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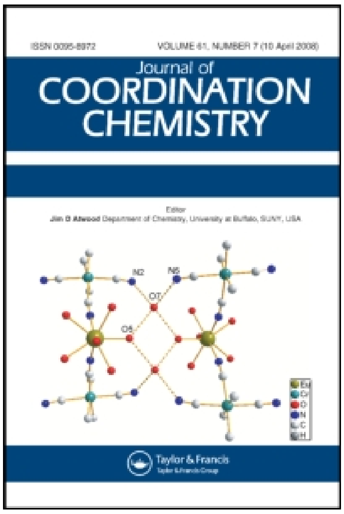

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Complexes of <i>cis</i>-dihalogenorhenium(V) with iminophenol

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Complexes of *cis*-dihalogenorhenium(V) with iminophenol

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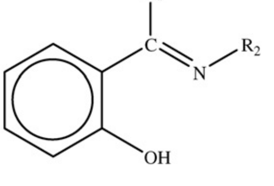
Complexes *cis*-$[ReOX_2(msa)(PPh_3)]$ [X = Cl(**1**), I(**2**)] were prepared from *trans*-$[ReOCl_3(PPh_3)_2]$ or *trans*-$[ReOI_2(OEt)(PPh_3)^2]$ with 2-(1-iminoethyl)phenol (Hmsa) in acetonitrile. An X-ray crystallographic study shows that the bonding distances and angles in **1** and **2** are nearly identical, and that the two halides in each complex are coordinated *cis* to each other in the equatorial plane *cis* to the oxo group. Rhenium(V) complexes with *cis* diiodides are rare. All bonding distances and angles are in the expected ranges.

Keywords: Rhenium(V); Iminophenol; *cis*-Diido; Crystal structures

1. Introduction

Schiff bases are versatile ligands in coordination chemistry, used in this role for the first time in 1933 [1]. Interest in these compounds as ligands stems from the biological and pharmaceutical applications of their metal complexes, which show increased antibiotic activity [2–4] after coordination of the ligands. For example, Schiff base complexes of iron(III) have exhibited widespread antiviral activity in biological systems [5, 6].

Substituents R_2 on the imino nitrogen of bidentate Schiff bases play a determining role in the geometry of the complexes formed [7, 8]. With large



R_1	R_2	Hnor
CH_3	H	Hmsa

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steric groups (like *t*-butyl), tetrahedral complexes of the type [M(nor)$_2$] [M = Ni(II), Cu(II)] are formed. However, with smaller substituents square-planar complexes are obtained [9–11].

Rhenium(V) complexes with potentially uninegative bidentate *N*,*O*-donor Schiff base ligands are well studied, and yield complexes with the formulae [ReOX$_2$(nor)(PPh$_3$)] and [ReOX(nor)$_2$] (X = Cl, Br) [12–15]. Similar products were obtained with 8-hydroxyquinoline as ligand [14]. In the case of [ReOX$_2$(nor)(PPh$_3$)], some systems have been isolated as *cis* and *trans* isomers [12–16]. Although diiodo complexes of Re(V) containing bidentate *N*,*O*-donor ligands are scarce in the literature, only *trans* isomers have been isolated [17].

In this study the synthesis and crystal structures of [ReOX$_2$(msa)(PPh$_3$)] [X = Cl(**1**), I(**2**)] are reported as products of the reactions of *trans*-[ReOX$_2$(Y)(PPh$_3$)$_2$] (X = Y = Cl for **1**; X = I, Y = OEt for **2**) with 2-(1-iminoethyl)phenol (Hmsa) in acetonitrile. In both products **1** and **2** the two halides are coordinated in *cis* positions relative to each other.

2. Experimental

2.1. *Reactants and methods*

Trans-[ReOCl$_3$(PPh$_3$)$_2$] [18] and *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$] [19] were synthesized by literature methods. Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. All manipulations were done under nitrogen using standard Schlenk and cannula techniques. Infrared spectra were obtained using KBr discs and ^{1}H NMR spectra (300 MHz) were run at room temperature in d$_6$-DMSO. The instrumentation used is the same as reported earlier [20].

2.2. *Synthesis*

2.2.1. Hmsa. A stream of ammonia (generated from heating a mixture of ammonium chloride and calcium hydroxide) was bubbled through a solution of 3.423 g of 2-hydroxyacetophenone in 25 cm^3 THF for 2 h, with a concomitant colour change to dark yellow. The solution was then heated under reflux overnight (~15 h). The partial removal of the solvent under vacuum, and the addition of *n*-heptane gave an oil, which was taken up in ethanol and left to evaporate slowly at room temperature to give yellow crystals. Yield = 2.206 g (64%); m.p. 124°C. Anal. Found (%): C, 71.12; H, 6.88; N, 10.48. Calcd: C, 71.09; H, 6.71; N, 10.36. IR(cm^{-1}): ν(OH) 3449; ν(NH) 2839; ν(C=N) 1608. ^{1}H NMR δ(ppm): 15.19 (br s, 1H, NH), 9.35 (br s, 1H, OH), 7.51 (d, 1H, H2), 7.36 (t, 1H, H4), 6.98 (d, 1H, H5), 6.82 (t, 1H, H3), 2.51 (s, 3H, CH$_3$).

