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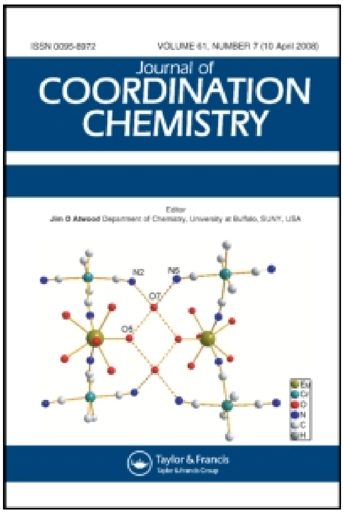

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Disproportionation of rhenium(V). Imidazolate coordination of pyridylbenzimidazole in a rhenium(III) complex

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Reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with 2-(2′-pyridyl)benzimidazole (pbiH) in methanol led to the isolation of the rhenium(III) compound [$ReCl_2$(pbi)$(PPh_3)_2$] (**1**). Complex **1** could also be prepared in better yield by the reduction of $[ReO_4]^-$ with PPh_3 in the presence of pbiH and hydrochloric acid. An X-ray crystallographic study showed that pbi is coordinated as a bidentate monoanionic chelate, with deprotonation of the imidazolyl NH group. The PPh_3 ligands are *trans* to each other.

Keywords: Rhenium(III); Pyridylimidazolate; Bidentate; Crystal structure

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1. Introduction

The recent advent of the two β-emitting isotopes ^{186}Re and ^{188}Re in the therapeutic field [1] has rekindled interest in the coordination chemistry of this metal. Part of our research effort in this field focusses on the coordination chemistry of rhenium(V) with multidentate ligands containing the imidazolyl group, and several accounts reflecting the results of our research have appeared [2–6]. We have earlier found that the reaction of the *N*,*N*-donor ligand 2-(2′-pyridyl)-imidazole (pimH) with *trans*-[$ReOCl_3(PPh_3)_2$]

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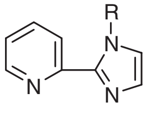
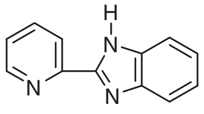
did not lead to the expected product [$ReOCl_3$(pimH)], as was found for 2,2′-bipyridyl [7], but to the formation of the Re(III) complex salt [$ReCl_2$(pimH)(PPh_3)$_2$](ReO_4) [2].



R=H(pimH), CH_3(pimMe)



pbiH

In the light of the propensity of Re(III) to form neutral octahedral complexes, the formation of the cationic complex was surprising, since a neutral complex could be obtained by the deprotonation of pimH to give an imidazolate coordination of pim$^-$. In contrast, with 2-(2′-pyridyl)-1-methylimidazole (pimMe) as ligand, the neutral Re(III) complex [$ReCl_3$(pimMe)(PPh_3)] was isolated [2]. Both compounds could also be prepared by the reaction of the chelates with [ReO_4]$^-$ in the presence of four equivalents of PPh_3 in methanol, containing a few drops of concentrated hydrochloric acid [2].

In this report, the reaction of 2-(2′-pyridyl)benzimidazole (pbiH) with [$ReOCl_3 \times (PPh_3)_2$] and [ReO_4]$^-$ is described. In both procedures the neutral Re(III) complex [$ReCl_2$(pbi)(PPh_3)$_2$] (**1**) was isolated, in which the pbiH iss deprotonated and is coordinated as a bidentate pyridylimidazolate.

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2. Experimental

2.1. *Reactants and methods*

Reagent-grade NH_4ReO_4, pbiH and deuterated solvents were purchased from Aldrich. Solvents and other chemicals (Aldrich) were used as received. IR spectra (KBr pellets) were recorded on a Nicolet 20 DXC FTIR spectrophotometer in the 4000–200 cm^{-1} range. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker AMX-300 spectrometer. All chemical shifts are relative to TMS, with DMSO-d_6 as solvent. Conductivity measurements were carried out with 10^{-3} M solutions in DMF at 293 K on a Philips PW9509 digital conductometer. Elemental analyses were carried out by the Department of Chemistry at the University of the Western Cape in Cape Town.

2.2. *Synthesis*

Trans-[$ReOCl_3$(PPh_3)$_2$] was prepared by a literature procedure [8]. [$ReCl_2$(pbi)(PPh_3)$_2$] (**1**) was prepared in two ways. To a suspension of 0.100 g (120 µmol) of *trans*-[$ReOCl_3$(PPh_3)$_2$] in 10 cm^3 of methanol was added 0.047 g (240 µmol) of pbiH, and the mixture was heated under reflux for an hour. The initial yellow-green colour of the mixture changed to dark orange when heating was stopped. After cooling to room temperature, the solution was filtered and left standing for 2 days, when orange crystals were collected by filtration. Recrystallization from a 1 : 2 acetone/methanol mixture gave crystals that were suitable for X-ray diffraction studies (yield 0.045 g, 46 µmol, 38% based on Re, m.p. = 184°C).

