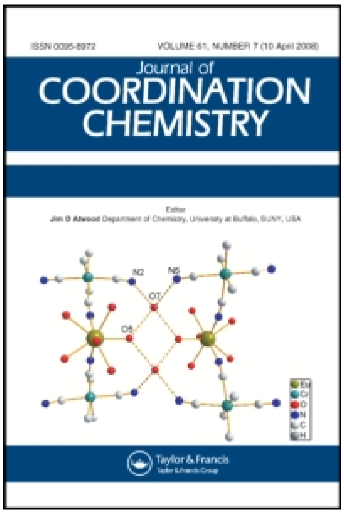

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Synthesis, molecular and electronic structure of $[ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$

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Synthesis, molecular and electronic structure of $[ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$

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A new organodiazenido rhenium complex, $[ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$ has been obtained from the direct reaction of $[ReCl_2(\eta^2\text{–}N_2COPh\text{–}N',O)(PPh_3)_2]$ with pyrazine in acetone. The complex has been characterized by spectroscopic methods and its structure determined using single-crystal X-ray diffraction techniques.

Keywords: Rhenium; Organodiazenido complexes; X-ray structure

1. Introduction

Rhenium possesses radioactive nuclides with potential for nuclear medicine applications. ^{186}Rhenium is one of the most promising radionuclides for palliative treatment of cancer and radioimmunotherapy. Detailed coordination chemical studies are required to explore possibilities for the designing of radio-pharmaceutical kits for both diagnosis and therapy [1]. Organodiazenido ligands, as well as others which contain multiple metal-nitrogen bonds, have been of great interest in recent years because of their amphoteric nature and close relationship to dinitrogen and nitrosyl ligands. Similar to the nitrosyl group, organodiazenido ligands (–NNR) display a variety of geometries: singly bent, doubly bent and bridging. Structural and synthetic studies of organodiazenido transition metal complexes have shown that the chemistry of these compounds is varied and interesting [2–4]. Considering that pyrazine ligands are an important group in organometallic chemistry and pyrazine metal complexes have attracted substantial interest considering their catalytic activity, the reactivity of $[ReCl_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2]$ towards pyrazine has been investigated. Here in this article is presented the synthesis of $[ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$, its spectroscopic characterization and a determination of its crystal and molecular structure.

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2. Experimental

All solvents were of reagent grade and used as received. Ammonium perrhenate, triphenylphosphine and pyrazine were purchased from Aldrich and used as received. $[ReCl_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2]$ was prepared according to literature methods [5]. Infrared spectra (KBr pellets) were recorded on a Nicolet Magna 560 spectrophotometer in the range 4000–400 cm^{-1}. Electronic spectra were measured on a Lab Alliance UV-vis 8500 spectrophotometer in the range 800–220 nm using deoxygenated dichloromethane as solvent. Elemental analyses (C, H, N) were performed on a Perkin–Elmer CHN-2400 instrument. Magnetic susceptibilities were measured at 296 K by the Faraday method.

2.1. $[ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$

A solution of pyrazine (0.25 g, 3.6 mmol) in acetone (10 cm^3) was added to $[ReCl_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2]$ (0.5 g, 0.55 mmol) suspended in acetone (30 cm^3) and the mixture stirred at room temperature for 48 h. The brown precipitate of $[ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$ was filtered off and the crystals suitable for X-ray structure determination were obtained by recrystallization from a mixture of chloroform and methanol (yield 75%). IR (KBr, cm^{-1}): 1648 (w), 1592 (s), 1566 (s), 1556 (s), 1483 (s), 1465 (s), 1434 (s), 1313 (m), 1261 (vs), 1172 (m), 1091 (s), 1062 (m), 858 (m), 743 (m), 693 (s), 645 (s), 602 (s), 520 (s), 493 (s). Anal. Calcd for $C_{47}H_{39}Cl_2N_4OP_2Re$ (%): C, 56.74; H, 3.95; N, 5.63. Found: C, 56.8; H, 4.0; N, 5.6.

2.2. *Determination of X-ray structure*

Intensity data were collected on a Kuma KM-4 diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Details concerning crystal data and refinement are given in table 1. The structure of the complex was

Table 1. Crystal data and structure refinement details for $[ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$.

