center is almost identical to those of $\text{ReOCl}_3(\text{PPh}_3)(\text{DMF})$ and $\text{ReOCl}_3(\text{PPh}_3)(\text{OPPh}_3)$ ($\text{OPPh}_3 = \text{triphenylphosphine oxide}$).^{15, 16} This is consistent with “the self-consistency rule”, where *trans* position to oxo group tends to be occupied by a σ -donor ligand.¹⁷ It is also worthy of note that the bond length of Re-Cl2 , where the Cl atom coordinates to the Re(V) center in the *trans* site to PPh_3 , is the shortest of the Re-Cl bonds in three complexes.

TABLE 2: Selected Bond Lengths and Bond Angles of $\text{ReOCl}_3(\text{PPh}_3)\text{L}$ Complexes

| L | NCP | DMF ^a | OPPh ₃ ^b |
|-----------------|-----------|------------------|--------------------------------|
| Bond length / Å | | | |
| Re1–O1 | 1.671(2) | 1.664(4) | 1.669(4) |
| Re1–O2 | 2.100(2) | 2.133(4) | 2.082(4) |
| Re1–Cl1 | 2.383(1) | 2.372(2) | 2.373(2) |
| Re1–Cl2 | 2.362(1) | 2.368(2) | 2.361(2) |
| Re1–Cl3 | 2.392(1) | 2.373(2) | 2.384(2) |
| Re1–P1 | 2.487(1) | 2.500(1) | 2.506(2) |
| Bond angle / ° | | | |
| O1–Re1–O2 | 168.34(9) | 170.8(2) | 171.35(18) |
| Cl1–Re1–Cl3 | 168.21(3) | 167.40(6) | 169.74(6) |
| Cl2–Re1–P1 | 165.32(3) | 166.02(5) | 171.52(6) |

^aRef. 15, ^bRef. 16.

Equilibrium constant for the reaction between $\text{ReOCl}_3(\text{PPh}_3)_2$ and NCP: As mentioned above, $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ is formed by mixing $\text{ReOCl}_3(\text{PPh}_3)_2$ with NCP in CH_2Cl_2 . We noticed that this reaction is reversible as follows.



The equilibrium (1) was examined in CH_2Cl_2 at 25 °C. Figure 3 shows each spectrum measured by adding NCP to a solution of $\text{ReOCl}_3(\text{PPh}_3)_2$. From the absorbance changes, the equilib-

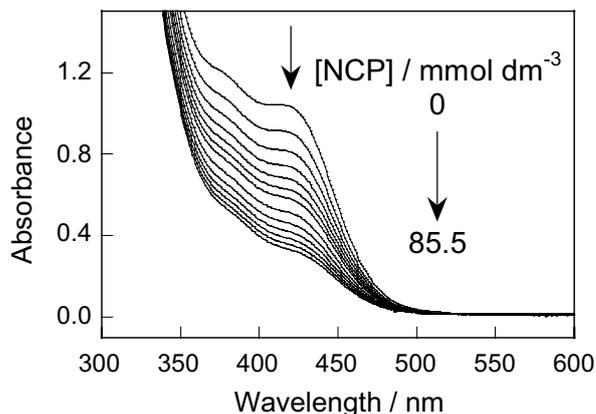


Figure 3. Spectral changes in the reaction of $\text{ReOCl}_3(\text{PPh}_3)_2$ with NCP in CH_2Cl_2 at 25 °C. $[\text{ReOCl}_3(\text{PPh}_3)_2]_0 = 0.94 \text{ mmol dm}^{-3}$ and $[\text{PPh}_3]_T = 10.2 \text{ mmol dm}^{-3}$.

rium constant of (1) was determined to be 0.33 ± 0.1 in CH_2Cl_2 at 25 °C. This indicates that donicity of NCP to the ReO^{2+} moiety is comparable to that of PPh_3 . The relatively high donicity of NCP is also observed in our previous work on the complex formation of UO_2^{2+} ion with NCP.¹¹

We also used TMTU as an unidentate ligand, and found that the reaction is not reversible in this case. This finding indicates that TMTU strongly coordinates to the Re(V) center. Some Re(V) complexes with TMTU have been reported.^{18, 19} We measured ³¹P NMR spectrum of a mixture of $\text{ReOCl}_3(\text{PPh}_3)_2$ with TMTU in CD_2Cl_2 , and observed two peaks at -23.7 and -2.3 ppm relative to the peak of 85% H_3PO_4 . Those peaks should be assigned to the coordinated and free PPh_3 , respectively. We have not obtained the crystal structure of the product yet. However, it is likely that the product with a formula of $\text{ReOCl}_3(\text{PPh}_3)(\text{TMTU})$ is formed by the reaction (2). The ³¹P chemical shifts of several compounds are listed in Table 3.



