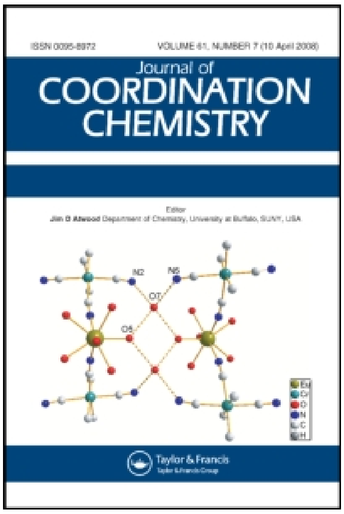

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# Synthesis and Characterization of Bisubstituted Rhenium(V) OXO Complexes with Benzimidazolylalcohol Ligands Containing the N,O Donor-Atom Set

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# SYNTHESIS AND CHARACTERIZATION OF BISUBSTITUTED RHENIUM(V) OXO COMPLEXES WITH BENZIMIDAZOLYLALCOHOL LIGANDS CONTAINING THE N,O DONOR–ATOM SET

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The reaction of the complex *trans*-$ReOCl_3(PPh_3)_2$ with potentially bidentate N,O-donor benzimidazolylalcoholate ligands (HL) in the presence of triethylamine in ethanol and benzene produces the complexes $ReO(OEt)(L)_2$ and $ReOCl(L)_2$, respectively. These compounds were characterized by elemental analysis, NMR, vibrational and optical spectroscopy. Mechanisms for the formation reactions and probable configurations of the complexes are proposed, and these are supported by qualitative and spectroscopic studies.

**Keywords:** Rhenium(V), benzimidazolylalcohols, complexes, mechanism, configuration

## INTRODUCTION

The chemistry of oxorhenium(V) complexes is receiving increased attention due to the potential application of the isotopes $^{186}Re$ and $^{188}Re$ as radiotherapeutic agents against cancer,[1] and because of similar chemical behaviour to technetium,[2] its second row congener, which has found major applications in diagnostic nuclear medicine.[3]

It has been shown that Schiff bases are suitable ligands to stabilize the $ReO^{3+}$ core, and complexes of the type $ReOX(L)_2$ and $ReOX_2(L)(PPh_3)$ (X = Cl, Br) have been prepared[4] by the reaction of $ReOX_3(PPh_3)_2$ with bidentate N,O-donor Schiff bases. These bidentate ligands always result in six-coordination, and crystal structure determinations have indicated that a phenolic oxygen is always coordinated *trans* to the rhenyl oxo oxygen.[5,6]

With the aim of attaining other stable configurations for the $ReO^{3+}$ core, we have produced complexes of the type $ReO(OEt)(L)_2$ and $ReOCl(L)_2$, which contain bidentate, N,O-donor benzimidazolylalcohols (HL; Figure 1) as ligands.

## EXPERIMENTAL

### *Materials*

The compound *trans*-$ReOCl_3(PPh_3)_2$ was prepared from ammonium perrhenate (Aldrich) according to literature procedures.[7] The benzimidazolylalcohol ligands were prepared as reported,[8] and their purity was checked by microanalyses, infrared

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spectroscopy and melting points. The ligand 2-(2-hydroxyphenyl)benzothiazole (HPBT) was obtained commercially (Aldrich), and was used without further purification. All solvents used were purified and dried by standard methods,[9] and all common laboratory chemicals were of analytical grade.

### *Apparatus*

Infrared spectra were recorded on Shimadzu FTIR-4100 and Nicolet 20 DXC FTIR spectrophotometers in the 4000–250 cm$^{-1}$ range in KBr pellets. Optical spectra were obtained with Shimadzu UV-3100 and Perkin-Elmer 330 spectrophotometers in the 200–800 nm range. $^1$H n.m.r. spectra were recorded at 300 K with a Varian Gemini 200 MHz spectrometer. A Philips PW 9509 digital conductometer was used to perform conductivity measurements, and elemental analyses were obtained with an Heraeus Rapid Analyzer. Chloride was determined by potentiometric titration with standard silver nitrate of solutions of the compounds decomposed by the Shoeniger method. These titrations were performed on a Metrohm-Herisau E536 potentiograph, using a Metrohm 665 Dosimat and a Metrohm-Herisau AG9100 $Ag^+/AgCl$ electrode. Melting points were determined in capillaries using a Gallenkamp apparatus, and are uncorrected.

