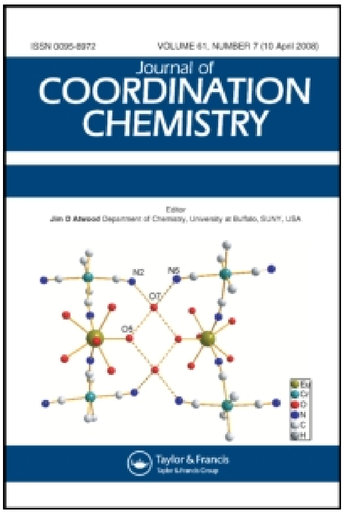


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis of Oxorhenium(V) Complexes of Heterocyclic-N,O and -N,S Ligands

J. G. H. Du Preez[a]; T. I. A. Gerber[a]; H. J. Kemp[a]; B. J. A. M. Van Brecht[a]
[a] Chemistry Department, University of Port Elizabeth, Port Elizabeth, South Africa

To cite this Article Preez, J. G. H. Du , Gerber, T. I. A. , Kemp, H. J. and Van Brecht, B. J. A. M.(1991) 'Synthesis of Oxorhenium(V) Complexes of Heterocyclic-N,O and -N,S Ligands', Journal of Coordination Chemistry, 24: 2, 159 — 168
To link to this Article: DOI: 10.1080/00958979109409458
URL: http://dx.doi.org/10.1080/00958979109409458

J. Coord. Chem. 1991, Vol. 24, pp. 159-168
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF OXORHENIUM(V) COMPLEXES OF HETEROCYCLIC-N,O AND -N,S LIGANDS

J. G. H. DU PREEZ, T. I. A. GERBER,* H. J. KEMP and
B. J. A. M. VAN BRECHT

Chemistry Department, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, 6000, South Africa

(Received November 16, 1990)

The complex *trans*-$ReOCl_3(PPh_3)_2$ reacts with potentially bidentate N,O- and N,S-donor benzimidazolylalcohols and benzimidazolylthiols (HL) in ethanol to produce the compounds $ReOCl_2(L)(PPh_3)$ or $ReOCl(OEt)(L)(PPh_3)$, depending on the reaction conditions. The complexes were characterized by elemental analysis, NMR, vibrational and optical spectroscopy. Mechanisms for the formation reactions and probable configurations of the products are proposed, and these are supported by qualitative studies and spectroscopy.

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

INTRODUCTION

The chemistry of oxorhenium(V) complexes has attracted increasing interest in recent years because of the attractive nuclear properties of the ^{186}Re and ^{188}Re isotopes, which make them useful as potential radiotherapeutic agents against cancer.[1] These two isotopes are strong β-emitters (2.12 and 1.07 MeV respectively), and radiopharmaceuticals based on these isotopes have been used for the treatment of malignant tumours of the kidney, liver, stomach, and organs of the pelvic cavity.[1]

Additional interest in the inorganic chemistry of rhenium centred on the similarity of its chemical behaviour to that of technetium,[2] its second row congener, which has found major applications in the field of diagnostic nuclear medicine.[3] It was envisaged that synthetic routes tested with rhenium may be applied for analogous preparations of ^{99m}Tc radiopharmaceuticals.

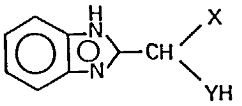
In the course of a systematic study of the nature of rhenium(V) and technetium(V) complexes with nitrogen heterocycles as ligands, we now report several new oxorhenium(V) complexes having heterocyclic N,O and -N,S donor benzimidazolylalcoholates and benzimidazolylthiols as ligands (Figure 1).

EXPERIMENTAL

The compound *trans*-$ReOCl_3(PPh_3)_2$ was prepared from ammonium perrhenate (Aldrich) according to literature procedures.[4] The benzimidazolylalcoholate and -thiolate ligands were prepared as reported,[5] and their purity was checked by microanalyses and melting points. All solvents used were purified and dried by standard methods.

---

* Author for correspondence.



X	Y	Abbvn
H	O	HBMA
CH_3	O	HBEA
C_6H_5	O	HBPA
H	S	HBMT
CH_3	S	HBET

FIGURE 1 Ligands used in the study: HBMA = benzimidazole-2'-ylmethanol; HBEA = 2-benzimidazole-2'-ylethanol; HBPA = 2-benzimidazole-2-ylbenzylalcohol; HBMT = benzimidazole-2-ylmethanethiol; HBET = 2-benzimidazole-2'-ylethanethiol.

