Chelation Processes to an Oxorhenium(V) Center by N,N,N,O-Tetradentate and N,N,O-Tridentate Ligands As Verified by Structural and Mechanistic Studies of Intermediate Species

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The reaction of $[ReO(OEt)Cl_2(PPh_3)_2]$ with *N*-(2-pyridylmethyl)-2-aminoethanol (mpenOH) afforded a mixture of Re^V−oxo complexes, from which the dichloro complex $[ReOCl_2(mpenO\text{-}N,N',O)]$ (**1**) and the chlorotriphenylphosphine complex $[ReOCl(PPh_3)(mpenO\text{-}N,N',O)]PF_6$ (**2**) were isolated by addition of NH_4PF_6. Similarly, $[ReO(OEt)Cl_2(PPh_3)_2]$ reacted with *N*,*N*-bis(2-pyridylmethyl)-2-aminoethanol (bpenOH) to give the dichloro complex $[ReOCl_2(bpenO\text{-}N,N',O)]$ (**3**) and the monochloro complex $[ReOCl(bpenO\text{-}N,N',N'',O)]PF_6$ (**4**). When ethylene glycol (H_2eg) was added to the mixture of $[ReO(OEt)Cl_2(PPh_3)_2]$ and bpenOH, $[ReO(eg)(bpenOH\text{-}N,N',N'')]ReO_4$ (**5**) was obtained. These five newly prepared complexes were structurally characterized. A mechanistic insight into the stepwise complex formation reaction of $[ReO(OEt)Cl_2(PPh_3)_2]$ with pyridylmethylamine derivatives (mpenOH and bpenOH) is discussed. Crystal data: $[ReOCl_2(mpenO)]$ (**1**), monoclinic, space group $P2_1/c$, $a = 8.632(1)$ Å, $b = 9.288(1)$ Å, $c = 14.802(1)$ Å, $\beta = 100.627(9)°$, $Z = 4$; $[ReOCl(PPh_3)(mpenO)](PF_6)\cdot 0.5CH_3CN$ (**2**·0.5CH_3CN), monoclinic, space group $P2_1/a$, $a = 19.758(6)$ Å, $b = 9.463(3)$ Å, $c = 16.297(4)$ Å, $\beta = 93.40(2)°$, $Z = 4$; $[ReOCl_2(bpenO)]$ (**3**), monoclinic, space group $P2_1$, $a = 6.577(1)$ Å, $b = 13.269(2)$ Å, $c = 9.686(2)$ Å, $\beta = 105.00(2)°$, $Z = 2$; $[ReOCl(bpenO)](PF_6)$ (**4**), triclinic, space group $P\bar{1}$, $a = 6.766(1)$ Å, $b = 14.538(2)$ Å, $c = 19.373(3)$ Å, $\alpha = 91.57(1)°$, $\beta = 97.43(1)°$, $\gamma = 91.62(1)°$, $Z = 4$; $[ReO(eg)(bpenOH)](ReO_4)$ (**5**), monoclinic, space group $P2_1/n$, $a = 12.691(2)$ Å, $b = 14.030(2)$ Å, $c = 11.153(2)$ Å, $\beta = 90.72(1)°$, $Z = 4$.

Introduction

The coordination chemistry of rhenium and technetium are of considerable interest due to the widespread use of $^{186/188}Re$ and ^{99m}Tc isotopes as therapeutic agents and diagnostic imaging agents, respectively, in nuclear medicine.[1−4] Despite the large number of rhenium and technetium complexes discovered thus far, the chemistry of these complexes is still restricted and much remains to be done. Thus there is an increasing demand for a fundamental knowledge about the structural and spectroscopic properties, redox reactivities, and mechanism of ligand substitution reactions to develop new and improved Re and Tc radiopharmaceuticals.

We have recently shown that the tetradentate ligand tris(2-pyridylmethyl)amine (tpa) gives a variety of rhenium complexes depending on the starting materials and reaction conditions. On reacting tpa with $[Re^VOCl_3(PPh_3)_2]$ in methanol, an oxorhenium(V) complex $[Re^VO(OCH_3)(tpa)]^{2+}$ was obtained, where the methoxide and amine nitrogen atom coordinate cis and trans, respectively, to the terminal oxide ion.[5] In the presence of some oxygen-donor chelating ligands such as catechol derivatives and ethylene glycol, a series of oxorhenium(V) complexes with tridentate tpa were obtained where one pyridylmethyl arm left uncoordinated.[5] Under different conditions, however, reduction of rhenium(V) occurred to give a rhenium(III) monomer $[ReCl_2(tpa)]^+$,[6] a μ-oxo rhenium(III) dimer $[Re_2(\mu\text{-}O)Cl_2(tpa)_2]^{2+}$,[7] and a di-$\mu$-oxo rhenium(IV) dimer $[Re_2(\mu\text{-}O)_2(tpa)_2]^{4+}$.[8,9] A similar reduction reaction was observed for the reaction of $[Re^VOCl_3(PPh_3)_2]$ with 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) to give μ-oxo rhenium(III) dimers $[Re_2(\mu\text{-}O)Cl_2(L)_4]^{2+}$ (L = bpy, phen).[10] It was found that the PPh_3 liberated from the starting complex acts as an oxygen abstracting reagent when the oxygen containing ligand is absent in the $O{=}Re^V$ moiety.[6] Therefore we planned to investigate the coordination of tpa-like ligands

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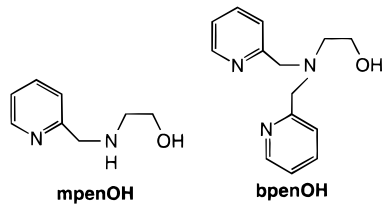
Chart 1



where parts of 2-pyridylmethyl groups are replaced by other groups to avoid reduction of rhenium(V).

We have synthesized a new N,N,N,O-tetradentate ligand, bpenOH (*N*,*N*-bis(2-pyridylmethyl)-2-aminoethanol), and investigated its reaction with $[Re^{V}O(OEt)Cl_2(PPh_3)_2]$. The ligand enabled us to isolate two products from the reaction mixture in which the bpenOH acts as a tridentate ligand (leaving one uncoordinated pyridine ring) and a tetradentate ligand (fully coordinated) with liberating an hydroxyl proton upon coordination through the oxygen atom. A different tridentate coordination mode of bpenOH, where the hydroxyl group left uncoordinated, was found when ethylene glycol (H_2eg) was used as a co-ligand. We have also synthesized a N,N,O-tridentate ligand, mpenOH (*N*-(2-pyridylmethyl)-2-aminoethanol), and investigated its reaction with the Re(V) starting material, $[Re^{V}O(OEt)Cl_2(PPh_3)_2]$. We wish to report here the preparation and structural characterization of several mononuclear Re(V) complexes which provide us some mechanistic information on the chelating process at the oxorhenium(V) center (Chart 1).