### *Synthesis of the complexes*

#### *ReO(OEt)(BMA)$_2$*

To a solution of 45 mg of the ligand HBMA (304 μmol) in 5 cm$^3$ ethanol was added 115 mg of *trans*-$ReOCl_3(PPh_3)_2$ (138 μmol) in 10 cm$^3$ ethanol with stirring. This was immediately followed by the addition of 3 drops of triethylamine, and the reaction mixture was heated under reflux for one hour. After about 15 min the colour of the solution changed from yellow-green to dark green, and a green solid started to precipitate. After cooling the mixture to room temperature, the green precipitate was filtered, washed with ethanol, benzene and diethylether, and dried under vacuum. This material is poorly soluble in polar organic solvents. The yield was 76%, based on Re; mp 201°C. Anal. Calcd. for $C_{18}H_{19}N_4O_4Re$: C, 39.92; H, 3.54; N, 10.35%. Found: C, 39.65; H, 3.52; N, 10.81; Cl, 0%. Infrared data (cm$^{-1}$): ν(Re=O) 946; ν(C–O) 1264; δ(OCH$_2$) 910. $^1$H n.m.r. [$(CD_3)_2SO$]: δ1.19 (t, 3H, $CH_3CH_2O$); 3.11 (q, 2H, $CH_3CH_2O$); 4.89 (s, 4H, $C_7H_5N_2$-$CH_2$-O); 7.36–7.70 (m, 8H, $C_6H_4$). Electronic spectrum (DMF) [$\lambda_{max}$, nm]: 397, 304, 283, 276 nm.

#### *ReO(OEt)(BEA)$_2$*

To 110 mg of $ReOCl_3(PPh_3)_2$ in 10 cm$^3$ ethanol was added a solution of 47 mg of HBEA (290 μmol) and 3 drops of triethylamine in 5 cm$^3$ ethanol. The reaction mixture was heated under reflux for one hour. After cooling to room temperature, the dark green solution was filtered, and the volume was reduced to 3 cm$^3$ under vacuum. After 5 cm$^3$ *n*-heptane was added and the solution stood overnight in a refrigerator, the green precipitate that deposited was collected and washed with water, methanol, benzene and diethylether. This material is moderately soluble in polar organic solvents like acetonitrile and chloroform, and slightly soluble in acetone and dichloromethane. The yield was 58%, based on Re; mp 155°C. Anal. Calcd. for $C_{20}H_{23}N_4O_4Re$: C, 42.17; H, 4.07; N, 9.83%. Found: C, 42.65; H, 3.75;

N, 9.68; Cl, 0%. Infrared data (cm$^{-1}$); ν(Re=O) 954; ν(C–O) 1273; δ(OCH$_2$) 911. $^1$H n.m.r [(CD$_3$)$_2$SO]: δ1.20 (t, 3H, C*H*$_3$CH$_2$O); 3.10 (q, 2H, CH$_3$C*H*$_2$O); 1.59 (d, 6H, C*H*$_3$); 5.13 (q, 2H, C*H*); 7.35–7.70 (m, 8H, C$_6$*H*$_4$). Electronic spectrum (DMF) [λ$_{max}$; nm]: 393, 300, 283, 276 nm.

### *ReO(OEt)(PBT)$_2$*

To a suspension of 100 mg of *trans*-ReOCl$_3$(PPh$_3$)$_2$ in 10 cm$^3$ of ethanol was added 60 mg (264 μmol) of HPBT in 5 cm$^3$ of ethanol, followed by the addition of 3 drops of triethylamine. The reaction mixture was heated under reflux for 30 min, during which time the colour of the solution changed to dark green. After cooling the solution to room temperature, the emerald green precipitate was filtered, washed with water, ethanol, benzene and diethylether, and dried under vacuum. The product is a non-electrolyte in DMF solution, and is poorly soluble in polar organic solvents. The yield was 68%, based on Re; mp 239°C. Anal. Calcd. for $C_{28}H_{21}N_2O_4S_2Re$: C, 48.06; H, 3.02; N, 4.00%. Found: C, 47.90; H, 3.09; N, 4.00; Cl, 0%. Infrared data (cm$^{-1}$); ν(Re=O) 949; ν(C-O) 1320, 1329; δ(OCH$_2$) 910. $^1$H n.m.r. (CDCl$_3$): δ1.24 (t, 3H, C*H*$_3$CH$_2$O); 3.72 (q, 2H, CH$_3$C*H*$_2$O); 6.80–8.04 (m, 16H, C$_6$*H*$_4$). Electronic spectrum (DMF) [λ$_{max}$, nm]: 380, 316, 284 nm.