Infrared spectra were recorded on Shimadzu FTIR-4100 and Beckman IR 4250 grating spectrophotometers in the range 4000–250 cm^{-1} in KBr pellets. Optical spectra were obtained with Shimadzu UV-3100 and Perkin-Elmer 330 spectrophotometers. Conductivity measurements were performed in acetonitrile using a Metrohm E518 conductometer. Elemental analyses were performed using a Heraeus Rapid Analyser. Chloride was determined by potentiometric titrations with standard silver nitrate solution of solutions of the compounds decomposed by the Shoeniger method. Melting points were determined in capillaries using a Gallenkamp apparatus, and are uncorrected.

Materials

$ReOCl_2(BMA)(PPh_3)$

A solution of 100 mg of $ReOCl_3(PPh_3)_2$ in 10 cm^3 ethanol was added to 53 mg (358 μmol) of the ligand HBMA in 5 cm^3 ethanol. After heating under reflux conditions for 45 min, the solution was cooled to room temperature, and a light blue precipitate was removed by filtration. The material was washed with ethanol, benzene and acetone, and dried under vacuum at 50°C. The yield was 64%, based on Re; mp 221°C. It is soluble in polar organic solvents and is a non-electrolyte in acetonitrile. Anal.: Calcd. for $C_{26}H_{22}N_2O_2Cl_2PRe$: C, 45.75; H, 3.25; N, 4.10; Cl, 10.39%. Found: C, 45.93; H, 3.39; N, 3.61; Cl, 10.12%.

$ReOCl_2(BEA)(PPh_3)$

To a solution of 100 mg of $ReOCl_3(PPh_3)_2$ in 10 cm^3 of ethanol was added 60 mg (370 μmol) of HBEA in 5 cm^3 ethanol. This mixture was heated under reflux conditions and within 20 min a light blue precipitate started to form. After heating for 1 hour, the solution was cooled to room temperature, and the precipitate was removed by filtration. It was washed with ethanol, benzene and acetone, and dried under vacuum. The yield was 82%, based on Re; mp 215°C. Anal.: Calcd. for $C_{27}H_{24}N_2O_2Cl_2PRe$: C, 46.57; H, 3.47; N, 4.02; Cl, 10.18%. Found: C, 46.44; H, 3.26; N, 4.36; Cl, 10.20%.

ReOCl$_2$(BPA)(PPh$_3$)

A mixture of 100 mg of ReOCl$_3$(PPh$_3$)$_2$ in 10 cm^3 of ethanol and 81 mg (360 μmol) of HBPA in 5 cm^3 ethanol was heated under reflux conditions for 30 min. During this ime the yellow-green solution assumed a blue colour, and a light blue precipitate was ormed. This material was filtered off after cooling to room temperature, and was washed with ethanol, benzene and acetone. It was recrystallized from CH$_2$Cl$_2$/EtOH. The yield was 73%, based on Re; mp 210°C. Anal.: Calcd. for C$_{32}$H$_{26}$N$_2$O$_2$Cl$_2$PRe: C, 50.66; H, 3.45; N, 3.69; Cl, 9.35%. Found: C, 50.71; H, 3.60; N, 3.69; Cl, 9.01%.

ReOCl(OEt)(BMA)(PPh$_3$)

To a solution of 100 mg (120 μmol) of *trans*-ReOCl$_3$(PPh$_3$)$_2$ in 10 cm^3 of ethanol was added 18 mg (120 μmol) of HBMA in 5 cm^3 ethanol. The mixture was heated under reflux conditions, and within 15 min a turquoise blue precipitate started to form. After heating was continued for 30 min, the solution was cooled to room temperature, and the precipitate was collected by filtration. It was washed with ethanol, benzene and acetone, and dried under vacuum to give a fine, light green precipitate. The yield was 52%, based on Re; mp 188°C. Anal.: Calcd. for C$_{28}$H$_{27}$N$_2$O$_3$ClPRe: C, 48.59; H, 3.93; N, 4.05; Cl, 5.12%. Found: C, 48.58; H, 3.56; N, 3.81; Cl, 5.09%.

