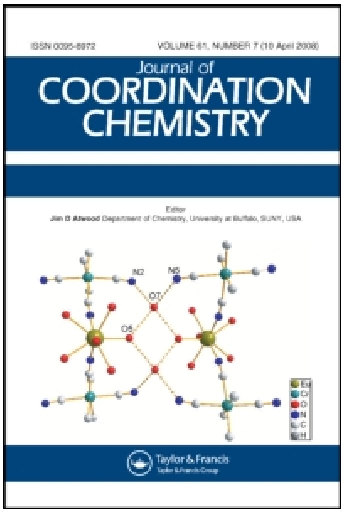


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Rhenium(V) Complexes with Bidentate *N,O*-Donor Imidazole Derivatives

T. I. A. Gerber[a]; Z. R. Tshentu[a]; S. Garcia-Granda[b]; P. Mayer[c]
[a] Department of Chemistry, University of Port Elizabeth, Port Elizabeth, South Africa [b] Facultad Quimica, Universidad Oviedo, Oviedo-Asturias, Spain [c] Deparment of Chemistry, Ludwig-Maximilians University, München, Germany

To cite this Article Gerber, T. I. A. , Tshentu, Z. R. , Garcia-Granda, S. and Mayer, P.(2003) 'Rhenium(V) Complexes with Bidentate *N,O*-Donor Imidazole Derivatives', Journal of Coordination Chemistry, 56: 12, 1093 — 1103
To link to this Article: DOI: 10.1080/00958970310001601820
URL: http://dx.doi.org/10.1080/00958970310001601820

J. Coord. Chem., Vol. 56, No. 12, 15 August 2003, pp. 1093–1103

Taylor & Francis
Taylor & Francis Group

RHENIUM(V) COMPLEXES WITH BIDENTATE *N,O*-DONOR IMIDAZOLE DERIVATIVES

T.I.A. GERBER[a,]*, Z.R. TSHENTU[a], S. GARCIA-GRANDA[b] and P. MAYER[c]

[a]*Department of Chemistry, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, South Africa;* [b]*Facultad Quimica, Universidad Oviedo, Cf Julian Claveria 8, 33006 Oviedo-Asturias, Spain;* [c]*Deparment of Chemistry, Ludwig-Maximilians University, D-81377 München, Germany*

(Received 01 March 2003; In final form 23 June 2003)

The reaction of a two-fold molar excess of the potential *N,O*-donor ligand 2-(hydroxymethyl)-1-methylimidazole (Hmi) with *trans*-[$ReOCl_3(PPh_3)_2$] led to the isolation of *cis*-[$ReOCl_2(mi)(PPh_3)$]. An X-ray structure determination indicated that the complex has distorted octahedral geometry, and that mi coordinates as a bidentate with the alcoholate oxygen *trans* to the oxo group. A similar reaction with 2-(1-ethyloxomethyl)-1-methylimidazole (eomi), the ethyl substituted analogue of Hmi, led to the formation of the oxo-bridged dinuclear complex [$(\mu\text{-O})\{ReOCl_2(eomi)_2\}_2$]. The ligand eomi coordinates as a monodentate *via* the imidazole nitrogen, with the "hard" ether oxygen uncoordinated. An X-ray crystal structure indicates that the chlorides are trans to each other in the ReN_2Cl_2 planes, which are orthogonal to the O=Re–O–Re=O backbone.

Keywords: Crystal structure; Rhenium(V); Imidazole *N,O*-donors

INTRODUCTION

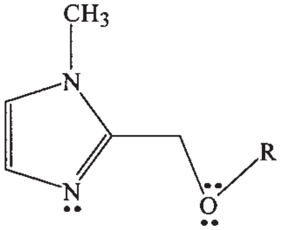
The chemistry of oxorhenium(V) complexes is receiving increasing attention because of the potential application of the isotopes ^{186}Re and ^{188}Re as radiotherapeutic agents against cancer [1], and because of its similar chemical behaviour to technetium, its second row congener, which has found major applications in diagnostic nuclear medicine [1]. The reactivity of the ReO^{3+} core with ligands containing the *N,O*-donor atom set has been thoroughly investigated, especially with Schiff-base ligands. These Schiff bases contain a phenolic oxygen from which the proton is abstracted to form negatively charged ligands upon coordination, and complexes of the type [$ReOCl(L)_2$] and [$ReOCl_2(L)(PPh_3)$] have been isolated by the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with bidentate Schiff bases, HL [2].

---

*Corresponding author.

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970310001601820

With the aim of attaining other stable configurations for the ReO^{3+} core, we have reacted *trans*-$[ReOCl_3(PPh_3)_2]$ with the potentially bidentate *N*,*O*-donor ligands 2-(1-hydroxymethyl)-1-methylimidazole (Hmi) and 2-(1-ethyloxomethyl)-1-methylimidazole (eomi). Reaction with Hmi led to the formation of the expected neutral monooxo product *cis*-$[ReOCl_2(mi)(PPh_3)]$. With eomi as ligand, the oxo-bridged $[(\mu\text{-}O)\{ReOCl_2(eomi)_2\}_2]$ was isolated, in which eomi acts as a neutral monodentate ligand through the imidazole nitrogen.