2.2.2. *cis*-[ReOX$_2$(msa)(PPh$_3$)] [X = Cl(1), I (2)]. Hmsa (39 mg, 289 µmol) was added to a solution of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] (100 mg, 120 µmol) for **1**, or *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$] (123 mg, 120 µmol) (for **2**), in 20 cm^3 acetonitrile and the mixtures were heated under reflux for 90 min. The colour of both reaction mixtures turned green, and after cooling to room temperature, the solutions were filtered and left to evaporate slowly at room temperature. After two days crystalline precipitates were collected by filtration, and washed with ethanol and diethyl ether. Recrystallization of **1** from a 2 : 1 v/v mixture of dichloromethane : ethanol, and of **2** from a 1 : 1 toluene : chloroform mixture gave green crystals suitable for X-ray crystallographic analysis. Yields = 58 mg of 1 (72%), 73 mg of **2** · ½ toluene(68%); m.p. 217°C(1), 191°C(**2** · ½ toluene). Anal. **1**: Found (%): C, 46.79; H, 3.48; N, 2.12. Calcd: C, 46.64; H, 3.46; N, 2.09. **2** · ½ toluene: Found: C, 39.63; H, 3.12; N, 1.78. Calcd: C, 39.43; H, 3.03; N, 1.56. IR(cm^{-1}) **1**: ν(Re=O) 956vs; ν(C=N) 1594vs; ν(Re=N) 528s; ν(Re–O) 494m; ν(Re–Cl) 322m, 314m. **2**: ν(Re=O) 949s; ν(C=N) 1594vs; ν(Re–N) 529m; ν(Re–O) 499m. ^{1}H NMR δ(ppm) **1**: 11.44 (br s, 1H, NH), 7.88 (d, 1H, H2), 7.56–7.67 (m, 15H, PPh_3), 7.52 (t, 1H, H4), 7.22 (d, 1H, H5), 7.06 (t, 1H, H3), 2.82 (s, 3H, CH_3). **2**: 11.67 (br s, 1H, NH), 7.92 (d, 1H, H2), 7.52–7.71 (m, 16H, PPh_3, H4), 7.31 (d, 1H, H5), 7.12 (t, 1H, H3), 2.85 (s, 3H, CH_3).

2.3. *Crystallography*

Intensity data for **1** and **2** were collected at 200(2) K on a Nonius Kappa CCD single-crystal diffractometer, using Mo-Kα radiation. Unit cell and space group determinations were carried out in the usual manner [21]. The structures were solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [22]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were geometrically constrained. ORTEP views of **1** and **2**, along with their numbering schemes, are given in figures 1 and 2 respectively. A summary of the crystal data and

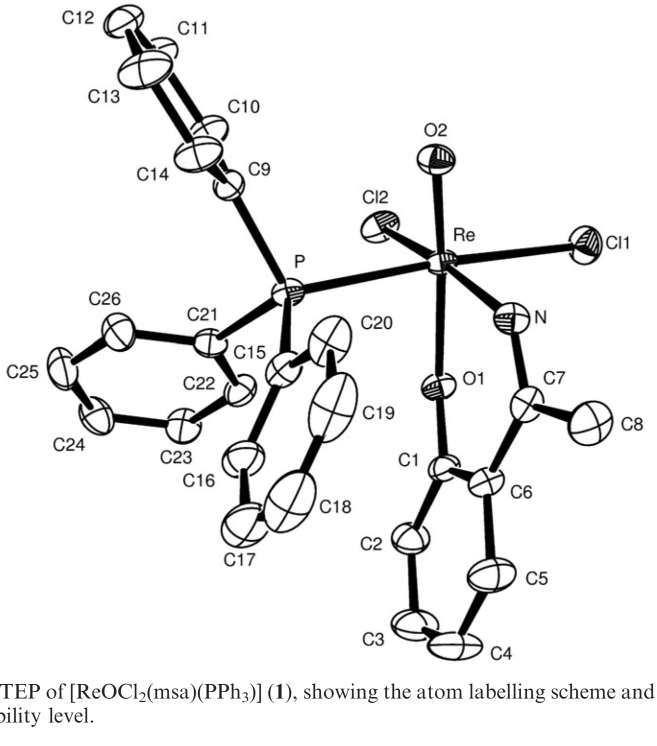

Figure 1. An ORTEP of [$ReOCl_2$(msa)(PPh_3)] (**1**), showing the atom labelling scheme and thermal ellipsoids at the 40% probability level.

