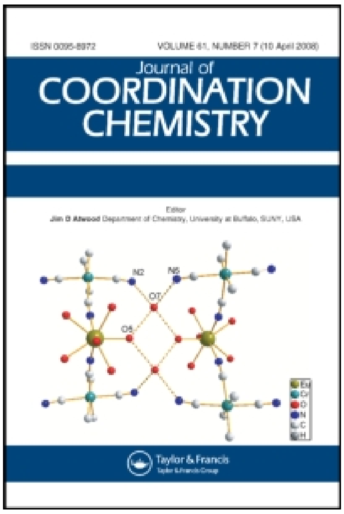

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article DziĘgielewski, J. O. , Michalik, S. , Kruszynski, R. and Bartczak, T. J.(2005) 'Synthesis, spectroscopic investigation and molecular structures of [ReBr$_2$(N$_2$COPh)(C$_3$N$_2$H$_4$)(PPh$_3$)$_2$] and [ReBr$_2$(N$_2$COPh)(bpy)(PPh$_3$)]', Journal of Coordination Chemistry, 58: 9, 741 — 749

To link to this Article: DOI: 10.1080/00958970412331336916

URL: http://dx.doi.org/10.1080/00958970412331336916

Journal of Coordination Chemistry
Vol. 58, No. 9, 15 June 2005, 741–749

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Synthesis, spectroscopic investigation and molecular structures of [$ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2$] and [$ReBr_2(N_2COPh)(bpy)(PPh_3)$]

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(*Received in final form 5 July 2004*)

[$ReBr_2(\eta^2$-N_2COPh-$N',O)(PPh_3)_2$] reacts with bipyridine (bpy) and pyrazole to give [$ReBr_2(N_2COPh)(bpy)(PPh_3)$] and [$ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2$], respectively. Both complexes have been characterized by IR, electronic and ^{1}H NMR spectroscopy, magnetic measurements and X-ray structure determination.

Keywords: Rhenium; Organodiazenido; X-ray structure; Electronic structure

1. Introduction

Organodiazenido ligands, as well as others containing 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, the organodiazenido ligand (–NNR) displays 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 [1–3]. Furthermore, the β-emitting radionucleides of rhenium, ^{186}Re and ^{188}Re, are of great interest in nuclear medicine, as they possess physical and nuclear properties favorable for use in systematic radiotherapy [4]. With the above in mind, we present the synthesis, spectroscopic and structural characterization of [$ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2$] (**1**) and [$ReBr_2(N_2COPh)(bpy)(PPh_3)$] (**2**).

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†Holder of a Foundation for Polish Science (FNP) scholarship.

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis Group Ltd
DOI: 10.1080/00958970412331336916

2. Experimental

Ammonium perrhenate and triphenylphosphine purchased from Aldrich and pyrazole purchased from P.O.Ch. Gliwice were used without further purification. [ReBr$_2$(η^2-N$_2$COPh-N',O)(PPh$_3$)$_2$] was prepared according to a literature method [5]. The solvent used in the reaction was argon saturated.

2.1. *[ReBr$_2$(N$_2$COPh)(C$_3$N$_2$H$_4$)(PPh$_3$)$_2$] (1)*

[ReCl$_2$(η^2-N$_2$COPh-N',O)(PPh$_3$)$_2$] (1 g, 1.1 mmol) was added to pyrazole (0.5 g, 7.2 mmol) in methanol (50 cm^3) and the reaction mixture was refluxed for 48 h. The resulting green, crystalline precipitate was collected by filtration and crystals suitable for X-ray structure determination were obtained by recrystallization from a mixture of chloroform and methanol. Yield: 70%.

^{1}H NMR (CD$_2$Cl$_2$, 293 K): 13.2 (1H , s N–H) 6.8–7.72 (m, 38H, CH of ArH and CH in pyrazole). ^{31}P NMR: −4.37 ppm. IR: (KBr, cm^{-1}) 3338 (s), 3053 (m), 1592 (s), 1551 (s), 1482 (s), 1462 (s), 1433(s), 1312 (m), 1263 (vs), 1171 (m), 1089 (s), 1061 (m), 855 (m), 746 (m), 693 (s), 518 (s), 494 (s). Calc. for C$_{46}$H$_{39}$Br$_2$N$_4$OP$_2$Re(%): C, 51.55; H, 3.67; N, 5.23. Found: C, 51.45; H, 3.70; N, 5.22.

