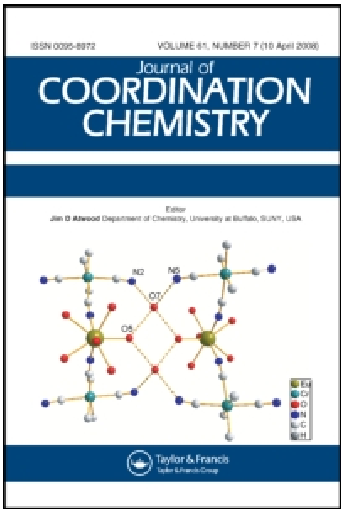

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectroscopic investigation, crystal and molecular structure of $[ReBr_2(N_2COPPh)(py)(PPh_3)_2]$

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To cite this Article Michalik, S. , DziĘgielewski, J. O. , Mrzigod, J. and Kruszynski, R.(2007) 'Synthesis, spectroscopic investigation, crystal and molecular structure of $[ReBr_2(N_2COPPh)(py)(PPh_3)_2]$', Journal of Coordination Chemistry, 60: 7, 771 — 776

To link to this Article: DOI: 10.1080/00958970600915397

URL: http://dx.doi.org/10.1080/00958970600915397

Journal of Coordination Chemistry
Vol. 60, No. 7, 10 May 2007, 771–776

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Synthesis, spectroscopic investigation, crystal and molecular structure of $[ReBr_2(N_2COPPh)(py)(PPh_3)_2]$

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(*Received in final form 10 May 2006*)

$[ReBr_2(N_2COPh)(py)(PPh_3)_2]$ complex has been obtained in the reaction of $[ReBr_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2]$ with excess pyridine. The complex was characterised by single-crystal X-ray structure analysis, IR and electronic spectroscopy and magnetic measurements.

Keywords: Rhenium; Organodiazenido; X-Ray structure

1. Introduction

The coordination chemistry of organodiazenides is a matter of current and growing interest in the field of nitrogen fixation. Furthermore, the β-emitting radionucleides of rhenium, ^{186}Re and ^{188}Re, are of great interest to nuclear medicine, as they possess physical and nuclear properties favourable for use in systematic radiotherapy [1]. In a search for suitable starting materials for the synthesis of Re complexes with this class of ligands, we have chosen the benzylhydrazido-Re(V) chelate $[ReBr_2(\eta^2\text{-}N_2COPh\text{-}N',O)(PPh_3)_2]$. This complex exhibits six-cordinate geometry as a consequence of chelate ring formation *via* the nitrogen and carbonyl oxygen atoms of the benzoyldiazenido ligand. The Re–O bond is relatively weak, and reaction with a variety of ligands yields benzoylazorhenium compounds of the type $[ReBr_2(N_2COPh)(PPh_3)_2L]$ [2]. Organodiazenido ligands, as well as others which contain metal-nitrogen multiple bonds, are of great interest because of their amphoteric nature and close relationship to dinitrogen and nitrosyl ligands. Similar to the nitrosyl group, organodiazenido ligands (–NNR) displays a variety of geometries. Structural and synthetic studies of organodiazenido metal transition complexes have shown that the chemistry of these compounds is varied and interesting [3–5]. In this article we

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970600915397

report the synthesis, spectroscopic and structural characterisation of the six-coordinate mononuclear rhenium diazenido complex [$ReBr_2(N_2COPh)(py)(PPh_3)_2$].

2. Experimental

2.1. *General procedures*

Ammonium perrhenate, triphenylphosphine and pyridine were commercially available and used without further purification. [$ReBr_2(\eta^2$-N_2COPh–N′,O)($PPh_3)_2$] was prepared according to a literature method [6]. The solvent used for the reaction was argon-saturated.

2.2. *[$ReBr_2(N_2COPh)(py)(PPh_3)_2$]*

[$ReBr_2(\eta^2$-N_2COPh–N′,O)($PPh_3)_2$] (1 g, 0.9 mmol) was added to py (0.25 g, 3.2 mmol) in methanol (50 cm^3) and the reaction mixture was refluxed for 48 h. The brown crystalline precipitate was collected by filtration and crystals suitable for X-ray structure determination obtained by recrystallization from a mixture of chloroform and methanol. Yield: 63%. IR (KBr, cm^{-1}): 1638 (s), 1575 (w), 1507 (s), 1481 (s), 1448 (w), 1435 (s), 1307 (w), 1235 (vs), 1168 (m), 1091 (m), 1050 (s), 1091 (s), 748 (m), 696 (s), 637 (m), 518 (s), 494 (m). Anal. Calcd for $C_{48}H_{40}Br_2N_3OP_2Re$ (%): C, 53.24; H, 3.72; N, 3.88. Found: C, 53.25; H, 3.75; N, 3.86.

