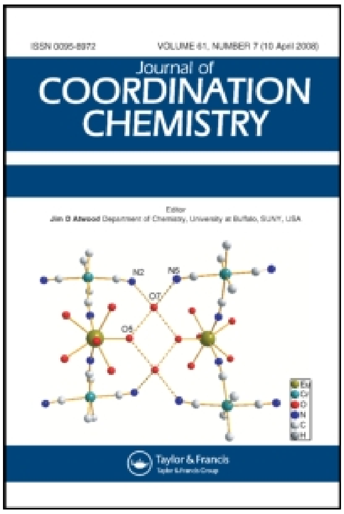

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Monodentate imido coordination of 1,2-diaminobenzene to rhenium(V)

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The complex *trans*-[Re(dab)$Cl_3(PPh_3)_2$] (H_2dab = 1,2-diaminobenzene) was prepared from the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with H_2dab in ethanol. The ligand dab is coordinated to the rhenium(V) centre only through a dianionic imido nitrogen to give a distorted octahedral coordination geometry around the metal ion.

Keywords: Rhenium(V); Monodentate imide; 1,2-Diaminobenzene; Crystal structure

1. Introduction

The current widespread interest in the coordination chemistry of rhenium is mainly due to the potential application of the radioisotopes ^{186}Re and ^{188}Re in radiotherapy [1]. Our interest is focused on the synthesis of rhenium(V) complexes containing the molecule 1,2-diaminobenzene (H_2dab) and its derivatives. Increasing attention has lately been devoted to metal complexes derived from H_2dab, mainly because of their unusual redox, magnetic and structural properties [2, 3]. In these compounds, H_2dab can be present as the 1,2-diamide dianion (dab), the 1,2-benzosemiquinone diimine π-radical monoanion (sbqdi), or the neutral 1,2-benzoquinone diimine (bqdi). These three forms are related by two one-electron oxidation–reduction steps, and there are several unusual examples in which the metal and/or the ligands are reduced or oxidized [4].

We have found that H_2dab and its derivatives are versatile ligands for rhenium(V). The sbqdi form has been found in the complex [Re^{IV}(sbqdi)$_3$]I [5], and the diamide form in the oxo-free complex [Re^V(dab)$_2$Cl(PPh_3)] [6]. The *cis*-dioxo complex [Re^VO_2(Hdab)(py)$_2$] contains the terminally reduced monoanionic monoamide form [7].

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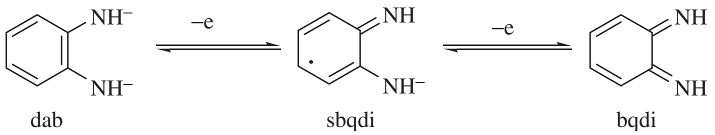

The simple substitution of $[ReOCl_4]^-$ with H_2dab leads to the formation [8] of $[Re^VO(dab)_2]^-$. We have now managed to prepare and structurally characterize the rhenium(V) complex $[Re(dab)Cl_3(PPh_3)_2]$, in which dab is present in the dianionic 1,2-imidoaminobenzene form, with coordination only through the imido nitrogen.

2. Experimental

Trans-$[ReOCl_3(PPh_3)_2]$ was prepared by a literature procedure [9]. The ligand H_2dab was obtained commercially (Aldrich). Scientific instrumentation used is the same as reported elsewhere [10]. Infrared spectra were obtained as KBr discs and ^{1}H NMR spectra were run in d_6-DMSO.

2.1. *Synthesis of [Re(dab)Cl$_3$(PPh$_3$)$_2$] (1)*

A mixture of *trans*-$[ReOCl_3(PPh_3)_2]$ (150 mg, 180 µmol), 1,2-diaminobenzene (23 mg, 213 µmol) and ethanol (20 cm^3) was heated under reflux for 1 h. The resulting green reaction mixture was allowed to cool to room temperature, and the dark red product **1** was filtered off, washed with ethanol and diethylether, and dried under vacuum. Further evaporation of the filtrate gave another batch of crystalline product; yield 113 mg (68%). Recrystallization from ethyl acetate/dichloromethane gave red parallelopipeds, m.p. 191–195°C (dec.). Anal. Calcd for $C_{42}H_{36}Cl_3N_2P_2Re$ (%): C, 54.64; H, 3.93; N, 3.03. Found: C, 54.72; H, 3.79; N, 2.89. IR (cm^{-1}): 3315w, 3061m, 1636s, 1578m, 1434s, 1363m, 1251m, 1190m, 1093s, 746s, 694vs, 523s, 453m, 320m, 278m; ^{1}NMR (300 MHz): δ_H 6.91 (2H, m, H(2), H(5)), 7.22(2H, m, H(3)H(4)), 7.32(2H, br s, NH_2), 7.56–7.68 (30H, m).

