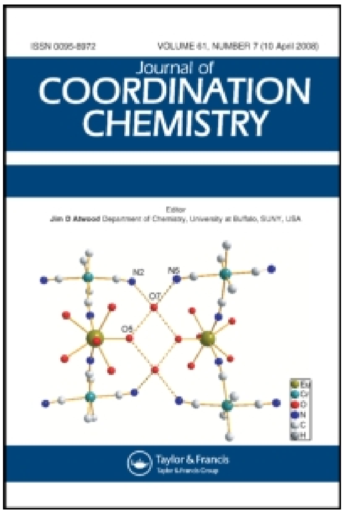

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Monodentate imido coordination of 2-aminodiphenylamine to rhenium(V)

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The complex *trans*-[Re(ada)$Cl_3(PPh_3)_2$] (H_2ada = 2-aminodiphenylamine) was prepared from the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with H_2ada in acetonitrile. The ligand ada is coordinated to the rhenium(V) centre solely through a dianionic imido nitrogen, with distorted octahedral coordination geometry around the metal ion. Surprisingly, the Re–Cl bond *trans* to the Re=N bond is shorter than the two equatorial Re–Cl bonds. The Re = N–C bond angle of the phenylimido moiety equals 178.7(4)°.

Keywords: Rhenium(V); Monodentate imido; 2-aminodiphenylamine; Crystal structure

1. Introduction

We have recently reported the coordination behaviour of 1,2-diaminobenzene (H_2dab) towards rhenium(V) [1–5], since metal complexes of H_2dab are of interest due to their unusual redox, magnetic and structural properties [6–8]. For example, H_2dab can be present in complexes 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 ligands are reduced or oxidized [4].

We note that H_2dab is a versatile ligand for rhenium(V). The sbqdi form has been found in the complex [Re^{IV}(sbqdi)$_3$]I [1], and the diamide form in the oxo-free complex [Re^V(dab)$_2$Cl(PPh_3)] [2]. The *cis*-dioxo complex [Re^VO_2(Hdab)(py)$_2$] contains the monoanionic amidoamino form [3]. We also managed to prepare 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 solely through the imido nitrogen [5]. Here, we report the product of the reaction of 2-aminodiphenylamine, a monophenyl derivative of H_2dab, with *trans*-[$ReOCl_3(PPh_3)_2$] in acetonitrile.

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2. Experimental

Trans-[$ReOCl_3(PPh_3)_2$] was prepared by a literature procedure [9]. H_2ada was obtained commercially (Aldrich). Scientific instrumentation used is the same as reported elsewhere [10]. IR spectra were obtained as KBr discs and ^1H NMR spectra were run in d_6-DMSO.

2.1. *[Re(ada)$Cl_3(PPh_3)_2$] (1)*

A mixture of *trans*-[$ReOCl_3(PPh_3)_2$] (150 mg, 180 μmol), 2-aminodiphenylamine (35 mg, 190 μmol) and acetonitrile (20 cm^3) was refluxed for 2 h under nitrogen. The resulting blue reaction mixture was allowed to cool to room temperature, and a violet precipitate was filtered off, washed with acetonitrile and diethylether, and dried under vacuum. Further evaporation of the filtrate gave another batch of crystalline product. Recrystallization from 1 : 2 dichloromethane/ethanol gave violet needles of **1** · $0.67CH_2Cl_2$; yield 139 mg (73%), m.p. 193–195°C. Anal. Calcd (%): C, 55.36; H, 3.94; N, 2.65. Found: C, 55.16; H, 3.87; N, 2.34. IR (cm^{-1}): ν(Re=N) 1092(s); ν(N–H) 3225(w); ν(Re–Cl) 297(m), 309(m). ^1H NMR (δ, ppm): 7.52–7.71(m, 32H); 7.21–7.35(m, 8H).

2.2. *X-ray structure*

X-ray diffraction studies on crystals of **1** · $2/3CH_2Cl_2$ 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 the 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.

3. Results and discussion

Reaction of H_2ada with *trans*-[$ReOCl_3(PPh_3)_2$] in equimolar quantities in boiling acetonitrile gave the product **1**. The rhenium(V) phenylimido complexes *trans*-[Re(NAr)$Cl_3(PPh_3)_2$] were 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 chloroform.

