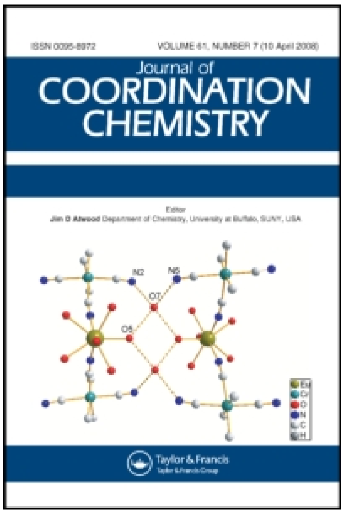

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SOLVENT DEPENDENCY OF SUBSTITUTION REACTIONS OF OXORHENIUM(V) COMPLEXES. THE CRYSTAL STRUCTURES OF *TRANS*-DICHLORO (*N*-PHENYSALICYLIDENEIMINATO)-TRIPHENYLPHOSPHINEOXORHENIUM(V) AND CHLORO(8-OXYQUINOLINE) [(2-OXYMETHYLINE-6-HYDROXYMETHYL)-PYRIDINE]OXORHENIUM(V)

G. Bandoli[a]; S. Gatto[a]; T. I. A. Gerber[b]; J. Perils[b]; J. G.H. Du Preez[b]
[a] Department of Pharmaceutical Science, University of Padova, Padova, Italy [b] Department of Chemistry, University of Port Elizabeth, Port Elizabeth, South Africa

To cite this Article Bandoli, G. , Gatto, S. , Gerber, T. I. A. , Perils, J. and Preez, J. G.H. Du(1996) 'SOLVENT DEPENDENCY OF SUBSTITUTION REACTIONS OF OXORHENIUM(V) COMPLEXES. THE CRYSTAL STRUCTURES OF *TRANS*-DICHLORO (*N*-PHENYSALICYLIDENEIMINATO)-TRIPHENYLPHOSPHINEOXORHENIUM(V) AND CHLORO(8-OXYQUINOLINE) [(2-OXYMETHYLINE-6-HYDROXYMETHYL)-PYRIDINE]OXORHENIUM(V)', Journal of Coordination Chemistry, 39: 3, 299 — 311

To link to this Article: DOI: 10.1080/00958979608024338

URL: http://dx.doi.org/10.1080/00958979608024338

J. Coord. Chem., 1996, Vol. 39, pp. 299–311
Reprints available directly from the publisher
Photocopying permitted by license only

SOLVENT DEPENDENCY OF SUBSTITUTION REACTIONS OF OXORHENIUM(V) COMPLEXES. THE CRYSTAL STRUCTURES OF *TRANS*-DICHLORO (*N*-PHENYLSALICYLIDENEIMINATO)-TRIPHENYLPHOSPHINEOXORHENIUM(V) AND CHLORO(8-OXYQUINOLINE) [(2-OXYMETHYLENE-6-HYDROXYMETHYL)-PYRIDINE]OXORHENIUM(V)

G. BANDOLI[a,*], S. GATTO[a], T.I.A. GERBER[b,*], J. PERILS[b]
and J.G.H. DU PREEZ[b]

[a]*Department of Pharmaceutical Science, University of Padova, Via Marzolo 5, 35131 Padova, Italy;* [b]*Department of Chemistry, University of Port Elizabeth, P.O. Box 1600, 6000 Port Elizabeth, South Africa*

(Received 12 March 1996)

The reaction of the complex $[ReOC\ell_2(HL)(PPh_3)]$ (**1**; H_2L = 2,6-*bis*(hydroxymethyl)pyridine), in which HL^- acts as a bidentate monoanionic N,O^--donor ligand, with the potentially bidentate N,O^--donor ligands *N*-phenylsalicylideneimine (PhsalH) and 8-hydroxyquinoline (oxineH) in ethanol led to the substitution of the chelate HL^- to produce *trans*-$[ReOC\ell_2(Phsal)(PPh_3)]$ (**2**) and *trans*-$[ReOC\ell_2(oxine)(PPh_3)]$ (**4**). In benzene the mixed *bis*(bidentate) ligand complexes $[ReOC\ell(Phsal)(HL)]$ (**3**) and $[ReOC\ell(oxine)(HL)]$ (**5**) were isolated. Complex **1** also reacts with a molar excess of PhsalH and oxineH(NOH) in ethanol to form $ReOC\ell(NO)_2$. All the complexes were characterized by various physical techniques, including IR and NMR. X-ray structures of **2** ($C_{31}H_{25}C\ell_2NO_2PRe$) and **5** ($C_{16}H_{14}C\ell N_2O_4Re$) were determined. Crystals of **2** are triclinic, $P\bar{1}$, $a = 8.813(4)$, $b = 10.200(4)$, $c = 16.913(7)$ Å, $\alpha = 84.90(3)$, $\beta = 80.81(3)$, $\gamma = 67.44(3)$°, $Z = 2$; those of **5** are monoclinic, $P2_1/c$, $a = 14.091(2)$, $b = 8.171(2)$, $c = 15.227(2)$ Å, $\beta = 115.48(2)$°, $Z = 4$. The structures were solved by the Patterson method and were refined by full-matrix least-squares procedures to $R = 0.0369$ ($R_w = 0.0469$) and 0.0619 (0.0770) for 3187 and 2858 reflections with $F > 4.0\sigma(F)$ for **2** and **5**, respectively.

Keywords: rhenium(V); bidentate ligands; substitution; solvent dependency; X-ray structure

---

*Authors for correspondence.