R = H (Hmi)
= CH_2CH_3 (eomi)

EXPERIMENTAL

Reagents

trans-$[ReOCl_3(PPh_3)_2]$ was synthesised using a published procedure [3]. The ligands Hmi and eomi were prepared according to a literature method [4]. Solvents were purified and dried before use. Laboratory chemicals were of reagent grade and were used without further purification.

Synthesis of Complexes

cis-[ReOCl₂(mi)(PPh₃)] (1)

To a 0.12 md solution of *trans*-$[ReOCl_3(PPh_3)_2]$ in 10 mL ethanol was added 0.24 mmol of Hmi in 5 mL of ethanol, and the resulting solution was heated under reflux for 90 min. During this period the yellow-green mixture changed to a blue solution. The solution was cooled to room temperature, and the blue precipitate was collected by vacuum filtration and washed with diethylether. The product was then recrystallised from CH_2Cl_2/EtOH (2:1) to yield intense blue crystals. The crystals were washed with ether and dried under vacuum. The complex is soluble in dichloromethane, DMF and DMSO, but is insoluble in alcohols, THF, benzene and water. The compound is slightly soluble in acetonitrile, acetone and hydrocarbons. Yield = 79%, m.p. = 239°C. Anal. Calcd.(%): C, 42.72 : H, 3.43; N, 4.33. Found: C, 42.71; H, 3.10; N, 4.25. IR (KBr): ν(C=N) 1621, ν(C=C) 1485, $\nu(H_2C\text{–}O)$ 1187, ν(Re=O) 952, ν(Re–N) 452, ν(Re–Cl) 328 cm^{-1}. ^1H NMR (295 K), ppm: 3.78 (3H, s, N–CH_3), 4.77 (2H, s, CH_2O), 7.50–7.68 (17H, m, PPh_3, *H*(2), *H*(3)). Conductivity (CH_3CN, 10^{-3} M) = 5.2 $ohm^{-1}\,cm^2\,mol^{-1}$.

[(μ-O){ReOCl₂(eomi)₂}₂] (2)

To a solution of 0.24 mmol of *trans*-$[ReOCl_3(PPh_3)_2]$ in 10 mL of acetone was added a two-fold molar excess of eomi, dissolved in 10 mL of acetone. The resulting mixture was refluxed for 40–50 min, and the mixture changed from yellow-green to blue-green. The solvent was removed under high vacuum, the oily residue dissolved in DMF/CH_2Cl_2 (3:7) and then allowed to stand in a closed vessel. After several days, bright blue-green crystals were obtained. The product was filtered, washed with acetone and finally dried under vacuum. The complex is soluble in DMF, DMSO and CH_3CN, partially soluble in CH_2Cl_2 and insoluble in water and alcohols. Yield = 72% (based on Re), m.p. = 226°C. Anal. Calcd. (%): C, 29.95; H, 4.30; N, 9.64. Found: C, 30.13; H, 4.16; N, 9.98. IR (KBr): ν(C=N) 1652, ν(C=C) 1499, ν(C–O–C) 1092, ν(Re=O) 971, ν(Re–O–Re) 720, ν(Re–N) 452, ν(Re–Cl) 310 cm^{-1}. ^1H NMR (295 K), ppm: 1.18 (3H, t, OCH_2CH_3), 3.50 (2H, q, OCH_2CH_3), 3.84 (3H, s, CH_3–N), 4.80 (2H, s, CH_2–O), 7.65 (1H, d, *H*(3)), 7.71 (1H, d, *H*(2)). Conductivity (CH_3CN, 10^{-3} M) = 100 $ohm^{-1}\,cm^2\,mol^{-1}$.

Physical Measurements

The instrumentation used in this study is the same as reported earlier [5]. IR spectra were obtained KBr discs and ^1H NMR spectra were run in d_6-DMSO.

X-ray Data Collection, Structure Solution and Refinement

Intensity data for **1** were collected at 293(2) K on a Nonius Kappa – CCD single crystal diffractometer, using Cu Kα radiation. Crystal–detector distance was fixed at 29 mm, and a total of 32 images were collected using the oscillation method, with 2° oscillation and 20 s exposure time per image. The crystal structure was solved by direct methods, using the program SHELXS-97 [6]. Anisotropic least-squares refinement was carried out with SHELXL-97 [7]. The hydrogen atoms were geometrically placed. During the final stages of the refinement, non-H atoms were anisotropically refined. The hydrogen atoms were isotropically refined with a common thermal parameter for each group of hydrogen atoms riding on the same atom.

Data collection for **2** was performed at 200 K on a Stoe IPDS using Mo Kα radiation. The structure was solved by direct methods and was refined by means of full-matrix least-squares procedures with SHELXL-97. All non-hydrogen atoms were refined anisotropically. Drawings were performed with the ZORTEP program [8]. Absorption corrections were performed using ψ-scans [9].

Relevant crystallographic data are listed in Table I (for Complexes **1** and **2**). For Complex **1**, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are given in Table II. These data are given in Table IV for Complex **2**. Bond lengths and angles for **1** and **2** are listed in Tables III and IV respectively.

