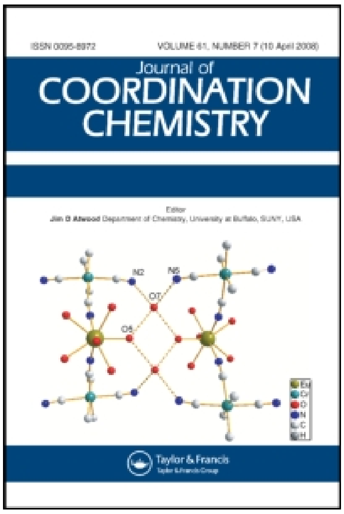

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A monooxorhenium(V) complex with an unusually long Re=O bond: the structure of [$ReOI_2$(ame)(PPh_3)] (Hame=2-(2-aminophenyl)ethanol)

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To cite this Article Gerber, T. I. A. , Luzipo, D. and Mayer, P.(2004) 'A monooxorhenium(V) complex with an unusually long Re=O bond: the structure of [$ReOI_2$(ame)(PPh_3)] (Hame=2-(2-aminophenyl)ethanol)', Journal of Coordination Chemistry, 57: 15, 1345 — 1349
To link to this Article: DOI: 10.1080/00958970412331303868
URL: http://dx.doi.org/10.1080/00958970412331303868

J. Coord. Chem., Vol. 57, No. 15, 15 October 2004, pp. 1345–1349

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A MONOOXORHENIUM(V) COMPLEX WITH AN UNUSUALLY LONG Re=O BOND: THE STRUCTURE OF [ReOI$_2$(AME)(PPh$_3$)] (HAME=2-(2-AMINOPHENYL)ETHANOL)

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(Received 31 March 2004)

The complex [ReOI$_2$(ame)(PPh$_3$)] (Hame=2-(2-aminophenyl)ethanol) was prepared from *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$] and Hame in benzene. It contains an unusually long Re=O bond (1.717(5) Å) and a large *trans* O=Re–O (ethanolate) bond angle of 171.4(2)°.

Keywords: Monooxorhenium(V); 2-(2-Aminophenyl)ethanol; Long Re=O bond; X-ray structure

INTRODUCTION

Oxorhenium(V) complexes with *N*,*O*-donor ligands containing the amino group (NH$_2$) as one of the donors have not been well studied. The few reports in the literature include the reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] with vinyl amides and 2-aminoalcohols (HL) to give products of the type [ReOCl$_2$(L)(PPh$_3$)], in which these ligands act as monoanionic bidentate chelates with a neutral amino group [1,2]. However, the reaction of *cis*-[ReO$_2$I(PPh$_3$)$_2$] with 3-methyl-2-aminophenol (H$_2$map) in ethanol led to the formation of *trans*-[Re(map)(Hmap)I(PPh$_3$)$_2$]I, where map is coordinated as a monodentate imide and Hmap as a bidentate aminophenolate [3]. In all these oxo complexes and others containing *N*,*O*-donor Schiff base ligands, a phenolate/alcoholate oxygen is always coordinated *trans* to the oxo group. The O=Re–O(phenolate/alcoholate) bond angles in these complexes vary in the range 158–166°, partly because of the five/six-membered metallocycles Re–N–O–Re, giving Re=O bond distances around 1.685(5) Å [2–5].

In this study we have increased the chelating metallocycle to seven members by using 2-(2-aminophenyl)ethanol (Hame) as a bidentate ligand in the complex [ReOI$_2$(ame)(PPh$_3$)], in order to investigate its influence on the O=Re–O bond angle and Re=O bond length.

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970412331303868

EXPERIMENTAL

Trans-[ReOI$_2$(OEt)(PPh$_3$)$_2$] was synthesised by a literature method [6]. 2-(2-Aminophenyl)ethanol (Hame) was obtained commercially (Aldrich). Solvents were purified and dried by standard methods. Infrared spectra were obtained using KBr discs. The instrumentation used is the same as reported earlier [7].

Synthesis of [ReOI$_2$(ame)(PPh$_3$)] · 0.5C$_6$H$_6$

Hame (40 mg, 293 µmol) was added to a solution of *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$] (150 mg, 146 µmol) in 20 cm^3 benzene and the mixture was heated under reflux for 30 mins. After cooling the solution to room temperature, a yellow-green solid was removed. Recrystallisation from dichloromethane/ethanol gave yellow crystals. Yield=71%; mp 201°C. Anal. Found(%): C, 38.93; H, 3.32; N, 1.22. Calc.: C, 38.98; H, 3.16; N, 1.57%. IR (cm^{-1}): ν(Re═O) 936 *vs*; ν(N–H) 3203, 3122; ν(Re–N) 530, ν(Re–O) 499. ^{1}H NMR δ(ppm): 9.79 (br s, 2H, NH_2), 7.36–7.80 (m, 19H, PPh_3, H(3), H(4), H(5), H(6)), 3.68 (t, 2H, C(7)H_2, J 6.1), 2.81 (t, 2H, C(8)H_2, J 6.1 Hz).