2.2. *[ReBr$_2$(N$_2$COPh)(bpy)(PPh$_3$)] (2)*

[ReBr$_2$(η^2-N$_2$COPh-N',O)(PPh$_3$)$_2$] (1 g, 1.1 mmol) was added to bipyridine (bpy) (0.5 g, 3.2 mmol) in toluene (50 cm^3) and the reaction mixture was refluxed for 1 h. The green, crystalline precipitate that formed was collected by filtration and crystals suitable for X-ray structure determination were obtained by recrystallization from a mixture of chloroform and methanol. Yield: 70%.

IR (KBr, cm^{-1}) 1638 (m), 1607 (m), 1523 (s), 1475 (s), 1436 (s), 1234 (vs), 1166 (m), 1048 (m), 1020 (m), 771 (m), 695 (s), 6362 (m), 534 (m). Calc. for C$_{35}$H$_{28}$Br$_2$N$_4$OPRe(%): C, 46.83; H, 3.14; N, 6.24. Found: C, 46.5; H, 3.1; N, 6.31.

2.3. *Physical measurements*

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the range 4000 to 400 cm^{-1} with the samples in the form of potassium bromide pellets. Electronic spectra were measured on a Lab Alliance UV–VIS 8500 spectrophotometer in the range 800 to 220 nm in deoxygenated dichloromethane. Magnetic susceptibilities were determined with a Quantum Design SQUID magnetometer. ^{1}H NMR spectra were recorded with a Bruker 400 MHz spectrometer at room temperature.

2.4. *Crystal structure determinations and refinement details*

Crystals of [ReBr$_2$(N$_2$COPh)(C$_3$N$_2$H$_4$)(PPh$_3$)$_2$] and [ReBr$_2$(N$_2$COPh)(bpy)(PPh$_3$)] suitable for X-ray structure determination were obtained by recrystallization from a mixture of chloroform and methanol. A crystal was mounted on a KM-4-CCD automatic diffractometer equipped with a CCD detector. X-ray intensity data were collected with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature with the ω scan mode. For [ReBr$_2$(N$_2$COPh)(C$_3$N$_2$H$_4$)(PPh$_3$)$_2$] a 50-s exposure time

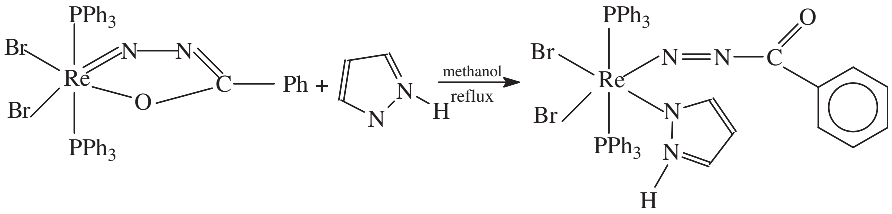
Table 1. Crystal data and structure refinement details for $[ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2]$ (**1**) and $[ReBr_2(N_2COPh)(bpy)(PPh_3)]$ (**2**).