RESULTS AND DISCUSSION

Syntheses

cis-[$ReOCl_2$(mi)(PPh_3)] was synthesised by reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with a two-fold molar excess of Hmi in dry ethanol as follows:

$$\mathrm{ReOCl_3(PPh_3)_2} + 2\mathrm{Hmi} \xrightarrow[\Delta]{\text{Ethanol}} \mathrm{ReOCl_2(mi)(PPh_3)} + [\mathrm{H_2mi^+}]\mathrm{Cl^-} + \mathrm{PPh_3}$$

TABLE I Crystal data and structure refinement details for *cis*-[$ReOCl_2$(mi)(PPh_3)] (**1**) and [(μ-O){$ReOCl_2(eomi)_2$}$_2$] (**2**)

	1	*2*
Empirical formula	$C_{23}H_{22}Cl_2N_2O_2PRe$	$C_{28}H_{48}Cl_4N_8O_7Re_2$
Formula weight	646.50	1122.95
Temperature (K)	293(2)	200
Wavelength (Å)	1.54184	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
Unit cell dimensions (Å,°)	$a=9.6510(1)$	$a=10.9608(5)$
	$b=10.6566(2)$	$b=14.8339(7)$
	$c=22.4188(3)$	$c=24.5063(13)$
	$\beta=96.121(10)$	$\beta=101.948(6)$
Volume (Å^3)	2292.56(6)	3898.2(3)
Z	4	4
Density (calc.) (Mg/m^3)	1.873	1.913
Absorption coefficient (μ) (mm^{-1})	13.364	6.531
F (000)	1256	2184
θ range for data collection (°)	3.97–70.01	2.3–27.9
Limiting indices	$-11 \le h \le 11$	$-14 \le h \le 14$
	$-12 \le k \le 12$	$-19 \le k \le 19$
	$-27 \le l \le 27$	$-32 \le l \le 32$
Reflections collected/unique	8126/4297 [R(int) = 0.035]	16705/4664 [R(int) = 0.039]
Data/restraints/parameters	4297/0/368	3751/0/222
Goodness-of-fit on F^2	1.041	0.94
Final R indices	$R1=0.0383$, $wR2=0.0783$	$R1=0.0251$, $wR2=0.0510$
Largest diff. peak and hole (e Å^{-3})	1.685, –0.926	0.89, –1.15

The dimeric species, [(μ-O){$ReOCl_2(eomi)_2$}$_2$] was prepared by the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with a two-fold molar excess of eomi in dry acetone, in a system that was open to the atmosphere. The reaction is proposed to proceed as follows:

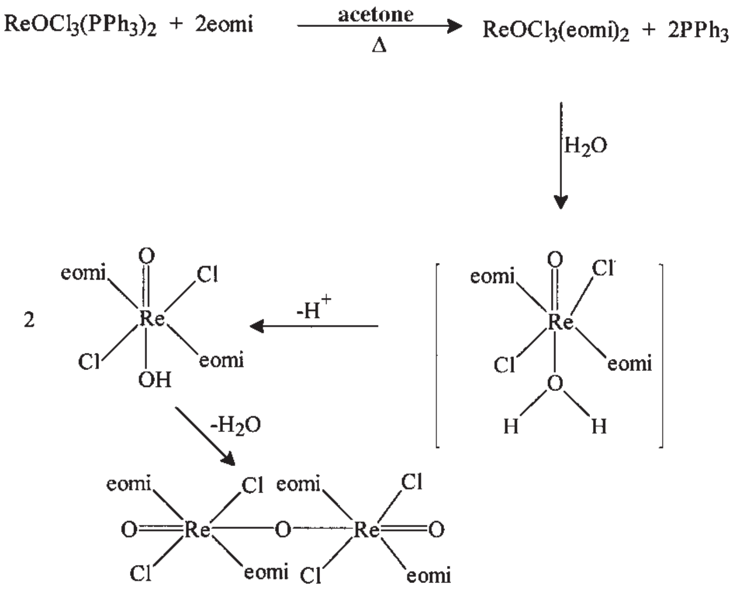


TABLE II Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **1**

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Re(1)	2002(1)	1427(1)	1719(1)	23(1)
Cl(1)	501(2)	−75(1)	1221(1)	30(1)
Cl(2)	2377(2)	86(1)	2598(1)	34(1)
P(1)	1283(2)	2889(1)	898(1)	23(1)
O(1)	3518(4)	1129(4)	1413(2)	29(1)
O(2)	571(4)	2311(3)	2093(2)	26(1)
N(1)	3101(5)	2807(4)	2263(2)	26(1)
N(2)	3096(5)	4500(4)	2818(2)	28(1)
C(1)	2313(6)	3606(5)	2523(3)	26(1)
C(2)	4468(7)	4227(6)	2742(3)	34(2)
C(3)	4443(6)	3186(6)	2398(3)	27(1)
C(4)	2619(8)	5603(7)	3114(3)	39(2)
C(5)	779(7)	3394(6)	2455(3)	28(1)
C(11)	2117(5)	2620(5)	220(2)	24(1)
C(12)	2459(7)	1412(6)	60(3)	33(2)
C(13)	3077(7)	1187(6)	−462(3)	37(2)
C(14)	3340(7)	2195(7)	−824(3)	38(2)
C(15)	3000(6)	3401(6)	−675(3)	31(1)
C(16)	2411(6)	3607(6)	−153(3)	28(1)
C(21)	−587(6)	2815(5)	676(2)	25(1)
C(22)	−1540(6)	3187(6)	1064(3)	28(1)
C(23)	−2952(7)	3101(6)	902(3)	33(2)
C(24)	−3461(7)	2624(6)	354(3)	36(2)
C(25)	−2533(7)	2212(7)	−29(3)	40(2)
C(26)	−1122(7)	2326(6)	122(3)	29(2)
C(31)	1698(6)	4501(5)	1100(2)	25(1)
C(32)	3107(6)	4792(6)	1263(3)	29(1)
C(33)	3483(8)	5974(6)	1472(3)	37(2)
C(34)	2507(8)	6887(6)	1525(3)	39(2)
C(35)	1116(8)	6626(6)	1352(3)	38(2)
C(36)	720(7)	5452(5)	1142(3)	30(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

