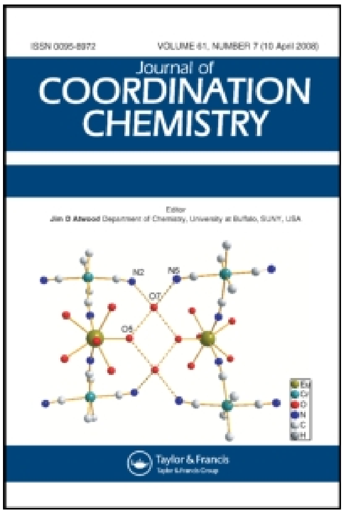

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Synthesis and characterization of a neutral rhenium(V) complex containing a tridentate chelate with an imido donor atom

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The six-coordinate complex *cis*-[Re(mps)Cl_2(PPh_3)] (**1**) (H_3mps = *N*-(2-amino-3-methylphenyl)-salicylideneimine) was prepared the reaction of *trans*-[ReOCl_3(PPh_3)$_2$] with a twofold molar excess of H_3mps in benzene. The compound was characterized by spectroscopy and single-crystal X-ray crystallography. Mps coordinates as a tridentate chelate *via* the doubly deprotonated 2-amino nitrogen (which is present in **1** as an imide), the neutral imino nitrogen and the phenolate oxygen atoms. The imide and phenolate oxygen atoms coordinate *trans* to each other in a distorted octahedral geometry around the rhenium(V) centre, with the two chlorides in *cis* positions.

Keywords: Rhenium(V); N,N,O trianion; Imide; Crystal structure

1. Introduction

Due to the prominence of the oxo-group in the coordination chemistry of rhenium(V) [1], much research effort is currently focussed on the synthesis of rhenium(V) moieties with metal nitrogen multiple bonds, such as metal-nitrido, metal-hydrazido and metal-imido, in order to produce substitution-inert complexes [2,3]. However, Re(V) imides have received the most attention because of the easy introduction of substituents on the imido moiety, and which may lead to a greater variety of complexes and consequently may "fine-tune" the biodistribution of these complexes in therapeutic applications. Our interest in this field concerns the synthesis of stable Re(V) complexes with multidentate ligands containing an amino group, which on deprotonation can lead to a coordinated chelate containing the phenylimido core Re = NC_6H_4–X. One of the major advantages of the phenylimido moiety is that it can be functionalized and derivatized. For example, the compound [^{188}Re(=NC_6H_4–X)Cl_3(PPh_3)$_2$] contains a *para*-substituted phenylimido group which was functionalized with a carboxylic group conjugated to various cholesterol derivatives [4]. However, it has also been shown that many

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phenylimidorhenium(V) compounds are hydrolytically unstable, ascribed to the presence of monodentate ligands in the coordination sphere [5]. For this reason, we believe that the use of multidentate imido ligands in the synthesis of rhenium(V) complexes can be advantageous.

We have recently reported the synthesis and structure of the rhenium(V) complex [Re(amb)(OEt)I(PPh_3)$_2$], in which the trianionic bidentate 2-imido-3-methylbenzoate (amb^{3-}) chelates *via* the imido nitrogen and deprotonated acetoxy oxygen atoms [6]. We have since extended this project by the isolation of the complex salt [Re(mps)Cl(PPh_3)$_2$](ReO_4), which was synthesized by reaction of *trans*-[$ReOCl_3$(PPh_3)$_2$] with the Schiff base *N*-(2-amino-3-methylphenyl)salicylideneimine (H_3mps) in ethanol [7]. Here we report the product isolated from the latter reaction carried out in benzene.

2. Experimental

Trans-[$ReOCl_3$(PPh_3)$_2$] was prepared by a literature procedure [8]. Scientific instrumentation used is the same as reported elsewhere [9]. IR spectra were obtained using KBr discs and ^{1}H NMR spectra were run in d$_6$-DMSO. Salicylaldehyde and 3-methyl-1,2-diaminobenzene were obtained commercially (Aldrich), and H_3mps was prepared as reported earlier [7].

2.1. *Cis-[Re(mps)Cl$_2$(PPh$_3$)] (1)*

A mixture of *trans*-[$ReOCl_3$(PPh_3)$_2$] (100 mg, 120 µmol) and 54 mg of H_3mps (239 µmol) was refluxed in 20 cm^3 of benzene for 90 mins. After heating was stopped, the hot solution was filtered and left to cool to room temperature. After 2 h a brown precipitate was removed by filtration, washed with benzene and diethylether. Recrystallization from 1 : 2 ethanol : benzene gave brown crystals. Yield 65 mg (73%), m.p. 171–175°C. Anal. Calcd (%): C, 51.75; H, 3.53; N, 3.37. Found: C, 51.66; H 3.59; N, 3.23. IR (cm^{-1}): ν(Re = N) 1100; ν(C = N) 1597; ν(Re–N) 517; ν(Re–O) 458; ν(Re–Cl) 306, 325. ^{1}H NMR (ppm): 13.66 (s, 1H, *H*(7)), 7.42–7.63 (m, 16H, PPh_3, *H*(2)), 7.18(d, 1H, *H*(11)), 7.08 (t, 1H, *H*(4)), 6.93 (t, 1H, *H*(3)), 6.83(d, 1H, *H*(13)), 6.75(d, 1H, *H*(5)), 6.67(t, 1H, *H*(12)), 2.05 (s, 3H, CH_3). Conductivity (10^{-3} M in CH_3CN): 48 ohm^{-1} cm^2 mol^{-1}.