INTRODUCTION

The coordination chemistry of rhenium is receiving increased attention due to the potential application of the β-emitting nuclides ^{186}Re ($\beta^- = 1.07$ MeV, *ca* 1.71×10^{-13} J, $t_{1/2} = 90$h) and ^{188}Re ($\beta^- = 2.12$ MeV, *ca* 3.40×10^{-13} J, $t_{1/2} = 17$h) as suitable radiotherapeutic agents,[1] and because of its similar chemical behaviour to technetium, its second row congener, which has found major application in diagnostic nuclear medicine.[2]

As part of a program to synthesize new rhenium and technetium complexes with possible nuclear medicinal applications, we are currently studying the formation of oxorhenium(V) complexes containing mixed bidentate ligands. Oxocomplexes of these two metals with bidentate ligands have been extensively studied during the last few years, but these ligands were mainly derivatives of *N*-phenylsalicylideneimine[3–5] and *S*-methyldithiocarbazate,[6–8] and generally contained the coordinating donor atom sets ON and SN. The reaction of $ReOC\ell_3(PPh_3)_2$ with bidentate N,O-donor Schiff bases (HL_2) has led to complexes[9–10] of the type $ReOC\ell(L_2)_2$ and $ReOC\ell_2(L_2)(PPh_3)$. Examples of oxorhenium(V) and -technetium(V) complexes containing mixed bidentate ligands are rare in the literature.

Our approach to the synthesis of 'mixed' complexes of rhenium(V) was to react *cis*-$[ReOC\ell_2(HL)(PPh_3)]$ (**1**; H_2L = 2,6-*bis*(hydroxymethyl)pyridine), in which HL^- acts as a bidentate N,O$^-$-donor ligand,[12] with the potentially bidentate N,O$^-$-donor ligands *N*-phenylsalicylideneimine (PhsalH) and 8-hydroxyquinoline (oxineH). In **benzene** the mixed *bis*(bidentate) ligand complexes $[ReOC\ell(NO)(HL)]$ (NOH = PhsalH, oxineH) **were** isolated, but in **ethanol** the bidentate HL^- was substituted to yield $[ReOC\ell_2(NO)(PPh_3)]$ as products.

EXPERIMENTAL

Materials

All chemicals were of reagent grade and were used as received. Solvents were purified and dried before use. *N*-Phenylsalicylideneimine was prepared by the condensation of aniline and salicylaldehyde in ethanol-benzene (50% v/v). A literature method[12] was used for the synthesis of *cis*-$[ReOC\ell_2(HL)(PPh_3)]$ (**1**).

Instrumentation

Scientific instrumentation used in this study is the same as reported elsewhere.[13] Infrared spectra were obtained in KBr discs and ^{1}H NMR spectra were run in d_6-DMSO. Electronic spectra were all obtained in acetonitrile, and data are given as λ_{max} with extinction coefficients (in the units $M^{-1}cm^{-1}$) in parentheses.

Synthesis of the Complexes

Trans-[$ReOC\ell_2(Phsal)(PPh_3)$] (2)

To complex **1** (101 mg, 148 μmol) and *N*-phenylsalicylideneimine (31 mg, 157 μmol) (PhsalH) was added 15 cm^3 of ethanol, the mixture was brought to reflux overnight (~18 h), then cooled to room temperature. A dark green product was filtered out and recrystallized from acetonitrile. The crystals were washed with ethanol and diethylether and dried *in vacuo* overnight. The product is soluble in DMF, DMSO, $CH_2C\ell_2$, $CHC\ell_3$, CH_3CN, and acetone, weakly soluble in benzene and THF and insoluble in diethylether and hydrocarbons; yield 69 mg(64%); m.p. 223°C. Anal. calcd. C, 50.9; H, 3.4; N, 1.9; Cℓ, 9.7%. Found: C, 51.0; H, 3.6; N, 2.1; Cℓ, 9.6%. IR:ν(Re=O) 972(s); ν(C=N) 1603(s); ν(C—O) 1304(s); ν(Re—Cl) 318(s); ν(P—C) 1096(s) cm^{-1}. ^{1}H NMR: δ8.56(d, 1H, *H*2); 8.10(s, 1H, C*H*=N); 7.68–7.80 (m, 3H, H^4, H^5, H^{11}); 7.62(m, 15H, P*Ph*$_3$); 7.52(d, 2H, H^9, H^{13}); 7.29 (t, 1H, H^3); 7.15(t, 2H, H^{10}, H^{12}) ppm. Electronic spectrum: 282(29100), 345(24400), 408(4500).

[$ReOC\ell(Phsal)(HL)$] (3)

A mixture of complex **1** (101 mg, 148 μmol) and PhsalH (32 mg, 162 μmol) in 10 cm^3 benzene was heated under reflux for 19h. After cooling to room temperature, a blue precipitate was filtered out from the green solution, and it was washed with benzene and diethylether. The mother liquor yielded another batch of blue crystals on slow evaporation. The compound is soluble in acetonitrile, DMF and DMSO, and insoluble in chloroform, acetone, cyclohexane and ethanol; yield 74%; m.p. 192°C. Anal. calcd. C, 42.0; H, 3.2; N, 4.9; Cℓ, 6.2%. Found: C, 42.0; H, 3.3; N, 4.8; Cℓ, 6.4%. IR: ν(Re=O) 951(vs); ν(C=N) 1610(s); ν(O—H) 3487(m); ν(C—O) of HL 1074(s); ν(C—O) of Phsal 1269 (m); ν(Re—Cl) 321(m) cm^{-1}. ^{1}H NMR: δ3.81(br s, 1H, O*H*); 4.83(s, 4H, 2CH_2); 8.52(t, 1H, H^3 of HL); 8.44 (d, 1H, H^2 of Phsal); 7.10–7.99(m, 11H) ppm. Electronic spectrum: 256sh, 328(16600), 362sh.

