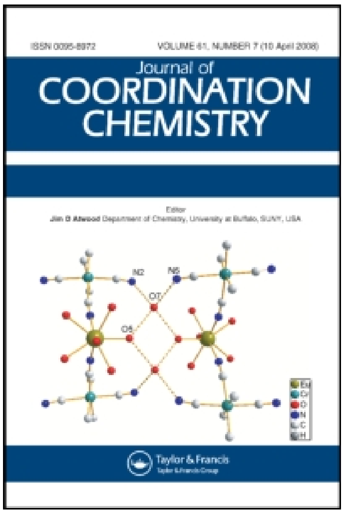

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Gerber, T. I. A. , Luzipo, D. and Mayer, P.(2003) 'The Reaction of the *cis*-ReO_2^+ Core with 2-Amino-3-Methylbenzoic Acid', Journal of Coordination Chemistry, 56: 18, 1549 — 1554
To link to this Article: DOI: 10.1080/00958970310001617067
URL: http://dx.doi.org/10.1080/00958970310001617067

J. Coord. Chem., Vol. 56, No. 18, 15 December 2003, pp. 1549–1554

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THE REACTION OF THE *cis*-ReO_2^+ CORE WITH 2-AMINO-3-METHYLBENZOIC ACID

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(Received 28 May 2003; In final form 11 August 2003)

The reaction of a twofold molar excess of 2-amino-3-methylbenzoic acid (H_3amb) with *cis*-[$ReO_2I(PPh_3)_2$] in ethanol led to the isolation and characterization of the six-coordinate [Re(amb)(OEt)I$(PPh_3)_2$] (**1**). The X-ray crystal structure of **1** illustrates that the trianionic ligand amb acts as a bidentate chelate via the doubly deprotonated amino nitrogen, which is present in **1** as an imide, and the deprotonated acetoxy oxygen. The Re=N bond length is 1.751(3) Å, and the Re=N–C angle [143.6(3)°] deviates considerably from linearity.

Keywords: Crystal structure; Rhenium(V)-imido complex; Potentially bidentate ligand

INTRODUCTION

Over recent years we have been investigating the unusual reactions of the oxorhenium(V) core with anilines that are substituted in positions 2 and/or 6. We have established that the reaction of the potentially bidentate ambidentate ligand 2,3-diaminophenol (H_2dap) with *trans*-[$ReOCl_3(PPh_3)_2$] in ethanol leads to the formation of the rhenium(V) imido complex *trans*-[Re(dap)$Cl_3(PPh_3)_2$], in which dap is coordinated monodentately via the doubly deprotonated nitrogen in the 2-position [1]. 2-Aminophenol (H_2ap) acts only as a monoanionic bidentate N,O-donor in the complex [$ReOCl_2$(ap)(PPh_3)] [2]. The substitution of the 3-amino group in H_2dab with a methyl, i.e., 2-amino-3-methylphenol (H_2amp), again led to imido formation in the complex [Re(amp)(Hamp)I$(PPh_3)_2$]I. Here amp is coordinated through the doubly deprotonated nitrogen only, and Hamp acts as dianionic N,O-donor, as would be expected [3].

Our interest in imido complexes of rhenium(V) originates from the possible therapeutic applications of rhenium radiopharmaceuticals in nuclear medicine [4,5]. The incorporation and modification of the Re=N–R core would allow manipulation of the biodistribution of the radiopharmaceutical.

We have now extended this project to the potential N,O-donor ligand 2-amino-3-methylbenzoic acid (H_3amb). The reaction of H_3amb with *cis*-[$ReO_2I(PPh_3)_2$] in ethanol

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970310001617067

gave the complex [Re(amb)I(OEt)(PPh$_3$)$_2$] (**1**) as product, in which amb acts as a trianionic N,O-donor chelate via the acetoxy oxygen and the doubly deprotonated (imido) nitrogen.

EXPERIMENTAL

Reagents

cis-[ReO$_2$I(PPh$_3$)$_2$] was prepared according to a literature procedure [6]. H$_3$amb was obtained commercially (Aldrich), and all other chemicals were of reagent grade and were used as received from commercial sources. Solvents were purified and dried by standard procedures. All reactions and manipulations were carried out under an inert argon atmosphere.

Instrumentation

Scientific instrumentation used is the same as reported elsewhere [7]. Infrared spectra were obtained in KBr discs and ^{1}H NMR spectra were run in d_6-DMSO.