### *ReO(OEt)(BPA)$_2$*

To 145 mg of ReOCl$_3$(PPh$_3$)$_2$ in 10 cm$^3$ ethanol were added a solution of 88 mg of HBPA (390 μmol) in 5 cm$^3$ ethanol and 3 drops of triethylamine. The reaction mixture was heated under reflux for one hour, during which time the colour of the solution turned to dark green. After cooling the solution to room temperature, the clear solution was filtered, and the volume was reduced to about 3 cm$^3$ under vacuum. The addition of 5 cm$^3$ *n*-heptane and cooling overnight in a refrigerator led to the depositing of an emerald green precipitate, which was filtered, washed with water, benzene, cold ethanol and diethylether, and dried under vacuum. It is a non-electrolyte in DMF solution and is poorly soluble in polar organic solvents. The yield was 68%, based on Re; mp 108°C. Anal. Calcd. for $C_{30}H_{27}N_4O_4Re$: C, 51.94; H, 3.92; N, 8.08%. Found: C, 51.69; H, 3.88; N, 7.93; Cl, 0%. Infrared data (cm$^{-1}$): ν(Re=O) 948; ν(C-O) 1283; δ(OCH$_2$) 910. $^1$H n.m.r. [(CD$_3$)$_2$SO]: δ1.19 (t, 3H, C*H*$_3$CH$_2$O); 3.12 (q, 2H, CH$_3$C*H*$_2$O); 6.23 (s, 2H, C*H*); 7.38–7.76 (m, 18H, C$_6$*H*$_4$, C$_6$*H*$_5$). Electronic spectrum (DMF) [λ$_{max}$, nm]: 395, 314, 273 nm.

### *ReOCl(BMA)$_2$*

To a solution of 108 mg of *trans*-ReOCl$_3$(PPh$_3$)$_2$ (130 μmol) in 10 cm$^3$ benzene was added 44 mg (298 μmol) of the ligand HBMA dissolved in 5 cm$^3$ benzene. This was followed by the addition of 4 drops of triethylamine, and the reaction mixture was heated under reflux for 30 min. Within 15 min, an olive green material precipitated out of the dark green solution. Heating was stopped, the solution cooled to room temperature, and the precipitate removed by filtration. It was washed successively with benzene, water, 2-propanol and diethylether, and dried under vacuum. The complex is poorly soluble in polar organic solvents but could be recrystallized from CH$_2$Cl$_2$. The yield was 72%, based on Re; mp 162°C. Anal. Calcd. for $C_{16}H_{14}N_4O_3ClRe$: C, 36.13; H, 2.65; N, 10.53; Cl, 6.66%. Found: C, 36.37; H, 2.47; N, 10.38; Cl, 6.81%. Infrared data (cm$^{-1}$): ν(Re=O) 951; ν(C–O) 1262, 1273:

ν(Re–Cl) 318. $^1$H n.m.r. [$(CD_3)_2SO$]: δ5.03 (s, 2H, C$H_2$); 5.08 (s, 2H, C$H_2$); 7.20–7.78 (m, 8H, $C_6H_4$). Electronic spectrum (DMF) [$\lambda_{max}$, nm (ε $M^{-1}$ $cm^{-1}$)]: 398 (278), 302 (1940), 282sh, 273 (7200).