TABLE 3: ³¹P chemical Shifts of Phosphorus Compounds

| Compound | δ / ppm^a |
|---|--|
| PPh_3 | -2.3 |
| $\text{ReOCl}_3(\text{PPh}_3)_2$ | -15.8^b |
| $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ | -16.6 |
| $\text{ReOCl}_3(\text{PPh}_3)(\text{TMTU})^c$ | -23.7 |
| $\text{ReOCl}_3(\text{PPh}_3)(\text{OPPh}_3)$ | $-30.8 (\text{PPh}_3)^b$ $52.5 (\text{OPPh}_3)^b$ |
| OPPh_3 | 30.5^b |

^aIn CD_2Cl_2 vs. external 85% H_3PO_4 ; ^bRef. 7; ^cPlausible formula.

Kinetics of the reaction of $\text{ReOCl}_3(\text{PPh}_3)_2$ with L (L = NCP and TMTU): The kinetic studies of the reactions of $\text{ReOCl}_3(\text{PPh}_3)_2$ with L were carried out spectrophotometrically in CH_2Cl_2 at various temperatures. The pseudo first-order rate constants (k_{obs}) were measured by following the absorbance changes at 416 nm after mixing a solution of $\text{ReOCl}_3(\text{PPh}_3)_2$ with excess L ($[\text{Re}] \ll [\text{L}]$). Each kinetic trace was nicely fitted by the first-order equation.²⁰ It was found that the k_{obs} values are independent of the concentrations of L. The plots of k_{obs} values against $[\text{NCP}]$ is shown in Figure 4. This result indicates that the rate-determining step (rds) of the *forward* reaction is ligand dissociation from the Re(V) center, and the dissociation group would be one of PPh_3 ligands in $\text{ReOCl}_3(\text{PPh}_3)_2$.



We assume that the PPh_3 dissociation reaction (3) involves

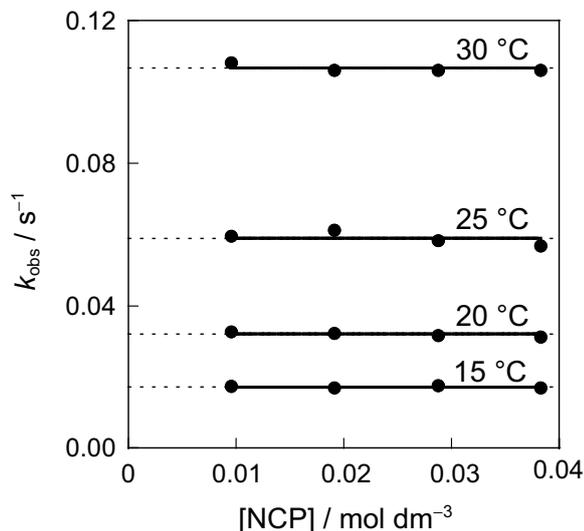
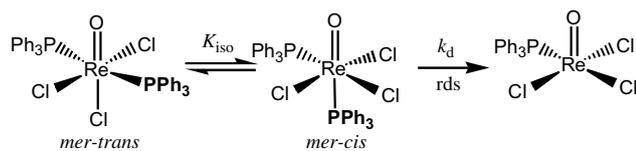


Figure 4. Plots of k_{obs} against $[\text{NCP}]$ for the *forward* reaction of (1). $[\text{ReOCl}_3(\text{PPh}_3)_2] = 0.1 \text{ mmol dm}^{-3}$ in CH_2Cl_2 .

mer-trans and *mer-cis* isomerization of $\text{ReOCl}_3(\text{PPh}_3)_2$. From recent ^{31}P NMR study, we have tentatively obtained evidence showing that such isomerization would exist in CD_2Cl_2 .²¹ Furthermore, it is also reported that *mer-trans* and *mer-cis* $\text{ReOCl}_3(\text{PPh}_3)_2$ complexes have been isolated.²²

Scheme 1



When reaction (3) proceeds in Scheme 1, the rate constant is expressed by eq 4,

$$k_{\text{obs}} = \frac{K_{\text{iso}} k_{\text{d}}}{1 + K_{\text{iso}}} \quad (4)$$

and if K_{iso} is fairly smaller than 1, eq 4 can give eq 5.²¹

$$k_{\text{obs}} = K_{\text{iso}} k_{\text{d}} \quad (5)$$

From the Eyring plot, the activation parameters were obtained as $\Delta H^\ddagger = 86.4 \pm 0.1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 21 \pm 1 \text{ J K}^{-1} \text{ mol}^{-1}$. We also investigated the forward reaction (1) by using TMTU as an entering ligand at various temperatures, and confirmed that the k_{obs} values at each temperature are independent of $[\text{TMTU}]$ and are almost the same as those in the reaction with NCP (We obtained ΔH^\ddagger and ΔS^\ddagger as $81 \pm 1 \text{ kJ mol}^{-1}$ and $2 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ for TMTU reaction).