Trans-[$ReOC\ell_2(oxine)(PPh_3)$] (4)

A solution of 8-hydroxyquinoline (22 mg, 152 μmol) in ethanol (5 cm^3) was added to an ethanolic solution (10 cm^3) of complex **1** (148 μmol). The mixture was heated under reflux for 45 min. After cooling to room temperature, a dark green precipitate was filtered out from the green solution. The product was washed with ethanol and diethylether, and dried *in vacuo*. Recrystallization from acetonitrile gave a mixture of green and brown crystals, with the latter being shown to be the *cis*-isomer. The green product (*trans*-isomer) is soluble in chloroform, dichloromethane, acetonitrile, DMF, DMSO and acetone, and insoluble in benzene, ethanol and hydrocarbons; yield 68%; m.p. 226°C. Anal. calcd. C, 47.7; H, 3.1; N, 2.1; Cl, 10.5%. Found: C, 47.1; H, 3.1; N, 2.2; Cl, 10.8%. IR: ν(Re═O) 974(vs); ν(C—O) 1314(s); ν(P—C) 1097(s); >(Re—Cl) 313(s) cm^{-1}. ^{1}H NMR.: δ8.39 (d, 1H, H^1); 8.22(d, 1H, H^7); 7.60(m, 15H, PPh_3); 6.80–7.50(m, 4H) ppm. Electronic spectrum: 251(23300), 392(7900).

The complex *cis*-[ReOCl$_2$(oxine)(PPh$_3$)] was obtained in good yield (71%) by heating under reflux a mixture of complex **1** and 8-hydroxyquinoline in an equimolar ratio in ethanol for 6h. Recrystallization from acetonitrile gave brown plates; m.p. 236°C. Anal. calcd. C, 47.7; H, 3.1; N, 2.1; Cl, 10. 5%. Found: C, 47.5; H, 3.4; N, 2.3; Cl, 10.1%. IR: ν(Re═O) 977(vs); ν(C—O) 1313(s); ν(Re—Cl) 305, 333(s) cm^{-1}.

[ReOCℓ(oxine)(HL)] (5)

A mixture of complex **1** (100 mg) and 8-hydroxyquinoline (22 mg) in benzene (12 cm^3) was heated under reflux for 1h, with the solution changing from purple to olive green. After heating was stopped and the solution cooled to room temperature, a green precipitate was collected by filtration. Slow evaporation of the mother liquor led to the formation of green parallelepipeds, which were suitable for X-ray crystal structure analysis. The product is soluble in acetone, DMF, chloroform, dichloromethane, DMSO and acetonitrile, and insoluble in ethanol and hydrocarbons; yield 73%; m.p. 210°C. Anal. calcd. C, 37.0; H, 2.7; N, 5.4; Cl, 6.8%. Found: C, 37.1; H, 2.9; N, 5.6; Cl, 6.8%. IR: ν(Reν═O) 962(vs); δ(C_5H_3N) 1636(vs); ν(O—H) 3437(m); ν(C—O) of HL 1099(m); ν(C—O) of oxine 1316(m); ν(Re—Cl) 323(m) cm^{-1}. ^{1}H NMR.: δ9.02(d, 1H,H^1); 8.15(m, 2H); 7.98(d 2H, H^{11}, H^{13}); 7.33–7.68(m, 3H); 6.64(d, 1H, H^7); 4.86(s, 4H, 2CH_2); 3.97(br s, 1H, OH) ppm. Electronic spectrum: 252(18700), 345sh, 399(6200).

Crystallographic Measurements and Structure Resolution of Trans-ReOCℓ$_2$(Phsal)(PPh$_3$) (2) and ReOCℓ(oxine)(HL) (5)

Crystals of **2** suitable for X-ray collection were obtained from the slow evaporation of acetonitrile solutions. Good quality crystals of **5** were obtained by cooling of a benzene solution of the complex. Details of crystal data, measurements of intensities and data processing are summarized in Table I. The structures were solved by standard Patterson and difference Fourier methods, while the full-matrix least-squares refinement minimized the function $\Sigma w(\backslash F_{0}\backslash\text{-}\backslash F_{c}\backslash)$.^{2} No anomalies in temperature factors or excursions of electron density in the final Fourier maps were observed.

TABLE I Structure determination of the complexes *trans*-[ReOCl$_2$(Phsal)(PPh$_3$)] (**2**) and [ReOCl(oxine)(HL)] (**5**)