	1	**2**
Empirical formula	$C_{46}H_{39}Br_2N_4OP_2Re$	$C_{35}H_{28}Br_2N_4OPRe$
Formula weight	1071.80	897.60
Temperature	291(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions	$a = 11.9280(9)$ Å	$a = 11.2990(7)$ Å
	$b = 12.4206(7)$ Å; $\beta = 100.308(6)^\circ$	$b = 16.2945(9)$ Å; $\beta = 101.416(5)^\circ$
	$c = 29.0211(19)$ Å	$c = 18.5528(11)$ Å
Volume	4230.2(5) Å^3	3348.2(3) Å^3
Z	4	4
Density (calculated)	1.681 Mg m^{-3}	1.781 Mg m^{-3}
Absorption coefficient	4.878 mm^{-1}	6.098 mm^{-1}
$F(000)$	2100	1736
Crystal size	0.17 × 0.14 × 0.14 mm	0.028 × 0.083 × 0.223 mm
θ range for data collection	2.94 to 25.10°	2.89 to 25.12°
Index ranges	$-14 \le h \le 14$	$-13 \le h \le 13$
	$-14 \le k \le 14$	$-17 \le k \le 19$
	$-34 \le l \le 34$	$-21 \le l \le 22$
Reflections collected	43 347	27 547
Independent reflections	7533 ($R_{int} = 0.1144$)	5973 ($R_{int} = 0.1057$)
Max. and min. transmission	0.5525 and 0.4964	0.8478 and 0.3433
Completeness to 2θ	95.1%	96.0%
Data/restraints/parameters	7533/0/551	5973/0/397
Goodness-of-fit on F^2	1.071	0.965
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0585$	$R1 = 0.0444$
	$wR2 = 0.1065$	$wR2 = 0.0444$
R indices (all data)	$R1 = 0.0927$	$R1 = 0.0929$
	$wR2 = 0.1201$	$wR2 = 0.0808$
Largest diff. peak and hole	1.860 and −1.622 e Å^{-3}	0.928 and −0.695 e Å^{-3}

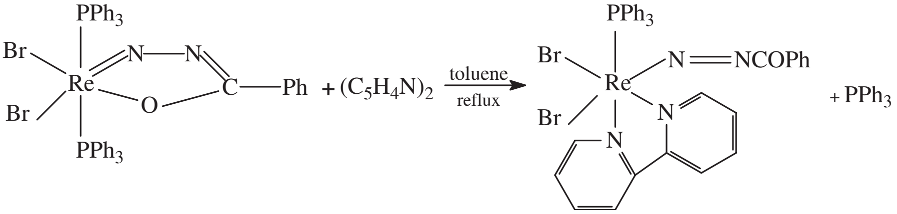
was used and a whole Ewald sphere was collected up to $2\theta = 50.2^\circ$. For $[ReBr_2(N_2COPh)(bpy)(PPh_3)]$ a 30-s exposure time was used and a whole Ewald sphere was collected up to $2\theta = 50.24^\circ$. Unit cell parameters were determined from least-squares refinement of the setting angles of the 8416 and 3835 strongest reflections for **1** and **2**, respectively. Details concerning crystal data and refinement for both complexes are given in table 1. The structures were solved by the Patterson method and subsequently completed by difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically using full-matrix, least-squares techniques. All hydrogen atoms were found in difference Fourier syntheses and refined as riding on their parent carbon atoms with geometry idealization after each cycle. They were assigned isotropic temperature factors equal to 1.2 times the value of equivalent temperature factor of the parent carbon atom. SHELXS97 [6], SHELXL97 [7] and SHELXTL [8] programs were used for all calculations.

3. Results and discussion

The reaction of $[ReBr_2(\eta^2\text{-}N_2COPh\text{-}N',O)(PPh_3)_2]$ with pyrazole results in the opening of the chelate ring through displacement of the coordinated carbonyl group by pyrazole and leads to $[ReBr_2(C_3N_2H_4)(N_2COPh)(PPh_3)_2]$ complex.



Refluxing [$ReBr_2(\eta^2$-N_2COPh-$N',O)(PPh_3)_2$] with an excess of bipyridine in toluene leads to [$ReBr_2(N_2COPh)(bpy)(PPh_3)$], according to the following scheme.



Complexes **1** and **2** are composed of discrete monomers with all atoms located in general positions. A perspective view of [$ReBr_2(C_3N_2H_4)(N_2COPh)(PPh_3)_2$] with the atom numbering scheme is shown in figure 1, and figure 2 presents a perspective drawing of [$ReBr_2(N_2COPh)(bpy)(PPh_3)$]. The coordination geometry about the rhenium center in [$ReBr_2(C_3N_2H_4)(N_2COPh)(PPh_3)_2$] shows mutually *trans* triphenylphosphine molecules minimizing steric congestion and bromine donors *trans* to the monodentate organodiazenido ligand and to the pyrazole molecule, which has displaced the carbonyl oxygen of the diazenido substituent. Bipyridine in [$ReBr_2(N_2COPh)(bpy)(PPh_3)$] forms a five-membered ring with the metal atom *trans* to the monodentate organodiazenido ligand and the bromide Br(1) ion. The pseudooctahedral environment of Re in

