

SYNTHESIS AND STRUCTURE OF A RHENIUM(V) COMPLEX CONTAINING A TRIDENTATE IMIDO-COORDINATED SCHIFF BASE

Irvin Booysen¹, Thomas I.A. Gerber^{1*}, Eric Hosten¹ and Peter Mayer²

¹Department of Chemistry, Nelson Mandela Metropolitan University, 6031 Port Elizabeth, South Africa

²Department of Chemistry, Ludwig-Maximilians University, D-81377 München, Germany

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ABSTRACT. The six-coordinate complex $[\text{Re}(\text{mps})\text{Cl}_2(\text{PPh}_3)]$ (**1**) ($\text{H}_3\text{mps} = N$ -(2-amino-3-methylphenyl)salicylideneimine) was prepared by the reaction of $[\text{NH}_4][\text{ReO}_4]$ with H_3mps in the presence of triphenylphosphine and hydrochloric acid in glacial acetic acid. Crystallization from acetonitrile gave the product **1**. CH_3CN . The compound was characterized by spectroscopy and X-ray crystallography. The results show that the tridentate mps ligand coordinates *via* the doubly deprotonated 2-amino nitrogen (which is present in **1** as an imide), the neutral imino nitrogen and the phenolate oxygen. The imide and phenolate oxygen are *trans* to each other in a distorted octahedral geometry around the rhenium(V) centre, with the two chlorides in *cis* positions.

KEY WORDS: Reduction of perrhenate, Rhenium(V), Imido donor atom, Crystal structure

INTRODUCTION

The use of compounds of the ^{186/188}Re isotopes as therapeutic agents in nuclear medicine has rekindled interest in the coordination chemistry of rhenium. Complexes are normally prepared from perrhenates, and usually have the oxo group as a ligand and the metal in the +5 oxidation state [1]. One of the disadvantages of this approach is that the oxo group dominates the structures, geometries, reactivity and magnetic properties, and puts limitations on the exploration of rhenium(V) coordination chemistry. For this reason current research efforts are focussing on oxo-free rhenium(V) compounds with metal-nitrogen multiple bonds, for example metal-nitrido, metal-hydrazido and metal-imido complexes [2, 3].

We have synthesized several stable Re(V) complexes containing the phenylimido core, $\text{Re}=\text{NC}_6\text{H}_4\text{-X}$, obtained by deprotonation of a precursor containing an amino group. An advantage of the phenylimido moiety is that it can be functionalized and derivatized, but a disadvantage is that phenylimidorhenium(V) compounds having monodentate ligands in the coordination sphere are hydrolytically unstable [4]. For this reason, the synthesis of rhenium(V) complexes containing multidentate imido-containing ligands is important.

We recently reported the structure of the rhenium(V) complex $[\text{Re}(\text{mps})\text{Cl}(\text{PPh}_3)_2][\text{ReO}_4]$, synthesized from the reaction of *trans*- $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with the Schiff base *N*-(2-amino-3-methylphenyl)salicylideneimine (H_3mps) in ethanol [5]. We now describe the reduction of $[\text{ReO}_4]^-$ with triphenylphosphine in the presence of H_3mps and hydrochloric acid.

EXPERIMENTAL

Ammonium perrhenate, salicylaldehyde and 3-methyl-1,2-diaminobenzene were obtained commercially from Aldrich. The scientific instrumentation used is the same as reported elsewhere [6]. Infrared spectra were obtained by use of KBr discs and ¹H NMR spectra were run in d₆-DMSO. The orange H_3mps ligand was synthesized by the condensation of salicylaldehyde and 3-methyl-1,2-diaminobenzene in a boiling ethanol/benzene mixture.

*Corresponding author. E-mail: thomas.gerber@nmmu.ac.za

[Re(mps)Cl₂(PPh₃)]·CH₃CN (1·CH₃CN)