ReOCl$_2$(BMT)(PPh$_3$)

A mixture of 100 mg of ReOCl$_3$(PPh$_3$)$_2$ in 10 cm^3 of ethanol and 59 mg (360 μmol) of HBMT in 5 cm^3 ethanol was heated under reflux conditions for 40 min. After cooling the solution to room temperature, the dark pink precipitate was collected by filtration, washed with ethanol, benzene and acetone, and dried under vacuum. The yield was 78%, based on Re; mp 201°C. Anal.: Calcd. for C$_{26}$H$_{22}$N$_2$OSCl$_2$PRe: C, 44.70; H, 3.17; N, 4.01; Cl, 10.15%. Found: C, 44.76; H, 3.03; N, 4.00; Cl, 10.02%.

ReOCl(OEt)(BMT)(PPh$_3$)

A mixture of 100 mg of ReOCl$_3$(PPh$_3$)$_2$ in 10 cm^3 of ethanol and 20 mg (122 μmol) of HBMT in 5 cm^3 ethanol was heated for 1 h under reflux conditions. After cooling the solution to room temperature, the solution was filtered to give a pink material, which was washed with ethanol, benzene and acetone, and dried under vacuum. The yield was 66%, based on Re; mp 189°C. Anal.: Calcd. for C$_{28}$H$_{27}$N$_2$O$_2$SClPRe: C, 47.49; H, 3.84; N, 3.96; Cl, 5.01%. Found: C, 47.21; H, 3.70; N, 4.00; Cl, 5.29%.

ReOCl$_2$(BET)(PPh$_3$)

To a suspension of 100 mg of ReOCl$_3$(PPh$_3$)$_2$ in 5 cm^3 of ethanol was added a solution of 64 mg (360 μmol) of HBET in 5 cm^3 ethanol. The mixture was heated under reflux conditions for 30 min, and after cooling to room temperature a small crop of mauve coloured precipitate was collected by filtration. It was washed with ethanol, benzene and acetone, and dried. No recrystallization was necessary to obtain a pure sample. Efforts to improve the yield by the manipulation of the mother liquor led to the isolation of impure product. The yield of pure product was 48%; mp 94°C. Anal.: Calcd. for C$_{27}$H$_{24}$N$_2$OSCl$_2$PRe: C, 45.51; H, 3.40; N, 3.93; Cl, 9.95%. Found: C, 45.32; H, 3.33; N, 3.73; Cl, 10.32%.

RESULTS AND DISCUSSION

Complexes with Benzimidazolylalcohols

The complex *trans*-$ReOCl_3(PPh_3)_2$ reacts in refluxing ethanol with a threefold excess of the substituted benzimidazole-N,O donor ligands HBMA, HBEA and HBPA (HL; Figure 1) to give compounds of general formula $ReOCl_2(L)(PPh_3)$. These complexes are all light blue in colour and are non-electrolytes in acetonitrile. They are soluble in CH_3CN, $CHCl_3$, acetone, THF, DMF, and CH_2Cl_2, and insoluble in benzene, diethyl ether, alcohol and *n*-pentane. The formation of these products is independent of the molar ratios of starting materials, and the same products were isolated even with a tenfold excess of the ligands LH and after prolonged heating (4 hours). It was thus impossible to isolate products of general formula $ReOClL_2$ from the simple addition and heating of the starting materials.

The reaction of equimolar quantities of *trans*-$ReOCl_3(PPh_3)_2$ with the ligand HMBA in refluxing ethanol led to the isolation of ReOCl(OEt)(BMA)(PPh_3) in 52% yield. It is light green in colour, and is only slightly soluble in CH_3CN, $CHCl_3$, acetone and CH_2Cl_2, and insoluble in benzene, ether, and alcohol. Efforts to synthesize similar compounds with the ligands HBEA and HBPA by using equimolar quantities of starting materials in refluxing ethanol were unsuccessful, and led to the isolation of impure products.

The most important infrared frequencies (in the solid state) for the complexes prepared in this study are given in Table I. The band due to the Re=O bond stretch was found in the range 953–965 cm^{-1}, 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 six-coordinate rhenium(V) complexes. There are no peaks in the infrared spectrum which could be ascribed to ν(O–H) vibrations. A band around 3200 cm^{-1} in the complexes is ascribed to the ν(N–H) vibration. These infrared data indicate that the ligands are coordinated to the rhenium through the deprotonated alcoholic oxygen and the neutral imidazole imine nitrogen atoms.