2.2. *X-ray structure*

X-ray diffraction studies on crystals of **1** were performed at 200(2) K using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods applying SIR97 [11] and refined by least-squares procedures using SHELXL-97 [12]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated in idealized geometrical positions. The data were corrected by a numerical absorption correction [13] after optimizing the crystal shape with XShape [14]. There are two molecules of **1** in the asymmetric unit. Crystal and structure refinement data are given in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystal data and structure refinement details for **1**.

Chemical formula	$C_{42}H_{36}Cl_3N_2P_2Re$
Formula weight	923.26
Temperature (K)	200(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 11.9701(2)$ $b = 14.2472(2)$, $\beta = 98.6995(6)$ $c = 2\ 1.7465(3)$
Crystal size (mm^3)	$0.04 \times 0.05 \times 0.15$
Volume ($Å^3$)	3665.99(9)
Z	4
Density (calcd), $Mg\,m^{-3}$	1.673
Absorption coefficient, mm^{-1}	3.655
Absorption correction	Numerical (XRed, rev. 1.09, STOE)
Diffractometer/scan	Nonius Kappa/CCD area detector
θ range for data collection (°)	3.2–27.5
Reflections measured	55982
Independent/observed reflections	8420 ($R = 0.090$)/6213[$I > 2\sigma(I)$]
Data/restraints/parameters	8420/0/461
Goodness of fit on F^2	1.02
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0392$, $wR_2 = 0.0862$

Table 2. Selected bond lengths [Å] and bond angles [°] for **1**.

Re–N(1)	1.731(4)	Re–Cl(1)	2.431(1)
Re–Cl(2)	2.417(1)	Re–Cl(3)	2.415(1)
Re–P(1)	2.498(1)	Re–P(2)	2.479(1)
C(1)–N(1)	1.361(6)	C(6)–N(2)	1.27(1)
N(1)–Re–Cl(1)	176.9(1)	Re–N(1)–C(1)	178.7(4)
N(1)–Re–P(1)	91.0(1)	N(1)–Re–P(2)	90.0(1)
N(1)–Re–Cl(2)	92.9(1)	N(1)–Re–Cl(3)	93.0(2)
P(1)–Re–P(2)	177.37(4)	Cl(2)–Re–Cl(3)	173.86(4)
P(1)–Re–Cl(2)	88.58(4)	P(2)–Re–Cl(3)	92.55(4)

3. Results and discussion

The reaction of H_2dab with *trans*-[$ReOCl_3(PPh_3)_2$] in equimolar quantities in boiling ethanol gave the product **1** in good yield. The rhenium(V) phenylimido complex *trans*-[$Re(NAr)Cl_3(PPh_3)_2$] was previously prepared by the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with a variety of reagents including $ArNH_2$ [15], ArNSO [16], $ArN = PPh_3$ [17] and 1-acetyl-2-phenylhydrazine [18]. Complex **1** is air-stable and diamagnetic, and a non-electrolyte in DMF. Its solubility in most polar solvents is low, but it can be recrystallized from ethylacetate and acetonitrile.

The IR spectrum of **1** is characterized by a strong absorption at $1093\,cm^{-1}$, which is within the region ($1000–1200\,cm^{-1}$) expected for the linearly coordinated phenylimido moiety with a Re–N triple bond. There are no peaks in the $890–1020\,cm^{-1}$ region, and which can be ascribed to a rhenium(V)-oxo stretch. There are two bands in the low frequency region at 320 and $278\,cm^{-1}$, corresponding to Re–Cl stretching modes. The lower value is indicative of a chloride *trans* to the imido nitrogen. In the ^1H NMR spectrum the signal due to the uncoordinated NH_2 group appears as a broad singlet at 7.32 ppm.