Synthesis of *trans*-[Re(amb)I(OEt)(PPh$_3$)$_2$] (1)

A mixture of 100 mg (115 µmol) of *cis*-[ReO$_2$I(PPh$_3$)$_2$] and 35 mg (232 µmol) of H$_3$amb in 20 cm^3 of ethanol was heated under reflux for 90 min. After heating was stopped and the green solution cooled to room temperature, the resulting dark green precipitate was isolated by filtration, washed with diethyl ether (2 cm^3), and dried. Crystals suitable for X-ray diffraction studies were grown from a 2 : 1 (v/v) benzene–ethanol mixture. Yield = 82 mg (69%), m.p. = 228°C. Anal. Calcd. (%) C, 53.60; H, 4.01; N, 1.36. Found: C, 53.77; H, 4.11; N, 1.66. IR (cm^{-1}): $\nu(CO_2^-)$ 1634; ν(C=C) 1582; ν(Re=N) 1062; ν(P–C) 1108; ν(Re–O) 459; ν(Re–I) 276. ^{1}H NMR (ppm): 1.08 (t, 3H, CH_3), 2.13 (s, 3H, CH_3), 3.41 (q, 2H, CH_2), 6.56 (t, 1H, J = 7.6 Hz, H(5)), 7.20 (d, 1H, J = 7.0 Hz, H(4)), 7.50–7.75 (m, 31H, H(6), 2 × PPh_3). UV-Vis (DMF; λ_{max}(ε, M^{-1}cm^{-1})): 351 (6800), 281 (12 000). Conductivity (DMF, 10^{-3} M) = 8 ohm^{-1}cm^2 mol^{-1}.

X-ray Determination of Crystal Structure

Data collection was performed at 200 K on a Nonius Kappa CCD using Mo Kα radiation. The structure of **1** was solved by direct methods and was refined by full-matrix least-squares procedures using SHELXL-97 [8]. All non-hydrogen atoms except the disordered carbon atoms of the ethoxy group were refined anisotropically. An ORTEP view of **1**, along with the atom numbering scheme, is given in Fig. 1. Relevant crystallographic data are given in Table I, with selected bond lengths and angles shown in Table II.

RESULTS AND DISCUSSION

The reaction of a twofold molar excess of 2-amino-3-methylbenzoic acid (H$_3$amb) with *cis*-[ReO$_2$I(PPh$_3$)$_2$] in dry ethanol under argon led to the isolation of the six-coordinate

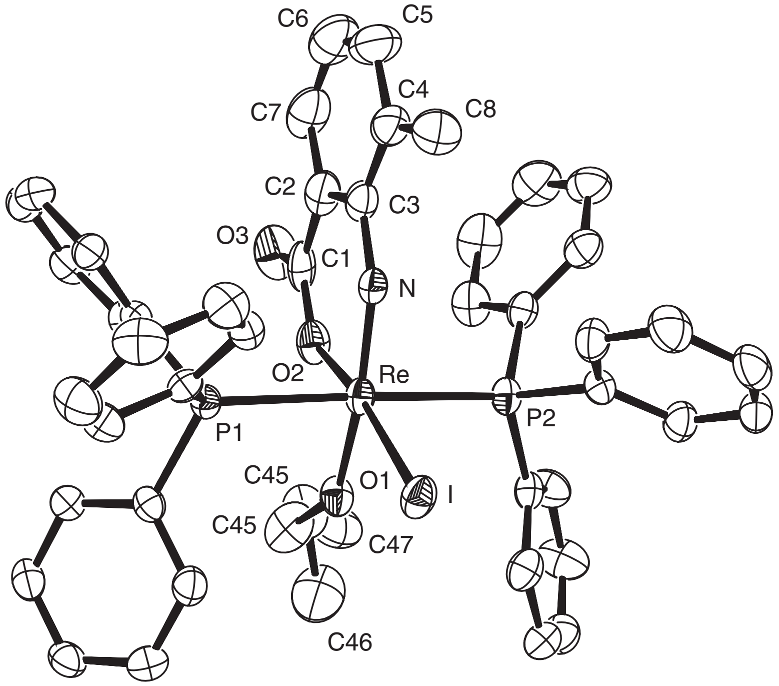

FIGURE 1 A view of the structure of [Re(amb)I(OEt)(PPh_3)$_2$] (**1**), showing the atom-labelling scheme and 50% thermal ellipsoids.