The complexes $ReOCl_2(L)(PPh_3)$ (L = BMA, BEA, BPA) have only one peak in the infrared spectrum, around 330 cm^{-1}, which can be ascribed with certainty to the ν(Re–Cl) vibration. The Re–Cl stretch in ReOCl(OEt)(BMA)(PPh_3) appears at 326 cm^{-1}, and a very strong band at 909 cm^{-1} is assigned to the ethoxy deformation mode.

TABLE I
Principal IR bands (cm^{-1}) of the complexes.*

Complex	ν(Re=O)	ν(N–H)	ν(Re–Cl)	ν(P–C)
$ReOCl_2$(BMA)(PPh_3)	964	3220	324	1097
$ReOCl_2$(BEA)(PPh_3)	963	3230	328	1096
$ReOCl_2$(BPA)(PPh_3)	953	3180	331	1096
ReOCl(OEt)(BMA)(PPh_3)	965	3240	326	1097
$ReOCl_2$(BMT)(PPh_3)	980	3250	328, 289	1094
$ReOCl_2$(BET)(PPh_3)	985	3245	328, 282	1090
ReOCl(OEt)(BMT)(PPh_3)	970	3250	324	1093

* In KBr disc.

^1H n.m.r. measurements in $CDCl_3$ solution showed that all the complexes are diamagnetic, a fact which is in agreement with previous observations of oxorhenium(V) species, and indicating some distortion from the octahedral configuration.[6] The ^1H n.m.r. spectrum of $ReOCl(OEt)(BMA)(PPh_3)$ exhibits a three proton triplet centred at 1.25 ppm due to the methyl group of the coordinated ethoxide, and a quartet at 3.73 ppm due to the methylene protons of the ethoxide.

The solution electronic spectra of the complexes $ReOCl_2(L)(PPh_3)$ (Table II) exhibit intense absorbances at *ca* 275 and 283 nm, with shoulders tailing into the visible region around 300 and 405 nm. 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 two additional peaks suggests that they are due to ligand-to-metal charge transfer.

TABLE II
Electronic absorption data for the complexes in DMF solution.

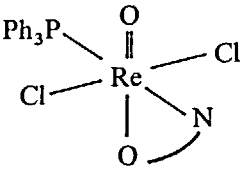
Complex	λ_{max}/nm (ε/M^{-1} cm^{-1})
$ReOCl_2(BMA)(PPh_3)$	404(1360), 301(2000), 282(14000), 276(15400), 271sh
$ReOCl_2(BEA)(PPh_3)$	410(1240), 305sh, 283(15100), 276(19600), 268sh
$ReOCl_2(BPA)(PPh_3)$	419(550), 304(2600), 281sh, 273(14300), 267sh
$ReOCl(OEt)(BMA)(PPh_3)$	400(2100), 305(2900), 283sh, 275(18700)
$ReOCl_2(BMT)(PPh_3)$	476(450), 346(5700), 285sh, 266(19200), 262sh
$ReOCl_2(BET)(PPh_3)$	474(500), 344(5200), 282sh, 266(21200), 262sh
$ReOCl(OEt)(BMT)(PPh_3)$	476(530), 349(3200), 285sh, 266(20400), 262sh

Complexes of general formula $ReOX_2(Rsal)(PPh_3)$ (X = Cl, Br; RsalH = bidentate N,O donor Schiff base ligand) were previously prepared by the reaction of *trans*-$ReOX_3(PPh_3)_2$ with the ligands RsalH.[7] It was found that in all these compounds the oxygen donor atom of the $Rsal^-$ ligand is coordinated in a position *trans* to the Re=O bond,[8,9] which is in accord with the well-established tendency of oxygen donor atoms in polydentate ligands to coordinate at this site.[10,11] The complex $ReOCl_2(Mesal)(PPh_3)$ (Mesal = *N*-methylsalicylideneamino) was isolated in both the *cis* and *trans* forms, which differ in the arrangement of the two chlorine atoms in the equatorial plane, but which are identical as far as the *trans* O–Re=O_{oxo} positions of the two oxygens on the axial vector are concerned.[12]