Experimental Section

Materials. *trans*-$[ReO(OEt)Cl_2(PPh_3)_2]$ was prepared by the literature method.[11] Acetonitrile and dichloromethane were dried over calcium hydride and phosphorus pentoxide, respectively. After drying, all solvents were distilled under an argon atmosphere. All other commercially available reagents were used as purchased.

Ligand Synthesis. (a) *N*-(2-Pyridylmethyl)-2-aminoethanol (mpenOH). A mixture of 2-picolyl chloride hydrochloride (2.00 g, 12.2 mmol), sodium hydroxide (488 mg, 12.2 mmol), and 2-aminoethanol (744 mg, 12.2 mmol) in 30 mL of water was stirred for 48 h at room temperature (25 °C). An aqueous solution of sodium hydroxide (488 mg, 12.2 mmol/10 mL) was added to the above solution. The solution was stirred for another 48 h. The reaction mixture was extracted with chloroform (3 × 100 mL), and the combined organic phase was washed once with water (50 mL). After drying the chloroform phase with Na_2SO_4 followed by evaporation, the product was isolated as a pale yellow oil (1.42 g, 77%). The product was used without further purification. ^{1}H NMR ($CDCl_3$)/ppm: δ 8.55−7.05 (m, 4H, aromatic H's), 3.92 (d, 2H, CH_2), 3.68−2.76 (m, 4H, CH_2).

(b) *N*,*N*-Bis(2-pyridylmethyl)-2-aminoethanol (bpenOH). A mixture of 2-picolyl chloride hydrochloride (10.00 g, 61 mmol), sodium hydroxide (2.44 g, 61 mmol), and 2-aminoethanol (1.86 g, 30.5 mmol) in 50 mL of water was stirred for 48 h at room temperature. An aqueous solution of sodium hydroxide (2.44 g, 61 mmol/10 mL) was added to the above solution. The solution was stirred for another 48 h. The reaction mixture was extracted with chloroform (3 × 100 mL), and the combined organic phase was washed once with water (50 mL). After the chloroform phase was dried with Na_2SO_4 and evaporated, the product was isolated as a dark orange oil. Further purification was carried out by column separation (silica gel, gradient of benzene−acetone starting with a ratio from 50:50 to 10:90) to give the desired product as a pale yellow oil (5.87 g, 40%). ^{1}H NMR ($CDCl_3$)/ppm: δ 8.58−7.05 (m, 8H, aromatic H's), 3.96 (s, 4H, CH_2), 3.68−2.80 (m, 4H, CH_2).

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Preparation of Complexes. (a) $[ReOCl_2(mpenO)]$ (1) and $[ReOCl(PPh_3)(mpenO)]PF_6$ (2). $[ReO(OEt)Cl_2(PPh_3)_2]$ (500 mg, 0.6 mmol) was added to a dichloromethane solution of mpenOH (90 mg, 0.6 mmol/20 mL). The mixture was stirred under argon for 1 h. A methanolic solution of NH_4PF_6 (96 mg, 0.6 mmol/5 mL) was added to the solution, and it was stirred for 10 min. Diethyl ether (50 mL) was added dropwise to the solution, and the resulting precipitate was collected by filtration and washed with acetonitrile to give **1** as a dark blue solid. Yield: 28.8 mg (11%). Anal. Calcd for $C_8H_{11}Cl_2N_2O_2Re$: C, 22.65; H, 2.61; N, 6.60; Cl, 16.71. Found: C, 23.14; H, 2.71; N, 7.10; Cl, 16.59. ^{1}H NMR (DMSO-d_6)/ppm: δ 9.32 (s, 1H, NH), 8.35−6.84 (m, 4H, aromatic H's), 4.18 (d, 2H, CH_2), 3.82−1.66 (m, 4H, CH_2). IR(KBr/cm^{-1}): 951 ($\nu_{Re=O}$). UV−vis (DMSO)/nm: 601 (ϵ = 7320 M^{-1} cm^{-1}). The ether-containing filtrate was allowed to evaporate slowly to give **2** as a purple solid. Yield: 198 mg (42%). Anal. Calcd for $C_{26}H_{26}ClF_6N_2O_2P_2Re$: C, 39.23; H, 3.29; N, 3.52; Cl, 4.45. Found: C, 38.80; H, 3.32; N, 3.57; Cl, 4.40. ^{1}H NMR ($CDCl_3$)/ppm: δ 9.82 (d, 1H, NH), 8.30−7.20 (m, 19H, aromatic H's), 5.28 (m, 2H, CH_2), 4.18−2.11 (m, 4H, CH_2). IR(KBr/cm^{-1}): 948 ($\nu_{Re=O}$). UV−vis (DMSO)/nm: 569 (ϵ = 11 700 M^{-1} cm^{-1}).