2.3. *Physical measurements*

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the range 4000–400 cm^{-1}. Electronic spectra were measured on a Lab Alliance 8500 spectrophotometer in the range 800–220 nm in deoxygenated dichloromethane. The magnetic susceptibility was determined with a Quantum Design SQUID magnetometer. Elemental analyses were performed on a Perkin-Elmer CHN-2400 analyzer.

2.4. *X-ray crystallography*

A crystal of [$ReBr_2(N_2COPh)(py)(PPh_3)_2$] was mounted on a KM-4-CCD automatic diffractometer equipped with a CCD detector, and used for data collection. X-ray intensity data were collected with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature with the ω scan mode. A 50 s exposure time was used and and the whole Ewald sphere was collected up to $2\theta = 50.20°$. Unit cell parameters were determined from least-squares refinement of the setting angles of the 4166 strongest reflections. Details concerning crystal data and refinement are given in table 1. The structure was solved by the Patterson method and subsequently completed by difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically using full-matrix, least-squares techniques. All hydrogen atoms were founded in different Fourier syntheses and refined as riding on their parent carbon atoms with geometry idealisation after each cycle and isotropic temperature factors

Table 1. Crystal data and structure refinement details for $[ReBr_2(N_2COPh)(py)(PPh_3)_2]$.

Empirical formula	$C_{48}H_{40}Br_2N_3OP_2Re$
Formula weight	1082.79
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	11.2899(15)
b	13.5051(17)
c	15.0147(19)
α	84.771(9)
β	89.204(8)
γ	72.120(9)
Volume ($Å^3$)	2169.4(5)
Z	2
Density (calculated) ($Mg\,m^{-3}$)	1.658
Absorption coefficient (mm^{-1})	4.756
$F(000)$	1064
Crystal size (mm^3)	0.098 × 0.074 × 0.061
θ range for data collection (°)	3.03–25.10
Index ranges	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$
Reflections collected	21442
Independent reflections	7716 ($R_{int} = 0.1167$)
Max. and min. transmission	0.741 and 0.473
Completeness to 2θ (%)	99.8
Data/restraints/parameters	7716/0/514
Goodness-of-fit on F^2	1.097
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0775$, $wR_2 = 0.1793$
R indices (all data)	$R_1 = 0.1028$, $wR_2 = 0.1969$
Largest diff. peak and hole ($e\,Å^{-3}$)	1.980 and 1.980

equal to 1.2 times that of the parent carbon. SHELXS97 [7], SHELXL97 [8] and SHELXTL [9] programs were used for all calculations.

3. Results and discussion

Reaction of $[ReBr_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2]$ with pyridine, results in the opening of the chelate ring through displacement of the coordinated carbonyl group by py and leads to the formation of $[ReBr_2(N_2COPh)(py)(PPh_3)_2]$. The complex crystallises in the triclinic space group $P\bar{1}$ and the structure is composed of discrete monomers with all atoms located in general positions. The molecular structure of the complex is shown in figure 1. The coordination geometry about rhenium exhibits mutually *trans* triphenylphosphine molecules minimizing steric congestion and chloride donors *trans* to the monodentate organodiazenido ligand and to a py molecule. Selected bond lengths and angles are summarized in table 2. Angular distortions from ideal octahedral are caused by the presence of the multiple bonding ligand (–NNR) *cis* to py. Re(1)–N(3)–N(4) is essentially linear and N(3)–N(4)–C(42) near 120°, indicating it is a 'singly bent' benzoyldiazenido complexes. The short Re–N(3) and N(3)–N(4) distances suggest extensive delocalization and multiple bonding in the N_2COPh unit, an observation confirmed by the virtual planarity of the entire Re–N–NCOPh fragment and the linearity of the Re–N–N unit. Re–N(3), N(3)–N(4) and N(4)–C