2.2. *X-ray structure*

Data collection was performed on a Nonius Kappa CCD diffractometer at 200 K with Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [10]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated in idealized geometrical positions. Data were corrected by a numerical absorption correction [11] after optimising the crystal shape with XShape [12]. Crystal and refinement data are given in table 1. Selected bond lengths and angles are given in table 2.

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

Chemical formula	$C_{32}H_{26}N_2OPCl_2Re$
Formula weight	742.65
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.2442(2)
b (Å)	11.6288(2)
c (Å)	13.6434(4)
α (°)	109.155(1)
β (°)	93.336(1)
γ (°)	116.961(1)
Volume (Å^3)	1455.96(6)
Z	2
Density (calcd) (Mg m^{-3})	1.694
Absorption coefficient (mm^{-1})	4.440
$F(000)$	728
Crystal size (mm^3)	$0.03 \times 0.10 \times 0.14$
θ range for data collection (°)	3.2–27.5
Index ranges	$-14 \le h \le 14$; $-14 \le k \le 14$; $-17 \le l \le 17$
Reflections measured	12258
Independent/observed reflections	6595/5884
Data/parameters	6595/352
Goodness-of-fit on F^2	1.06
Final R indices $[I > 2\sigma(I)]$	0.0276, $wR_2 = 0.0611$
Largest diff. peak and hole (e Å^{-3})	1.50/−1.23

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

Re–O	1.928(2)	Re–N(2)	1.762(3)
Re–Cl(1)	2.445(1)	Re–N(1)	2.169(3)
Re–Cl(2)	2.352(1)	Re–P	2.424(1)
C(1)–O	1.332(5)	C(7)–N(1)	1.292(5)
N(1)–C(8)	1.432(5)	N(2)–C(9)	1.401(6)
P–Re–Cl(1)	173.15(3)	Cl(2)–Re–N(2)	103.2(1)
O–Re–N(2)	158.9(1)	Cl(1)–Re–N(1)	87.57(9)
Cl(1)–Re–O	86.62(7)	Cl(2)–Re–P	91.24(3)
Cl(1)–Re–N(2)	96.5(1)	C(1)–O–Re	137.4(2)
Re–N(2)–C(9)	128.6(2)	C(7)–N(1)–C(8)	119.9(3)
N(1)–Re–N(2)	76.7(1)	C(6)–C(7)–N(1)	125.5(4)
N(1)–Re–O	82.6(1)	N(2)–Re–P	90.2(1)

3. Results and discussion

The compound *cis*-[Re(mps)Cl_2(PPh_3)] (**1**) was prepared by the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with two mol equivalents of H_3mps in benzene, heated at reflux. Spectroscopic and X-ray crystallographic results indicate that the chelate mps is present in **1** as a trinegative tridentate ligand, with coordination through the doubly deprotonated amino nitrogen (to form a coordinated imido group), the imino nitrogen and the deprotonated phenolic oxygen atom. Complex **1** is diamagnetic and a non-electrolyte in acetonitrile, and is soluble in a wide variety of solvents such as ethanol, chloroform, DMF, DMSO and acetonitrile. The IR spectrum of **1** displays the Re = N