The complex is monomeric and neutral, and exhibits approximately octahedral coordination geometry. The structure is disordered, with 42% of the molecules having the free NH_2 group above Cl(3), and 58% with $N(2)H_2$ above the Cl(2) atom (see figure 1). The Re atom is displaced from the mean P(1)Cl(2)P(2)Cl(3) plane by 0.073(1) Å towards N(1). The *trans* phosphorus donors are displaced from the equatorial plane by 0.05(1) Å, and the chloride ligands by −0.05(1) Å. As a measure of the geometrical distortion, the metal in the coordination polyhedron is 1.44(2) Å from the Cl(1)Cl(3)P(2) plane and −1.20(2) Å from the N(1)P(1)Cl(2) plane, the angle between the two triangular faces being 10.9(1)°. The diaminobenzene ligand acts as a dianionic moiety; the Re–N(1)–C(1) bond angle [178.7(4)°] emphasizes the linear coordination mode of the triply bonded phenylimido unit, and the Re–N(1) distance of 1.731(4) Å agrees with values found in other rhenium(V)-phenylimido octahedral complexes (1.726(6) Å in $[Re(NPh)Cl_3(PPh_3)_2]$ [19], 1.740(6) Å [20] in $[Re(NPh)(OEt)(bpy)_2]^{2+}$ and 1.709(8) Å in $[Re(NPh)(maltol)_2(PPh_3)_2]^+$ [21]). The phenylimido moiety is virtually perpendicular to the mean equatorial plane (dihedral angle 89.6(1)°), and to minimize steric congestion around the metal atom, the ligand fits between two phenyl rings (figure 1), so that the C(1)–C(6) ring centroid is 3.65(2) Å from the C(19)–C(24) centroid and 3.59(2) Å from that of C(25)–C(30); it makes a dihedral angle of 14.8° with the first phenyl and 13.7° with the second phenyl group.

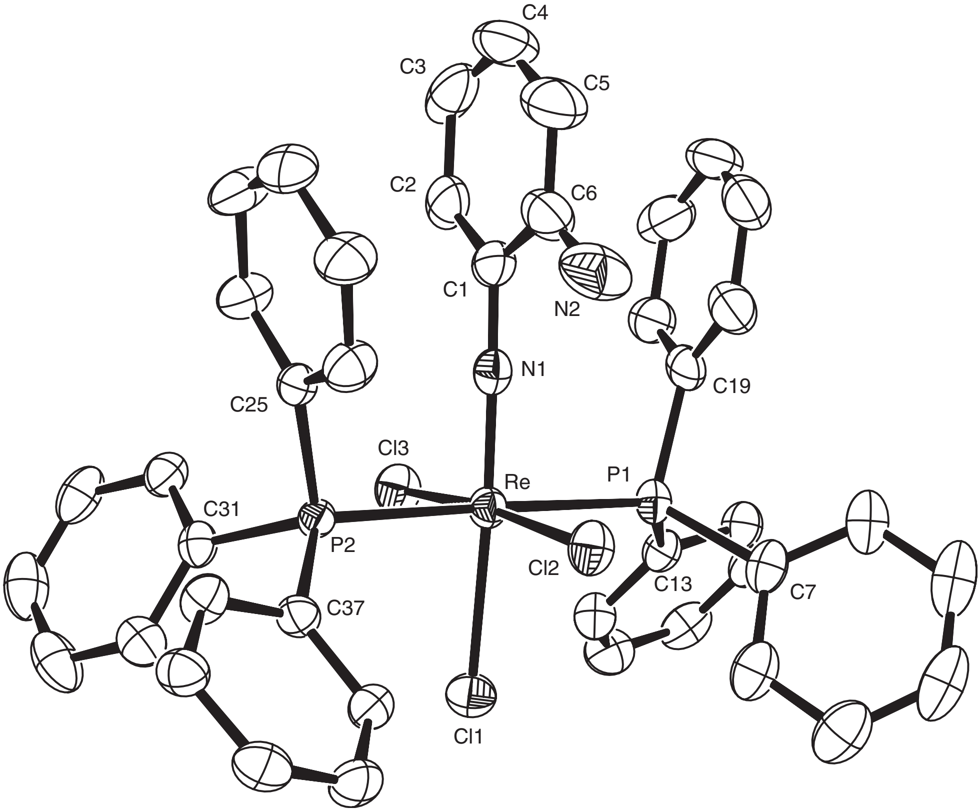

Figure 1. An ORTEP view of complex **1**, showing 40% probability displacement ellipsoids and the atom labelling. Hydrogen atoms have been omitted for clarity.

In addition, an intramolecular hydrogen bond between N(2)H(2B) and Cl(2) (2.652 Å), with the N(2)–H(2B)–Cl(2) angle equalling 135.1(1)°, consolidates the crystal packing. Bond lengths and angles within the inner core show no unusual features, being within the range expected by comparison to other six-coordinated rhenium(V) complexes containing similar ligands [22].

The monodentate coordination of 1,2-diaminobenzene in the monoimido form is unusual, and presents another mode of coordination for this molecule, one which has not been structurally characterized hitherto. Monodentate coordination of the 1,2-diaminobenzene entity has previously been observed in the square pyramidal cobalt(II) complex [Co(bqdi)$_2$(sbqdi)]BPh$_4$, in which the 1,2-benzosemiquinone diimine sbqdi anion is coordinated by only one nitrogen [23].

Supplementary material

CCDC-283381 contains 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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