Crystallography

Intensity data were collected on a Nonius Kappa CCD diffractometer at 200(2) K with Mo Kα radiation ($\lambda = 0.71073$ Å). Further details are given in Table I. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [8]. All non-hydrogen atoms were refined anisotropically. Selected bond lengths and angles are given in Table II.

TABLE I Crystal data and structure refinement data for **1** · 0.5C$_6$H$_6$

Chemical formula	C$_{29}$H$_{28}$I$_2$NO$_2$PRe
Formula weight	893.53
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.7334(5)$ Å
	$b = 10.8150(6)$ Å
	$c = 14.2199(8)$ Å
	$\alpha = 77.265(2)°$
	$\beta = 69.053(2)°$
	$\gamma = 69.446(2)°$
Volume (Å^3)	1434.9(1)
Z	2
Absorption coefficient (mm^{-1})	6.468
F(000)	842
θ range for data collection (deg)	3.17–27.46
Crystal size (mm)	0.06 × 0.03 × 0.02
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-18 \le h \le 18$
Reflections measured	20300
Independent/observed reflections	6431/3972
Data/restraints/parameters	6431/0/325
Goodness of fit on F^2	1.023
Final R indices [$I > 2\sigma(I)$]	0.0532, $wR_2 = 0.0822$
Largest diff. peak and hole (e/Å^3)	1.280, −1.300

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

Re–O(1)	1.717(5)	Re–O(2)	1.860(5)
Re–I(1)	2.7264(6)	Re–I(2)	2.8397(6)
Re–N	2.256(6)	Re–P	2.449(2)
C(1)–N	1.46(1)	C(8)–O(2)	1.406(9)
C(7)–C(8)	1.51(1)	C(1)–C(2)	1.42(1)
C(2)–C(3)	1.39(1)	C(1)–C(6)	1.38(1)
C(2)–C(7)	1.51(1)	P–C(15)	1.839(8)
O(1)–Re–O(2)	171.4(2)	I(1)–Re–I(2)	172.2(2)
O(1)–Re–I(1)	95.5(2)	N–Re–P	172.5(2)
O(1)–Re–I(2)	88.3(2)	Re–O(2)–C(8)	149.5(5)
O(1)–Re–N	92.0(2)	O(2)–C(8)–C(7)	108.9(6)
O(1)–Re–P	95.3(2)	Re–N–C(1)	119.5(5)
N–C(1)–C(2)	120.4(7)	Re–P–C(15)	117.4(2)

RESULTS AND DISCUSSION

The complex [ReOI$_2$(ame)(PPh$_3$)] (**1**) was prepared by the reaction of *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$] with a twofold molar excess of 2-(2-aminophenyl)ethanol (Hame) at reflux in benzene. With an equimolar ratio of reactants, coordination of ame could not be achieved, and only the starting materials were recovered.

Spectroscopic evidence suggests that ame acts as a monoanionic bidentate *N*,*O*-donor chelate, with deprotonation of the alcoholate oxygen. In the infrared spectrum of **1** the asymmetric Re=O stretching frequency appears as a very strong band at 936 cm^{-1}, which falls below the range (950–968 cm^{-1}) normally observed for neutral six-coordinate monooxorhenium(V) complexes having an anionic oxygen atom coordinated *trans* to the oxo group [7]. Two bands of medium intensity at 3203 and 3122 cm^{-1} are indicative of the presence of the coordinated neutral NH$_2$ group. The ν(Re–N) and ν(Re–O) stretches appear at 530 and 499 cm^{-1}, respectively. Full assignment of the peaks in the ^{1}H NMR spectrum was not possible due to overlap of signals in the aromatic region. A broad singlet at δ9.79 ppm is attributed to the protons of the amino group. Two two-proton triplets at δ2.81 and 3.68 ppm are assigned to the two methylene protons.