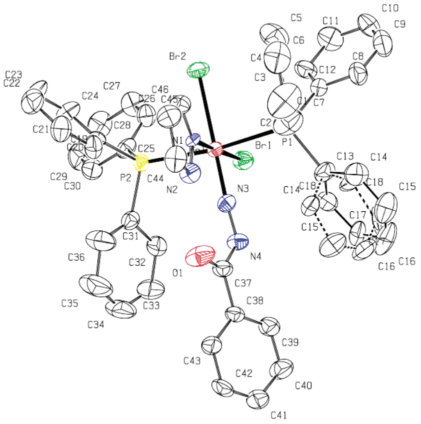


Figure 1. ORTEP view of the structure of **1** showing 50% probability thermal ellipsoids and the atom numbering scheme.

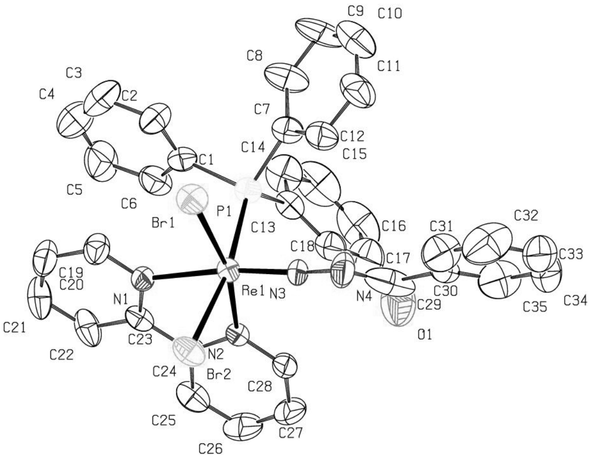


Figure 2. ORTEP view of the structure of **2** showing 50% probability thermal ellipsoids and the atom numbering scheme.

Table 2. Selected bond lengths [Å] and angles [°] for $[ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2]$, **1**.

Re(1)–N(3)	1.736(6)	N(3)–Re(1)–N(1)	92.3(3)
Re(1)–N(1)	2.188(6)	N(3)–Re(1)–P(1)	92.6(2)
Re(1)–P(1)	2.474(2)	N(1)–Re(1)–P(1)	88.67(17)
Re(1)–P(2)	2.476(2)	N(3)–Re(1)–P(2)	94.6(2)
Re(1)–Br(2)	2.5641(9)	N(1)–Re(1)–P(2)	91.35(17)
Re(1)–Br(1)	2.5844(9)	P(1)–Re(1)–P(2)	172.84(7)
N(1)–N(2)	1.327(9)	N(3)–Re(1)–Br(2)	179.2(2)
N(1)–C(46)	1.338(10)	N(1)–Re(1)–Br(2)	86.89(16)
N(2)–C(44)	1.357(10)	P(1)–Re(1)–Br(2)	87.40(6)
N(3)–N(4)	1.252(8)	P(2)–Re(1)–Br(2)	85.45(5)
N(4)–C(37)	1.382(10)	N(3)–Re(1)–Br(1)	87.6(2)
C(37)–O(1)	1.233(9)	N(1)–Re(1)–Br(1)	179.03(16)
C(37)–C(38)	1.477(11)	P(1)–Re(1)–Br(1)	90.37(6)
		P(2)–Re(1)–Br(1)	89.62(5)
		Br(2)–Re(1)–Br(1)	93.21(3)
		N(2)–N(1)–C(46)	107.9(7)
		N(2)–N(1)–Re(1)	120.4(5)
		C(46)–N(1)–Re(1)	131.6(6)
		N(1)–N(2)–C(44)	109.2(7)
		C(45)–C(44)–N(2)	108.5(8)
		N(4)–N(3)–Re(1)	169.3(6)
		N(3)–N(4)–C(37)	118.8(7)
		O(1)–C(37)–N(4)	123.1(7)
		O(1)–C(37)–C(38)	121.8(8)
		N(4)–C(37)–C(38)	115.1(7)
		O(1)–C(29)–C(30)	114.0(13)

$[ReBr_2(N_2COPh)(bpy)(PPh_3)]$ shows clear distortions, induced mainly by the bite angle of chelating bipyridine – *cis* angles vary between 75.0 and 97.0° and *trans* angles range from 166.1 to 171.8°. Selected bond lengths and angles for $[ReBr_2(C_3N_2H_4)(N_2COPh)(PPh_3)_2]$ and $[ReBr_2(N_2COPh)(bpy)(PPh_3)]$ are summarized in tables 2 and 3, respectively. Angular distortion from an ideal octahedron is caused by the presence of the multiply bonding ligand (–NNR) *cis* to pyrazole and bpy.