TABLE III Selected bond lengths (Å) and angles (°) for **1**

Re(1)–O(1)	1.692(4)	C(15)–C(16)	1.372(8)
Re(1)–O(2)	1.935(4)	N(1)–C(1)	1.319(7)
Re(1)–N(1)	2.122(5)	N(1)–C(3)	1.360(7)
Re(1)–Cl(1)	2.3586(14)	N(2)–C(1)	1.345(7)
Re(1)–Cl(2)	2.4306(14)	N(2)–C(2)	1.384(8)
Re(1)–P(1)	2.4546(14)	N(2)–C(4)	1.449(8)
O(2)–C(5)	1.414(7)	C(1)–C(5)	1.488(8)
C(2)–C(3)	1.349(9)	C(2)–C(3)	1.349(9)
O(1)–Re(1)–O(2)	160.62(17)	N(1)–Re(1)–Cl(1)	170.72(13)
O(1)–Re(1)–N(1)	87.15(18)	O(1)–Re(1)–Cl(2)	98.02(13)
O(2)–Re(1)–N(1)	75.48(16)	O(2)–Re(1)–Cl(2)	89.21(11)
O(1)–Re(1)–Cl(1)	101.80(14)	N(1)–Re(1)–Cl(2)	85.35(13)
O(2)–Re(1)–Cl(2)	96.00(11)	Cl(1)–Re(1)–Cl(2)	90.91(5)
C(11)–P(1)–C(21)	106.2(3)	O(1)–Re(1)–P(1)	91.11(13)
C(5)–O(2)–Re(1)	125.6(3)	O(2)–Re(1)–P(1)	81.84(11)
C(1)–N(1)–C(3)	106.9(5)	N(1)–Re(1)–P(1)	94.31(13)
C(1)–N(1)–Re(1)	115.2(4)	Cl(1)–Re(1)–P(1)	88.02(5)
N(1)–C(1)–N(2)	110.7(5)	Cl(2)–Re(1)–P(1)	170.83(5)

TABLE IV Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **2**

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Re(1)	3954(1)	−1072(1)	6763(1)	14(1)
Cl(1)	5780(9)	−1337(6)	6397(4)	23(3)
Cl(2)	2171(9)	−871(6)	7197(4)	22(3)
O(1)	5000(9)	−1060(2)	7500(4)	16(9)
O(2)	3005(3)	−1066(19)	6124(11)	24(8)
O(3)	1961(3)	1349(2)	5763(12)	35(10)
O(4)	2870(3)	−3570(2)	5584(12)	33(10)
N(1)	4334(3)	337(2)	6741(12)	16(9)
N(2)	4257(3)	1805(2)	6652(13)	22(10)
N(3)	3736(3)	−2475(2)	6875(12)	17(9)
N(4)	3698(3)	−3940(4)	6791(13)	21(9)
C(1)	3579(4)	1038(3)	6573(15)	20(1)
C(2)	5511(4)	682(3)	6923(16)	20(11)
C(3)	5473(4)	1588(3)	6872(17)	22(11)
C(4)	3799(5)	2729(3)	6542(2)	35(16)
C(5)	2216(4)	1029(3)	6319(16)	25(11)
C(6)	2251(4)	723(4)	5373(2)	50(19)
C(7)	1973(10)	1139(6)	4816(3)	101(4)
C(8)	3808(4)	−3158(3)	6526(16)	18(10)
C(9)	3563(4)	−2841(2)	7369(15)	18(10)
C(10)	3545(4)	−3747(2)	7318(16)	21(11)
C(11)	3751(5)	−4849(3)	6568(2)	33(14)
C(12)	3879(4)	−3106(3)	5923(16)	24(11)
C(13)	1717(5)	−3102(4)	5534(2)	41(16)
C(14)	699(6)	−3710(6)	5233(3)	79(3)

U(eq) = one-third of the trace of the orthogonalised U_{ij} tensor.

Characterization of the Complexes

In the IR spectrum of Complex **1** there is a very strong absorption at 952 cm^{-1}, assigned to the Re=O stretch. This is supported by the observation that monooxo-rhenium(V) complexes with an anionic oxygen atom *trans* to the oxo group have ν(Re=O) typically in the range 950–968 cm^{-1} [10]. The spectrum shows that coordination of mi takes place through the unsaturated nitrogen atom of the imidazole ring and the deprotonated alcoholate oxygen. This is indicated by the change in frequency of the C=N stretching band upon formation of the metal complex. In rings systems [11], ν(C=N) is usually observed at about 1650 cm^{-1}. Chelation of Hmi to Re(V) results in lowering from 1645 cm^{-1} in the free ligand to 1621 cm^{-1} in the complex. The ν(Re–N) mode is evidenced by a weak absorption at 452 cm^{-1}. Coordination of the alcoholate oxygen atom is also indicated by the lowering of ν(CH$_2$–O) from 1247 cm^{-1} in the free ligand to 1187 cm^{-1} in the complex. The presence of triphenylphosphine is indicated by the strong band at 1095 cm^{-1}. Far IR spectra of monosubstituted Schiff-base complexes usually show two ν(Re–Cl) in the 345–286 cm^{-1} region for the cis chloro species [2]. The IR spectrum of this cis complex surprisingly shows only one band of medium intensity at 328 cm^{-1}.