### *ReOCl(BEA)$_2$*

To 108 mg of *trans*-$ReOCl_3(PPh_3)_2$ dissolved in 10 cm$^3$ benzene were added 45 mg of the ligand HBEA dissolved in 10 cm$^3$ benzene. After the addition of 4 drops triethylamine, the mixture was heated under reflux for 30 min, and after cooling a green precipitate was collected. This product was washed with benzene, water, 2-propanol and diethylether, and dried under vacuum. The complex is poorly soluble in polar organic solvents, and was recrystallized from $CH_2Cl_2/Et_2O$. The yield was 63%, based on Re: mp 163°C. Anal. Calcd. for $C_{18}H_{18}N_4O_3ClRe$: C, 38.61; H, 3.24; N, 10.00; Cl, 6.33%. Found: C, 38.47; H, 3.33; N, 10.14; Cl, 6.09%. Infrared data (cm$^{-1}$): ν(Re=O) 960; ν(C–O) 1273, 1291; ν(Re–Cl) 318. $^1$H n.m.r. [$(CD_3)_2SO$]: δ1.08 (d, 3H, C$H_3$); 1.33 (d, 3H, C$H_3$); 4.75–4.96 (m, 2H, C$H$); 7.28–7.70 (m, 8H, $C_6H_4$). Electronic spectrum (DMF) [$\lambda_{max}$, nm (ε $M^{-1}$ $cm^{-1}$)]: 405 (830), 303 (2500), 280sh, 273 (13800).

### *ReOCl(PBT)$_2$*

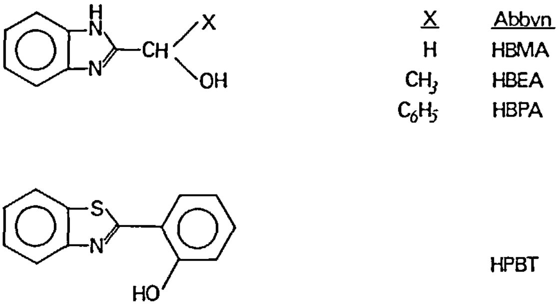
Four drops of triethylamine were added to a mixture of 100 mg of *trans*-$ReOCl_3(PPh_3)_2$ and 64 mg of the ligand HPBT in 15 cm$^3$ benzene. The reaction solution was heated under reflux for 30 min, during which time its colour changed to dark red-brown. After cooling to room temperature, the clear solution was filtered and left overnight to evaporate. The resultant green precipitate was filtered, washed with ethanol and diethylether, and dried under vacuum. The complex is moderately soluble in acetonitrile, chloroform, acetone and dichloromethane, and was recrystallized from $CH_2Cl_2$. The yield was 69%, based on Re; mp 141°C. Anal. Calcd. for $C_{26}H_{16}N_2O_3S_2ClRe$: C, 45.25; H, 2.34; N, 4.06; Cl, 5.14%. Found: C, 45.77; H, 2.62; N, 4.32; Cl, 5.29%. Infrared data (cm$^{-1}$): ν(Re=O) 955; ν(C–O) 1292; 1325; ν(Re–Cl) 328. $^1$H n.m.r. [$(CD_3)_2SO$]:δ6.75–8.23 (m, 16H, $C_6H_4$). Electronic spectrum (DMF) [$\lambda_{max}$, nm (ε $M^{-1}$ $cm^{-1}$]: 378 (960), 328 (4300), 290 (4200), 273 sh.

### *ReOCl(BPA)$_2$*

A mixture of 105 mg of *trans*-$ReOCl_3(PPh_3)_2$, 56 mg of the ligand HBPA and 4 drops of triethylamine in 20 cm$^3$ benzene was heated under reflux for 30 min. After cooling the reaction solution to room temperature, the dark green precipitate was removed by filtration, and it was washed with benzene, 2-propanol and diethylether. It was dried under vacuum. The complex is weakly soluble in ethanol, acetonitrile, chloroform and acetone, and insoluble in dichloromethane. It was recrystallized from $CH_3CN$. The yield was 68%, based on Re; mp 139°C. Anal. Calcd. for $C_{28}H_{22}N_4O_3ClRe$: C, 49.16; H, 3.24; N, 8.19; Cl, 5.18%. Found; C, 49.44; H, 3.06; N, 8.54; Cl, 5.32%. Infrared data (cm$^{-1}$): ν(Re=O) 951; ν(C–O) 1272; 1281; ν(Re–Cl) 317. $^1$H n.m.r. [$(CD_3)_2SO$]: δ6.00 (s, 1H, C$H$); 6.12 (s, 1H, C$H$); 7.18–7.77 (m, 18H, $C_6H_4$, $C_6H_5$). Electronic spectrum (DMF) [$\lambda_{max}$, nm (ε, $M^{-1}$ $cm^{-1}$)]: 410 (1200), 326 (2250), 282 sh, 273 (12000).