To [NH₄][ReO₄] (100 mg, 0.37 mmol) in 0.34 mL of concentrated HCl and 10 mL of glacial acetic acid was added a mixture of 0.098 g (0.37 mmol) of PPh₃ and 0.169 g of H₃mps (0.75 mmol), dissolved in 10 mL of glacial acetic acid. The mixture was stirred for 3 h at room temperature, during which time an orange precipitate of **1** formed (0.127 g; 48 %). This was filtered off and washed with acetic acid and diethyl ether. To the mother liquor was added 5 mL of acetonitrile, and slow evaporation of this mixture at room temperature gave orange crystals, which were washed with diethyl ether, then dried under vacuum. Yield of **1**·CH₃CN = 0.106 g (37 %), m.p. 198-200 °C. Anal. calcd. (%): C, 52.11; H, 3.73; N, 5.36. Found: C, 52.36; H 3.61; N, 5.22. IR (cm⁻¹): ν(C=N) 1598; ν(Re=N) 1096, ν(Re-N) 534; ν(Re-O) 466; ν(Re-Cl) 324, 318. ¹H NMR (ppm): 13.66 (s, 1H, *H*(7)), 7.61-7.33 (m, 16H, PPh₃, *H*(2)), 7.17 (d, 1H, *H*(11)), 7.08 (t, 1H, *H*(4)), 6.96 (t, 1H, *H*(3)), 6.82 (d, 1H, *H*(13)), 6.74 (d, 1H, *H*(5)), 6.66 (t, 1H, *H*(12)), 2.08 (s, 3H, CH₃). UV-Vis (DMF) (λ (ε, M⁻¹cm⁻¹)): 329 (7400), 375 (3400), 491 (800). Conductivity (10⁻³ M, CH₃CN) = 31 ohm⁻¹cm²mol⁻¹.

X-ray structure

Data collection was on a Nonius Kappa CCD diffractometer at 200K with Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [7]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated in idealized geometrical positions. Data were corrected by a numerical absorption correction [8] after optimising the crystal shape with XShape [9]. 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**·CH₃CN.

Chemical formula	C ₃₄ H ₂₉ N ₃ OPCl ₂ Re
Formula weight	783.70
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions (Å)	<i>a</i> = 18.4648(2) <i>b</i> = 15.2651(1) <i>c</i> = 22.0463(2)
Volume (Å ³)	6214.1(1)
<i>Z</i>	8
Density (calc.) (Mg/m ³)	1.675
Absorption coefficient (mm ⁻¹)	4.167
<i>F</i> (000)	3088
Crystal size (mm)	0.09 x 0.18 x 0.22
θ range for data collection (°)	3.2 – 27.5
Index ranges	-23 ≤ <i>h</i> ≤ 23; -19 ≤ <i>k</i> ≤ 19; -28 ≤ <i>l</i> ≤ 28
Reflections measured	13521
Independent/observed reflections	7100/5706
Data/parameters	7100/380
Goodness-of-fit on <i>F</i> ₂	1.07
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0348, <i>wR</i> ₂ = 0.0809
Largest diff. peak and hole (e/Å ³)	1.42/-2.06

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

Re-O	1.926(3)	Re-N(2)	1.768(4)
Re-Cl(1)	2.373(1)	Re-N(1)	2.162(3)
Re-P	2.420(1)	Re-Cl(2)	2.422(1)
C(1)-O	1.343(6)	C(7)-N(1)	1.311(6)
N(1)-C(8)	1.422(6)	N(2)-C(9)	1.448(6)
Cl(1)-Re-Cl(2)	88.85(4)	Cl(2)-Re-N(1)	85.2(1)
O-Re-N(2)	157.8(2)	Cl(2)-Re-P	175.09(4)
Cl(1)-Re-O	96.52(9)	Cl(1)-Re-P	93.30(4)
Cl(1)-Re-N(2)	105.3(2)	C(1)-O-Re	136.0(3)
Re-N(2)-C(9)	127.7(3)	C(7)-N(1)-C(8)	113.3(3)
N(1)-Re-N(2)	76.1(2)	C(6)-C(7)-N(1)	126.8(4)
N(1)-Re-O	82.6(1)	N(1)-Re-P	92.6(1)

RESULTS AND DISCUSSION

The complex *cis*-[Re(mps)Cl₂(PPh₃)] (**1**) was prepared in good yield (85 %) by the reduction of [NH₄][ReO₄] with triphenylphosphine in the presence of two mole equivalents of H₃mps in glacial acetic acid, according to the equation



Spectroscopic and X-ray crystallographic results indicate that the 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 it is only soluble in the polar solvents, e.g. DMF, DMSO and acetonitrile.

The IR spectrum of **1** displays the Re=N stretching frequency as a medium-intensity band at 1096 cm⁻¹, with no band in the 920-990 cm⁻¹ region that can be ascribed to ν(Re=O). The Re-N and Re-O stretches appear at 534 and 466 cm⁻¹, respectively, and medium-intensity bands at 324 and 318 cm⁻¹ are typical of ν(Re-Cl). Although the ¹H NMR spectrum of the complex is dominated by the signals of the phosphine protons, the aromatic region integrates for 23 protons. 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 7.33-7.61 ppm. The signals of the other protons of the mps ligand are clearly distinguishable as a doublet-triplet-triplet-doublet-triplet sequence in the region 6.66-7.17 ppm.