IR spectra of Complex **2** show a very intense band at 720 cm^{-1}, assigned to ν_{as}(Re–O–Re) and within the typical range of 700–740 cm^{-1} observed for this band [12–14]. A weak absorption at 971 cm^{-1} is assigned to the Re=O stretch, in agreement with observations that ν(Re=O) shows weak or medium absorption for dimeric species containing the imidazole lignd [12]. The frequency of the C–O–C stretching mode at

TABLE V Selected bond lengths (Å) and angles (°) for **2**

Re(1)–Cl(1)	2.3893(10)	N(2)–C(3)	1.369(6)
Re(1)–Cl(2)	2.4286(10)	N(2)–C(4)	1.465(5)
Re(1)–O(1)	1.9280(2)	N(3)–C(8)	1.339(5)
Re(1)–O(2)	1.691(3)	N(3)–C(9)	1.375(5)
Re(1)–N(1)	2.134(3)	N(4)–C(8)	1.347(5)
Re(1)–N(3)	2.119(3)	N(4)–C(10)	1.365(5)
O(3)–C(5)	1.415(5)	N(4)–C(11)	1.461(5)
O(3)–C(6)	1.416(6)	C(1)–C(5)	1.495(6)
O(4)–C(12)	1.416(5)	C(2)–C(3)	1.350(6)
O(4)–C(13)	1.425(7)	C(6)–C(7)	1.471(9)
N(1)–C(1)	1.339(5)	C(8)–C(12)	1.497(5)
N(1)–C(2)	1.374(5)	C(9)–C(10)	1.350(4)
N(2)–C(1)	1.351(5)	C(13)–C(14)	1.504(9)
Cl(1)–Re(1)–Cl(2)	175.63(3)	C(1)–N(2)–C(4)	127.2(4)
Cl(1)–Re(1)–O(1)	88.34(3)	C(3)–N(2)–C(4)	124.1(4)
Cl(1)–Re(1)–O(2)	93.19(11)	Re(1)–N(3)–C(8)	129.6(3)
Cl(1)–Re(1)–N(1)	88.17(9)	Re(1)–N(3)–C(9)	122.8(2)
Cl(2)–Re(1)–N(3)	90.73(9)	C(8)–N(3)–C(9)	107.5(3)
Cl(2)–Re(1)–O(1)	88.03(3)	C(8)–N(4)–C(10)	108.4(3)
Cl(2)–Re(1)–O(2)	90.47(11)	C(8)–N(4)–C(11)	126.9(3)
Cl(2)–Re(1)–N(1)	94.02(9)	C(10)–N(4)–C(11)	124.7(3)
Cl(2)–Re(1)–N(3)	86.65(9)	N(1)–C(1)–N(2)	108.9(4)
O(1)–Re(1)–O(2)	178.35(12)	N(1)–C(1)–C(5)	128.4(4)
O(1)–Re(1)–N(1)	86.20(12)	N(2)–C(1)–C(5)	122.7(4)
O(1)–Re(1)–N(3)	87.08(12)	N(1)–C(2)–C(3)	109.4(4)
O(2)–Re(1)–N(1)	93.22(12)	N(2)–C(3)–C(2)	106.2(4)
O(2)–Re(1)–N(3)	93.52(13)	O(3)–C(5)–C(1)	112.3(3)
N(1)–Re(1)–N(3)	173.22(12)	O(3)–C(6)–C(7)	108.6(5)
Re(1)–O(1)–Re(1)	178.93(18)	N(3)–C(8)–N(4)	108.7(3)
C(5)–O(3)–C(6)	113.8(3)	N(3)–C(8)–C(12)	127.9(4)
Re(1)–N(1)–C(1)	131.1(3)	N(3)–C(9)–C(10)	108.2(3)

1092 cm^{-1} is nearly identical to that of the free ligand (1095 cm^{-1}), which is a possible indication of non-coordination. A weak absorption at 452 cm^{-1} is assigned to ν(Re–N), while the band at 310 cm^{-1} is assigned to ν(Re–Cl).

^{1}H NMR spectra for both complexes were run in d_6-DMSO. The aromatic region for **1** shows a multiplet in the region δ7.50–7.68 that integrates for 17 protons, ascribed to the 15 protons of PPh_3 and the two of the imidazole ring. The singlets at δ3.78 and 4.77 correspond to the CH_3–N and CH_2O protons, respectively. The signal at δ4.10 in the spectrum of the free ligand, due to O*H*, disappears in the spectrum of **1**. The dimeric complex **2** is only slightly soluble in DMSO and was dissolved with heating. The aromatic region shows two doublets at δ7.65 and 7.71 assignable to the two imidazole ring protons. The CH_3–N and CH_2–O signals appear at δ3.84 and 4.80, respectively.