TABLE I Crystal data and structure refinement for **1**

Formula	$C_{46}H_{41}NO_3IP_2Re$
Formula weight	1030.88
Temperature (K)	200
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*1
Unit cell dimensions (Å, °)	$a = 9.6912$ (2)
	$b = 12.2604$ (2)
	$c = 17.5970$ (3)
	$\alpha = 76.7396$ (8)
	$\beta = 84.1802$ (8)
	$\gamma = 87.8604$ (7)
Volume (Å^3)	2024.39(6)
Z	2
Density (calc; Mg m^{-3})	1.691
Crystal size (mm)	0.07 × 0.10 × 0.13
Absorption coefficient (mm^{-1})	3.885
F(000)	1012
θ range	3.2–27.5°
Index ranges	$-12 \leq h \leq 12$; $-15 \leq k \leq 15$; $-22 \leq l \leq 22$
Reflection collected/unique/*R*(int)	41 730/9208/0.077
Observed data [$I > 2.0\sigma(I)$]	6851
Data/parameters	9208/506
Goodness-of-fit on F^2	1.02
R, wR_2	0.0383/0.0751
Largest diff. peak and hole (e Å^{-3})	0.77 and −1.20

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

Re–N	1.751 (3)	Re–P(1)	2.4895 (11)
Re–O(2)	2.108 (3)	Re–P(2)	2.4880 (13)
Re–I	2.7382 (3)	Re–O(1)	1.885 (3)
C(1)–O(2)	1.297 (6)	C(1)–O(3)	1.227 (6)
N–C(3)	1.399 (6)	C(4)–C(8)	1.483 (8)
I–Re–P(1)	89.21 (3)	P(1)–Re–P(2)	177.68 (4)
I–Re–P(2)	90.92 (3)	P(1)–Re–O(1)	88.72 (8)
I–Re–O(1)	91.25 (9)	P(1)–Re–O(2)	89.17 (10)
I–Re–O(2)	171.79 (9)	P(1)–Re–N	91.92 (12)
I–Re–N	104.90 (12)	P(2)–Re–O(1)	88.96 (8)
O(1)–Re–O(2)	80.66 (12)	P(2)–Re–O(2)	90.37 (10)
O(1)–Re–N	163.84 (15)	P(2)–Re–N	90.28 (13)
O(2)–Re–N	83.20 (15)	Re–O(2)–C(1)	132.2 (3)
Re–N–C(3)	143.6 (3)	O(2)–C(1)–O(3)	121.4 (4)
N–C(3)–C(4)	120.1 (4)		

rhenium(V) complex $[Re(amb)(OEt)I(PPh_3)_2]$ (**1**), according to the equation

$$[ReO_2I(PPh_3)_2] + H_3amb + EtOH \rightarrow [Re(amb)(OEt)I(PPh_3)_2] + 2H_2O$$

In the infrared spectrum of the complex the stretching frequency of the rhenium–imido nitrogen multiple bond is displayed at $1062\,cm^{-1}$, with $\nu(CO_2^-)$ and ν(Re–O) at 1634 and $459\,cm^{-1}$ respectively. The presence of the ethoxide is shown by an intense band at $922\,cm^{-1}$, which corresponds to the ethoxy bending mode.

The ^1H NMR spectrum clearly establishes the presence of the ethoxide, with the typical quartet–triplet signals at δ 3.41 and 1.08 ppm respectively. The methyl group of the amb ligand appears as a three-proton singlet at δ 2.13 ppm. The H(5) and H(4) ring protons give rise to a triplet (at δ 6.56 ppm) and doublet (at δ 7.20 ppm) respectively, with the H(6) proton's signal hidden under the 31 proton multiplet at δ 7.50–7.75 ppm.

An ORTEP perspective view of the asymmetric unit is shown in Fig. 1. The rhenium atom is at the centre of a distorted octahedron. The basal plane is defined by the acetoxy oxygen of amb, two *trans* phosphorus atoms and the iodide. The ethoxide oxygen and imido nitrogen are in *trans* axial positions. The ethoxide molecule is distorted, but it has no influence on any of the parameters of the structure.