(b) $[ReOCl_2(bpenO)]$ (3) and $[ReOCl(bpenO)]PF_6$ (4). $[ReO(OEt)Cl_2(PPh_3)_2]$ (500 mg, 0.6 mmol) was added to a dichloromethane solution of bpenOH (144 mg, 0.6 mmol/20 mL). The solution was stirred under argon for 8 h. A methanolic solution of NH_4PF_6 (96 mg, 0.6 mmol/5 mL) was added to the solution, and the mixture was stirred for 10 min. Diethyl ether (50 mL) was added dropwise to the solution, and the resulting precipitate was collected by filtration and then washed with acetonitrile to give **3** as a dark blue solid. Yield: 19.8 mg (6%). Anal. Calcd for $C_{14}H_{16}Cl_2N_3O_2Re$: C, 32.63; H, 3.13; N, 8.15; Cl, 13.76. Found: C, 32.47; H, 3.18; N, 8.58; Cl, 13.40. ^{1}H NMR (DMSO-d_6)/ppm: δ 9.38−7.46 (m, 8H, aromatic H's), 5.22 (m, 4H, CH_2), 4.69−2.59 (m, 4H, CH_2). IR(KBr/cm^{-1}): 951 ($\nu_{Re=O}$). UV−vis (DMSO)/nm: 586 (ϵ = 8670 M^{-1} cm^{-1}). A second crop of **3** was isolated from the ether-containing filtrate. Yield: 43.8 mg (14%). Slow evaporation of the acetonitrile washings gave **4** as a dark blue solid. Yield: 110 mg (29%). Anal. Calcd for $C_{14}H_{16}ClF_6N_3O_2PRe$: C, 26.91; H, 2.58; N, 6.72; Cl, 5.67. Found: C, 27.26; H, 2.63; N, 6.96; Cl, 5.54. ^{1}H NMR (acetone-d_6)/ppm: δ 9.47−8.18 (m, 8H, aromatic H's), 6.52 (d, 2H, CH_2), 5.41 (d, 2H, CH_2), 3.74 (m, 4H, CH_2). IR (KBr/cm^{-1}): 954 ($\nu_{Re=O}$). UV−vis (DMSO)/nm: 605 (ϵ = 9230 M^{-1} cm^{-1}).

(c) $[ReO(eg)(bpenOH)](ReO_4)$ (5). A mixture of $[ReO(OEt)Cl_2(PPh_3)_2]$ (500 mg, 0.6 mmol), bpenOH (144 mg, 0.6 mmol), ethylene glycol (40 mg, 0.6 mmol), and triethylamine (120 mg, 0.6 mmol) in 50 mL of acetone was refluxed under an argon atmosphere for 1 h. The solvent was removed under vacuum, and the remaining solid was dissolved into acetonitrile (20 mL). The acetonitrile solution was allowed to evaporate slowly to give, after 5 days, green crystals suitable for X-ray analysis. Yield: 103 mg (23%). Anal. Calcd for $C_{16}H_{21}N_3O_8Re_2$: C, 25.43; H, 2.80; N, 5.56. Found: C, 25.64; H, 2.82; N, 5.85. ^{1}H NMR (acetone-d_6)/ppm: δ 8.78−7.64 (m, 8H, aromatic H's), 5.19−2.81 (m, 12H, CH_2). IR (KBr/cm^{-1}): 978 ($\nu_{Re=O}$). UV−vis (acetone)/nm: 512 (ϵ = 252 M^{-1} cm^{-1}).

(d) Conversion of $[ReOCl_2(bpenO)]$ (3) to $[ReOCl(bpenO)]PF_6$ (4). The conversion of $[ReOCl_2(bpenO)]$ to $[ReOCl(bpenO)]^+$ was monitored by ^{1}H NMR by dissolving $[ReOCl_2(bpenO)]$ in deuterated DMSO. After 5 days at room temperature, 80% conversion was accomplished. The same transformation can be achieved by subtracting one of the equatorial chloride ligands on **3** (40 mg, 0.078 mmol) with $AgPF_6$ (19 mg, 0.078 mmol) in 20 mL of acetonitrile. The latter method afforded the formation and isolation of **4** in 73% yield after filtration and evaporation of the solvent.

X-ray Structural Determinations. Crystals of **1** and **3** suitable for X-ray structural analyses were obtained by the slow vapor diffusion of diethyl ether into the DMF solution. Crystals of **2** and **4** suitable for X-ray structural analysis were obtained by recrystallization from acetonitrile. **2** was obtained as acetonitrile solvate, **2**·0.5CH_3CN. The crystals **1**−**5** were mounted on glass fibers and the crystal of **2**·0.5CH_3-CN was coated with a viscous perfluoroether due to inclusion of CH_3-CN molecule as a crystallizing solvent. All data were collected on a Rigaku AFC-5R (**1** and **3**) or MacScience MXC18 diffractometer

Table 1. Crystallographic Data for $[ReOCl_2(mpenO)]$ (**1**), $[ReOCl(PPh_3)(mpenO)](PF_6)\cdot 0.5CH_3CN$ (**2**·0.5CH_3CN), $[ReOCl_2(bpenO)]$ (**3**), $[ReOCl(bpenO)](PF_6)$ (**4**), and $[ReO(eg)(bpenOH)](ReO_4)$ (**5**)

	1	**2**·0.5CH_3CN	**3**	**4**	**5**
empirical formula	$C_8H_{11}Cl_2N_2O_2Re$	$C_{27}H_{27.5}ClF_6N_{2.5}O_2P_2Re$	$C_{14}H_{16}Cl_2N_3O_2Re$	$C_{14}H_{16}ClF_6N_3O_2PRe$	$C_{16}H_{21}N_3O_8Re_2$
fw	423.29	816.63	515.41	516.98	755.77
space group	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a/Å	8.632(1)	19.758(6)	6.577(1)	6.766(1)	12.691(2)
b/Å	9.288(1)	9.463(3)	13.269(2)	14.538(2)	14.030(2)
c/Å	14.802(1)	16.297(4)	9.686(2)	19.373(3)	11.153(2)
α/deg	90	90	90	91.57(1)	90
β/deg	100.627(9)	93.40(2)	105.00(2)	97.43(1)	90.72(1)
γ/deg	90	90	90	91.62(1)	90
V/Å^3	1166.5(2)	3041(1)	816.5(2)	1887.9(5)	1985.8(6)
Z	4	4	2	4	4
T/°C	23	−70	23	20	20
λ/Å	0.710 69	0.710 73	0.710 69	0.710 73	0.710 73
d_{calcd}/(g/cm^3)	2.41	1.78	2.10	1.82	2.53
μ(Mo Kα)/cm^{-1}	110.03	43.07	77.80	68.17	123.97
R^a	0.029	0.059	0.028	0.041	0.043
$R_w{}^b$	0.025	0.069	0.021	0.045	0.051

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + p|F_o|^2$ ($p = 2.25 \times 10^{-6}$ for **1**, 1.0×10^{-6} for **3**, and 0.001 for **2**·0.5CH_3CN, **4**, and **5**).