The conductivity of the monomeric Complex **1** in acetonitrile [$\Lambda_m = 5.24(1)$ ohm^{-1} cm^2 mol^{-1}] confirms that is is a non-electrolyte; conductivity readings between 120 and 160 ohm^{-1} cm^2 mol^{-1} are consistent with a 1 : 1 electrolyte in acetonitrile [15]. The dimeric species **2** shows a high conductivity reading in acetonitrile [$\Lambda_m =$ 100 ohm^{-1} cm^2 mol^{-1}] but falls below the range generally accepted for a 1:1 electrolyte.

Description of the Structure of *cis*-[$ReOCl_2$(mi)(PPh_3)] (1)

X-ray-quality, single crystals of **1** were obtained by slow evaporation of a 2 : 1 (v/v) dichloromethane/ethanol solution of the complex. An ORTEP perspective view of the asymmetric unit along with the atom numbering scheme is given in Fig. 1.

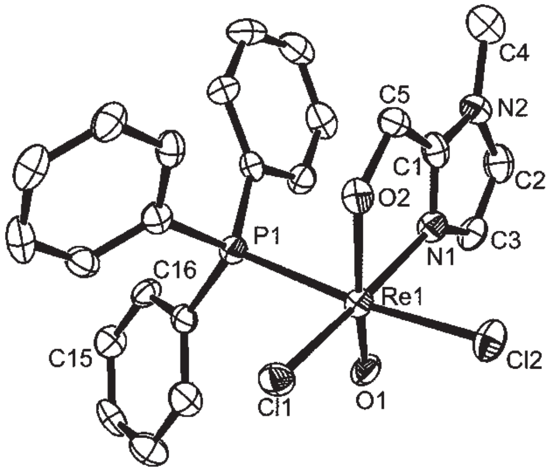


FIGURE 1 An ORTEP view of *cis*-[$ReOCl_2(mi)(PPh_3)$] (**1**), showing the atom labelling scheme. Atomic displacement ellipsoids are drawn at the 50% probability level.

The rhenium atom lies at the centre of a distorted octahedron. The basal plane is defined by the imidazole nitrogen of the mi ligand, two chlorides and the phosphorus atom of PPh_3. The deprotonated alcoholate oxygen of mi and the oxo group lie in trans axial positions. The two chlorides are coordinated to the metal centre cis to each other, with a Cl(1)–Re–Cl(2) angle of 90.9(1)°.

The rhenium(V) atom deviates from the mean equatorial plane by 0.1917(3) Å towards the oxo oxygen, and the Cl_2NP donor atoms deviate by some 0.004 Å from this plane as well. Deviation of rhenium from this plane results in the O(1)–Re–N(1), O(1)–Re–Cl(2) and O(1)–Re–P(1) angles being larger than 90° [101.8(1), 98.0(1) and 91.1(1)°, respectively]. The O(1)–Re–O(2) angle deviates considerably from linearity [160.6(2)°] the smallest ever found for *N*,*O*-donor ligands of this type. The bite angle of the bidentate mi ligand is relatively small [75.5(2)°], which contributes considerably to the distortion of the complex.

The Re–Cl(2) bond, trans to P(1), at 2.455(1) Å, is significantly longer than the chloride trans to imidazolyl N(1) [2.359(1) Å], which confirms the lower trans influence of the nitrogen. The Re–O(1) distance of 1.692(4) Å is slightly longer than the average (1.675 Å) normally expected for monooxorhenium(V) complexes in a distorted octahedral environment. The Re–O(2) distance of 1.935(4) Å also deserves comment, since it is shorter than expected on the basis of the trans labilising effect exerted by the oxo group [16,17].

Bond distances in the imidazolyl ring clearly show localised double and single bonds. C(1)–N(1) and C(2)–C(3) bonds are localised double bonds at 1.319(7) and 1.349(9) Å, respectively. The three other are localised C–N single bonds, which vary in distance from 1.345 Å [C(1)–N(2)] to 1.384(8) Å [C(2)–N(2)].

Complexes of formula [$ReOCl_2(Rsal)(PPh_3)$] (RsalH = bidentate *N*,*O*-donor Schiff base) were previously prepared by the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with RsalH. It was also found that in all these compounds the oxygen donor atom of the Rsal ligands of coordinated trans to the Re=O bond [18]. The complex [$ReOCl_2(Mesal)(PPh_3)$] (Mesal = *N*-methylsalicylideneimino) was isolated in both the cis and trans forms, which differ in the arrangement of the two chlorine atoms in the equatorial plane. In this study, no evidence for the formation of the trans dichloro isomer could be found. It was also impossible to isolate the bisubstituted product [ReOCl(mi)$_2$], even under extreme conditions. It was, however, shown previously [19] that the *N*,*O*-donor 3-hydroxypicolinic acid (HL) in its reaction with (*n*-Bu$_4$N)[ReOCl$_4$] in benzene and ethanol yielded (*n*-Bu$_4$N)[ReOCl$_3$(L)] and [ReOCl(L)$_2$], respectively. It was also found that [ReOCl$_4$]$^-$, reacts with bidentate ligands RsalH (R = Me, Ph) in THF and EtOH to produce [ReOCl$_3$(Rsal)]$^-$, which on prolonged heating in the presence of RsalH gave [ReOCl(Rsal)$_2$] in ethanol. The crystal structure [2] of the Mesal$^-$ derivative showed an octahedral environment around the metal, with the phenolate oxygen trans to the oxo group and the two imine nitrogens cis to each other.