The alternate method is as follows. To a mass of 0.50 g (186 µmol) of the salt (NH_4)[ReO_4] in 5 cm^3 of methanol was added 0.17 cm^3 of concentrated HCl. To this mixture was added 5 cm^3 of a methanolic solution of PPh_3 (195 mg, 760 µmol) and

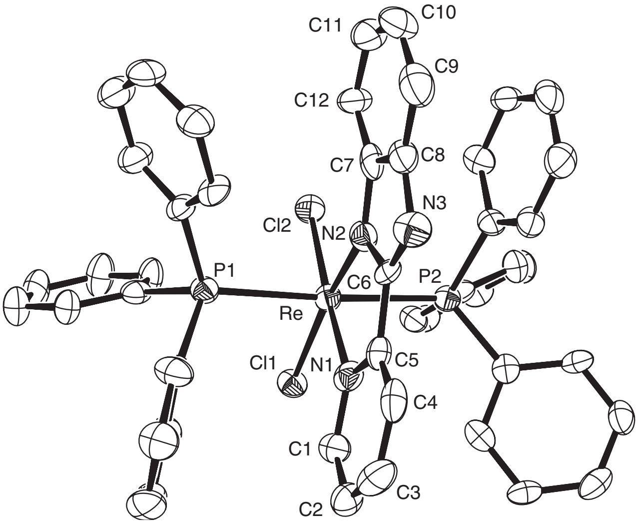

Figure 1. An ORTEP view of complex **1**, showing 40% probability displacement ellipsoids and the atom labelling. Hydrogen atoms have been omitted for clarity.

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pbiH (73 mg, 370 µmol). The resulting solution was heated under reflux for 90 mins. After cooling to room temperature, the orange solution was filtered to remove a small amount of green material. Slow evaporation of the filtrate over 2 days gave an orange, crystalline solid, which was recrystallized from a 1 : 2 acetone/methanol mixture (yield 0.126 g, 129 µmol, 69% based on Re, m.p. = 184°C). Anal. Calcd for $ReC_{48}H_{38}N_3Cl_2P_2$ (%): C, 59.08; H, 3.92; N, 4.31%. Found: C, 59.21; H, 3.83; N, 3.77. ^1H NMR δ(ppm): 13.24 (d, PPh_3*ortho*), 8.71(t, PPh_3*meta*), 8.48(t, PPh_3*para*), 3.44(s, H2), 3.38(s, H9, H12), 3.29(s, H10, H11), 2.88(s, H4), 2.71(s, H3), 1.25(s, H1). IR(ν_{max}/cm^{-1}): 1481 (C=C), 455, 499 (Re–N), 297, 305 (Re–Cl).

2.3. *X-ray crystallography*

Intensity data for **1** were collected at 200(2) K on a Nonius Kappa CCD single-crystal diffractometer, using Mo-Kα radiation. Unit cell and space group determinations were carried out in the usual manner [9]. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-96 [10]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were geometrically constrained. An ORTEP view of **1**, along with the atom numbering scheme, is given in figure 1. A summary of crystal data and refinement details is shown in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis*

Complex **1** with pbi$^-$ as a chelating ligand was synthesized by reaction of $[ReOCl_3(PPh_3)_2]$ with two equivalents of pbiH in methanol, heated at reflux in air.

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Table 1. Crystallographic data for **1**.

Chemical formula	$C_{48}H_{38}N_3Cl_2P_2Re$
Formula weight	975.90
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å,°)	$a = 13.8856(3)$
Volume (Å^3)	$b = 10.5556(2)$ $\beta = 99.709(1)$
	$c = 27.7446(6)$
	4008.3(2)
Z	4
Density (Calcd) (Mg m^{-3})	1.617
Crystal size (mm)	0.02 × 0.08 × 0.10
μ (mm^{-1})	3.284
F(000)	1944
Theta min-max (°)	3.5–22.5
Index ranges	$-14 \leq h \leq 14$
	$-11 \leq k \leq 11$
	$-29 \leq \ell \leq 29$
Observed data	27035
N_{ref}, N_{par}	5218, 505
$R1$, $wR2$, S	0.0440, 0.0876, 1.02
Min./max. resd. density (e Å^{-3})	−1.04/0.90

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

Re–Cl(1)	2.378(2)	Re–Cl(2)	2.384(2)
Re–P(1)	2.478(2)	Re–P(2)	2.500(2)
Re–N(1)	2.149(6)	Re–N(2)	2.072(6)
N(2)–C(6)	1.37(1)	N(3)–C(6)	1.33(1)
N(1)–C(5)	1.37(1)	N(3)–C(8)	1.40(1)
P(1)–Re–P(2)	176.75(7)	N(1)–Re–N(2)	76.2(2)
Cl(1)–Re–Cl(2)	94.67(7)	Cl(1)–Re–N(2)	167.3(2)
Cl(2)–Re–N(1)	174.2(2)	N(1)–C(5)–C(6)	112.2(7)
P(1)–Re–Cl(1)	88.50(7)	P(2)–Re–Cl(2)	85.55(7)