## RESULTS AND DISCUSSION

Complexes of the type $ReO(OEt)(L)_2$ and $ReOCl(L)_2$ are formed readily by the reaction of an excess of the ligands HL (HL = HBMA, HBEA, HBPA, HPBT; Figure 1) with *trans*-$ReOCl_3(PPh_3)_2$ in the presence of triethylamine in refluxing ethanol and benzene, respectively. These complexes are all green, and are non-electrolytes in DMF. They are not particularly soluble in common organic solvents; the best solubility is in DMF and DMSO. All complexes are stable in the solid state, but $ReO(OEt)(L)_2$ complexes decompose slowly in solution. This instability and their low solubility precluded their recrystallization, but they precipitated out of solution analytically pure. The characterization of the complexes was achieved on the basis of elemental analysis, infrared and $^1H$ n.m.r. spectra. (See Experimental section.)



| X | Abbvn |
|---|---|
| H | HBMA |
| $CH_3$ | HBEA |
| $C_6H_5$ | HBPA |

FIGURE 1 Ligands used in the study (HBMA = 2-benzimidazole-2′-ylmethanol; HBEA = 2-benzimidazole-2′-ylethanol; HPBT = 2-(2-hydroxyphenyl)benzothiazole; HBPA = 2-benzimidazole-2′-ylbenzylalcohol).

The infrared spectra show Re=O bond stretches in the 946–961 $cm^{-1}$ range, while the corresponding value in the starting complex *trans*-$ReOCl_3(PPh_3)_2$ is 968 $cm^{-1}$. These values are in agreement with those found for other six-coordinate rhenium(V) complexes. There are no peaks in the infrared spectrum which could be ascribed to ν(O–H) vibrations, and a band around 3200 $cm^{-1}$ is assigned to the ν(N–H) vibration [absent in $ReOX(PBT)_2$ (X = Cl, OEt)]. These data indicate that the ligands $L^-$ are coordinated to rhenium(V) through the deprotonated alcoholate/phenolate oxygen and the neutral imidazole imine nitrogen. A single peak around 318 $cm^{-1}$ in the far-infrared region of the $ReOCl(L)_2$ complexes is indicative of a ν(Re–Cl) vibration, with the chloride coordinated *cis* to the oxo oxygen. The $ReO(OEt)(L)_2$ complexes have no peaks in this region which could be ascribed to a Re–Cl bond stretch, but have a very strong peak around 910 $cm^{-1}$ which is assigned to the ethoxy deformation mode. Each of the complexes $ReOCl(L)_2$ and $ReO(OEt)(PBT)_2$ exhibits two peaks in the region 1260–1330 $cm^{-1}$, which are ascribed to ν(C–O) vibrations, and thereby indicating the presence of two molecules of the ligands $L^-$ in asymmetric positions in these complexes. On the other hand, the infrared spectra of the complexes $ReO(OEt)(L)_2(L \neq PBT)$ show only a single peak in the region 1260–1285 $cm^{-1}$, which is ascribed to ν(C–O) stretching vibrations of two $L^-$ ligands in symmetric positions.

$^1H$ n.m.r. spectra of all the $ReO(OEt)(L)_2$ complexes in $(CD_3)_2SO$ indicate the presence of a coordinated ethoxide, with a three proton triplet centred around δ1.20 ppm and a quartet in the region δ3.10–3.72 ppm due to the methylene protons of ethoxide. The spectrum of $ReO(OEt)(BMA)_2$ exhibits only one band at δ4.89 ppm attributable to the $CH_2$ protons of the two coordinated $BMA^-$ ligands, and thereby indicating that the two $BMA^-$ ligands are equivalent. The complex $ReO(OEt)(BEA)_2$ exhibits a single doublet at δ1.59 ppm and a single quartet at δ5.13 ppm attributable to the $CH_3$ and CH protons, respectively, of the two coordinated $BEA^-$ ligands, and thus indicating similar magnetic properties of these protons in the two bidentate chelates in the complex. Magnetic equivalence of the two $BPA^-$ ligands in the complex $ReO(OEt)(BPA)_2$ is confirmed by the appearance of a single singlet at δ6.23 ppm, attributable to two equivalent, non-aromatic CH protons of the two ligands.