It has been shown in the reaction of acetylacetone with *trans*-$ReOCl_3(PPh_3)_2$ or *trans*-$ReOCl_2(OEt)(PPh_3)_2$, that the group *trans* to the oxo group is very susceptible to attack, and that initial attack would involve the replacement of the group *trans* to the oxo-oxygen.[13] Information concerning the reaction mechanism was obtained by carrying out the reaction of a twofold excess of the ligand HBMA and $ReOCl_3(PPh_3)_2$ in refluxing ethanol in the presence of a tenfold excess of triphenylphosphine. No reaction was observed, and only the starting complex was recovered. On this basis, the first step in complex formation of $ReOCl_2(L)(PPh_3)$ is probably the substitution of a PPh_3 group by the ligand LH, which will coordinate to the rhenium(V) centre *via* the benzimidazole nitrogen atom. To account for this step, it is necessary to refer to the harder basic character of the imidazole imine nitrogen atom in comparison with the softer PPh_3 base. This means that the interaction between the harder Re(V) acid and the imine nitrogen is stronger than with PPh_3,[14] and hence favours this substitution step. Substitution of a PPh_3 ligand by a nitrogen atom has already been observed using Schiff base ligands. The complex $[ReOCl_3(PPh_3)(Hsal)]$ (Hsal = *N*-methylsalicylideneimine) has the Schiff base coordinated as a unidentate ligand through the aldimine nitrogen.[15]

The intermediate product that is thus formed by the substitution of PPh_3 by the imidazole imine nitrogen then gives the final product $ReOCl(X)(L)(PPh_3)$ by chelation, where the alcoholic oxygen of the ligand substitutes the more reactive chloride, probably the chloride *trans* to the Re=O bond, followed by deprotonation of the oxygen. No evidence could be found for the possible alternative mechanism of substitution starting with a prior attack of the protonated alcoholic oxygen and subsequent elimination of HCl, thereby indicating that OH is a weaker base than the imidazole imine nitrogen.

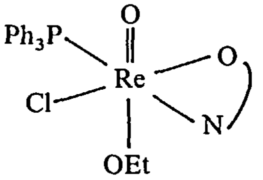
A consideration of all the above circumstantial data for the complexes $ReOCl_2(L)(PPh_3)$ suggests the following possible configuration.



The production of $ReOCl(OEt)(BMA)(PPh_3)$ from the reaction of equimolar quantities of *trans*-$ReOCl_3(PPh_3)_2$ and the ligand HBMA in refluxing ethanol was rather surprising. The Re–Cl stretch at 326 cm^{-1} in the infrared spectrum indicates that the chlorine atom is coordinated in a *cis* position to the oxo oxygen. Previous results also indicate that the imidazole nitrogen and PPh_3 molecule will coordinate in *cis* positions to the oxo oxygen, and the question arises as to which atom (the ethoxide oxygen or the alcoholic oxygen of the ligand BMA^-) coordinates in the position *trans* to the Re=O bond.

There is no direct evidence which can be used to assign the coordinating atom in the position *trans* to the Re=O bond. Our rationale is that, due to the low activity of the ligand HBMA relative to the activity of ethanol, the driving force of the reaction of the HBMA ligand with *trans*-$ReOCl_3(PPh_3)_2$ would be low. The complex intermediate *trans*-$ReOCl_2(OEt)(PPh_3)_2$ would then form, and which will then react with HBMA to form the isolated product $ReOCl(OEt)(BMA)(PPh_3)$. The electron-withdrawing effect of the imidazole nitrogen atoms will make the benzimidazole hydroxyl group more acidic than the corresponding group in ethanol. The positive inductive effect of the ethyl group in ethanol results in the poor acidity of ethanol. The delocalization of electron density from the benzimidazole imine nitrogen to the rhenium atom upon coordination further enhances the acidic properties of the benzimidazole hydroxyl. However, the increase in acidic property is accompanied by a simultaneous decrease in σ donor strength. We therefore propose that the ethoxide will cooordinate *trans* to the Re=O bond in the complex $ReOCl(OEt)(BMA)(PPh_3)$.

The oxygen of the BMA$^-$ ligand readily displaces an equatorial chloride, which is a weaker base than the oxygen donor atom of the BMA$^-$ ligand. The benzimidazole oxygen atom will thus be in a *cis* position with respect to the Re=O bond, since the stronger σ donor strength of the ethoxide will not allow its displacement by the benzimidazole oxygen. We therefore propose the following configuration for the complex ReOCl(OEt)(BMA)(PPh_3).