Crystal Data		
Compound	**2**	**5**
Empirical formula	$C_{31}H_{25}C\ell_2NO_2PRe$	$C_{16}H_{14}ClN_2O_4Re$
Colour; Habit	green parallelepipeds	brown parallelepipeds
Crystal size, mm	0.1 0 × 0.20 × 0.25	0.12 × 0.16 × 0.20
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a, Å	8.813(4)	14.091(2)
b, Å	10.200(4)	8.171(2)
c, Å	16.913(7)	15.227(2)
α, deg	84.90(3)	
β, deg	80.81(3)	115.48(2)
γ, deg	67.44(3)	
Volume, Å^3	1385(1)	1582.8(4)
Z	2	4
Formula weight	731.6	519.9
Density (calc.), Mg/m^3	1.754	2.182
Absorption coefficient, mm^{-1}	4.67	7.87
F(000)	716	992
Data Collection		
Diffractometer used	SiemensR3m/V	
Radiation	Mo Kα	
Wavelength, Å	0.71073	
Temperature, K	294	294
Monochromator	Highly oriented graphite crystal	
2θ range	4.5 to 45.0°	4.5 to 55.0°
Scan type	ω-2θ	ω-2θ
Scan speed	Variable; 4.51 to 14.65°/min in ω	Variable; 3.50 to 14.65°/min in ω
Index ranges	$-9 \le h \le 9$	$-18 \le h \le 16$
	$-10 \le k \le 10$	$0 \le k \le 10$
	$0 \le \ell \le 18$	$0 \le \ell \le 19$
Independent reflections	3628	3649
Observed reflections	3187 ($F > 4.0\sigma(F)$)	2858 ($F > 4.0\sigma(F)$)
Solution and Refinement		
System used	Siemens SHELXTL PLUS (Release 4.2) (1990)	
Solution	Heavy atom methods	
Refinement method	Full-matrix least-squares	
Quantity minimized	$\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2$	
Hydrogen atoms	Riding model, common variable isotropic *U*	
Weighting scheme	$w^{-1} = \sigma^2(F)+0.0036F^2$	$w^{-1} = \sigma^2(F)+0.0055\,F^2$

TABLE I (*Continued*)

No. of parameters refined	344	218
Final R indices (obs. data)	R = 0.037, Rw = 0.047	R = 0.062, Rw = 0.077
R indices (all data)	R = w = 0.042, Rw = 0.049	R = 0.074, Rw = 0.087
Goodness-of-fit	0.73	0.95
Data-to-parameter ratio	9.3:1	13.1:1

Final fractional atomic coordinates are given in Table II, while selected bond distances and angles are reported in Table III. The molecular structures are shown in Figures 1 and 2, which also define the atom numbering scheme. Additional material available comprises anisotropic thermal parameters (Tables A1 and A2 for **2** and **5**, respectively), H-atom coordinates (Tables B1 and B2), bond lengths (Tables C1 and C2), bond angles (Tables D1 and D2), listings of the observed/calculated structure factors (Tables E1 and E2) and finally packing diagrams for **2** (Figure S2) and **5** (Figure S3). The supplementary data are available from the authors upon request.

TABLE II Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2× 10^3)^a

trans-[ReOCℓ$_2$(Phsal)(PPh$_3$)] (2)

	x/a	y/b	z/c	U_{eq}
Re	2522(1)	1374(1)	2794(1)	25(1)
Cl(1)	3882(3)	2559(2)	3401(1)	41(1)
Cl(2)	963(3)	605(3)	2037(1)	46(1)
P(1)	5220(2)	-557(2)	2411(1)	24(1)
O(1)	2170(7)	456(6)	3622(3)	38(2)
O(2)	3060(6)	2311(6)	1786(3)	32(2)
N(1)	380(8)	3281(7)	2938(4)	33(3)
C(1)	2344(9)	3467(8)	1341(5)	29(3)
C(2)	3079(10)	3664(9)	580(5)	35(4)
C(3)	2330(11)	4874(10)	134(5)	40(4)
C(4)	865(11)	5903(10)	450(5)	41(4)
C(5)	121(11)	5707(10)	1190(6)	43(4)
C(6)	827(10)	4514(8)	1663(5)	30(3)
C(7)	-30(10)	4357(9)	2442(5)	37(3)
C(8)	-747(10)	3409(9)	3675(5)	34(3)
C(9)	-1506(10)	2433(10)	3870(6)	44(4)
C(10)	-2590(12)	2573(14)	4555(7)	63(5)
C(11)	-2958(13)	3672(13)	5048(7)	66(5)
C(12)	-2229(13)	4643(12)	4859(6)	62(5)
C(13)	-1089(12)	4523(10)	4164(6)	48(4)

TABLE II (*Continued*)

trans-[ReOCℓ$_2$(Phsal)(PPh$_3$)] (**2**)

	x/a	*y/b*	*z/c*	U_{eq}
C(1a)	6316(9)	–86(8)	1497(5)	27(3)
C(2a)	6773(10)	1080(9)	1532(5)	34(3)
C(3a)	7584(11)	1499(10)	849(6)	43(4)
C(4a)	7889(11)	824(11)	135(6)	47(4)
C(5a)	7468(11)	–332(11)	109(6)	48(4)
C(6a)	6680(11)	–789(9)	793(5)	37(4)
C(1b)	5040(9)	–2232(8)	2272(5)	27(3)
C(2b)	5609(10)	–3390(9)	2794(5)	34(3)
C(3b)	5392(12)	–4631(9)	2698(6)	46(4)
C(4b)	4619(12)	–4740(10)	2071(7)	55(5)
C(5b)	4026(12)	–3623(10)	1565(6)	47(4)
C(6b)	4211(11)	–2346(9)	1660(5)	38(4)
C(1c)	6643(10)	–981(9)	3152(5)	29(3)
C(2c)	6038(11)	–1021(10)	3953(5)	41(4)
C(3c)	7090(13)	–1377(10)	4529(6)	52(4)
C(4c)	8761(14)	–1667(11)	4293(7)	60(5)
C(5c)	9378(13)	–1639(12)	3499(7)	59(5)
C(6c)	8324(10)	–1291(10)	2920(6)	40(4)