Table 3. Selected bond lengths [Å] and angles [°] for [$ReBr_2(N_2COPh)(bpy)(PPh_3)$], **2**.

Re(1)–N(3)	1.739(7)	N(3)–Re(1)–N(2)	97.0(2)
Re(1)–N(2)	2.087(5)	N(3)–Re(1)–N(1)	171.8(2)
Re(1)–N(1)	2.223(6)	N(2)–Re(1)–N(1)	75.0(2)
Re(1)–P(1)	2.402(2)	N(3)–Re(1)–P(1)	93.2(2)
Re(1)–Br(1)	2.5496(8)	N(2)–Re(1)–P(1)	98.01(16)
Re(1)–Br(2)	2.5869(9)	N(1)–Re(1)–P(1)	89.87(16)
P(1)–C(1)	1.810(9)	N(3)–Re(1)–Br(1)	95.28(19)
P(1)–C(7)	1.822(9)	N(2)–Re(1)–Br(1)	166.09(16)
P(1)–C(13)	1.832(8)	N(1)–Re(1)–Br(1)	92.46(16)
N(3)–N(4)	1.249(10)	P(1)–Re(1)–Br(1)	87.87(5)
N(4)–C(29)	1.250(14)	N(3)–Re(1)–Br(2)	96.3(2)
C(29)–O(1)	1.296(12)	N(2)–Re(1)–Br(2)	83.75(16)
		N(1)–Re(1)–Br(2)	81.10(16)
		P(1)–Re(1)–Br(2)	170.06(6)
		Br(1)–Re(1)–Br(2)	88.37(3)
		C(1)–P(1)–Re(1)	110.3(3)
		C(7)–P(1)–Re(1)	118.9(3)
		C(13)–P(1)–Re(1)	116.5(3)
		C(19)–N(1)–Re(1)	125.4(5)
		C(23)–N(1)–Re(1)	114.6(5)
		C(28)–N(2)–Re(1)	124.2(5)
		C(24)–N(2)–Re(1)	118.5(5)
		N(4)–N(3)–Re(1)	167.4(7)
		N(3)–N(4)–C(29)	121.0(12)
		N(4)–C(29)–O(1)	126.6(12)
		O(1)–C(29)–C(30)	114.0(13)

Re–N(3)–N(4) angles are essentially linear and N(3)–N(4)–C angles are near 120°, indicating a "singly bent" benzoyldiazenido mode. The 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 [3, 9, 10].

The significant lengthening of Re–Br in **1** results from the *trans* location of bromine donors with respect to the strongly π-interacting benzoyldiazenido group and the pyrazole ligand. The Re–Br(2) distance *trans* to the NNR ligand is shorter than Re–Br(1) *trans* to pyrazole, indicating the stronger *trans* influence of the heterocycle in comparison to the benzoyldiazenido group. The Re–N(1) bond length of **1** agrees well with appropriate values found previously in similar rhenium compounds containing coordinated pyrazole [11, 12].

The bipy bite angle of **2** is typical of complexes containing polypyridine ligands: 75.5° for [$Re(bpy)(CO)_4(COCH_3)$] [13], 72.9° for [$ReOBr_3(bipy)$] [14] and 77.9° for [$ReBr_4(bipy)$] [14]. The significant lengthening of the Re–N(1) bond results from the *trans* location of bromide, but the Re–N(1) distance in **2** is determined by the presence of the strong π-acceptor benzoyldiazenido group in the *trans* position.