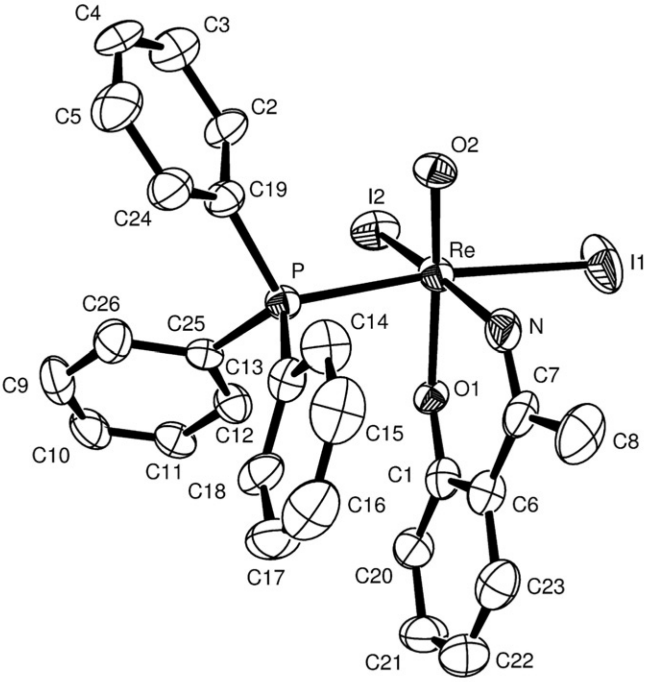

Figure 2. ORTEP drawing of the structural unit of [ReOI$_2$(msa)(PPh$_3$)] (**2**) (40% probability ellipsoids).

refinement details is given in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis*

The Schiff-base ligand Hmsa was prepared by reaction of ammonia with 2-hydroxyacetophenone in THF. Complexes **1** and **2** were obtained from reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] and *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$], respectively, with a twofold molar excess of Hmsa in acetonitrile. Pure products could not be isolated from the reaction of equimolar quantities. Both complexes are diamagnetic and are non-electrolytes in DMF, and they are soluble in a wide variety of polar solvents.

3.2. *Structures*

Perspective views of the asymmetric units of **1** and **2** are shown in figures 1 and 2, respectively. The complexes exhibit distorted octahedral geometries about the central rhenium(V). The basal planes are defined by the phosphorus atom of the PPh$_3$, two halides *cis* to each other, and the neutral imino nitrogen of msa. The oxo group and phenolate oxygen lie in *trans* axial positions. Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear O(2) = Re–O(1) axis of 167.02(9)° in **1**

Table 1. Crystal and structure refinement data for **1** and **2**.

	1	**2** · ½C_7H_8
Chemical formula	$C_{26}H_{23}NO_2PCl_2Re$	$C_{29.5}H_{27}NO_2PI_2Re$
Formula weight	669.55	898.53
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	10.4089(1)	10.0828(3)
b	11.0423(2)	12.1823(3)
c	12.7589(2)	13.8432(4)
α	83.188(1)	74.736(2)
β	70.954(1)	69.832(1)
γ	63.254(1)	68.416(2)
Volume (Å^3)	1237.20(4)	1465.96(7)
Z	2	2
Density (Calcd) (Mg m^{-3})	1.797	2.026
Absorption coefficient (mm^{-1})	5.216	6.332
$F(000)$	652	838
Crystal size (mm^3)	0.03 × 0.05 × 0.08	0.04 × 0.09 × 0.13
θ range for data collection (°)	3.2–27.5	3.2–24.0
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-15 \le l \le 16$	$-11 \le h \le 11$, $-13 \le k \le 13$, $-15 \le l \le 15$
Reflections measured	25,607	8944
Independent/observed reflections	5647/5308	4590/3845
Data/parameters	5647/303	4590/350
Goodness-of-fit on F^2	1.07	1.06
Final R indices $[I > 2\sigma(I)]$	0.0210($wR_2 = 0.0450$)	0.0415($wR_2 = 0.1122$)
Largest diff. peak and hole (e Å^{-3})	1.05, −1.00	3.03, −2.11