(**2**·0.5CH_3CN, **4**, and **5**) using graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation at 293 K except for **2**·0.5CH_3CN (203 K). The unit cell parameters of **1** and **3** were obtained by least-squares refinement of 25 reflections ($25 \le 2\theta \le 30°$), while those of **2**·0.5CH_3CN, **4**, and **5** were obtained by least-squares refinement of 26 reflections ($30 \le 2\theta \le 35°$). The intensities of three standard reflections for each compound, monitored every 150 reflections, showed no appreciable decay during the data collection. All data were corrected for Lorentz and polarization effects. Absorption corrections were applied for each compound.[12]

The crystal structures of **1**, **2**·0.5CH_3CN, and **3** were solved by direct method (SIR92).[13] Those of **4** and **5** were solved by heavy-atom method by using DIRDIF[14] and SHELXS-86,[15] respectively. The positional and thermal parameters of non-H atoms were refined anisotropically by the full-matrix least-squares method. The minimized function was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + p|F_o|^2$ ($p = 2.25 \times 10^{-6}$ for **1**, 1.0×10^{-6} for **3**, and 0.001 for **2**·0.5CH_3CN, **4**, and **5**). H atoms were included at calculated positions with fixed displacement parameters (1.2 (for **1** and **3**) or 1.3 (for **2**·0.5CH_3CN, **4**, and **5**) times the displacement parameters of the host atom). In the final cycle of the refinement, parameter shifts were less than 0.1σ. No correction was made for secondary extinction.

All calculations were performed using TEXSAN[16] for **1** and **3** and CRYSTAN[17] for **2**·0.5CH_3CN, **4**, and **5**. Further crystallographic data are given in Table 1. Listings of the selected bond distances and angles are summarized in Table 2. Non-hydrogen atom coordinates, anisotropic thermal parameters, and full listings of bond distances and angles for **1**−**5** are included as Supporting Information.

Other Measurements. UV−visible spectra were recorded on a GBC 916 spectrophotometer at 20 °C. IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer. The ^{1}H NMR spectra were obtained at 270 MHz with a JEOL JNM-EX270 spectrometer.

Results and Discussion

Structure. We have isolated five products as single crystals from the reaction of *trans*-$[ReO(OEt)Cl_2(PPh_3)_2]$ with mpenOH and bpenOH. For clarity, we first describe their structures before discussing the stepwise chelation steps of mpenOH and bpenOH ligands to the Re═O moiety. The molecular structures of **1**−**5** are shown in Figures 1−5, respectively. Because the asymmetric unit of **4** consists of two crystallographically independent molecules, one of the molecules of **4** is illustrated in Figure 4. All the structures consist of discrete distorted octahedral rhenium(V) complexes, which are neutral in **1** and **3** and are monocationic in **2**, **4**, and **5**. In complex **1**, the deprotonated mpenOH ligand ($mpenO^-$) acts as a tridentate ligand and coordinates facially to the Re(V) center in which the oxyethyl group of $mpenO^-$ occupies the trans position of the terminal oxygen atom. The two chloro groups have a cis configuration. This is interesting since the starting complex $[ReO(OEt)Cl_2(PPh_3)_2]$ has a trans configuration. In complex **2**, the $mpenO^-$ also acts as a tridentate ligand and coordinates facially to the Re(V) center. The coordination mode of $mpenO^-$ is very similar to that in **1**. The nitrogen atom in the pyridyl group coordinates to Re atom at the position trans to the triphenylphosphine ligand. In the complex **3** which has an uncoordinated pyridylmethyl group, the deprotonated bpenOH ligand ($bpenO^-$) acts as a tridentate ligand and coordinates facially to the Re(V) center. The oxyethyl group of $bpenO^-$ occupies the trans position to the terminal oxygen atom. The two chloro groups again have a cis configuration. In complex **4**, the $bpenO^-$ acts as a tetradentate ligand. The oxyethyl group occupies the trans position to the terminal oxygen atom. Three N atoms coordinate to the Re(V) center meridionally, where two pyridyl groups are trans to each other. On the other hand, in complex **5**, the neutral ligand bpenOH coordinates facially to the Re(V) center as a tridentate ligand with an uncoordinated hydroxyethyl group, in which the tertiary amine nitrogen occupies the trans position of the terminal oxygen atom. The two pyridyl groups have a cis configuration.

Apart from **5**, which has the bent (155.3(4)°) *trans*-$[O{=}Re{-}N]^{3+}$ group, the complexes **1**−**4** contain the bent *trans*-$[O{=}Re{-}O]^{2+}$ moiety (Table 2). The O═Re−O angles of them are almost the same (162.7(3)−163.7(3)°) regardless of the equatorial ligands and are very similar to those in $[ReOCl_2\{Ph(O)CNNCMe_2\}(PPh_3)]$ (163.6(3)°),[18] $[ReOCl_2(HL)(PPh_3)]$ (H_2L =

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[ReOCl_2(mpenO)]$ (**1**), $[ReOCl(PPh_3)(mpenO)](PF_6)\cdot 0.5CH_3CN$ (**2**), $[ReOCl_2(bpenO)]$ (**3**), $[ReOCl(bpenO)](PF_6)$ (**4**), and $[ReO(eg)(bpenOH)](ReO_4)$ (**5**)