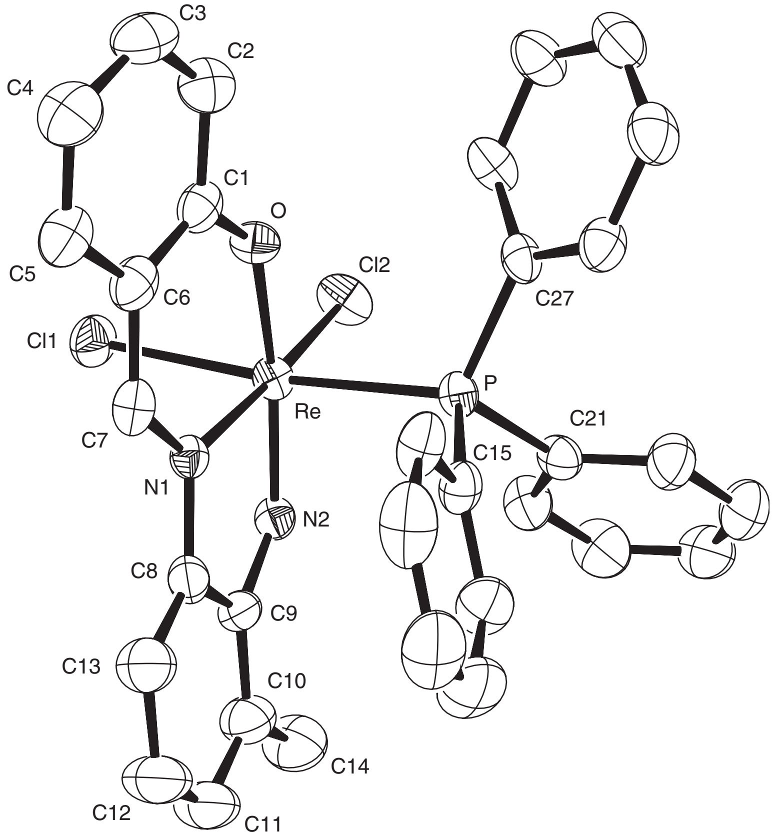

Figure 1. ORTEP drawing of the molecular structure of *cis*-[Re(mps)$Cl_2(PPh_3)$] showing the atom labelling scheme; thermal ellipsoids are drawn at the 40% probability level.

stretching frequency as a medium-intensity band at 1100 cm^{-1}, with no band in the 920–990 cm^{-1} region that can be ascribed to ν(Re = O). Re–N and Re–O stretches occur at 517 and 458 cm^{-1}, respectively, and two medium intensity band at 306 and 325 cm^{-1} are typical of ν(Re–Cl), with two *cis* Re–Cl bonds. Although the ^{1}H NMR spectrum is dominated by the signals of the phosphine protons, the aromatic region integrates for 23 hydrogens. The signal of the methine proton H(7) appears far downfield as a singlet at 13.66 ppm, and the signal of H(2) is hidden under a sixteen-proton multiplet at 7.42–7.63 ppm. The signals of the other protons of the mps ligand are clearly distinguishable as a doublet-triplet-triplet-doublet-doublet-triplet sequence in the region 6.67–7.18 ppm.

X-ray crystallographic analysis of **1** shows that the rhenium(V) ion is centred in an octahedral environment with the equatorial plane formed by the $PCl_2N(1)$ donor set (figure 1). The octahedron is distorted, with the Cl(2)–Re–P [91.24(3)°], Cl(1)–Re–Cl(2) [88.58(4)°], Cl(1)–Re–N(1) [87.57(9)°] and N(1)–Re–P [92.64(9)°] bond angles remarkably close to orthogonality. The equatorial plane is strictly planar, and the rhenium atom is displaced from this plane by 0.0695 Å towards the N(2) atom. This displacement leads to the non-orthogonal angles N(2)–Re–Cl(1) = 96.5(1)°, N(2)–Re–Cl(2) = 103.2(1)°, N(2)–Re–N(1) = 76.7(1)° and N(2)–Re–P = 90.2(1)°. This distortion results in a nonlinear N(2)–Re–O axis of 158.9(1)°. The two phenyl rings of mps make a dihedral angle of 13.14°. The two bite angles of mps are N(1)–Re–O = 8 2.6(1)° and N(1)–Re–N(2) = 76.7(1)°.

The mps ligand acts as a trianionic tridentate, with N(2) coordinated to Re as a dinegative imido nitrogen atom. The Re–N(2) bond length of 1.762(3) Å is slightly longer than normally observed for the phenylimido unit [1.726–1.740 Å] [3,13], but is considerably shorter than the values usually found for Re^V–NH and Re^V–NH_2 bonds [1.98–2.05 Å and 2.15–2.23 Å, respectively] [14]. The Re–N(2)–C(9) bond angle of 128.6(2)° indicates significant deviation from linearity of the coordination mode of the phenylimido unit, with a reduction in bond order. These data intimate that the imido nitrogen is doubly, rather than triply, bonded to the rhenium, thereby making the complex a sixteen-electron species. The Re–N(1) bond length of 2.169(3) Å is typical of Re^V–N(imine) bonds [14], and the Re–O bond length of 1.928(2) Å falls at the lower end of the range normally observed for Re–O (phenolate) bonds [15]. The C(7)–N(1)–C(8) bond angle of 119.9(3)° is close to the ideal for a sp^2 hybridized nitrogen atom and the C(7)–N(1) bond length of 1.292(5) Å is typical of a carbon-nitrogen double bond. Re–Cl bond lengths [2.445(1) and 2.352(1) Å] are within the range [2.34(2)–2.44(2) Å] found normally for Re(V) complexes containing phosphine ligands [16]. A weak intramolecular hydrogen bond exists between C(7)H(7) and Cl(1) [3.715(4) Å].

It was shown earlier that in the salt $[Re(mps)Cl(PPh_3)_2](ReO_4)$, obtained when the reaction was carried out in ethanol, mps is also coordinated as a trianionic tridentate chelate [7]. However, there are significant differences in the Re–N(2) [1.82(2) Å] and Re–O [1.85(2) Å] bond lengths of mps, when compared to those of **1**.

Supplementary data

File CCDC-613411 contains crystallographic data for this article. 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; e-mail: deposit @ccdc.cam.ac.uk].

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