Empirical formula	$C_{47}H_{39}Cl_2N_4OP_2Re$
Formula weight	994.86
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 12.944(4)$ Å $\alpha = 75.41(2)^\circ$
	$b = 13.137(4)$ Å $\beta = 70.29(3)^\circ$
	$c = 13.782(4)$ Å $\gamma = 81.19(2)^\circ$
Volume	2129.1(10) $Å^3$
Z	2
Calculated density	1.552 mg m^{-3}
Absorption coefficient	3.095 mm^{-1}
$F(000)$	992
Crystal size	$0.32 \times 0.05 \times 0.04$ mm^3
θ range for data collection	2.79°–25.10°
Index ranges	$-15 \leq h \leq 15, -15 \leq k \leq 15, -16 \leq l \leq 16$
Reflections collected/unique	21 982/7597 [$R_{(int)} = 0.1624$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7597/0/502
Goodness-of-fit on F^2	0.979
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0880$, $wR_2 = 0.2050$
R indices (all data)	$R_1 = 0.1863$, $wR_2 = 0.2669$
Largest diff. peak and hole	1.722 and -1.692 e $Å^{-3}$

solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically using full-matrix, least-squares techniques. A numerical absorption correction was used. Hydrogen atom positions of the phenyl rings were found from subsequent difference Fourier syntheses and were treated as riding on the adjacent carbon atom [$d(C–H) = 0.96$ Å] and refined with individual isotropic temperature factors equal to 1.2 times the value of equivalent isotropic temperature factor of the parent carbon atom. SHELXL-97 [6] and SHELXTL [7] programs were used for all calculations. Atomic scattering factors were those incorporated in the computer programs.

3. Results and discussion

$[ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$ was obtained from the direct reaction of $[ReCl_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2]$ with pyrazine in acetone. The complex is triclinic, space group $P\bar{1}$. Accurate cell parameters, crystal data and related details are given in table 1. A perspective view of the compound, together with the atom numbering scheme, is shown in figure 1. The coordination geometry about rhenium involves mutually *trans* triphenylphosphine molecules, minimizing steric congestion, and chloride donors *trans* to the monodentate organodiazenido ligand and the pyrazine molecule,

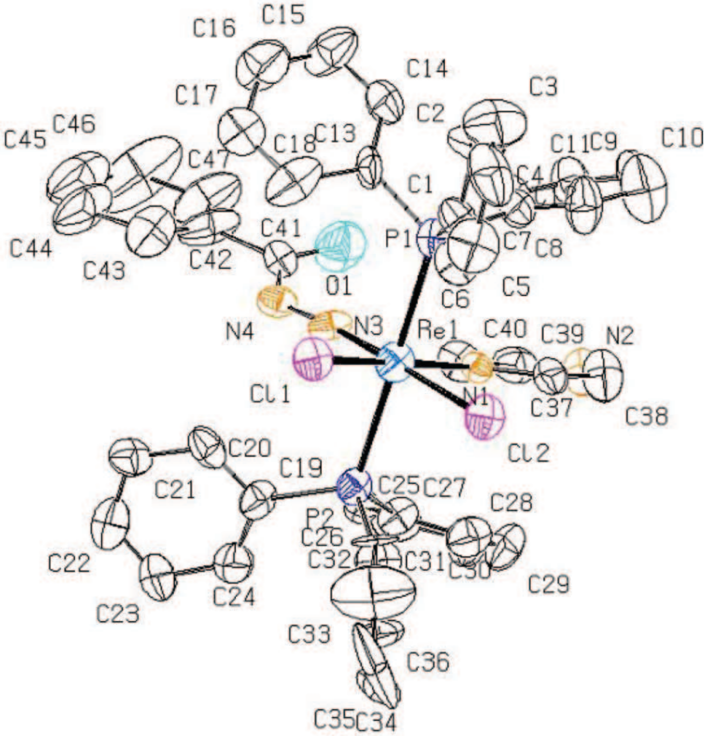

Figure 1. ORTEP view of the structure of $[ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond lengths (Å) and angles (°) for $ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$.