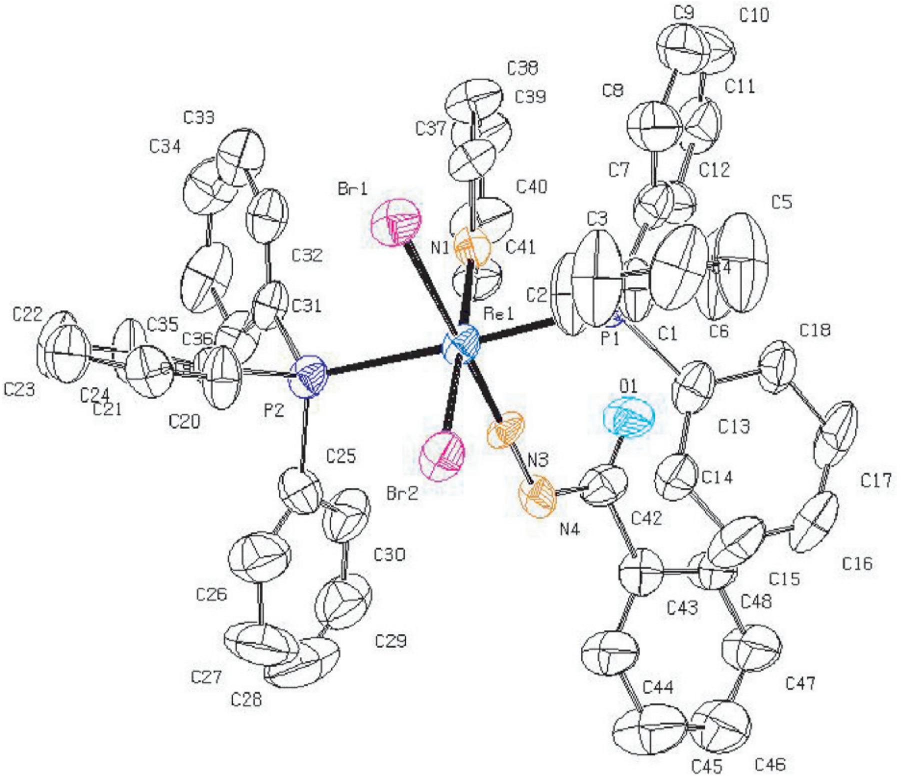

Figure 1. The molecular structure of [$ReBr_2(N_2COPh)(py)(PPh_3)_2$] showing the atom numbering scheme.

Table 2. Selected bond lengths (Å) and angles (°) for [$ReBr_2(N_2COPh)(py)(PPh_3)_2$].

Re(1)–N(3)	1.747(8)	N(3)–Re(1)–N(1)	92.9(3)
Re(1)–N(1)	2.196(9)	N(3)–Re(1)–P(2)	92.5(3)
Re(1)–P(1)	2.487(3)	N(1)–Re(1)–P(2)	88.8(2)
Re(1)–P(2)	2.485(3)	N(3)–Re(1)–P(1)	90.8(3)
Re(1)–Br(1)	2.5721(13)	N(1)–Re(1)–P(1)	91.2(2)
Re(1)–Br(2)	2.5812(12)	P(2)–Re(1)–P(1)	176.70(9)
N(1)–C(37)	1.331(14)	N(3)–Re(1)–Br(1)	178.5(3)
N(1)–C(41)	1.371(13)	N(1)–Re(1)–Br(1)	88.6(2)
N(4)–C(42)	1.400(14)	P(2)–Re(1)–Br(1)	87.54(8)
N(3)–N(4)	1.236(11)	P(1)–Re(1)–Br(1)	89.17(8)
N(4)–C(42)	1.400(14)	N(3)–Re(1)–Br(2)	89.0(3)
C(42)–O(1)	1.170(14)	N(1)–Re(1)–Br(2)	177.6(2)
C(37)–N(1)–C(41)	118.7(9)	P(2)–Re(1)–Br(2)	89.68(7)
C(37)–N(1)–Re(1)	124.0(6)	P(1)–Re(1)–Br(2)	90.19(7)
C(41)–N(1)–Re(1)	117.2(7)	Br(1)–Re(1)–Br(2)	89.47(4)
N(1)–C(37)–C(38)	122.2(10)	C(13)–P(1)–Re(1)	112.7(5)
N(4)–N(3)–Re(1)	171.4(8)	C(7)–P(1)–Re(1)	112.4(4)
N(3)–N(4)–C(42)	118.8(9)	C(1)–P(1)–Re(1)	122.5(4)
O(1)–C(42)–N(4)	124.9(11)	C(25)–P(2)–Re(1)	110.0(4)
O(1)–C(42)–C(43)	122.5(11)	C(31)–P(2)–Re(1)	113.6(4)
N(4)–C(42)–C(43)	112.6(10)	C(19)–P(2)–Re(1)	121.6(4)