The IR spectrum of **1** is characterized by a strong absorption at 1092 cm^{-1}, which is within the region expected (1000–1200 cm^{-1}) for the linearly coordinated phenylimido moiety with a Re–N triple bond. There are no peaks in the 890–1020 cm^{-1} region which can be ascribed to a rhenium(V)-oxo stretching vibration. There are two bands in the

Table 1. Crystal data and structure refinement data for **1** · 2/3CH_2Cl_2.

Chemical formula	$C_{48}H_{40}Cl_3N_2P_2Re.0.67CH_2Cl_2$
Formula weight	1055.9
Temperature (K)	200(2)
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions (Å)	
a	33.8259(3)
b	24.2755(2)
c	10.9213(1)
Crystal size (mm^3)	0.02 × 0.03 × 0.17
Volume (Å^3)	8967.9(1)
Z	8
Density (Calcd) (Mg m^{-3})	1.564
Absorption coefficient (mm^{-1})	3.076
$F(000)$	4208
θ range for data collection (°)	3.2–24.1
Index ranges	$-38 \le h \le 38$; $-27 \le k \le 27$; $-12 \le l \le 12$
Reflections measured	93235
Independent/observed reflections	14046($R = 0.049$)/11901[$I > 2\sigma(I)$]
Data/restraints/parameters	14046/0/1035
Goodness of fit on F^2	1.03
Final R indices [$I > 2\sigma(I)$]	0.0305, $wR_2 = 0.0645$
Largest diff. peak/hole (e Å^{-3})	0.81/−0.54

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

Re–N(1)	1.706(4)	Re–Cl(1)	2.397(2)
Re–Cl(2)	2.438(2)	Re–Cl(3)	2.420(1)
Re–P(1)	2.498(1)	Re–P(2)	2.486(1)
C(1)–N(1)	1.387(7)	C(6)–N(2)	1.376(7)
N(1)–Re–Cl(1)	177.8(2)	Re–N(1)–C(1)	178.7(4)
N(1)–Re–P(1)	95.4(2)	N(1)–Re–P(2)	94.3(2)
N(1)–Re–Cl(2)	91.2(2)	N(1)–Re–Cl(3)	91.7(2)
P(1)–Re–P(2)	169.40(5)	Cl(2)–Re–Cl(3)	177.11(5)
P(1)–Re–Cl(2)	94.76(5)	P(2)–Re–Cl(3)	90.64(5)

low-frequency region at 309 and 297 cm^{-1}, corresponding to Re–Cl stretching modes. The lower value is indicative of a chloride *trans* to the imido nitrogen. The ^{1}H NMR spectrum of **1** is not informative with respect to the coordination mode of ada, since only two multiplets in the regions 7.21–7.35 (8H) and 7.52–7.71 ppm (32H) are present.

X-ray crystallographic analysis of **1** showed that two molecules of the compound exist in the asymmetric unit. These have different orientations in the lattice, and are mirror images of each other with comparable bond lengths and angles; these do not differ by more than their estimated standard deviations. The complex is monomeric and neutral, and exhibits approximately octahedral coordination geometry (figure 1). The octahedron is distorted, with the Cl(2)–Re–P(1) [94.76(5)°], Cl(2)–Re–P(2) [89.34(5)°], P(2)–Re–Cl(3) [90.64(5)°] and P(1)–Re–Cl(3) [84.77(5)°] bond angles close to orthogonality. The Re atom is displaced from the mean P(1)Cl(2)P(2)Cl(3) equatorial plane by 0.135(1) Å towards N(1). This leads to the non-orthogonal angles N(1)–Re–P(1) = 95.4(2)°, N(1)–Re–P(2) = 94.3(2)°, N(1)–Re–Cl(2) = 91.2(2)° and N(1)–Re–Cl(3) = 91.7(2)° and results in a nonlinear N(1)–Re–Cl(1) axis of 177.8(2)°. The *trans* phosphorus donors lie out of this equatorial plane by 0.074(1) Å, while the chloride