Table 2. Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

	1	**2**
Re–O(2)	1.688(2)	1.696(5)
Re–O(1)	1.942(2)	1.925(5)
Re–X(1)	2.410(1)	2.767(1)
Re–X(2)	2.373(1)	2.674(1)
Re–N	2.089(3)	2.11(1)
Re–P	2.465(1)	2.492(2)
C(1)–O(1)	1.346(4)	1.35(1)
N–C(7)	1.286(4)	1.27(2)
C(6)–C(7)	1.458(4)	1.46(1)
O(1)–Re–O(2)	167.02(9)	167.7(3)
X(1)–Re–O(2)	97.83(7)	97.5(2)
X(2)–Re–O(2)	100.23(8)	99.1(3)
N–Re–O(2)	90.3(1)	89.7(3)
P–Re–O(2)	86.69(7)	88.3(2)
X(1)–Re–X(2)	88.88(3)	88.77(3)
X(1)–Re–P	175.47(2)	173.44(7)
X(2)–Re–N	168.78(7)	169.7(2)
O(1)–Re–N	80.64(9)	81.0(3)
Re–O(1)–C(1)	137.1(2)	138.5(6)
Re–N–C(7)	134.3(2)	133.6(7)
N–C(7)–C(6)	121.7(3)	123(1)

[167.7(3)° in **2**], accomplished by Cl(1)–Re–P and Cl(2)–Re–N angles of 175.47(2)° [I(1)–Re–P = 173.44(7)° in **2**] and 168.78(7)° [I(2)–Re–N = 169.7(2)°], respectively. The metal shifts out of the mean equatorial plane formed by X_2PN by 0.136 and 0.128 Å in **1** and **2**, respectively, towards O(2), which is the result of the non-orthogonal angles O(2)–Re–X(1) = 97.83(7)° in **1** [97.5(2)° in **2**], O(2)–Re–Cl(2) = 100.23(8)° [O(2)–Re–I(2) = 99.1(3)°], O(2)–Re–P = 86.69(7)° in **1** [88.3(2)° in 2] and O(2)–Re–N = 90.3(1)° in **1** [89.7(3)° in **2**]. The Re=O(2) axis is inclined at 177.3° and 176.7° with respect to the equatorial plane in 1 and 2, respectively.

The Re=O(2) bond lengths of 1.688(2) and 1.696(5) Å are within the range expected with a phenolate oxygen *trans* to the oxo group [14,23,24]. The Re–O(1) bond lengths of 1.942(2) **1** and 1.925(5) Å **2** are shorter than the accepted length for a Re–O single bond [2.04 Å] [25]. The Re–X(1) bond length is significantly longer than Re–X(2), due to the larger *trans* effect of P compared to the imino N. The bite angle of the msa ligand is practically identical in the two complexes. C(7)–N is a double bond [1.286(4) Å in **1**, 1.27(2) Å in **2**], and the N–C(7)–C(6) bond angle around 122° is indicative of the sp^2 hybridization of C(7). In both complexes there is an intramolecular hydrogen-bond between NH and O(2) [3.045(3) Å in **1**, 2.990(9) Å in **2**].

3.3. *Spectral characterization*

The infrared spectra of **1** and **2** display Re=O stretching frequencies at 956 and 949 cm^{-1}, respectively, which fall in the observed region of 945–968 cm^{-1} for neutral six-coordinate monooxorhenium(V) complexes having an anionic phenolate oxygen atom coordinated *trans* to the oxo group [26,27]. The Re–N and Re–O stretches appear around 530 and 495 cm^{-1}, respectively. The spectrum of **1** displays two distinct peaks at 314 and 322 cm^{-1}, typical for ν(Re–Cl) with the two chlorides in *cis* positions to the oxo group, and in *cis* sites to each other. In the ^{1}H NMR spectra of the complexes the broad singlets far downfield around 11.5 ppm are attributed to the imino proton. A fifteen proton multiplet in the range 7.5–7.7 ppm illustrates the presence of PPh_3. The four phenyl protons of msa give rise to a set of doublet-triplet-doublet-triplet signals in the range 7.92–7.06 ppm.

We have previously synthesized $[ReOI_2(ame)(PPh_3)]$ (**3**), with the iodides in *trans* positions to each other, from the reaction of *trans*-$[ReOI_2(OEt)(PPh_3)_2]$ with 2-(2-aminophenyl)ethanol (Hame) in benzene [17]. The ame ligand coordinates to rhenium(V) *via* the neutral sp^3-hybridized amino nitrogen atom [Re–N = 2.256(6) Å] and a deprotonated alcoholate oxygen *trans* to the oxo group [Re–O = 1.860(5) Å]. These two bonding distances reflect the significant donor properties of an imino and amino nitrogen on the one hand, and of a phenolate and alcoholate oxygen on the other. Therefore, from a comparison of the bonding parameters of complexes **2** and **3**, an imino nitrogen is a stronger Lewis base than an amino nitrogen, and an alcoholate oxygen is a better σ and π-donor than a phenolate oxygen in rhenium(V) complexes.

Supplementary material

CCDC-623909 (for **1**) and CCDC-623910 (for **2**) contain the crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk.

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