A perspective view of the asymmetric unit of [ReOI$_2$(ame)(PPh$_3$)] (**1**) is shown in Fig. 1. It exhibits distorted octahedral geometry about the central rhenium ion. The basal plane is defined by the phosphorus atom of the PPh$_3$ group, two iodide ions *trans* to each other, and the neutral amino nitrogen of ame. The oxo group and alcoholate oxygen lie in *trans* axial positions. Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear O(1)=Re–O(2) axis of 171.4(2)°, accomplished by I(1)–Re–I(2) and N–Re–P angles of 172.77(2)° and 172.5(2)°, respectively. The metal is shifted out of the mean equatorial plane formed by I$_2$PN by 0.1251 Å towards O(1), which is the result of the non-orthogonal angles O(1)–Re–I(1) 95.5(2), O(1)–Re–I(2) 88.3(2)°, O(1)–Re–N 92.0(2)° and O(1)–Re–P 95.3(2)°. In the O$_2$I$_2$PN polyhedron the rhenium ion is 1.177 Å from the I(1)–O(1)–N plane, and –1.344 Å from I(2)–O(2)–P, with the dihedral angle being 5.30°. The Re=O(1) axis is inclined at 176.00° with respect to the equatorial plane. The bite angle (i.e. N–Re–O(2)) of ame is 83.5(2)°.

The Re=O(1) bond length of 1.717(5) Å is considerably longer than that normally observed for monomeric six-coordinate monooxorhenium(V) complexes (average

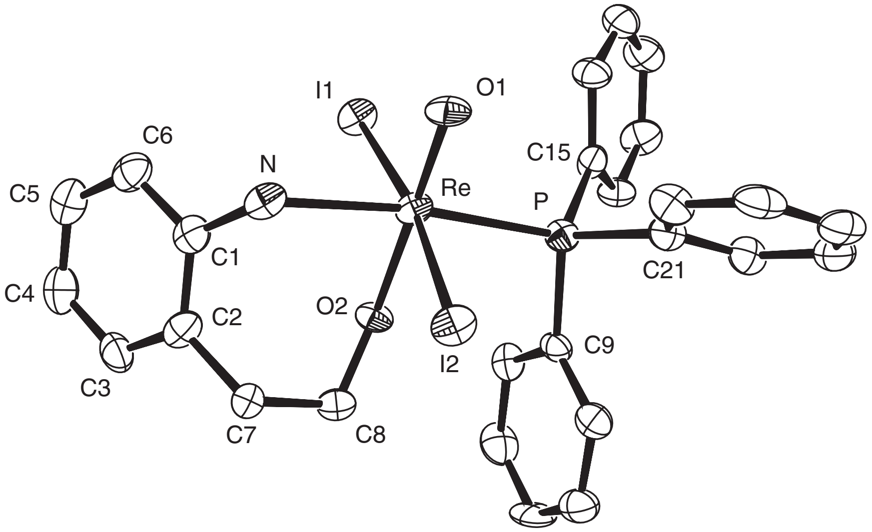

FIGURE 1 An ORTEP view of the structure, showing the atom labelling scheme and thermal ellipsoids drawn at the 40% probability level. The benzene molecule is omitted for clarity.

1.685(5)Å) [2–5], and shorter than the average of 1.76 Å for this bond in *trans*-dioxorhenium(V) complexes [9]. This longer Re=O(1) bond in **1** is reflected by the weaker Re=O stretching frequency of 936 cm^{-1} in the infrared spectrum. Also, the Re–O(2) bond length is 1.860(5) Å, considerably shorter than the accepted length for a Re–O single bond (2.04 Å) [10]. Partial double bond character in the Re–O(2) bond is consistent with the large Re–O(2)–C(8) angle of 149.5(5)°. This same effect has been observed in the complex $[ReOCl_2(OEt)(dpa)]$ (dpa=2,2′-dipyridylamine), where the Re–O(ethoxide) bond length is 1.866(5) Å with a Re–O–C_2H_5 angle of 149.8(5)° [11].

The two *trans* Re–I bond lengths are significantly different, and are around the upper limit of the observed range of 2.664(2)–2.789(3) Å [6]. The Re–P distance of 2.449(2) Å is within the expected range for Re(V)–P bond lengths with a σ-donor ligand *trans* to it [12]. Re–N (2.256(6) Å) is just outside the range of (2.10–2.22 Å) observed for Re(V)–NH_2 bonds [2, 13]. The N–C(1) bond has a typical single bond length value of 1.46(1) Å.

The bidentate ame$^-$ ligand forms a seven-membered ring with a boat formation around the Re ion, with N(1) and C(7) as "bow" and "stern" atoms (up by 0.398 and 0.421 Å, respectively, and torsion angles in the range –57.3, 53.4°); the mean plane makes a dihedral angle of 70.07° with the mean equatorial plane. We rationalise the fact that the Re=O(1) bond is significantly longer than in other similar related complexes due to the increased O(1)=Re–O(2) bond angle of 171.4(2)°, which will lead to better orbital overlap between O(2) and Re and will result in stronger Re–O(2) bonding, and resultant weaker Re=O(1) bonding.

Supplementary Material

CCDC-225319 contains 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; E-mail: deposit@ccdc.cam.ac.uk.

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