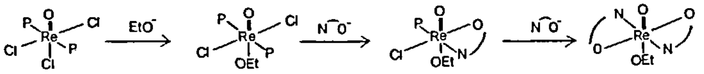
The appearance of two doublets at δ1.08 and 1.33 ppm in the $^1H$ n.m.r. spectrum of $ReOCl(BEA)_2$ in $(CD_3)_2SO$ is attributed to the $CH_3$ protons of two inequivalent $BEA^-$ ligands. Two singlets in the spectrum of $ReOCl(BMA)_2$ at δ5.03 and 5.10 ppm are ascribed to the $CH_2$ protons of two inequivalent $BMA^-$ ligands. The spectrum of $ReOCl(BPA)_2$ also exhibits two singlets for the nonaromatic CH proton at δ6.00 and 6.12 ppm, indicating different magnetic behaviour of this proton in the two coordinated $BPA^-$ ligands.

The proton n.m.r. spectra of the complexes $ReOX(PBT)_2$ ($X = OEt$, Cl) are too complex to accurately assign any signals or derive any conclusions about possible configurations. It would appear, however, that due to the complexity of the spectra and number of peaks in the aromatic region, the two benzimidazolylalcoholate ligands $PBT^-$ are not in the same plane of the octahedron in these two complexes.

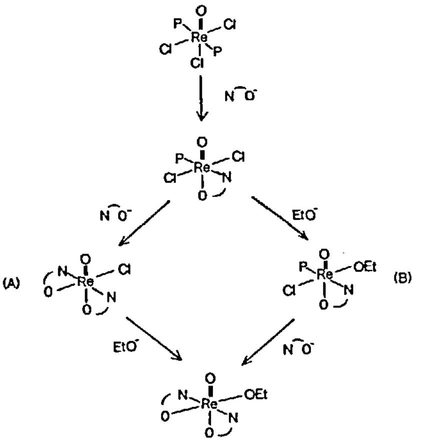
The solution electronic spectra of the complexes in DMF exhibit intense absorbances at *ca* 275 and 283 nm, with shoulders tailing into the visible region. The peak around 283 nm is ascribed to an intraligand $\pi \rightarrow \pi^*$ transition, with the high energy peak around 275 nm due to oxo oxygen-to-rhenium(V) charge transfer. The intensity of the additional peaks suggests that they are due to ligand-to-metal charge transfer. Due to the slow decomposition of the $ReO(OEt)(L)_2$ complexes in DMF solution, the extinction coefficients of their absorption peaks could not be determined accurately.

Information concerning the reaction mechanism of the formation of the complexes $ReO(OEt)(L)_2$ was obtained by carrying out the reaction of a twofold excess of the ligand HPBT and *trans*-$ReOCl_3(PPh_3)_2$ in the presence of triethylamine and a tenfold excess of triphenylphosphine in boiling ethanol. The excess $PPh_3$ did not affect the reaction, and the previously isolated product $ReO(OEt)(PBT)_2$ was obtained in good yield. On this basis, the first step in complex formation for $ReO(OEt)(L)_2$ must be the substitution of a labile chloride, probably the chloride *trans* to the Re=O bond in *trans*-$ReOCl_3(PPh_3)_2$, by a charged oxygen atom. This charged oxygen can be the deprotonated alcoholate/phenolate oxygen of the ligands HL, or the charged oxygen of ethoxide, which will both be present due to the presence of base triethylamine. The presence of the oxo oxygen and a charged oxygen, both hard bases, in the apical positions around the hard acid Re(V) will result in the weakening of the remaining Re–Cl and Re–$PPh_3$ bonds in the equatorial positions, and their substitution can then easily occur by the chelate ligand $L^-$ and/or $EtO^-$. From the above considerations, two different possible mechanisms can be postulated (Scheme 1), leading to two different products, with the ethoxide either in a position *trans* or *cis* to the oxo oxygen.

Spectroscopic evidence, however, supports the configuration of the products $ReO(OEt)(L)_2$ ($L \neq PBT$) with the ethoxide in the *trans* position and the charged alcoholate oxygen of the chelate ligands *cis* to the rhenyl oxo oxygen, and hence mechanism (a) in Scheme 1. This configuration is supported by the appearance of only one peak in the infrared spectra that can be ascribed to ν(C–O) vibrations, and thereby indicating that the two $L^-$ ligands ($L^- \neq PBT^-$) in the complexes are in symmetric positions. Further evidence for this configuration is provided by the proton n.m.r. results, which indicated the presence of the chelate ligands in magnetically equivalent positions in the complexes.