The electronic spectrum of **1** in DMF shows two intense absorptions at 329 and 375 nm, with a weaker one at 491 nm. With reference to previous spectroscopic studies [10], the intense band at 329 nm, with an extinction coefficient of 7400 M⁻¹cm⁻¹, is tentatively assigned to a ligand-to-metal charge transfer transition [p_π(N²⁻) → d*_π(Re)], and the one at 375 nm to the p_π(Cl⁻) → d*_π(Re) (d*_π=d_{xz}, d_{yz}). The weak absorption at 491 nm is probably due to a (d_{xy})² → (d_{xy})¹(d*_π)¹ transition.

X-ray crystallographic analysis of **1**.CH₃CN shows that the rhenium(V) ion is in an octahedral environment with the equatorial plane formed by the PCl₂N(1) donor set (Figure 1). The octahedron is severely distorted with large deviations from orthogonality for Cl(1)-Re-N(2) [105.3(2)°], Cl(1)-Re-O [96.52(9)°] and Cl(2)-Re-N(2) [96.3(1)°]. The N(2)-Re-O angle is 157.8(2)° and the P-Re-Cl(2) angle 175.09(4)°. The dihedral angle between two phenyl rings of mps is 13.65° and the two bite angles of mps are N(1)-Re-O = 82.6(1)° and N(1)-Re-N(2) = 76.1(2)°.

The mps ligand acts as a terdentate trianionic moiety, with N(2) coordinated to Re as a dinegative imido nitrogen atom. The Re–N(2) bond length [1.768(4) Å] is slightly longer than normally observed [1.726 – 1.740 Å] for the phenylimido unit [3, 11], but considerably shorter than the values found for Re^V–NH and Re^V–NH₂ bonds [1.98–2.05 Å and 2.15–2.23 Å, respectively] [12]. The Re–N(2)–C(9) bond angle [127.7(3)°] deviates significantly from 180° and shows that the imido nitrogen is doubly, rather than triply, bonded to the rhenium, making the complex a sixteen-electron species. The Re–N(1) bond length of 2.162(3) Å is typical of Re^V–N (imine) bonds [12], and the Re–O bond length of 1.926(3) Å falls at the lower end of the range normally observed for Re–O (phenolate) bonds [13]. The C(7)–N(1)–C(8) bond angle [120.5(4)°] is close to that for a sp²-hybridized nitrogen atom and the C(7)–N(1) bond length [1.311(6) Å] is normal for a carbon–nitrogen double bond. The Re–Cl bond lengths are within the range [2.34(2)–2.44(2) Å] found for Re(V) complexes containing phosphine ligands [14].

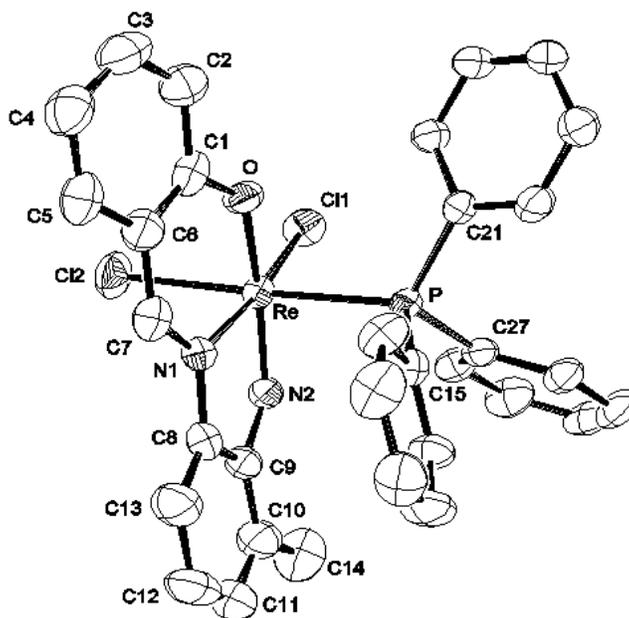


Figure 1. ORTEP drawing of the molecular structure of [Re(mps)Cl₂(PPh₃)] showing the atom labelling scheme; thermal ellipsoids are drawn at 40 % probability level.

We have recently reported the reaction between *trans*-[ReOCl₃(PPh₃)₂] and *N*-(2-aminophenyl)salicylideneamine (H₃apa), which gave *cis*-[Re(apa)Cl₂(PPh₃)] as product [15]. Like the mps in **1**, the apa acts as a tridentate ligand *via* the doubly-deprotonated amino nitrogen (which is coordinated as an imide), the neutral secondary amino nitrogen and the deprotonated phenolic oxygen.

Supplementary data

File CCDC-643782 contains the 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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