bond lengths and N(3)–N(4)–C(47), Re–N(3)–N(4) angles are in good agreement with values found by others for 'singly bent' organodiazenido complexes [10–13]. Significant lengthening of Re–Br results from the location of bromine *trans* to the strongly π-interacting benzoyldiazenido group and py ligand. Re–Br(1) distance *trans* to NNR is shorter than the Re–Br(2) *trans* to py, indicating the stronger *trans* influence of the heterocyclic molecule in comparison with the benzoyldiazenido group. Re–N(1) (2.196(9) Å) agrees well with appropriate values found previously in similar rhenium compounds containing monodentate *N*-heterocyclic ligands [12]. Bond valences were computed as $\nu_{ij} = \exp[(R_{ij} - d_{ij})/b]$ [14–16], where R_{ij} is the bond-valence parameter (in the formal sense the R_{ij} parameter value can be considered as the idealised single-bond length between *i* and *j* atoms). $R_{\text{Re–N}}$, $R_{\text{Re–P}}$, $R_{\text{Re–Br}}$ were taken as 2.06, 2.45 and 2.45 [17] respectively and *b* was taken as 0.37 [14, 16]. The computed bond valences for rhenium are $\nu_{\text{Re–N(py)}} = 0.69$, $\nu_{\text{Re–N(N}_2\text{COPh)}} = 2.33$, $\nu_{\text{Re–P}} = 0.930$ and 0.935; $\nu_{\text{Re–Br}}$ 0.719 and 0.701 v.u. which means that Re–$\text{N}_{(\text{N}_2\text{COPh})}$ bond is almost three times stronger than other bonds and can be formally considered as a double bond. Re–$\text{N}_{(\text{py})}$ bond is the weakest one, and the strengths of Re–Br bonds are between those of Re–$\text{N}_{(\text{py})}$ and Re–P. The structure is stabilized by multiple weak intramolecular hydrogen bonds [18, 19], whose geometries are given in table 3.

In contrast to the starting [ReBr$_2$(η^2-N$_2$COPh–N′,O)(PPh$_3$)$_2$] complex, IR spectra shows several bands in the range 1550–1650 cm^{-1} range assigned to ν(N=N), ν(C–N) and ν(C=O), which confirm the opening of the chelate ligand and the presence of py [5]. The complex contains triphenylphosphine and thus shows the characteristic pair of bands at approximately 1430 and 1480 cm^{-1}; typically, the lower frequency band is more intense. Considering diamagnetism and the linear Re=N=N– configuration, one can assume that the N$_2$COPh ligand is a donor of four electrons and Re(I) has a 5d^6 configuration. Taking into account the possible d–d, charge–transfer and intra-ligand electron transitions, absorption bands were assigned as shown in table 4. Charge–transfer transitions are of MLCT character, and N$_2$COPh is a stronger acceptor than py, as proven by the fact that Re–N(3) is shorter than Re–N(1) bond, and the Re–Br(1) bond *trans* to N$_2$COPh is longer than Re–Br(2) *trans* to py. The data of table 4 show a pseudooctahedral electronic configuration with a moderate degree of covalency, with ligand fields parameters $10Dq = 25025\,\text{cm}^{-1}$, $B = 690\,\text{cm}^{-1}$ and $C = 2760\,\text{cm}^{-1}$. Coupled π* orbitals in py and N$_2$COPh cause a significant delocalization of 5d donor electrons onto these ligands, thus lowering the covalency of the Re–N(1), Re–N(3), and Re–P bonds.

Table 3. Hydrogen-bond details for [ReBr$_2$(N$_2$COPh)(py)(PPh$_3$)$_2$] (Å, °).

D–H···A	H···A	D···A	∠(DHA)
C2–H2···Br1	2.89	3.560(15)	130.4
C2–H2···Br2	2.88	3.551(18)	129.8
C20–H20···Br2	2.70	3.536(13)	150.2
C37–H37···Br1	2.67	3.281(10)	124.2
C38–H38···Br1*	2.91	3.600(12)	132.4
C41–H41···O1	2.56	3.093(15)	117.0
C41–H41···N3	2.51	3.009(14)	113.6
C44–H44···N4	2.48	2.800(15)	100.5

*At $-x$, $-y$, $-z$.

Table 4. Electronic spectrum details for [$ReBr_2(N_2COPh)(py)(PPh_3)_2$].

Band position (cm^{-1})	ε ($M^{-1} cm^{-1}$)	Assignment
15,398	759	$^1A_1 \rightarrow {}^3T_1, {}^3T_2$, $5d \rightarrow \pi^*_{(pyridine)}$
22,292	6610	$^1A_1 \rightarrow {}^1T_1, {}^3T_2$, $5d \rightarrow \pi^*_{(pyridine)}$
24,704	9950	$5d \rightarrow \pi^*_{(=N=N-COPh)}$
33,333	16,120	$^1A_1 \rightarrow {}^3T_2$, $\pi \rightarrow \pi^*_{(pyridine)}$
39,620	27,550	$\pi \rightarrow \pi^*_{(PPh_3)}$
46,598	72,320	$\pi \rightarrow \pi^*_{(=N=N-COPh)}$, $\delta \rightarrow \delta^*_{(Re-Br)}$

Supplementary data

Supplementary data for [$ReBr_2(N_2COPh)(py)(PPh_3)_2$] complex are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting deposition number 605764.

Acknowledgements

The crystallographic study was financed by funds allocated by the Ministry of Education and Science to the Institute of General and Ecological Chemistry, Technical University of Łódź.

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