	1	**2**·0.5CH_3CN	**3**	**4**[a]	**5**
Re1−O1	1.690(4)	1.70(3)	1.675(5)	1.685(8)	1.681(10)
Re1−O2	1.947(3)	1.91(3)	1.904(6)	1.915(7)	
Re1−O3					1.903(9)
Re1−O4					1.938(9)
Re1−Cl1	2.357(1)	2.362(10)	2.350(2)	2.354(4)	
Re1−Cl2	2.382(2)		2.390(2)		
Re1−P1		2.445(10)			
Re1−N1	2.182(4)	2.20(3)	2.214(7)	2.143(8)	2.317(10)
Re1−N11	2.124(4)	2.17(4)	2.125(6)	2.127(9)	2.169(10)
Re1−N21				2.109(9)	2.139(10)
O1−Re1−O2	163.5(2)	163.3(10)	162.7(3)	163.1(4)	
O1−Re1−O3					111.0(4)
O1−Re1−O4					107.3(5)
O1−Re1−Cl1	105.4(1)	104.1(8)	104.7(2)	105.5(3)	
O1−Re1−Cl2	95.6(1)		95.1(2)		
O1−Re1−P1		93.5(8)			
O1−Re1−N1	87.1(2)	85.9(11)	85.3(2)	85.5(4)	155.3(4)
O1−Re1−N11	88.6(2)	92.1(11)	89.1(3)	87.9(4)	89.0(4)
O1−Re1−N21				89.8(4)	94.4(5)
O2−Re1−Cl1	90.0(1)	92.4(7)	91.0(2)	90.7(3)	
O2−Re1−Cl2	90.5(1)		92.6(2)		
O2−Re1−P1		90.3(7)			
O2−Re1−N1	77.1(1)	77.3(10)	78.4(3)	78.3(3)	
O2−Re1−N11	84.1(1)	84.2(10)	82.4(2)	85.0(3)	
O2−Re1−N21				92.4(4)	
O3−Re1−O4					82.5(4)
O3−Re1−N1					89.8(4)
O3−Re1−N11					159.5(4)
O3−Re1−N21					83.2(4)
O4−Re1−N1					87.9(4)
O4−Re1−N11					87.1(4)
O4−Re1−N21					157.2(4)
Cl1−Re1−Cl2	89.20(6)		87.79(9)		
Cl1−Re1−P1		86.4(4)			
Cl1−Re1−N1	166.3(1)	167.2(8)	168.5(2)	168.9(3)	
Cl1−Re1−N11	94.7(1)	92.8(9)	94.7(2)	99.0(3)	
Cl1−Re1−N21				98.1(3)	
Cl2−Re1−N1	95.4(1)		97.1(2)		
Cl2−Re1−N11	173.3(1)		174.4(2)		
P1−Re1−N1		101.1(8)			
P1−Re1−N11		174.4(8)			
N1−Re1−N11	79.6(2)	78.7(12)	79.6(3)	82.1(4)	72.1(4)
N1−Re1−N21				80.7(4)	74.4(4)
N11−Re1−N21				162.8(4)	100.5(4)

[a] Selected bond lengths (Å) angles (deg) around Re2 atom in **4**: Re2−O3, 1.698(7); Re2−O4, 1.904(7); Re2−Cl2, 2.376(3); Re2−N2, 2.134(8); Re2−N31, 2.131(9); Re2−N41, 2.135(9); O3−Re2−O4, 163.7(3); O3−Re2−Cl2, 102.2(3); O3−Re2−N2, 86.4(4); O3−Re2−N31, 92.7(4); O3−Re2−N41, 88.3(4); O4−Re2−Cl2, 93.0(3); O4−Re2−N2, 78.4(3); O4−Re2−N31, 90.4(4); O4−Re2−N41, 83.7(4); Cl2−Re2−N2, 171.4(3); Cl2−Re2−N31, 99.8(3); Cl2−Re2−N41, 98.4(3); N2−Re2−N31, 80.3(4); N2−Re2−N41, 81.0(4); N31−Re2−N41, 161.2(4).

2,6-bis(hydroxymethyl)pyridine) (167(1)°),[19] and $[ReOCl(PO)_2]$ (POH = (*o*-hydroxyphenyl)diphenylphosphine) (163.7(4)°).[20] The Re═O distances in **1**−**4** are very similar (1.675(5)−1.70(3) Å) and fall into the range which is commonly found for the complexes having a $[O{=}Re{-}O]^{2+}$ moiety.[18−22] The Re−O(oxyethyl) distances in **2**−**4** are similar to each other, while that in **1** is ca. 0.04 Å longer than those in the others despite the similar Re═O distances in **1**−**4**. The Re−N(py) distances in **1**, **3**, and **4** are close to each other and are slightly shorter than those in **2** and **5** which are trans to PPh_3 and ethylene glycolate, respectively. In the dichloro complexes **1** and **3**, the Re−Cl bond (2.357(1) Å for **1**; 2.350(2) Å for **3**) which is trans to the Re−N(tertiary amine) bond is slightly shorter than that (2.382(2) Å for **1**; 2.390(2) Å for **3**) which is trans to the Re−N(py) bond, due to lesser extent of trans influence of the tertiary amine nitrogen. Except for the difference of the uncoordinated arm, the structure of **5** is very similar to that of $[ReO(eg)(tpa\text{-}N,N',N'')]^+$ in which tpa acts as a tridentate ligand. The structural parameters such as the Re═O and Re−N(amine) distances and O═Re−N(amine) angle in **5** are comparable to those in $[ReO(eg)(tpa\text{-}N,N',N'')]^+$ and $[Re(O)(cat)(tpa\text{-}N,N',N'')]^+$ (cat = *o*-catecholate dianion).[5] The Re═O distance in **5** is also very close to that in **1**−**4**. However, the Re−N(amine) distance in **5** (2.317(10) Å) is ca. 0.1 Å longer than those in **1**−**4** (2.134(8)−2.214(7) Å) and that in $[ReO(DL\text{-}ECH_3)]$ (DL-ECH_3 = trianionic form of ethylenedi-DL-cysteine) (2.217(5) Å)[23]

(18) Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans*. **1979**, 279.
(19) Gerber, T. I. A.; Bruwer, J.; Bandoli, G.; Perils, J.; du Preez, J. G. H. *J. Chem. Soc., Dalton Trans.* **1995**, 2189.
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(23) Hansen, L.; Lipowska, M.; Taylor, A., Jr.; Marzilli, L. G. *Inorg. Chem.* **1995**, *34*, 3579.

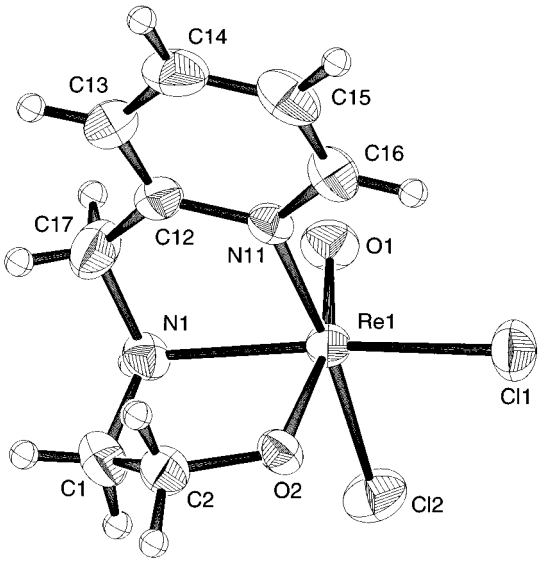


Figure 1. Molecular structure of [$ReOCl_2$(mpenO)] (**1**) with the atomic numbering scheme showing 50% probability thermal ellipsoids.