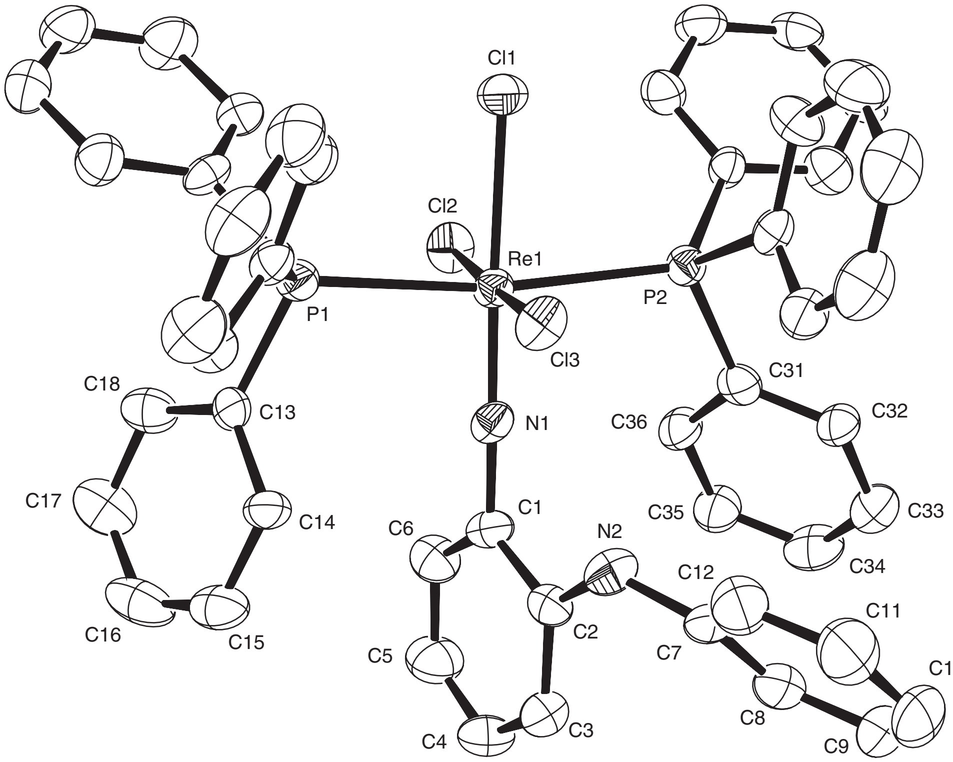

Figure 1. An ORTEP view of complex **1**, showing 40% probability displacement ellipsoids and the atom labelling scheme. Hydrogen atoms are omitted for clarity.

ligands are out by −0.074(2) Å. As a measure of the geometrical distortion, the metal in the coordination polyhedron is 1.466(1) Å from the Cl(1)Cl(3)P(2) plane and −1.141(1) Å from the N(1)P(1)Cl(2) plane, the angle between the two triangular faces being 7.83°. The imidodiphenylamino 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 1.706(4) Å agrees with the 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 89.45(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 3.30(2) Å from the C(13)–C(18) centroid and 3.57(2) Å from that of C(31)–C(36); it makes a dihedral angle of 19.89° with the first phenyl ring and 36.48° with the second. The C(7)–C(12) phenyl ring makes a dihedral angle of 22.12° with the C(31)–C(36) ring, and their ring centroids are separated by 3.10(2) Å. In addition, intramolecular hydrogen bonds between N(2)H(2) and Cl(3) [3.280(5) Å], with the N(2)–H(2)–Cl(2) angle equalling 173.0(1)°, and between N(2)H(2) and N(1) [2.732(7) Å] consolidate the crystal packing. The bond lengths and angles within the inner core are within the range expected from the comparison of other six-coordinated rhenium(V) complexes containing similar ligands [22]. However, and surprisingly, the Re–Cl(1) bond [2.397(2) Å] is shorter than the equatorial Re–Cl bonds

[2.429(2) Å average]. The C(2)–N(2)–C(7) bond angle [127.7(5)°] is considerably larger than that expected for an sp^3-hybridized nitrogen atom, and this is ascribed to structural and electronic effects involving the C(7)–C(12) and C(31)–C(36) phenyl rings.

Monodentate coordination of 1,2-diaminobenzene in the monoimido form to rhenium(V) was first observed in the complex *trans*-$[Re(dab)Cl_3(PPh_3)_2]$ [5], and it shows many similarities with complex **1**. For example, the Re–N(1)–C(1) angle [178.7(4)°] is identical in both complexes, although Re–N(1) bond lengths vary considerably [1.731(4) *vs.* 1.706(4) Å in **1**]. 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-614011 contains crystallographic data for this article. 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; Email: deposit@ccdc.cam.ac.uk].

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