The first step in the formation of **1** is probably the substitution of a PPh$_3$ group by the ligand Hmi, which coordinates to rhenium(V) *via* the imidazolyl nitrogen. The harder basic character of this nitrogen compared to the softer PPh$_3$ base means that the interaction will be stronger than with PPh$_3$. In support of this first reaction step, it was shown that in the complex [ReOCl$_3$(MesalH)(PPh$_3$)] the Schiff base is coordinated as a unidentate through the aldimine nitrogen [20]. The final product **1** is then formed by chelation and deprotonation of the alcoholate oxygen by substitution of the more reactive chloride trans to the Re=O bond.

Description of the Structure of [(μ-O){ReOCl$_2$(eomi)$_2$}$_2$] (2)

Single crystals of **2** suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane/DMF solution of the complex. An ORTEP plot of **2** is shown in Fig. 2. The complex consists of two independent [ReOCl$_2$(eomi)$_2$] units bridged by an oxygen atom, around which the two metal units are centrosymmetric.

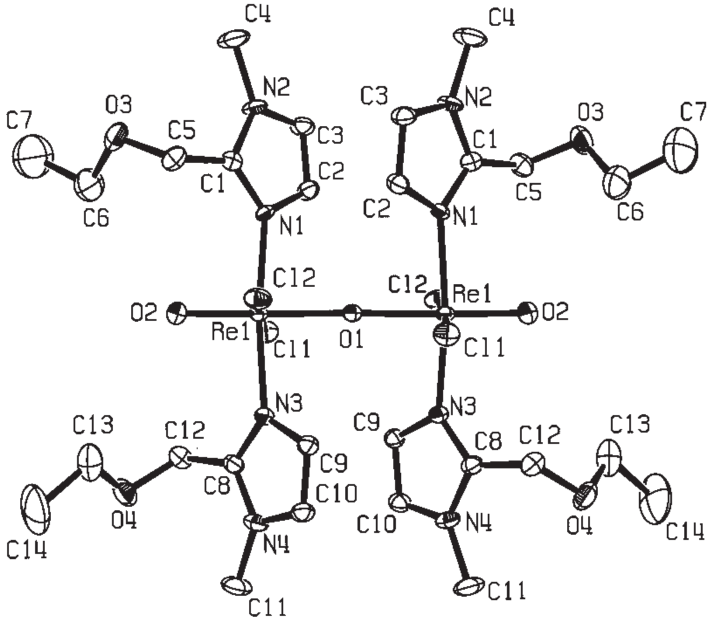


FIGURE 2 An ORTEP view (at 50% probability) of [(μ-O){ReOCl$_2$(eomi)$_2$}$_2$] (**2**).

The O=Re–O–Re=O backbone shows very little deviation from linearity, with the Re–O(1)–Re angle equal to 178.9(2)°.

As illustrated in Fig. 2, the rhenium atoms are centred in an octahedron with the equatorial plane formed by an N_2Cl_2 donor set. The angles in the $ReCl_2N_2$ planes are all very close to 90° [average = 89.9(9)°], and the Re–N and Re–Cl bonds are displaced towards the bridging Re–O(1) and away from the terminal O(2) [average O(2)–Re–N = 93.4(1)°; O(2)–Re–Cl = 91.8(1)°]. This distortion of the four equatorial ligands is highly common in rhenium(V) oxo-bridged dimers, and in all previous examples [10,21] of this type the equatorial ligands are displaced away from the Re=O bond. This latter distortion is ascribed to the relatively high double bond character of the terminal bonds compared to the longer Re–O bonds, which can be classified as single bonds. In **2**, the Re–O(2) bond equals 1.691(3) Å, clearly having double bond character, and the Re–O(1) bond equals 1.928(2) Å, definitely on the single bond side. The O(2)–Re–O(1) unit is virtually linear at 178.4(1)°.

Re–N distances [mean 2.127(3) Å] are normal and practically identical with the value found in Complex **1** [2.122(5) Å]. Re–Cl bonds [mean 2.414(1) Å] are slightly longer than those in Complex **1**, but differ insignificantly from those in $[Re_2O_3Cl_4(py)_4]$, which also contains the chloride ligands trans to each other [22].

The conformation of the complex is very similar to that of $[Re_2O_3Cl_4(py)_4]$ [22]. Within each octahedron, the plane of each imidazole ring roughly bisects the angles defined by the two adjacent Cl–Re–O bonds, thus avoiding extremely short contacts between ortho hydrogens and cis ligands. In this situation the two imidazole rings are nearly orthogonal to each other, with a dihedral angle of 87.1(2)°. In the two $ReCl_2N_2$ planes the imidazole rings face each other in an eclipsed orientation (Fig. 3), in spite of the fact that steric interaction can be reduced by rotating one of the $ReCl_2N_2$ units about the backbone. In this conformation, strong stabilizing stacking interactions can also take place between the π-electron clouds. It can also be envisaged that an eclipsed orientation of the Re–N bonds in one half with the Re–Cl bonds in the

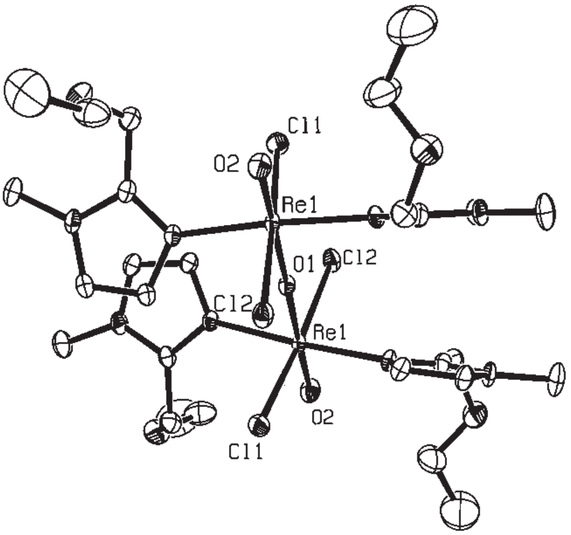


FIGURE 3 An ORTEP plot (at 50% probability) of **2**, showing the eclipsed orientation of the imidazole rings.

other would create unfavourable short contacts between ortho groups of imidazole and with Cl ligands in the two halves.