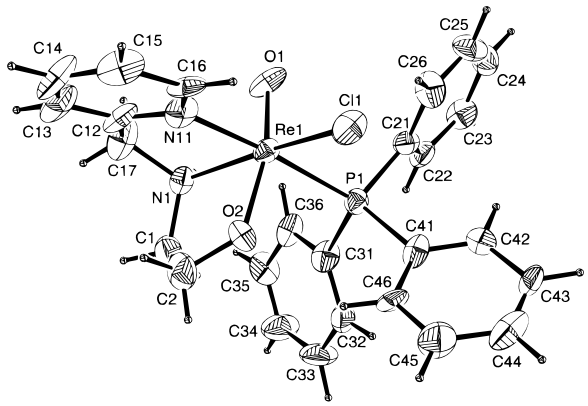


Figure 2. ORTEP drawing of the complex cation in [$ReOCl(PPh_3)$(mpenO)](PF_6) (**2**) with the atomic numbering scheme showing 50% probability thermal ellipsoids.

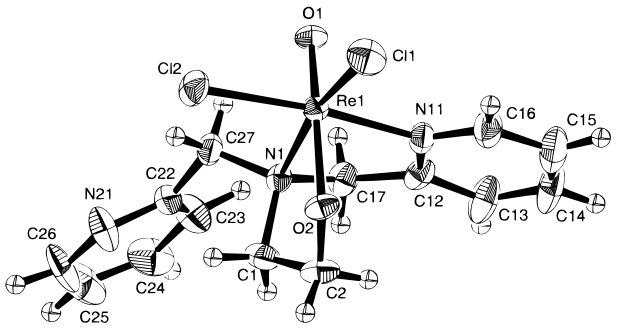


Figure 3. Molecular structure of [$ReOCl_2$(bpenO)] (**3**) with the atomic numbering scheme showing 50% probability thermal ellipsoids.

which has a similar O═Re−N(amine) bond angle (151.6(2)°) with that in **5**. This is probably due to a strong trans influence of the Re═O bond in **5**.

Stepwise Chelation Steps of the Chelating Ligands. The *trans*-dichloro(ethoxo)oxobis(triphenylphosphine)rhenium(V), [$ReO(OEt)Cl_2(PPh_3)_2$] complex has proven, in our case, to be a better starting material for ligand substitution reactions than the *trans*-[$ReOCl_3(PPh_3)_2$] complex. This is due to the fact that the liberated ethoxide ion can act as a base to remove a proton from the mpenOH and bpenOH ligand and improve the nucleophilicity thereof.

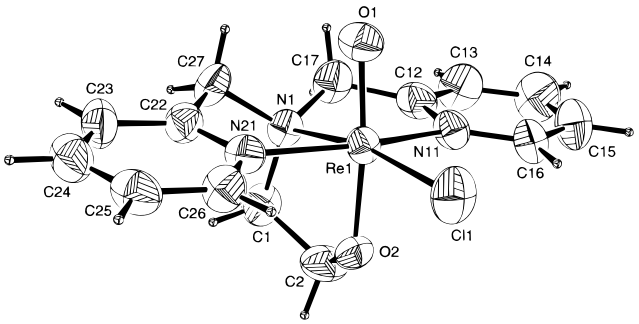


Figure 4. ORTEP drawing of the complex cation in [ReOCl(bpenO)](PF_6) (**4**) with the atomic numbering scheme showing 50% probability thermal ellipsoids.

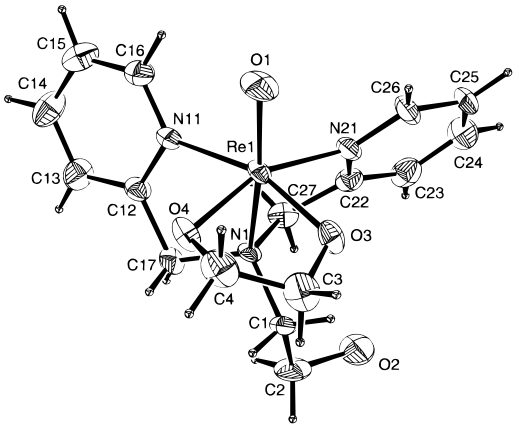


Figure 5. ORTEP drawing of the complex cation in [ReO(eg)(bpenOH)](ReO_4) (**5**) with the atomic numbering scheme showing 50% probability thermal ellipsoids.

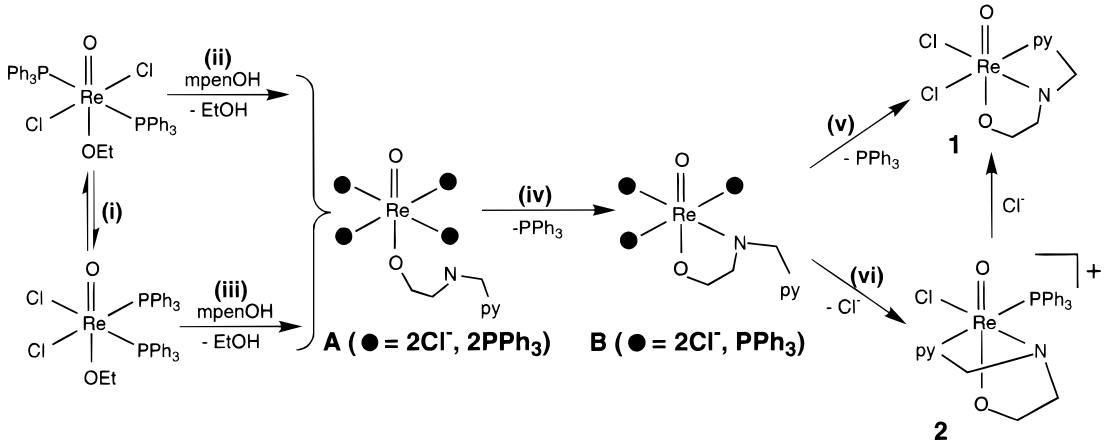
The reaction between *trans*-[$ReO(OEt)Cl_2(PPh_3)_2$] and mpenOH (molar ratio 1:1) in dichloromethane resulted in the formation of a mixture of two compounds, [$ReOCl_2$(mpenO)] (**1**) and [$ReOCl(PPh_3)$(mpenO)]PF_6 (**2**) in 11 and 42% yield, respectively. In our procedure of isolation of **1** and **2**, we added a PF_6^- salt before isolating neutral **1**. If the volume of the reaction mixture is reduced or diethyl ether is added to the reaction mixture, [$ReOCl(PPh_3)$(mpenO)]Cl coprecipitates with **1**. The addition of PF_6^- salt improves the solubility of the [$ReOCl(PPh_3)$(mpenO)]$^+$ cation and **1** is obtained without coprecipitation of [$ReOCl(PPh_3)$(mpenO)]$^+$ salt.