Previous work has shown that $ReOCl_4^-$ reacts with the potentially terdentate N,O,S-donor ligand *N*-(2-sulphidophenylsalicylideneimine) (H_2L') in methanol or ethanol to form complexes of the general formula ReOCl(X)(L′) (X = MeOH or EtOH).[16] In these two complexes the phenolic oxygen is coordinated in a position *cis* to the oxo oxygen, with the solvent molecule bound *trans* to the Re=O bond. The five-coordinate compound ReOCl(L′) also reacts with methanol or ethanol to yield a six-coordinate complex with a molecule of solvent *trans* to the oxo oxygen.[16] It was also found[16] that the reaction of $ReOCl_4^-$ with H_2L' in acetone, acetonitrile or dichloromethane leads to the formation of $ReOCl_2(L')$. In this compound, the phenolic oxygen is not coordinated *trans* to the Re=O bond. The latter position is occupied by chlorine, which can easily be displaced by alcohols.

Complexes with benzimidazolylthiols

The reaction of an excess of the potentially bidentate N,S-donor benzimidazolylthiol ligands HBMT and HBET with *trans*-$ReOCl_3(PPh_3)_2$ in ethanol forms the monosubstituted $ReOCl_2(L)(PPh_3)$ complexes (L = BMT, BET) in good yields. The formulation of these complexes was supported by elemental analyses. They are stable in the solid state, but are not indefinitely stable in solution. Their solubilities are very similar, and they are moderately soluble in chloroform, DMF and acetone, slightly soluble in acetonitrile and dichloromethane, and insoluble in ether, alcohol, benzene and hydrocarbons. They are diamagnetic and their non-conductivity in acetonitrile indicates their non-ionic character.

Reaction of the ligand HBMT with *trans*-$ReOCl_3(PPh_3)_2$ in equimolar quantities in refluxing ethanol led to the isolation of the pink complex ReOCl(OEt)-(BMT)(PPh_3). This compound is slightly soluble in benzene, dichloromethane, DMF and chloroform, and insoluble in acetonitrile, acetone, alcohol, and hydrocarbons. It is stable both in the solid state and in solution. Conductivity measurements in DMF indicate that it is a non-conductor. The corresponding reaction with the ligand HBET does occur, but no pure products could be isolated.

The infrared band due to the Re=O stretch in the two complexes $ReOCl_2(L)(PPh_3)$ (L = BMT, BET) was found in the 980–985 cm^{-1} range, and which differs significantly from the corresponding band in the starting complex. This increase in ν(Re=O) was also observed in analogous six-coordinate dithiocarbamate complexes[17] and in the compound $ReOCl_2(PPh_3)$ {p-MeC_6H_4N=C(OEt)-S}.[18] The ν(Re=O) stretch in the complex ReOCl(OEt)(BMT)(PPh_3) appears at 970 cm^{-1}.

There are no peaks in the spectrum which could be ascribed to ν(S–H) vibrations, and a band around 3200 cm^{-1} is due to the ν(N–H) vibration. The far-infrared stretching frequencies of the two $ReOCl_2(L)(PPh_3)$ complexes show two ν(Re–Cl) bands, one at 328 cm^{-1} and the other in the range 280–290 cm^{-1}. The compound ReOCl(OEt)(BMT)(PPh_3) has a single band at 324 cm^{-1}.

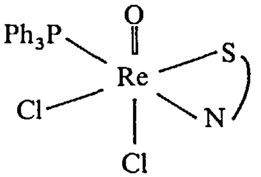
The ^1H n.m.r. spectrum of ReOCl(OEt)(BMT)(PPh_3) in $CDCl_3$ solution indicates a three proton triplet centred at 1.25 ppm, and a quartet at 3.72 ppm, due to the methyl and methylene protons of the ethoxide, respectively.

The electronic absorption spectra of these complexes exhibit an intense absorbance at 266 nm, with shoulders tailing into the visible region around 350 and 476 nm. The high energy peak at 266 nm is ascribed to the oxo oxygen-to-rhenium(V) charge transfer transition. Peaks in the range 320–380 nm have previously been found for complexes containing a thiolic sulphur as donor atom,[16] and we assign the peak around 350 nm to a sulphur-to-rhenium(V) charge transfer.