Bond distances in imidazolyl rings clearly show localized double [C(1)=N(1) = 1.339(5) Å, C(2)=C(3) = 1.350(6) Å] and single bonds [C(1)–N(2) = 1.351(5) Å, C(3)–N(2) = 1.369(6) Å, C(2)–N(1) = 1.374(5) Å]. The imidazolyl rings are also very planar, with the largest torsion angle being 0.6(4)° [C(1)–N(1)–C(2)–C(3)]. The uncoordinated neutral ethereal oxygens O(3) and O(4) are too weak as Lewis base to form coordination covalent bonds to the hard acid Re(V). C–O–C bond angles [mean 113.2(3)°] are indicative of sp^3 hybridization of the oxygen atoms.

Complex **2** has the *trans,trans*-$ReCl_2N_2$ arrangement of formulation $Re_2O_3Cl_4N_4$. In contrast, the oxo-bridged dinuclear (μ-O)[$ReOCl_2(py)_2$]$_2$ was shown to contain the *cis,cis*-$ReCl_2N_2$ arrangement [22]. However, refluxing the oxo-alkoxo complexes [$ReO(OR)Cl_2(py)_2$] ($R = CH_3$ or C_2H_5) in toluene yielded a dinuclear compound, (μ-O)[$ReOCl_2(py)_2$]$_2$, in which a *trans,trans* arrangement of pyridine and chloride ligands around rhenium was found by X-ray diffraction studies. The two $ReCl_2N_2$ planes are rotated with respect to each other by 27° about the backbone axis [21].

References

[1] J.R. Dilworth and S.J. Parrot, *Chem. Soc. Rev.* **27**, 13 (1998).
[2] U. Mazzi, R. Roncari, R. Rossi, V. Bertolasi, O. Traverso and L. Magon, *Transition Met. Chem.* **5**, 289 (1980).
[3] N.P. Johnson, C.J.L. Lock and G. Wilkinson, *Inorg. Synth.* 145 (1967).
[4] M.M. Mtotywa, PhD. Thesis, University of Port Elizabeth (2002).
[5] T.I.A. Gerber, A.J. Kemp, G. Bandoli, A. Dolmella and J.G.H. du Preez, *Inorg. Chim. Acta* **202**, 191 (1992).
[6] G.M. Sheldrick, *Acta Crystallogr.* **A46**, 467 (1999).
[7] G.M. Sheldrick, SHELX-97, Programs for Structure Solution and Refinement (University of Göttingen, Germany, 1997).
[8] L. Zsolnai and H. Pritzkow, ZORTEP. An Interactive ORTEP Program (University of Heidelberg, Germany, 1995).
[9] MSC/AFC Diffractometer Control Software, Version 5.1.0 (Molecular Structure Corporation, Research Forest Drive, The Woodlands, TX 77381, USA, 1993).
[10] A. Marchi, A. Duatti, R. Rossi, L. Magon, U. Mazzi and U. Pasquetto, *Inorg. Chim. Acta* **15**, 81 (1984).
[11] T.J. Lane, I. Nakagawa, J.L. Walker and A.J. Kandathil, *Inorg. Chem.* **1**, 267 (1962).
[12] S. Fortin and A.L. Beauchamp, *Inorg. Chem.* **39**, 4886 (2000).
[13] N.P. Johnson, F.I.M. Taha and G. Wilkinson, *J. Chem. Soc.* 2614 (1964).
[14] H. Pietzsch, H. Spies, P. Leibnitz and G. Reck, *Polyhedron* **14**, 1849 (1995).
[15] W.J. Geary, *Coord. Chem. Rev.* 7, **81** (1971).
[16] F. Tisato, U. Mazzi, G. Bandoli and M. Nicolini, *J. Chem. Soc., Dalton Trans.* 1693 (1987).
[17] A. Abrahams, G. Bandoli, S. Gatto, T.I.A. Gerber and J.G.H. du Preez, *J. Coord. Chem.* **43**, 297 (1998).
[18] C.J.L. Lock and C. Wang, *Can. J. Chem.* **53**, 1548 (1975).
[19] S. Gatto, T.I.A. Gerber, G. Bandoli, J. Perils and J.G.H. du Preez, *Inorg. Chim. Acta* **269**, 235 (1998).
[20] E. Roncari, U. Mazzi, R. Rossi, A. Duatti and L. Magon, *Transition Met. Chem.* **6**, 169 (1981).
[21] S. Fortin and A.L. Beauchamp, *Inorg. Chim. Acta.* **279**, 159 (1998).
[22] C.J.L. Lock and G. Turner, *Can. J. Chem.* **56**, 179 (1978).