As X-ray analyses revealed, the compound **1**, having two chloro groups in a cis configuration, and **2** were obtained from the same reaction mixture. It indicates that the trans to cis rearrangement must take place during the chelation step to form **1** from the *trans*-[$ReO(OEt)Cl_2(PPh_3)_2$] and that the precursor **B** should contain two chloro groups and a PPh_3 (trans and cis notation refers to the arrangement of the chloro ligands) (Scheme 1). Although the configuration of the chloro groups in **B** is ambiguous, both cis and trans isomers are possible, to give **1** and **2**, by considering an association mechanism, since it is known that the Re(V) forms seven-coordinate structure such as [ReO(tpen)]$^{3+}$ (tpen = *N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-ethylenediamine)[24] and [ReO(2,2′:6′,2″:6″,2‴-quaterpyridine)(OCH_3)$_2$]$^+$.[25]

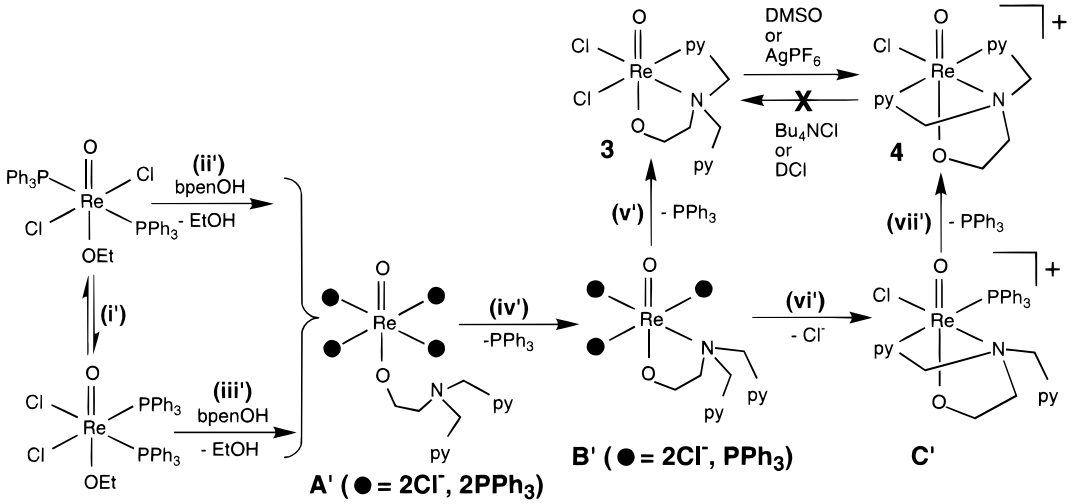
It has been reported that trans−cis equilibration is established in the solution of *trans*-[$ReO(OEt)Cl_2(PPh_3)_2$] (Scheme 1i).[26]

(24) Jin, H.-Y.; Ikari, S.; Kobayashi, K.; Umakoshi, K.; Sugimoto, H.; Sasaki, Y.; Ito, T. *Inorg. Chem.* Submitted.
(25) Che, C.-M.; Wang, Y.-P.; Yeung, K.-S.; Wong, K.-Y.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1992**, 2675.

Scheme 1



Scheme 2



It is tempting to consider that the cis isomer of $[ReO(OEt)Cl_2(PPh_3)_2]$ is the initial reactant.[27] However, the trans isomer could also be a reactant, since trans-cis rearrangement is possible in each chelation step of monodentate to bidentate (Scheme 1iv) and bidentate to tridentate (Scheme 1v or vi). The initial step of the complex formation should be the substitution of the oxygen atom in the mpenOH ligand for the OEt^- possibly with the proton transfer to give monodentate intermediate **A** (Scheme 1ii or iii). **A** may be considered as a trans or a cis isomer or a mixture of them, since we cannot assign geometrical isomers for this intermediate. One of the PPh_3 ligands would be liberated by the attack of the amino nitrogen to give bidentate intermediate **B** (Scheme 1iv). Since we could not isolate intermediate **A** and **B**, it is not clear in which step the trans-cis rearrangement occurred.

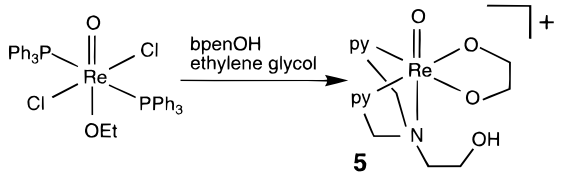
Since triphenylphosphine is a better leaving group than the chloride ion, the reaction of **2** with chloride ion (Bu_4NCl) was followed by ^1H NMR in CD_3CN. After 1 h of incubation of the sample tube at 50 °C, an 86% conversion of **2** to **1** was observed. This solution is unstable when it is brought in contact with air. We have not yet succeeded in isolating **1** from this solution due to unknown factor of its instability. On the other hand, the compound **1** did not react with PPh_3. The compound **2** can be converted to **1**, but **1** cannot be converted back to **2**.

The reaction between *trans*-$[ReO(OEt)Cl_2(PPh_3)_2]$ and bpenOH (molar ratio 1:1) in dichloromethane again resulted in the formation of a mixture of two compounds, $[ReOCl_2(bpenO)]$ (**3**) and $[ReOCl(bpenO)]PF_6$ (**4**) in 20 and 29% yield, respectively. Similarly to the stepwise chelate formation of mpenOH toward *trans*-$[ReO(OEt)Cl_2(PPh_3)_2]$ (Scheme 1), the chelate formation of bpenOH toward *trans*-$[ReO(OEt)Cl_2(PPh_3)_2]$ may be represented by Scheme 2. Again the initial step of the complex formation should be the substitution of the oxygen atom in the bpenOH ligand for the OEt^- possibly with the proton transfer to give monodentate intermediate **A′** which are corresponding to **A** in Scheme 1ii′ and iii′. One of the PPh_3 ligands would be liberated by the attack of amino nitrogen to give bidentate intermediate **B′** (Scheme 2iv′).