Mechanism A



Mechanism B

SCHEME 1 Possible mechanisms for complex formation.

The formation of this configuration (*i.e.* $EtO^-$ *trans* to the Re=O bond) can be rationalized in terms of the fact that the anionic oxygen donor atoms of the ligands $L^-$, due to the electron-withdrawing effect of the imidazole nitrogen atoms, will be weaker σ-donors than the oxygen atoms of the ethoxide. This, together with the higher activity of $EtO^-$, would lead to the displacement of the chloride *trans* to rhenyl oxo in *trans*-$ReOCl_3(PPh_3)_2$ by ethoxide. The anionic oxygen donor atom of the $L^-$ ligand then readily displaces an equatorial chloride, which is a weaker base. The benzimidazole oxygen atom will thus be *cis* to the Re=O bond, since the stronger σ donor strength of the ethoxide will not allow its displacement by the benzimidazole oxygen.

Although the n.m.r. results for $ReO(OEt)(PBT)_2$ were rather inconclusive regarding its configuration, the infrared data suggest that the two $PBT^-$ ligands are present in asymmetric positions in the complex, with the ethoxide coordinated *cis* and a charged phenolate oxygen coordinated *trans* to the oxo oxygen. It would thus appear that mechanism (b) in Scheme 1 is operative for the formation of $ReO(OEt)(PBT)_2$.

An excess of $PPh_3$ also has no influence on the formation of the complexes $ReOCl(L)_2$ in benzene, and we in fact found an increase in reaction yield in the presence of excess free $PPh_3$. Spectroscopic evidence supports the formation of the products $ReOCl(L)_2$ with the chloride *cis*, and an anionic oxygen donor atom of one of the two $L^-$ ligands *trans* to the rhenyl oxo oxygen. Evidence for this configuration is provided by the facts that two ν(C–O) vibrations and a relatively strong Re–Cl bond are implicated by the infrared data, as well as the proton n.m.r. spectra that indicate that the two $L^-$ ligands are in inequivalent positions in the $ReOCl(L)_2$ complexes. These data suggest that mechanism (b) in Scheme 1 is operative for the formation of $ReOCl(L)_2$ in benzene, with the configuration illustrated by product A.

We are of the opinion that the Re=O stretching frequency can be a valuable indicator in establishing the nature of the coordinating group *trans* to the rhenyl oxo group in distorted octahedral rhenium(V) complexes containing polydentate ligands. The ν(Re=O) stretch in complexes with a chloride in the *trans* position[10–12] occurs in the 970–990 $cm^{-1}$ range, while in complexes with a neutral solvent molecule in that position it occurs in the narrow range[13,14] 980–985 $cm^{-1}$. Complexes containing a charged phenolate oxygen in the *trans* position[2,4,15,16] have ν(Re=O) in the range 950–970 $cm^{-1}$. Although information on rhenium(V) complexes having an alkoxide in the *trans* position is scarce in the literature, it is to be expected that such complexes would display ν(Re=O) in a region slightly lower in frequency than in the case of a charged phenolate oxygen in that position. This lowering of the Re=O stretching frequency with a methoxide or ethoxide *trans* to the oxo group can be ascribed to the fact that better overlap will be obtained by the methoxide/ethoxide oxygen than by the phenolate oxygen due to the positive inductive effects of the methyl/ethyl groups of the alkoxides and the negative inductive effect of a phenyl group. Steric effects in polydentate chelate ligands may also decrease the extent of the overlap of the phenolate oxygen in Re–OR bond formation. The increased overlap of the methoxide/ethoxide oxygen with the bonding orbitals of rhenium(V) will lead to a weaker *trans* Re=O bond, and hence a decrease in its stretching frequency. This rationale is evident in the infrared data of the complexes prepared in this study, where complexes having an ethoxide *trans* to the oxo oxygen [*i.e.* $ReO(OEt)(L)_2$ ($L \neq PBT$)] show a slightly lower Re=O stretching frequency than complexes containing an anionic alcoholate/phenolate oxygen donor in this position (*i.e.* $ReOCl(L)_2$).