Reduction to Re(III) is somewhat surprising, since the phenomenon was not observed with the bidentate *N*,*N*-donors 2,2′-bipyridine (bipy) or 1,10-phenanthroline [7]. The low yield of **1** is the result of the disproportionation mechanism which also produces perrhenate as by-product. Complex **1** could also be prepared in higher yield by the reaction of $[ReO_4]^-$ with pbiH in the presence of four equivalents of PPh_3 in methanol, acidified with hydrochloric acid, with the excess phosphine acting as reducing agent. The complexes $[ReCl_3(bipy)(PPh_3)]$ and $[ReCl_3(imMe)_2(PPh_3)]$ (imMe = 1-methylimidazole) have also been synthesized by the reduction of $[ReOCl_3(PPh_3)_2]$ with additional excess PPh_3 [11, 12]. The conductivity of **1** in DMF [$\Lambda_M = 18\,\mathrm{Ohm^{-1}\,mol^{-1}\,cm^2}$] confirms that it is a non-electrolyte. It is soluble in a wide variety of solvents, including acetone, acetonitrile, dichloromethane, DMF and DMSO, but is insoluble in water, alcohols and benzene. It is stable for months in the solid state, and for days in solution.

3.2. *Spectroscopic characterization*

Even though complex **1** is paramagnetic, its ^{1}H NMR signals are surprisingly sharp and clear. Protons of the PPh_3 groups lead to the typical pattern observed previously for Re(III)–PPh_3 complexes [12]. The *ortho* protons of the phosphine

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phenyl rings are shifted far downfield, to δ 13.24 ppm, from their normal position at *ca* 7.6 ppm in diamagnetic complexes. The *meta* and *para* protons are also shifted downfield, although to a lesser extent, to δ 8.71 and 8.48 ppm, respectively. The pyridyl protons H1 and H3 (see figure 1 for labelling) are shifted upfield (at δ 1.25 and 2.71 ppm, respectively) by *ca* 6 ppm from their expected diamagnetic positions, with upfield shifts also observed for H2, H4 and the benzimidazole protons.

There is no evidence in the infrared spectrum of **1** for the existence of an N–H bond, with no bands in the region 3000–3300 cm^{-1}. Two medium intensity bands for the Re–Cl stretches at 297 and 305 cm^{-1} indicate the presence of the two chlorides in non-equivalent *cis* positions.

3.3. *Crystal structure*

In the complex the Re atom lies in a distorted octahedral environment. The two PPh_3 ligands lie *trans* to each other, with the two *cis* chlorides, imidazole nitrogen N(2) and pyridinic nitrogen N(1), forming a square plane. Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear P(1)–Re–P(2) axis of 176.75(7)°, accomplished by N(1)–Re–Cl(2) and N(2)–Re–Cl(1) angles of 174.2(2)° and 167.3(2)°, respectively. The rhenium atom is displaced slightly out of the mean equatorial N_2Cl_2 plane by 0.0090 Å towards P(2), the result of the non-orthogonal angles P(2)–Re–Cl(1) = 93.63(7)°, P(2)–Re–Cl(2) = 85.55(7)°, P(2)–Re–N(1) = 94.3(2)° and P(2)–Re–N(2) = 88.2(2)°. The bite angle of pbi [N(1)–Re–N(2)] equals 76.2(2)°, which is not significantly different from that of 2-(2′-pyridyl)imidazole and 2,2′-diimidazole in other rhenium(III) complexes (75.2–76.5°) [13]. The pyridine and benzimidazole rings of pbi are not coplanar, with a dihedral angle of 10.7° between their least-squares planes. They make dihedral angles of 4.7 and 6.4° with the mean equatorial plane, respectively. Both the benzimidazole and pyridine rings are planar, as expected. Due to chelation, the C–C–N angles at the ring junctions of pbi deviate markedly from 120° [N(1)–C(5)–C(6) = 112.2(7)°, C(5)–C(6)–N(2) = 117.0(7)°], and the rhenium atom lies about 3° off the lone-pair directions [C(5)–N(1)–Re = 117.1(5)°, C(6)–N(2)–Re = 117.2(5)°]. Intraligand distances show that N(3)–C(6) is a localized double bond [1.33(1) Å] and that deprotonation of N(2) has not led to delocalization [C(6)–N(2) = 1.37(1) Å, C(8)–N(3) = 1.40 Å].

Re–Cl distances are just outside the range of 2.349–2.374 Å found in other rhenium(III) complexes [13]. The average Re–P distance of 2.489(2) Å deviates little from the average of 2.483(2) Å found in other Re(III) complexes with two PPh_3 ligands *trans* to each other. The Re–N(1) bond [2.149(6) Å] is longer than the Re–N(2) bond [2.072(6) Å], reflecting the stronger basic properties of the imidazolate nitrogen.

Supplementary material

CCDC-286382 contains crystallographic data for complex **1**. 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 1 EZ, UK; fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk].

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