In the next step, one of the uncoordinated pyridyl groups would either substitute another equatorial phosphine to form **3** (Scheme 2v′), or substitute one of the equatorial chloride ligands to form the intermediate **C′**, $[ReOCl(PPh_3)(bpenO)]^+$ (Scheme 2vi′). The intermediate **C′** was not isolated but is probable, since the corresponding complex $[ReOCl(PPh_3)(mpenO)]^+$ (**2**) was isolated as described above. This may react further with the other uncoordinated pyridyl group in the bpenO ligand to form the $[ReOCl(bpenO)]^+$ complex where the bpenO ligand acts as a tetradentate ligand (Scheme 2vii′). The $[ReOCl(bpenO)]^+$ cation complex was isolated as the hexafluorophospate salt.

(26) Grove, D. E.; Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *J. Chem. Soc.* **1965**, 490.
(27) Battistuzzi, G.; Borsari, M.; Battistuzzi, R. *Polyhedron* **1997**, *16*, 2093.

Scheme 3



5

The dichloro complex **3** is soluble only in DMSO and DMF. The DMF solution of **3** is stable for more than a week at room temperature. The DMSO solution of **3**, however, is not so stable, and **3** converts to $[ReOCl(bpenO)]^+$ (**4**). The transformation of **3** to **4** was monitored by ^1H NMR in deuterated DMSO. After 5 days at room temperature, an 80% conversion was accomplished. The same transformation can be achieved by subtracting one of the equatorial chloride ligands on **3** with $AgPF_6$ in acetonitrile. This afforded the formation of **4** in 73% yield. On the other hand, **3** could not be accessed via ligand substitution reactions on **4** with an excess amount of Bu_4NCl (5 equiv in CH_3CN). Similarly, in CD_3CN with an excess amount of DCl, no back-conversion of **4** to **3** could be observed on ^1H NMR even after 5 days at room temperature. This suggested that the dichloro complex **3** is the kinetically stable intermediate because the formation of **3** is much faster than the conversion from **3** to **4**. The complex **3** eventually converted completely to the thermodynamically stable complex $[ReOCl(bpenO)]^+$. Since **3** has poor solubility in dichloromethane, it could be isolated in 20% yield before it was converted to **4**.

When the *trans*-$[ReO(OEt)Cl_2(PPh_3)_2]$ was reacted with bpenOH in the presence of ethylene glycol, the complex with chelated ethylene glycolate dianion $[ReO(eg)(bpenOH)](ReO_4)$ (**5**) was obtained, in which the neutral bpenOH acted as a tridentate ligand and coordinates to the Re(V) center through two pyridyl groups and an amine nitrogen (Scheme 3). It is possible that the deprotonation of bpenOH by EtO^- does not proceed in the presence of ethylene glycol and the more basic amino nitrogen substitute first for EtO^- at the oxorhenium(V) center. It is also noteworthy that some of the starting material was oxidized to Re(VII) to give the ReO_4^- ion which acts as counteranion in **5**. Similar oxidation of the Re(V) ion to ReO_4^- was also found in the reaction of $[ReOCl_3(PPh_3)_2]$ with Me_2tpa (bis(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine) in ethanol−water mixture.[9] In that case, the disproportionation of Re(V) to Re(IV) and Re(VII) which produces the $Re^{IV}_2(\mu\text{-}O)_2$ unit and ReO_4^- has been suggested.

The reactions of **3** and **4** with ethylene glycol were conducted in order to check their reactivity. We found that the reaction of **4** with ethylene glycol did not proceed even though the reaction mixture was refluxed for 5 h. The reaction of **3** with ethylene glycol had less reproducibility, but at least this reaction did not give **5**. These observations indicate that the ethylene glycol molecule or its anion reacts with Re center before the reaction with bpenOH. This is in contrast with the reaction of $[ReOCl_3(PPh_3)_2]$ with 1,4,7-triazacyclononane (tacn) in the presence of ethylene glycol in which the reaction is expected to proceed via the $[(tacn)ReOCl_2]^+$ intermediate to give $[(tacn)ReO(eg)]^+$.[28]

Preference of Re(V) Oxidation State During the Present Reactions. It is well-known that a phosphine ligand such as PPh_3 abstracts oxygen from rhenium(V) oxo-complexes to give a rhenium(III) compound.[27,29] Indeed, we have found that upon ligand substitution reactions involving tpa (tris(2-pyridylmethyl)amine) and $[ReOCl_3(PPh_3)_2]$ or $[ReOCl_2(OEt)(PPh_3)_2]$, reduction of the Re(V) center proceeded by the oxide abstraction by the liberated PPh_3 ligands.[6] However, no reduction by the liberated PPh_3 was observed during the formation of compounds **1**−**5**. This observation indicates that the O═Re−O moiety, which is present in all of the isolated compounds (**1**−**5**), stabilizes the Re(V) oxidation state in the ligand substitution reactions involving *trans*-$[ReO(OEt)Cl_2(PPh_3)_2]$. A similar preference of the Re(V) oxidation state was observed for $[ReOCl_2\{Ph(O)CNNCMe_2\}(PPh_3)]$,[18] $[ReOCl_2(HL)(PPh_3)]$ (H_2L = 2,6-bis(hydroxymethyl)pyridine),[19] $[ReOCl(L')]$ (L′ = 1,3-(*N*,*N*′-bis(salicylidene)diamino)-2,2-dimethylpropyl and its derivative),[21] and $[ReOCl(PO)_2]$ (POH = (*o*-hydroxyphenyl)diphenylphosphine).[20] The involvement of ethylene glycol or catecholate in the reaction of tpa with $[ReOCl_3(PPh_3)_2]$ or $[ReOCl_2(OEt)(PPh_3)_2]$ also afforded Re(V) complexes.[5] It is concluded that the existence of hydroxy group in the chelating ligands precludes the reduction of the metal center to Re(III). It is also concluded in this study that initial attack of the chelating ligands occurs at the trans position to the terminal oxide which is perhaps the most labile site for the substitution by the oxygen or amino nitrogen of the chelating ligands. Subsequent chelating process is not straightforward but proceeds possibly via a few processes.

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Supporting Information Available: Five X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

IC971477N

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