The presence of an excess of PPh_3 has no effect on the reaction of a threefold excess of ligands HBMT and HBET with *trans*-$ReOCl_3(PPh_3)_2$ in ethanol, and in each case the complexes $ReOCl_2(L)(PPh_3)$ were isolated. We in fact found that the yield of product increases when the reactions are carried out in the presence of excess free PPh_3. It is thus obvious that a different mechanism is operative for the reaction of the benzimidazolylthiols with *trans*-$ReOCl_3(PPh_3)_2$ than for the benzimidazolylalcohols. Since the thiols will be stronger acids than the alcohols, the activity of the deprotonated form of the N,S-donor ligands will be higher than for the N,O-donor ligands. On these grounds, the first step in the formation of the complexes $ReOCl_2(L)(PPh_3)$ (L = BMT, BET) will be nucleophilic attack of the deprotonated thiolic sulphur. This can occur to form a seven-coordinate intermediate, which can then rearrange by chelation with the loss of a chloride and a phosphine to give the product $ReOCl_2(L)(PPh_3)$. Heptacoordination has been found to be fairly common for rhenium.[19,20]

The possibility that the initial step in the mechanism may be the substitution of the most reactive chlorine, lying *trans* to the Re=O bond, by the deprotonated thiolic sulphur also seems plausible. In our opinion this mechanism seems unlikely, since it would result in the charged sulphur atom being in the *trans* position to the oxo oxygen in the product, which has never been found before. Structural studies of the complex $ReOCl_2(PPh_3)$(*p*-$MeC_6H_4N{=}C(OEt){-}S$)[18] showed that the bidentate chelate ligand coordinates in the equatorial plane with a Cl atom in the apical position *trans* to the Re=O bond. This situation is in contrast with the analogous bidentate N,O-donor Schiff base complexes, where the charged donor atom is always found *trans* to the Re=O bond.[8,9] This difference can be explained by the *trans* effect that is caused by the Re=O bond, and which increases according to the *trans* ligand in the order $RO^- < Cl^- < RN < RS^-$, in agreement with the hard acid character of Re(V).[21]

All the above data support the following configuration for the complexes $ReOCl_2(L)(PPh_3)$ (L = N,S^--donor ligand).



The isolation of the complex ReOCl(OEt)(BMT)(PPh$_3$) by heating the isolated omplex ReOCl$_2$(BMT)(PPh$_3$) in EtOH under reflux conditions or by the reaction of *ans*-ReOCl$_3$(PPh$_3$)$_2$ and HBMT at equimolar ratios in ethanol, indicates the lative ease with which the reactive chloride *trans* to the oxo oxygen can be isplaced, and supports the above configuration for the complexes containing the ,S$^-$-donor ligands.

In the complex [ReO(OMe){2-NC$_4$H$_3$CH=N(CH$_2$)$_3$NMe(CH$_2$)$_3$N=CHC$_4$H$_3$-H-2}], where the tetradentate ligand lacks an anionic oxygen donor atom, only *mer* ites are occupied by the neutral and anionic nitrogen donor atoms of the chelate gand.[10] The methoxide ligand completes six-coordination by occupying the site *ans* to the rhenyl oxo group.

Our study, considered as a whole, seems consistent with the principle of HSAB[14] s already applied to rhenium(V) complexes.[21] It is clear that the repulsion exerted y the oxo oxygen group on the equatorial ligands increases in the order P < N(imio < S$^-$ < Cl$^-$ < O$^-$, an order which corresponds to that of increasing hardness of he ligand as a base. The increasing hardness of the base leads to increasing ionic haracter of its bond with the hard acid rhenium(V), with the result that the harder asic ligands gain steric bulk as a consequence of the higher population of their rbitals. This effect will mean that the affinity of the above groups to occupy the oordination site *trans* to the oxo group in six-coordinate rhenium(V) complexes will e in the order O$^-$ > Cl$^-$ > S$^-$ > N > P. This and other studies[7,10,11,16] show once gain that in efforts to achieve particular configurational arrangements for the inding of facultative ligands to the ReO^{3+} function, the selection of the donor atom ype appears to be crucial.

CKNOWLEDGEMENTS

he authors wish to thank the Medical Research Council of South Africa, the oundation for Research Development and the University of Port Elizabeth for inancial support.