[ReOCℓ(oxine)(HL)] (*5*)

	x/a	*y/b*	*z/c*	U_{eq}
Re	7791(1)	7130(1)	2764(1)	29(1)
Cl	6506(2)	9078(4)	1855(2)	53(1)
O(1)	7460(7)	6937(11)	3701(6)	49(3)
O(2)	7954(5)	6518(9)	1548(5)	33(2)
O(3)	8811(6)	8890(9)	3033(5)	39(3)
O(4)	8752(7)	1573(11)	4017(6)	47(3)
N(1)	6627(6)	5250(10)	2074(6)	32(3)
N(2)	9234(6)	5765(11)	3457(5)	31(3)
C(1)	5932(8)	4602(16)	2368(9)	45(4)
C(2)	5207(9)	3446(16)	1827(11)	52(5)
C(3)	5177(10)	2849(15)	989(11)	51(5)
C(4)	5908(8)	3511(14)	647(8)	40(4)
C(5)	5944(9)	3019(15)	–230(9)	50(4)
C(6)	6648(9)	3724(5)	–488(8)	43(4)
C(7)	7352(8)	4961(14)	86(7)	39(4)
C(8)	7325(7)	5415(12)	940(6)	30(3)
C(9)	6596(7)	4965(12)	1220(7)	31(3)
C(10)	10067(8)	6723(14)	3619(7)	35(4)
C(11)	11091(9)	6087(15)	3989(8)	42(4)
C(12)	11246(8)	4439(15)	4199(8)	44(4)
C(13)	10388(9)	3508(15)	4070(8)	43(4)
C(14)	9399(8)	4144(13)	3699(6)	33(3)
C(15)	9881(9)	8495(14)	3432(8)	43(4)
C(16)	8450(9)	3089(13)	3533(8)	35(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Selected bond lengths (Å) and bond angles (°)

trans-[ReOCℓ$_2$(Phsal)(PPh$_3$)]			
Re—Cl(1)	2.383(3)	Re—N(1)	2.127(6)
Re—Cl(2)	2.390(3)	N(1)—C(7)	1.29(1)
Re—P(1)	2.469(2)	C(6)—C(7)	1.44(1)
Re—O(1)	1.668(6)	O(2)—C(1)	1.333(9)
Re—O(2)	1.962(5)	P(1)—C(mean)	1.817(8)
Cl(1)—Re—Cl(2)	168.9(1)	P(1)—Re—N(1)	168.3(2)
Cl(1)—Re—P(1)	89.8(1)	P(1)—Re—O(1)	90.7(2)
Cl(1)—Re—N(1)	86.6(2)	P(1)—Re—O(2)	85.1(1)
Cl(1)—Re—O(1)	95.2(3)	O(1)—Re—N(1)	100.7(2)
Cl(1)—Re—O(2)	86.5(2)	O(2)—Re—N(1)	83.6(2)
Cl(2)—Re—P(1)	96.2(1)	O(1)—Re—O(2)	175.5(2)
Cl(2)—Re—N(1)	85.6(2)	Re—N(1)—C(7)	127.3(5)
Cl(2)—Re—O(1)	94.0(3)	N(1)—C(7)—C(6)	127.8(7)
Cl(2)—Re—O(2)	84.8(2)	Re—O(2)-C(1)	138.7(4)
[ReOCℓ(oxine)(HL)]			
Re—Cl	2.360(3)	Re—N(1)	2.162(8)
Re—O(1)	1.69(1)	Re—N(2)	2.156(8)
Re—O(2)	2.023(8)	O(2)—C(8)	1.32(1)
Re—O(3)	1.948(7)	O(3)—C(15)	1.40(1)
Cl—Re—O(1)	97.9(3)	O(2)—Re—N(1)	75.0(3)
Cl—Re—O(2)	89.5(2)	O(2)—Re—N(2)	82.3(3)
Cl—Re—O(3)	86.3(2)	O(3)—Re—N(1)	164.6(4)
Cl—Re—N(1)	87.9(2)	O(3)—Re—N(2)	79.8(3)
Cl—Re—N(2)	163.8(3)	N(1)—Re—N(2)	103.3(3)
O(1)—Re—O(2)	158.6(4)	Re—N(2)—C(10)	110.8(7)
O(1)—Re—O(3)	109.7(4)	Re—O(3)—C(15)	118.7(6)
O(1)—Re—N(1)	85.2(4)	Re—N(1)—C(9)	114.0(7)
O(1)—Re—N(2)	94.8(4)	Re—O(2)—C(8)	120.2(7)
O(2)—Re—O(3)	90.7(3)		

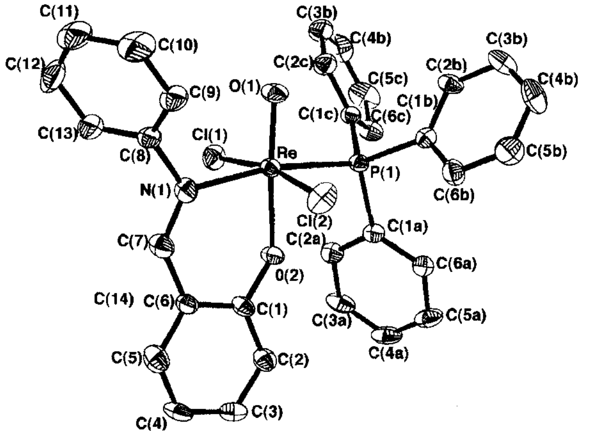

FIGURE 1 ORTEP drawing of trans-[ReOCℓ$_2$(C(7)Phsal)(PPh$_3$)] (2); 40% probability thermal ellipsoids are shown.

