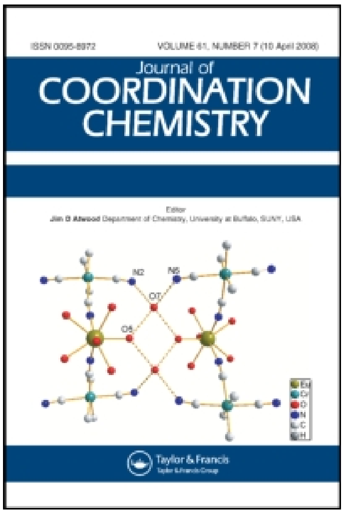

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FORMATION OF AN OXO-FREE RHENIUM(V) COMPLEX WITH 2-AMINOTHIOPHENOL

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The reaction of a twofold molar excess of 2-aminothiophenol (H_2L) with *trans*-$[ReOCl_3(PPh_3)_2]$ in benzene led to the isolation of the oxo-free rhenium(V) complex $[ReCl(PPh_3)L_2]$ (**1**). IR, ^1H NMR and X-ray crystallographic results indicate that the ligands L coordinate in a dianionic amidothiolate form to the metal and that the complex has the unusual skew-trapezoidal bipyramidal geometry. The ligands L have an average bite angle of 78.8(1)°, with average Re–N and Re–S bond lengths equal to 1.978(5) and 2.297(1) Å, respectively.

Keywords: Oxo-free; Rhenium(V); Crystal structure; Skew-trapezoidal bipyramid

INTRODUCTION

There is currently considerable interest in the coordination chemistry of rhenium, especially in its +V oxidation state, because of its potential applications in radiotherapy [1] and because it is easily obtained from the reduction of perrhenate and is stabilized by a large variety of ligands. However, the most distinctive feature of Re(V) chemistry is the existence of a large number of stable complexes in which the metal forms multiple bonds to oxygen, nitrogen or sulfur. These complexes are mostly octahedral and contain one of the $[ReO]^{3+}$, $[ReO_2]^+$, $[Re_2O_3]^{4+}$, $[ReN]^{2+}$, $[Re{=}NR]^{3+}$ or $[ReS]^{3+}$ moieties [2]. These multiply bonded donor atoms severely restrict the structure, geometry, reactivity and magnetic properties of Re(V) complexes.

Re(V) complexes without oxo, nitrido, imido or sulfido groups are rare. The few examples in the literature ($ReCl_5$, $[ReX_4(diars)_2]^+$, $[Re(HNC_6H_4S)_3]^-$, $[ReH_5(PPh_3)_2(py)]$ and its derivatives) were synthesized by either the reduction of Re(VI) and Re(VII) or the oxidation of Re(III) and Re(IV) species under extreme conditions [3]. Only two examples in the literature have been prepared with the ligand substitution of a Re(V) compound; $[ReH_5(PPh_3)_3]$ [4] and $[ReCl(PPh_3)L'_2]$ [5] were made by treating

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trans-[$ReOCl_3(PPh_3)_2$] with $LiAlH_4$ and 3-nitro-1,2-diaminobenzene (H_2L'), respectively.

This report describes the complex [$ReCl(PPh_3)L_2$] (**1**), which is the product of the reaction of 2-aminothiophenol (H_2L) with *trans*-[$ReOCl_3(PPh_3)_2$] in benzene. In **1**, the ligands L act as bidentate dianionic amidothiolate chelates.

EXPERIMENTAL

Reagents

Trans-[$ReOCl_3(PPh_3)_2$] was synthesized by a published procedure [6]. Solvents were of reagent grade, and were purified, dried and deoxygenated before use. All other reagents were obtained commercially (Aldrich), and their purity was checked by ^{1}H NMR and melting point.

Synthesis

A mixture of 100 mg (120 µmol) of *trans*-[$ReOCl_3(PPh_3)_2$] and 30 mg (240 µmol) of 2-aminothiophenol (H_2L) in 20 cm^3 of benzene was heated under reflux for 90 min. After cooling the solution to room temperature, a red precipitate was removed by filtration, washed with benzene and diethylether, and dried under vacuum. Recrystallization from acetonitrile gave brown plates. Yield 68% (based on Re), mp 178°C. *Anal.* Calcd (%): C, 49.34; H, 3.45; N, 3.84; S, 8.78. Found: C, 49.47; H, 3.51; N, 3.91; S, 8.36. IR: ν(NH) 3274; ν(Re–N) 482; ν(Re–S) 354; ν(Re–Cl) 308 cm^{-1}. ^{1}H NMR (295 K) ppm: 6.52 (2H, t, H^{23}/H^{29}), 6.77 (2H, t, H^{22}/H^{28}), 6.91 (d, 2H, H^{24}/H^{30}), 7.40–7.65 (17H, m, P*Ph*$_3$, H^{21}/H^{27}), 14.22 (2H, s, N*H*). UV–Vis nm (ε/M cm^{-1}): 578 (14 100), 454 (64 000).