Re–N(3)	1.769(12)	N(3)–Re(1)–N(1)	91.2(5)
Re(1)–N(1)	2.190(10)	N(3)–Re(1)–Cl(2)	177.6(3)
Re(1)–Cl(1)	2.428(4)	N(1)–Re(1)–Cl(2)	87.5(3)
Re(1)–Cl(2)	2.428(4)	N(3)–Re(1)–Cl(1)	93.8(4)
Re(1)–P(1)	2.473(4)	N(1)–Re(1)–Cl(1)	174.9(3)
Re(1)–P(2)	2.477(4)	Cl(2)–Re(1)–Cl(1)	87.45(15)
N(3)–N(4)	1.189(15)	N(3)–Re(1)–P(1)	90.0(4)
N(4)–C(41)	1.42(2)	N(1)–Re(1)–P(1)	91.5(3)
O(1)–C(41)	1.23(2)	Cl(2)–Re(1)–P(1)	92.16(15)
N(1)–C(40)	1.278(18)	Cl(1)–Re(1)–P(1)	87.64(14)
N(1)–C(37)	1.394(18)	N(3)–Re(1)–P(2)	90.6(4)
N(2)–C(39)	1.27(2)	N(1)–Re(1)–P(2)	90.1(3)
C(38)–N(2)	1.31(2)	Cl(2)–Re(1)–P(2)	87.32(14)
		Cl(1)–Re(1)–P(2)	90.68(15)
		P(1)–Re(1)–P(2)	178.26(13)
		C(19)–P(2)–Re(1)	117.3(6)
		C(25)–P(2)–Re(1)	109.7(6)
		C(40)–N(1)–Re(1)	122.0(11)
		C(37)–N(1)–Re(1)	121.4(10)
		C(39)–N(2)–C(38)	114.3(18)
		N(1)–C(40)–C(39)	119.6(17)
		N(4)–N(3)–Re(1)	166.3(11)
		N(3)–N(4)–C(41)	122.4(14)
		O(1)–C(41)–N(4)	119.4(17)
		O(1)–C(41)–C(42)	125(2)
		N(4)–C(41)–C(42)	115.4(18)

which displaces the carbonyl oxygen of the diazenido ligand. Selected bond lengths and angles are given in table 2. Angular distortions from ideal octahedral geometry is caused by the presence of the multiply bonding ligand (–NNR) *cis* to pyrazine. The Re(1)–N(3)–N(4) angle is essentially linear and N(3)–N(4)–C(37) is near 120°, indicating the "singly bent" coordination mode. Short Re–N(3) and N(3)–N(4) distances suggest extensive delocalization and multiple bonding throughout the N_2COPh unit, an observation confirmed by the virtual planarity of the entire Re–N–NCOPh group and the linearity of the Re–N–N unit. Re–N(3), N(3)–N(4) and N(4)–C bond lengths and N(3)–N(4)–C, Re–N(3)–N(4) angles are in good agreement with values found by others for "singly bent" organodiazenido complexes [4,8]. The structure is stabilized by multiple, weak intramolecular hydrogen bonds, geometries of which are given in table 3. A packing diagram is depicted in figure 2.

In contrast to the starting $[ReCl_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2]$ complex, IR spectra show several bands in the range 1550–1650 cm^{-1} range assigned to $\nu(N{=}N)$, $\nu(C\text{–}N)$ and $\nu(C{=}O)$, confirming the opening of the chelate ligand and the presence of pyrazole [4]. The complex contains triphenylphosphine ligands and thus shows the characteristic pair of bands at 1434 and 1483 cm^{-1}; typically the lower frequency band is more intense. Diamagnetism of $[ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2]$ and the linear configuration of Re–N–N atoms proves that N_2COPh ligand is a four-electron donor and the central ion has $5d^6$ configuration [2]. Electronic absorption bands may be only of MLCT type and band assignments in table 4 have only qualitative character. N_2COPh and $C_4N_2H_4$ have comparable π-acceptor ability for $5d$ electrons, as confirmed by the same lengths for Re–Cl bonds *trans* to these ligands (lack of *trans* influence). The $C_4N_2H_4$ ligand is on the other hand a weaker π-acceptor, compared to the $C_3N_2H_4$ ligand, and this lowers the covalency of

Table 3. Hydrogen-bonding geometry for [$ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2$] (bond lengths in angstroms, bond angles in degrees).