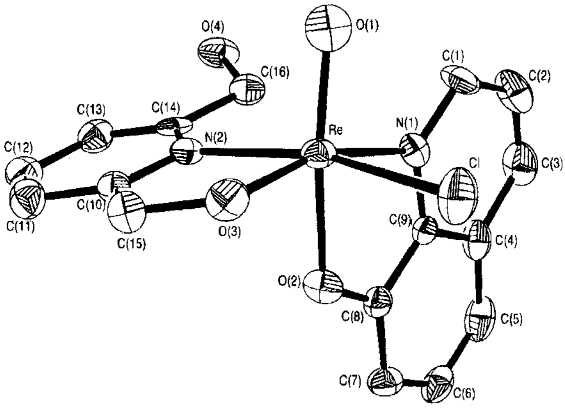

FIGURE 2 An ORTEP drawing of the complex [ReOCℓ(oxine)(HL)] (**5**). The atom-numbering scheme and thermal ellipsoids drawn at the 40% probability level are shown.

RESULTS

The reaction of *cis*-[ReOCℓ_2(HL)(PPh$_3$)] (**1**) with *N*-phenylsalicylideneimine (PhsalH) and 8-hydroxyquinoline (oxineH) in equimolar quantities under reflux in ethanol led to the formation of *trans*-[ReOCℓ_2(Phsal)(PPh$_3$)] (**2**) and *trans*-[ReOCℓ_2(oxine)(PPh$_3$)] (**4**), respectively. The latter complex was isolated after only 45 min of heating, but when heating was continued for 6h, the *cis* isomer was obtained in good yield. The products ReOCℓ(Phsal)$_2$ and ReOCℓ(oxine)$_2$ were isolated in good yield when a three-fold molar excess of PhsalH and oxineH were reacted with **1** under reflux conditions in ethanol.

Complexes **2** and **4**, as well as the *cis* isomer of **4**, were previously[14] obtained after the prolonged heating of *trans*-ReOCℓ_2(X)(PPh$_3$)$_2$ (X=Cl or OEt) with the N,O$^-$-donor ligands PhsalH and oxineH in ethanol and benzene, respectively. The *bis*(bidentate) ligand complex ReOCℓ(Phsal)$_2$ was reported earlier [10] as the product of the reaction of *trans*-ReOCℓ_3(PPh$_3$)$_2$ with a molar excess of PhsalH in the presence of triethylamine in benzene. The mixed *bis*(bidentate) ligand complexes [ReOCℓ(Phsal)(HL)] (**3**) and [ReOCl(oxine)(HL)] (**5**) were isolated from the reactions of **1** with PhsalH and oxineH, under reflux conditions, respectively, in benzene. Reactions of complexes **2** and **4** with an excess of H$_2$L in benzene led to the isolation of **3** and **5**, respectively, after prolonged heating. The melting points and infrared and proton nuclear magnetic resonance spectra of the products were identical to those prepared from **1** in benzene. All the complexes in this study are diamagnetic and are non-electrolytes in acetonitrile and DMF. In solution they are stable for days, and for months in the solid state.

Characterization of the Complexes

All complexes were characterized by elemental analyses, infrared and ^{1}H NMR spectroscopy, and X-ray crystallography in the cases of *trans*-ReOCℓ_2(Phsal)(PPh$_3$) (**2**) and ReOCℓ(oxine)(HL) (**5**). Infrared measurements confirmed the existence of rhenium-ligand multiple bonds and proved that the multidentate ligands were coordinated, as were shown by shifts in absorptions of the complexes in comparison with those of the free ligands and starting materials; the elemental analyses established the formulation of all the products. Full assignments of the ^{1}H NMR spectra were in most cases impossible due to the overlapping of multiplets in the aromatic hydrogen region (6.0–8.8 ppm); however, the spectra were nevertheless still useful in verifying the nature of the complexes.

Trans-[ReOCℓ_2(Phsaℓ)(PPh$_3$)] (2) and trans-[ReOCℓ_2(oxine)(PPh$_3$)] (4)

These two complexes were reported earlier in the literature as the products of the reaction of *trans*-ReOCℓ_3(PPh$_3$)$_2$ with PhsalH and oxineH, and melting points and infrared data were given.[14] The values for ν(Re═O) (at 972 and 974 cm^{-1} for **2** and **4** respectively) suggest that the anionic phenolic oxygen donor atom, which coordinates *trans* to the Re═O bond, is a harder base than the aliphatic alcoholic oxygen of HL. All the infrared data correspond to those reported earlier [14] for **2** and **4**, within experimental error. The far-infrared spectra show only one absorption in the 285–340 cm^{-1} region which could be assigned to ν(Re—Cl), thus suggesting a *trans* disposition of the chlorides in **2** and **4**.

The ^{1}H NMR spectrum of **2** shows the presence of 25 protons in the aromatic region. The proton attached to C(2) (see Figure 1) and the azomethine proton appear as a doublet and singlet the furthest downfield at δ8.56 and 8.10 ppm respectively. The signal for the two equivalent protons H^9 and H^{13} appears at δ7.52 ppm, and the magnetic equivalence of protons H^{10} and H^{12} is evidenced by a two-proton triplet the furthest upfield at δ 7.15 ppm.

A full assignment of the ^{1}H NMR spectrum of **4** is problematic due to the overlapping of several signals. However, the presence of the oxine ligand is established beyond doubt by the chemical shift of proton H^1 (see Figure 2 for the atom numbering of oxine$^-$), which appears as a doublet the furthest downfield at δ 8.39 ppm. Furthermore, the aromatic region integrates for a total of 21 protons, equivalent to the presence of oxine and PPh$_3$.