Complexes of general formula $ReOX(Rsal)_2$ (X = Cl or Br; RsalH = *N*-methyl- and *N*-phenylsalicylideneimine) and $ReOX(oxine)_2$ (oxineH = 8-hydroxyquinoline) were previously prepared by the reaction of *trans*-$ReOX_3(PPh_3)_2$ or *trans*-$ReOBr_2(OEt)(PPh_3)_2$ with the lithium salts of the Schiff base ligands or by adding triethylamine to the Schiff bases in the reaction mixture.[4] With the pure Schiff bases only the monosubstituted $ReOX_2(Rsal)(PPh_3)$ species could be isolated.[4] Crystal structure determinations[5,6] of these complexes indicate that the phenolate oxygen donor atom of the $Rsal^-$ ligand is coordinated *trans* to the Re=O bond, in accord with the well-established tendency of oxygen donor atoms in bidentate ligands to coordinate at this site.[17] The complex $TcOCl(PBT)_2$ has also been isolated previously, and a crystal structure determination indicated that the coordination of the $PBT^-$ ligands occurs through the phenolate oxygen atoms and the nitrogen atoms of the benzothiazole rings, and that one of the phenolate oxygen atoms is coordinated *trans* to Tc=O.[18]

Not all rhenium(V) complexes containing ligands with a negatively charged oxygen donor atom have the *trans* O=$\mathrm{Re^V}$–OR arrangement. In ReOCl(X)(L) [X = MeOH or EtOH, L = *N*-(2-sulphidophenylsalicylideneiminato)] the phenolic oxygen of the tridentate N,O,S-donor ligand L is coordinated *cis* to the rhenyl oxo group, with the solvent molecule bound to the rhenium in the *trans* position.[14]

Recent studies on the reaction of $[\mathrm{MOCl_4}]^-$ (M = Re or Tc) with terdentate N,N,O-donor Schiff bases, HL, in dichloromethane led to the isolation of the neutral complexes, $\mathrm{MOCl_2(L)}$ [L = 1-(8′-quinolyl)salicylideneiminate, *N*-8′-quinolyl)salicylideneiminate, 3-methoxy-*N*-(8′-quinolyl)salicylideneiminate, *N*-(2′-dimethylaminoethyl)salicylideneiminate]. Although only one of the $\mathrm{TcOCl_2L}$ complexes was studied in detail, a crystal structure determination indicated that the charged phenolate oxygen is coordinated *cis* and the imino nitrogen *trans* to the oxo group.[19] Infrared and $^1$H n.m.r. data indicate that the analogous rhenium complexes have the same configuration.[19] The dissolution of the complexes $\mathrm{MOCl_2(L)}$ in alcohols (ROH) leads to the formation of the species $[\mathrm{MOCl_2(OR)(L)}]^-$, with $\mathrm{L^-}$ now acting as a bidentate chelate ligand,[19] and with the alcoholate oxygen being coordinated *cis* to the oxo oxygen atom. The affinity for rhenium(V) to have the *trans* O = Re–OR arrangement in its complexes is illustrated by the complex $[\mathrm{ReO(OMe)\{2\text{-}NC_4H_3CH = N(CH_2)_3NMe(CH_2)_3N = CHC_4H_3NH\text{-}2\}}]$, where the tetradentate lacks an anionic oxygen donor atom.[16] Only *mer* sites are occupied by the neutral and anionic nitrogen donor atoms of the chelate ligand, with the methoxide completing six-coordination by occupying the site *trans* to the rhenyl oxo oxygen.

Our study, as a whole, seems consistent with the principle of HSAB[20] as already applied to rhenium(V) complexes.[5] This principle has the effect that the affinity of donor atoms to occupy the coordination site *trans* to the rhenyl oxo group in six-coordinate rhenium(V) complexes will be in the order $\mathrm{O^-} > \mathrm{Cl^-} > \mathrm{N} > \mathrm{P}$, which is also the order of decreasing hardness of the donor atoms as bases. Since the anionic oxygen donor in $\mathrm{CH_3CH_2O^-}$ is a harder base than the oxygen in $\mathrm{L^-}$ ($\mathrm{L^-} \neq \mathrm{PBT^-}$), it follows that the hard Re=O group would show a higher affinity towards the hardest $\mathrm{RO^-}$ species in the complexes $\mathrm{ReO(OEt)(L)_2}$. Thus the ethoxide group lies *trans* to the rhenyl oxo oxygen.

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