EFERENCES

1. E. Deutsch, K. Libson and J-L. Vanderheyden, "Technetium and Rhenium in Chemistry and Nuclear Medicine", M. Nicolini, G. Bandoli and U. Mazzi, Eds., (Cortina International, Verona, Italy, 1989), 3, 13 (1989); A.R. Fritzberg, J-L. Vanderheyden, A.C. Morgan, R.W. Schroff and P.G. Abrams, *ibid*, 3, 615 (1989); J-L. Vanderheyden, T.N. Rao, S. Kasina, D. Wester, F-M. Su and A.R. Fritzberg, *ibid*, 3, 623 (1989); G.J. Ehrhardt, A.R. Ketring, T.A. Turpin, M-S. Razavi, J-L. Vanderheyden, F-M. Su and A.R. Fritzberg, *ibid.*, 3, 631 (1989); H.R. Maxon III, L.E. Schroder, S.R. Thomas, V.S. Hertzberg, E. Deutsch, R.C. Samaratunga, K. Libson, C.C. Williams, J.S. Moulton and H.J. Schneider, *ibid.*, 3, 733 (1989).
2. R. Rossi, A. Marchi, L. Magon, A. Duatti, U. Casellato and R. Graziani, *Inorg. Chim. Acta*, **160**, 23 (1989); F. Tisato, F. Refosco, U. Mazzi, G. Bandoli and M. Nicolini, *ibid.*, **157**, 227 (1989); F. Tisato, F. Refosco, U. Mazzi, G. Bandoli and A. Dolmella, *ibid.*, **164**, 127 (1989); F. Tisato, F. Refosco, U. Mazzi, G. Bandoli and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 1693 (1987); J.-L. Vanderheyden, M. Heeg and E. Deutsch, *Inorg. Chem.*, **24**, 1666 (1985).
3. B.L. Holman, A.G. Jones, J. Lister-James, A. Davison, M.J. Abrams, J.M. Kirschenbaum, S.S. Timeh and R.J. English, *J. Nucl. Med.*, **25**, 1350 (1984); P.J. Ell, J.M.L. Hocknell, P.H. Jarrit, I. Cullum, D. Lui, D. Campos-Costa, D.P. Nowotnik, R.D. Pickett, L.R. Canning and R.D. Neirinckx, *Nucl. Med. Commun.*, **6**, 437 (1985).
4. N.P. Johnson, C.J.L. Lock and G. Wilkinson, *Inorganic Syntheses*, **9**, 145 (1967); J. Chatt and G. A. Rowe, *J. Chem. Soc. A*, 4019 (1962).

5. M.A. Phillips, *J. Chem. Soc.*, 2393 (1928).
6. J. Chatt, J.D. Garforth, N.P. Johnson and G.A. Rowe, *J. Chem. Soc.*, 1012 (1964).
7. U. Mazzi, E. Roncari, R. Rossi, V. Bertolasi, O. Traverso and L. Magon, *Transition Met. Chem.*, **5**, 289 (1980).
8. M. Sacerdoti, V. Bertolasi, G. Gilli and A. Duatti, *Acta Cryst.*, **C40**, 968 (1984).
9. V. Bertolasi, M. Sacerdoti, G. Gili and U. Mazzi, *Acta Cryst.*, **B38**, 426 (1982).
10. H.J. Banbery, W. Hussain, T.A. Homer, C.J. Jones and J.A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 657 (1990).
11. U. Mazzi, F. Refosco, F. Tisato, G. Bandoli and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 1623 (1986).
12. V. Bertolasi, V. Ferretti, M. Sacerdoti and A. Marchi, *Acta Cryst.*, **C40**, 971 (1984).
13. C.J.L. Lock and C. Wan, *Can. J. Chem.*, **53**, 1548 (1975).
14. R.G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
15. E. Roncari, U. Mazzi, R. Rossi, A. Duatti and L. Magon, *Transition Met. Chem.*, **6**, 169 (1981).
16. F. Tisato, F. Refosco, U. Mazzi, G. Bandoli and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 1693 (1987).
17. J.F. Rowbottom and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 826 (1972).
18. R. Rossi, A. Marchi, A. Duatti, L. Magon, U. Casellato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1857 (1988).
19. R.J. Mawsky and L.M. Venazi, *J. Chem. Soc.*, 4447 (1962).
20. D.E. Grove, N.P. Johnson, C.J.L. Lock and G. Wilkinson, *J. Chem. Soc.*, 490 (1965).
21. G. Gilli, M. Sacerdoti, V. Bertolasi and R. Rossi, *Acta. Cryst.*, **B38**, 100 (1982).