[ReOCℓ(Phsal)(HL)] (3) and [ReOCℓ(oxine)(HL)] (5)

In the infrared spectra of **3** and **5** the Re═O stretching frequencies appear in the expected range (945–965 cm^{-1}) for neutral six-coordinate rhenium(V) complexes with an anionic oxygen donor *trans* to the oxo group.[15-16] Broad bands of medium intensity at 3487 cm^{-1} and 3437 cm^{-1} in the spectra of **3** and **5** respectively suggest that an OH group of HL^- in the complexes is not coordinated. The strong band at 1096 cm^{-1} (>(P—C)) in **1** is absent in the spectra of **3** and **5**, and in the far-infrared region a single band of medium intensity around 321 cm^{-1} is indicative of the presence of a single chloride in the complexes.

^1H NMR spectra provide definite evidence for the presence of HL^- in the complexes. The free OH protons of the coordinated HL^- ligands appear as broad singlets at δ3.81 and 3.97 ppm in **3** and **5**, respectively (at δ4.48 ppm in **1**), and it seems unlikely that it is involved in hydrogen bonding. The chemical shifts of the methylene protons (a four proton singlet at δ4.83 and 4.86 ppm, respectively) differ little from that in **1**. A full assignment of the spectra was complicated by overlapping signals in the aromatic region, although the doublet the furthest downfield in **5** at δ9.02 ppm is assigned to H^1 (see Figure 2 for atom numbering).

X-ray Structure of trans-[ReOCℓ$_2$(Phsal)(PPh$_3$)] (2)

The complex is built up by the juxtaposition at van der Waals distances of well-separated neutral rhenium(V) molecules (Figure 1). The coordination geometry about the Re is distorted octahedral, and in the coordination polyhedron the Re atom is 0.20 Å from the Cℓ(1)P(1)Cℓ(2)N(1) equatorial plane, towards the O(1) oxo-atom. The 'inner core' is distorted mainly by this movement, with the result that the angles Cℓ(1)–Re—Cℓ(2) and P(1)–Re—N(1) are 168.9(1) and 168.3(2)°, respectively. The O(oxo)–Re—O(2) angle is also non-linear at 175.5(2)°, while the bond angles in the equatorial plane are rather close to 90°. The $Phsal^-$ ligand bridges an equatorial and an apical position, with quite normal structural parameters (see, for comparison, $ReOC\ell(Phsal)_2$ [17] and $TcOC\ell(Phsal)_2$).[3] The six-membered [ReO(2)C(1)C(6)C(7)N(1)] planar ring is virtually perpendicular to the mean equatorial plane, the dihedral angle being 93.3°. In the $C\ell_2PNO_2$ polyhedron the Re atom is +1.15 Å away from the Cℓ(1)P(1)O(1) plane and −1.34 Å from the Cℓ(2)N(1)O(2) one, the angle between the two triangles being 6.1°. The bond lengths and angles in the 'inner core' (Table III) fall within the range reported for other six-coordinate monooxorhenium(V) complexes and they do not merit any comment.[18-19] Moreover, the Re—O(2) bond length (1.962(5) Å) seems to exclude any *trans* weakening effect due to the strong π–bonding of the oxo-group.

X-ray Structure of [ReOCℓ(oxine)(HL)] (5)

The molecular geometry and the atom numbering of the complex are shown in Figure 2. The structure consists of discrete neutral molecules. The internal geometrical parameters indicate a distorted octahedral geometry around the rhenium. The N(2) and O(3) donor atoms of the HL^- ligand, together with the Cℓ and N(1) atom of the oxine ligand, form the equatorial plane, with the oxo-O(1) and the O(2) atoms *trans* to each other in axial positions. In this manner the two organic ligands act as bidentate uninegative moieties. Distortions from the ideal Re-centered octahedron result in (i) the Re atom lying out of the mean equatorial plane by 0.23Å towards the oxo-atom; (ii) a non-linear O(1)—Re—O(2) axis of 158.6(4)° accompanied by Cl—Re—N(2) and N(1)—Re—O(3) angles of 163.8(3) and 164.6(4)°, respectively; (iii) the N(1) KO(2) distance is 2.55Å, and consequently the N(1)—Re—O(2) 'bite' angle (75.0°) is narrower than the N(2)—Re—O(3) angle (79.8°; N(2) KO(3) 2.64 Å); (iv) in the $C\ell N_2O_3$ polyhedron the Re atom is +1.14 Å away from the CℓN(1)O(1) plane and −1.28 Å from the N(2)O(3)O(2) one, the angle between the two triangles being 9.1°. In the 'inner core', the two five-membered rings, *i.e.*, ReN(2)C(10)C(15)O(3) and ReN(1)C(9)C(8)O(2), are quasi-orthogonal, with a dihedral angle of 81.0°, and the Re—O(2) distance (2.023(8) Å), *trans* to the oxo atom, seems somewhat sensitive to *trans* influence.

DISCUSSION

The bidentate coordination of HL^- in **1** enabled the preparation of mixed bidentate ligand complexes of rhenium(V), of which no examples could be found in the literature. Simple reaction of **1** with the bidentate N,O^--donor ligands *N*–phenylsalicylideneimine (PhsalH) and 8-hydroxyquinoline (oxineH) in *benzene* led to the substitution of Cl- and PPh_3 to form [ReOCℓ(Phsal)(HL)] (**3**) and [ReOCℓ(oxine)(HL)] (**5**), respectively. A crystal structure analysis of **5** (Figure 2) indicates that the coordination site *trans* to the rhenyl oxo oxygen is occupied by the deprotonated oxygen of the *o*-hydroxyphenyl group of $Phsal^-$, and not the deprotonated anionic aliphatic alcoholate oxygen of HL^-, as was the case in **1**.