X-ray Data Collection, Structure Solution and Refinement

Crystals of **1**, suitable for X-ray diffraction studies, were grown from acetonitrile. Crystallographic data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation. The structure was solved by direct methods [7] and refined by full-matrix least-squares procedures using SHELXL-97 [8]. All non-hydrogen atoms were refined anisotropically. Crystal data and details of the structure determination are given in Table I, with selected bond distances and angles shown in Table II.

RESULTS AND DISCUSSION

The rhenium(V) complex [$ReCl(PPh_3)L_2$] (**1**) was prepared in good yield from the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with 2-aminothiophenol (H_2L) in a 1:2 molar ratio in boiling benzene as follows:

$$ReOCl_3(PPh_3)_2 + 2H_2L \xrightarrow[\Delta]{} [ReCl(PPh_3)L_2] + 2HCl + H_2O + PPh_3.$$

TABLE I Crystal and structure refinement data for [ReCl(PPh$_3$)L$_2$] (**1**)

Empirical formula	$C_{30}H_{25}ClN_2S_2PRe$
Formula weight	730.30
Temperature (*K*)	200
Wavelength	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	$a = 14.918(1)$ $b = 10.323(1)$ $c = 19.187(2)$ $\beta = 105.14(1)$
Volume (Å^3)	2852.1(5)
Z	4
Density (calc.) (Mg m^{-3})	1.701
Crystal size (mm)	0.07 × 0.14 × 0.21
Absorption coefficient (mm^{-1})	4.579
F(000)	1432
Theta range	2.2–25.8
Index range	$-17 \leq h \leq 18$ $-12 \leq k \leq 12$ $-23 \leq l \leq 23$
Reflections collected/unique	19409/5441
Data/restraints/parameters	365/0/342
Goodness-of-fit on F^2	0.86
Final R indices	$R = 0.0310$, $wR_2 = 0.0564$
Largest diff. peak and hole (e Å^{-3})	0.68 and −2.02

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

Re–Cl	2.444(1)	Re–P	2.449(2)
Re–S(1)	2.297(1)	Re–S(2)	2.297(1)
Re–N(1)	1.979(5)	Re–N(2)	1.976(4)
N(1)–C(20)	1.370(7)	N(2)–C(26)	1.359(7)
S(1)–C(19)	1.733(6)	S(2)–C(25)	1.727(6)
C(25)–C(26)	1.394(8)	C(26)–C(27)	1.399(9)
C(27)–C(28)	1.369(8)	C(28)–C(29)	1.39(1)
C(29)–C(30)	1.373(9)	C(25)–C(30)	1.388(7)
N(1)–H(71)	0.89(6)	N(2)–H(72)	0.87(3)
Cl–Re–P	77.65(5)	Re–S(1)–C(19)	104.0(2)
N(1)–Re–S(1)	78.7(1)	Re–S(2)–C(25)	103.3(2)
N(2)–Re–S(2)	78.9(1)	Re–P–C(1)	108.5(2)
Cl–Re–S(1)	130.28(5)	Cl–Re–N(1)	82.1(1)
Cl–Re–S(2)	137.02(5)	Cl–Re–N(2)	82.2(1)
N(1)–C(20)–C(19)	115.7(5)	S(1)–C(19)–C(24)	126.0(5)
Re–N(1)–C(20)	127.2(4)	Re–N(2)–C(26)	126.7(4)
Re–N(2)–H(72)	111(3)	Re–N(1)–H(71)	119(4)

The diamagnetic compound is soluble in a variety of solvents such as acetone, acetonitrile, chloroform, dichloromethane and ethyl acetate. It is stable in solution for days, and for months in the solid state.

The crystal structure shows that **1** (Fig. 1) is monomeric and neutral, and exhibits skew-trapezoidal bipyramidal geometry. The complex contains two dinegative L ligands symmetrically coordinated to the Re(V) center. The coordinating mode of L is evidenced by the two Re–NH bond distances (both equal within the range of