Kinetics of the reaction of $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ with PPh_3 : The *backward* reaction of (1) was also examined by the absorbance changes at 416 nm after mixing a solution of $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ with PPh_3 under the condition of $[\text{Re}] \ll [\text{PPh}_3]$. Figure 5 shows that the rate constants (k_{obs}) are not affected by $[\text{PPh}_3]$. Therefore, it is also proposed that ligand dissociation should be the rate-determining step in the backward reaction. From the Eyring plot, the values of ΔH^\ddagger and ΔS^\ddagger were obtained as $90 \pm 2 \text{ kJ mol}^{-1}$ and $48 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

Reaction mechanism of reaction (1): From the kinetic data, it is presumed that the rate-determining steps of both directions of reaction (1) are dissociation of the leaving ligand (PPh_3 from $\text{ReOCl}_3(\text{PPh}_3)_2$ in the *forward* reaction, and NCP from $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ in the *backward* reaction).

Considering this finding and geometrical aspect of Re complexes, we propose a mechanism of the ligand substitution reaction of $\text{ReOCl}_3(\text{PPh}_3)_2$ with NCP as shown in Scheme 2.

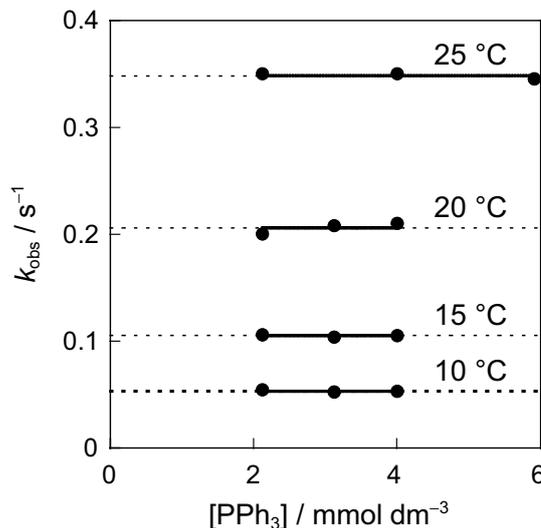
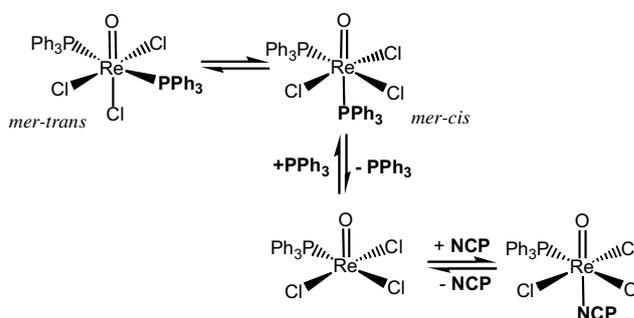


Figure 5. Plots of k_{obs} against $[\text{PPh}_3]$ for the *backward* reaction of (1). $[\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})] = 0.1 \text{ mmol dm}^{-3}$ in CH_2Cl_2 .

Scheme 2



4. Summary

The results of present study are summarized as follows. The $\text{ReOCl}_3(\text{PPh}_3)_2$ complex reacts with NCP in CH_2Cl_2 to form $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$. The resulting $\text{ReOCl}_3(\text{PPh}_3)(\text{NCP})$ complex has a distorted octahedral geometry and NCP coordinates to the *trans* position of $\text{Re} = \text{O}$ group. The equilibrium constant of $\text{ReOCl}_3(\text{PPh}_3)_2 + \text{NCP} \leftrightarrow \text{ReOCl}_3(\text{PPh}_3)(\text{NCP}) + \text{PPh}_3$ was determined as 0.33 ± 0.1 in CH_2Cl_2 at 25 °C. The rate-determining steps of forward and back-ward reactions in the above equilibrium are proposed to be the dissociation of PPh_3 and NCP coordinated to the *trans* position of the oxo group in $\text{Re} = \text{O}$ moiety.

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