When the reactions of **1** with PhsalH and oxineH were performed in ethanol, it was surprisingly found that the bidentate HL^- ligand was substituted in **1** by $Phsal^-$ and $oxine^-$ to form the *trans* isomers of [ReOCℓ2(Phsal)(PPh_3)] (**2**) and [$ReOC\ell_2$(oxine)(PPh_3)] (**4**). This unusual substitution of HL^- by other bidentate N,O^--donors in ethanol is in our opinion partly the result of strong hydrogen-bonding that exists between the free OH group in the coordinated HL^- and the ethanol molecules of the solvent. These hydrogen-bonds will weaken the N,O^--coordination of HL^-, and this, coupled with the fact that the negatively charged phenolic oxygen is a harder base than the anionic aliphatic oxygen of HL^-, facilitates the displacement of HL^- rather than $C\ell^-$ and PPh_3. In benzene, hydrogen bonding is absent, and no substitution of coordinated HL^- occurs.

Reaction of **1** with a three-fold molar excess of PhsalH and oxineH with prolonged heating in ethanol gave $[\mathrm{ReOC}\ell(\mathrm{Phsal})_2]$ and $[\mathrm{ReOC}\ell(\mathrm{oxine})_2]$ as products.

Another interesting aspect of this work is that although a *cis* orientation of the two chlorides exists in **1**, *trans* isomers are obtained for **2** and **4**. Both isomers (*i.e.*, *trans* and *cis*) have previously[14] been observed for both complexes, which were obtained by the reaction of *trans*-$\mathrm{ReOC}\ell_3(\mathrm{PPh}_3)_2$ and the bidentate ligands. It was found that the *cis*-isomer of $\mathrm{ReOC}\ell_2(\mathrm{Phsal})(\mathrm{PPh}_3)$ is obtained from benzene or THF at room temperature or upon heating under reflux for a short time.[14] In refluxing ethanol the *trans* isomer was the principal product, and its yield increased as the reaction time was increased. This correlates with the observations in this study.

Acknowledgments

T.I.A.G and J.P. are grateful to the Foundation for Research Development and the University of Port Elizabeth for financial support.

References

[1] W. Jia and G.J. Ehrhardt, *J. Nucl. Biol. Med.*, **38**, 447 (1994); F.-M. Su, L. Lyen, H.B. Breitz, P.L. Weiden and R. Fritzberg, *J. Nucl. Biol. Med.*, **38**, 485 (1994).

[2] *Technetium and Rhenium in Chemistry and Nuclear Medicine 4*, eds. M. Nicolini, G. Bandoli, and U. Mazzi, (SG Editoriali, Padova, Italy, 1995).

[3] G. Bandoli, U. Mazzi, D.A. Clemente and E. Roncari, *J. Chem. Soc., Dalton Trans.*, 2455 (1982).

[4] G. Bandoli, M. Nicolini, U. Mazzi and F. Refosco, *J. Chem. Soc., Dalton Trans*, 2505 (1984).

[5] F. Tisato, F. Refosco, U. Mazzi, G. Bandoli and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 1693 (1987).

[6] J.G.H. du Preez, T.I.A. Gerber and O. Knoesen, *J. Coord. Chem.*, **16**, 285 (1987).

[7] J.G.H. du Preez, T.I.A. Gerber and O. Knoesen, *Inorg. Chim. Acta*, **133**, 3 (1987).

[8] A. Marchi, R. Rossi, L. Magon, A. Duatti, R. Pasqualini, V. Ferretti and V. Bertolasi, *J. Chem. Soc., Dalton Trans.*, 1411 (1990).

[9] J.G.H. du Preez, T.I.A. Gerber, H.J. Kemp and B.J.A.M. van Brecht, *J. Coord. Chem.*, **24**, 159 (1991).

[10] U. Mazzi, E. Roncari, R. Rossi, V. Bertolasi, O. Traverso and L. Magon, *Transition Met. Chem.*, **5**, 289 (1980).

[11] V. Bertolasi, V. Ferretti, M. Sacerdoti and A. Marchi, *Acta Cryst.*, **C40**, 971 (1984).

[12] T.I.A. Gerber, J. Bruwer, G. Bandoli, J. Perils and J.G.H. du Preez, *J. Chem. Soc., Dalton Trans.*, 2189 (1995).

[13] J.G.H. du Preez, T.I.A. Gerber and H.J. Kemp, *J. Coord. Chem.*, **25**, 139 (1992).

[14] E. Roncari, U. Mazzi, R. Rossi, A. Duatti and L. Magon, *Transition Met. Chem.* **6**, 169 (1981).

[15] S. Jurisson, L.F. Lindoy, K.P. Dancy, M. McPartlin, P.A. Tasker, D.K. Uppal and E. Deutsch, *Inorg. Chem.*, **23**, 227 (1984).

[16] G. Bandoli, U. Mazzi, E. Roncari and E. Deutsch, *Coord. Chem. Rev.*, **44**, 191 (1982).

[17] G. Gilli, M. Sacerdoti, V. Bertolasi and R. Rossi, *Acta Cryst.*, **B38**, 100 (1982).

[18] G. Bandoli, T.I.A. Gerber, R. Jacobs and J.G.H. du Preez, *Inorg. Chem.*, **33**, 178 (1994), and refs therein.

[19] F. Tisato, F. Refosco, A. Moresco, G. Bandoli, A. Dolmella and C. Bolzati, *Inorg. Chem.*, **34**, 1779 (1995); G. Bandoli, A. Dolmella, T.I.A. Gerber, J.G.H. du Preez and H.J. Kemp, *Inorg. Chim. Acta*, **217**, 141 (1994).