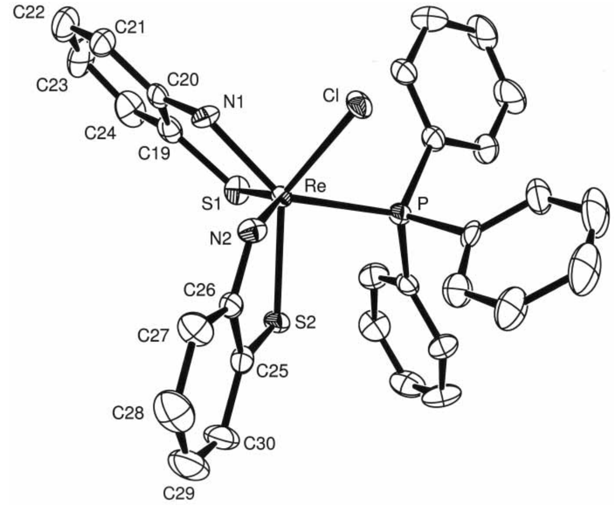

FIGURE 1 The molecular structure of $[ReCl(PPh_3)L_2]$ (**1**) showing the atom numbering scheme and 40% displacement ellipsoids.

the e.s.d. values; mean value 1.978(5) Å) and the two Re–S distances (average value 2.297(1) Å). These values are consistent with those found in the literature for these particular bonds [9]. Re–P (2.449(2) Å) and Re–Cl bond lengths (2.444(1) Å) are within the ranges observed for a large variety of Re(V) oxo, nitrido and imido complexes [9,10]. The Re, Cl and P atoms are above the N(1)N(2)S(1)S(2) mean plane by 0.767, 2.549 and 2.781 Å, respectively. The Re atom is 1.330 Å from the N(1)N(2)Cl plane and 1.462 Å from the S(1)S(2)P plane; the dihedral angle between these two planes is 7.43°.

The average bite angle of the L ligands is 78.8(1)° [S(1)–Re–N(1) = 78.7(1)°; S(2)–Re–N(2) = 78.9(1)°], which is some 3.9° smaller than in the anion $[TcOL_2]^-$ [11]. The Cl–Re–P angle of 77.65(5)° scarcely differs from the L bite angles. The average C–N bond distance of 1.364(7) Å is considerably shorter than a characteristic C–N single bond of 1.45 Å, and noticeably longer than the expected double bond length of 1.28 Å [12]. In addition, the C–S bond length (average 1.730(6) Å) is significantly shorter than the C–S single bond length of 1.76(1) Å and longer than the double bond length of 1.69(1) Å found in *N*,*S*-coordinated 2-aminothiophenol anions [13]. These deviations may be attributed to delocalization in the chelate rings ReNCCS.

Stereochemistries usually envisaged for six-coordinate complexes of the type $[M(bidentate)_2(monodentate)_2]$ are *cis*- and *trans*-octahedral. However, for bidentate ligands of small normalized bite b $[b = 2\sin(i - \mathrm{M} - j/2)]$ these structures become distorted; for example, the *trans*-octahedral structure distorts to the skew-trapezoidal bipyramidal structure [14]. Surprisingly, this distortion occurs in **1** with a rather large value of $b = 1.27$. In six-coordinate complexes of known crystal structure with two identical bidentate ligands, the *cis*-octahedral geometry is preferred with small normalized bite ligands ($b < 1.30$). The *trans* structure remains possible, however, at low b if the effective bond length ratio R (monodentate/bidentate) > 1.0 [14]. In **1**, R equals 1.14.

The infrared spectrum of **1** contains no band in the region 770–980 $\mathrm{cm^{-1}}$ that can be ascribed to a Re=O stretching frequency. A single N–H absorption occurs at 3274 $\mathrm{cm^{-1}}$, and Re–N and Re–S bands occur at 482 and 354 $\mathrm{cm^{-1}}$, respectively. The Re–Cl stretch appears as a band of medium intensity at 308 $\mathrm{cm^{-1}}$. The proton NMR spectrum of **1** clearly illustrates the presence of two chemically equivalent ligands L and one PPh_3 group. The triplets at δ6.52 and 6.77 ppm integrate for two protons each, and they are assigned to the protons H^{23}/H^{29} and H^{22}/H^{28}, respectively. The doublet for H^{24}/H^{30} occurs at δ6.91 ppm, while the expected doublet for H^{21}/H^{27} is buried under the 17-proton multiplet in the range δ7.40–7.56 ppm. The signals of the two NH protons appear as a singlet at 14.22 ppm. The crystallographic, infrared and NMR data unambiguously establish that the two H_2L ligands in **1** are doubly deprotonated and that the rhenium is in the +V formal oxidation state.

The isolation of complex **1** presents an interesting example of an oxo-free complex of rhenium(V) that is easily prepared by ligand substitution of the oxo compound *trans*-$[ReOCl_3(PPh_3)_2]$. The substitution of an oxo group from Re(V) is not often observed, and Re(V) complexes without a multiply bonded donor atom are unusual.

Supplementary Material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with deposit no. CCDC-231986. This information may be obtained free of charge from The Director, CCDC, 12 Union Rd, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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