D–H···A	H···A	D···A	∠(DHA)
C6–H6···Cl1	2.82	3.478(17)	129.0
C6–H6···Cl2	2.74	3.460(18)	134.8
C18–H18···Cl1	2.76	3.60(2)	151.2
C20–H20···Cl1	2.81	3.539(16)	136.6
C20–H20···N3	2.60	3.24(2)	126.8
C20–H20···N4	2.56	3.18(2)	123.9
C29–H29···Cl2†	2.80	3.696(19)	162.2
C32–H32···Cl1	2.69	3.532(9)	151.1
C32–H32···Cl2	2.53	3.064(12)	116.4
C37–H37···Cl2	2.49	3.117(19)	124.5
C40–H40···O1	2.41	3.10(2)	130.8
C40–H40···N3	2.52	3.01(2)	112.7
C43–H43···N4	2.41	2.77(3)	102.6

†Equivalent atom at $-x$, $-y$, $-z$.

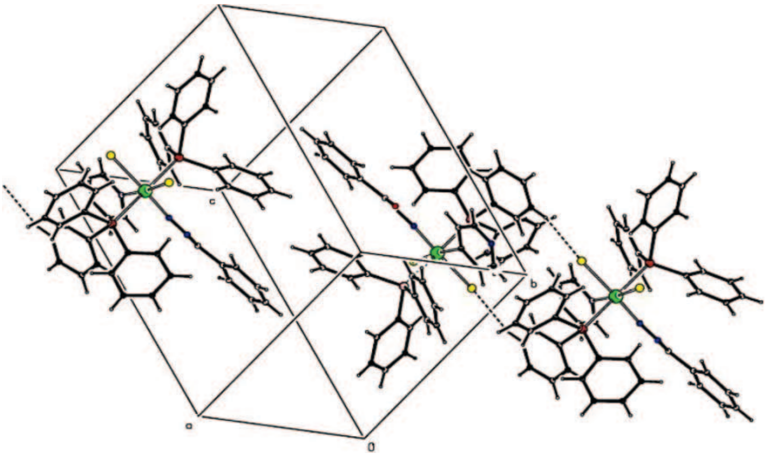

Figure 2. Packing diagram for [$ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2$]. Hydrogen bonds are shown as dashed lines.

Table 4. Electronic absorption band positions (cm^{-1}), molar absorption coefficients ($M^{-1}\,cm^{-1}$) and assignments for [$ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2$].

ν_{max}	ε	Assignment
19,230	1295	${}^1A_1 \rightarrow {}^3T_1$ $5d \rightarrow \pi^*_{C=C}$
22,593	7240	${}^1A_1 \rightarrow {}^3T_2$ $5d \rightarrow \pi^*_{N=C}$
25,614	6680	${}^1A_1 \rightarrow {}^1T_1$ $5d \rightarrow \pi^*_{N=N-C}$
35,137	16 895	${}^1A_1 \rightarrow {}^1T_2$ $\pi \rightarrow \pi^*_{C_6H_5}$
43,554	34 425	$\pi^b \rightarrow 3d_p$ $\pi \rightarrow \pi^*_{N_2COPh}$

[$ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2$] in comparison with [$ReCl_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2$]. Parameters for [$ReCl_2(N_2COPh)(C_4N_2H_4)(PPh_3)_2$] complex, calculated using the data of table 4 are $Dq = 2800\,cm^{-1}$, $B = 596\,cm^{-1}$, and $C = 2384\,cm^{-1}$; for [$ReCl_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2$]: $Dq = 2930\,cm^{-1}$, $B = 578\,cm^{-1}$ and $C = 2312\,cm^{-1}$. Conclusions resulting from the spectroscopic data are confirmed by the structure, according to which the Re–N bond in [$ReCl_2(N_2COPh)$ $(C_4N_2H_4)(PPh_3)_2$] is 0.04 Å longer than in [$ReCl_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2$].

Supplementary material

Supplementary data of [$ReCl_2(C_4N_2H_4)(N_2COPh)(PPh_3)_2$] complex are available from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 25813.

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