Selected bond distances and angles are given in Table II. Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear N=Re–O(1) axis of 163.84(15)°, accomplished by O(2)–Re–I and P–Re–P angles of 171.79(9) and 177.68(4)° respectively. The rhenium atom is lifted out of the mean equatorial P_2IO plane by 0.108(1) Å towards N, which is the result of the non-orthogonal angles N–Re–I = 104.90(12); N–Re–P(1) = 91.92(12), N–Re–P(2) = 90.28(13) and N–Re–O(2) = 83.20(15)°.

The ethoxo group is distorted over two equally populated orientations about the axis. This type of disorder has also been observed for the complexes $[ReO(OEt)X_2(PPh_3)_2]$ (X = Cl, Br) [9,10]. A broad range (138–176°) is found in the literature for the Re–O–Et angle; in **1** the angles are 135.3(10) and 144.3(14)° for the refined positions.

Iodide is rarely found as a ligand in rhenium(V) complexes, and the Re–I distance of 2.7382(3) Å falls in the observed range of 2.664(2)–2.789(3) Å [3,6]. The two PPh_3

ligands are coordinated to the metal centre *trans* to each other, with the P(1)–Re–P(2) angle practically linear at 177.68(4)°, in order to minimize steric hindrance. The average Re–P distance equals 2.4888(13) Å, which is identical to that in the *trans*-biphosphine imido complex [Re(dap)$Cl_3(PPh_3)_2$] [2.489(3) Å] [1].

The amb ligand acts as a bidentate trianionic moiety, with coordination to rhenium through the doubly deprotonated imido nitrogen and the acetoxy oxygen O(2). The Re–N–C(3) bond angle of 143.6(3)° is rather acute, and illustrates an unusual significant deviation from linearity of the coordination mode of the triply bonded phenylimido unit. The Re–N distance of 1.751(3) Å is significantly longer than the normally observed range of 1.726(6)–1.740(6) Å [11,12], and the N–C(3) distance of 1.399(6) Å is longer than the mean value reported for phenylimido-alkoxo compounds [13,14]. These data intimate that the imido nitrogen is doubly, rather than triply, bonded to the rhenium.

The axial Re–O(1) (ethoxo) bond [1.885(3) Å] is considerably shorter than those found for alkoxo groups *trans* to the Re=NPh bond [13,14]. Distances of 2.04, 1.86 and 1.75 Å have been proposed for typical single, double and triple bonds respectively [6], meaning a significant double-bond character for the Re–O(1) bond. Another indication of its double-bond character is that the Re–O(1)–C(1) angle is splayed to 135.3(10)°/144.3(14)° when no apparent intramolecular nonbonding contacts exist. It is also interesting to note that the O(1)–C(45) bond is coplanar with the Re–O(2) bond [C(45)–O(1)–Re–O(2) torsion angle = 0.9(13)°] and the Re–I bond [C(45)–O(1)–Re–I torsion angle = 179.5(13)°]. As was pointed out earlier [12], this orientation and the relatively large angle at the ethoxy oxygen present favourable conditions for bonding interactions between the π orbitals of the ethoxide and the empty d_{xz} and d_{yz} orbitals of rhenium.

The Re–O(2) bond length of 2.108(3) Å is clearly indicative of a single bond, and the C(1)–O(2) bond length of 1.297(6) Å is in the normal range found previously [15]. The average C–C bond length in the ring of the amb ligand is 1.392(10) Å, which is identical to the average value for the C–C bond length in benzene. The C(2)–C(7) phenyl ring also maintains its planarity and aromaticity. For example, the torsion angles C(2)–C(3)–C(4)–C(5) and N–C(3)–C(4)–C(5) are −0.3(8) and −179.3(5)°, respectively.

Rhenium(V) complexes containing chelating imido ligands are not common, the first example being [Re(ana)Cl(OEt)$(PPh_3)_2$], which was synthesized by the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with anthranilic acid (H_3ana) in ethanol [16]. Another example is [Re(dpa)Cl_2(Hdpa)], prepared from *trans*-[$ReOCl_3(PPh_3)_2$] and 2-diphenylphosphinoaniline (H_2dpa), which contains the N,P-chelated imido ligand dpa [17].

Acknowledgements

T.I.A.G. and D.L. are grateful to the University of Port Elizabeth for financial support.

Supplementary Material

Additional material, available from the Cambridge Crystallographic Data Centre, comprises detailed information on structure data collection and structure refinement, final fractional atomic coordinates, thermal parameters, a full listing of bond lengths/angles, torsion angles, contact distances and hydrogen bonds.

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