Bond valences were computed as $\nu_{ij} = \exp[(R_{ij} - d_{ij})/B]$ [15–17], where R_{ij} is the bond-valence parameter (in the formal sense R_{ij} is the single-bond length between i and j atoms) [18]. $R_{\text{Re–N}}$, $R_{\text{Re–P}}$, $R_{\text{Re–Br}}$ values were taken as 2.06, 2.46 and 2.45 [18], respectively, and the value of B was taken as 0.37 [16]. Computed bond valences, $\nu_{\text{Re–}j}$, are gathered in table 4. The total valence of Re is 6.458 and 6.580 v.u. (valence units),

Table 4. Rhenium bond valences, $\nu_{\mathrm{Re}-j}$ [v.u.].

Bond	$[\mathrm{ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2}]$	$[\mathrm{ReBr_2(N_2COPh)(bpy)(PPh_3)}]$
Re–Br(1)	0.735	0.764
Re–Br(2)	0.694	0.691
Re–P(1)	0.963	1.170
Re–P(2)	0.958	
Re–N(1)	0.708	0.644
Re–N(2)		0.930
Re–N(3)	2.400	2.381

Table 5. Hydrogen-bonding geometries for $[\mathrm{ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2}]$ and $[\mathrm{ReBr_2(N_2COPh)(bpy)(PPh_3)}]$ [Å,°].

D–H···A	H···A	D···A	∠(DHA)
$[\mathrm{ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2}]$			
C(12)–H(12)···Br(1)	2.87	3.584(9)	134.0
C(18)–H(18)···Br(1)	2.81	3.668(19)	154.5
C(20)–H(20)···N(1)	2.62	3.162(11)	118.1
C(20)–H(20)···N(2)	2.60	3.414(11)	146.4
C(26)–H(26)···Br(2)	2.77	3.549(9)	141.9
C(46)–H(46)···Br(2)	2.82	3.329(9)	115.9
$[\mathrm{ReBr_2(N_2COPh)(bpy)(PPh_3)}]$			
C12–H12···N3	2.48	3.268(11)	143.1
C12–H12···N4	2.45	3.327(13)	158.3
C16–H16···Br2$^{\#1}$	2.79	3.652(10)	155.3
C18–H18···O1	2.39	3.214(13)	147.3
C19–H19···Br1	2.79	3.434(9)	127.8
C25–H25···Br2$^{\#2}$	2.78	3.594(8)	146.5
C28–H28···O1	2.38	3.262(10)	158.5
C28–H28···N3	2.62	3.112(9)	113.9
C31–H31···N4	2.51	2.829(16)	100.5

$^{\#1}$: $+x-1, y, z$; $^{\#2}$: $-x, -y, -z$.

respectively, for compounds **1** and **2**. This indicates that rhenium substituents in $[\mathrm{ReBr_2(C_3N_2H_4)(N_2COPh)(PPh_3)_2}]$ are more weakly bonded than in $[\mathrm{ReBr_2(N_2COPh)(bpy)(PPh_3)}]$. The structures are stabilized by multiple, weak, intramolecular hydrogen bonds [19, 20], whose geometries are given in table 5.

In contrast to the starting $[\mathrm{ReBr_2}(\eta^2\text{-}\mathrm{N_2COPh}\text{-}N',O)(\mathrm{PPh_3})_2]$ complex, infrared spectra show several bands in the 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 [3]. The complexes contain triphenylphosphine ligands and thus show the characteristic pair of bands at approximately 1430 and 1480 cm^{-1} and, typically, the lower frequency band is more intense.

The strong band at 3338 cm^{-1} for **1** is assignable to N–H vibrations and the ^{1}H NMR spectrum of **1** exhibits a singlet at 13.3 ppm, confirming the presence of pyrazole in the coordination sphere [21, 22]. Table 6 lists the positions and molar absorption coefficients of electronic bands and the electronic transitions assigned to them for compounds **1** and **2**. Considering the diamagnetism of the complexes and linear configuration of the Re=N=N– group, it can be assumed that the $\mathrm{N_2COPh}$ ligand is a four-electron donor and Re(I) has electron configuration 5d^6 [1].

Table 6. Electronic spectra, band positions, molar absorption coefficients and assignments for $[ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2]$ and $[ReBr_2(N_2COPh)(bpy)(PPh_3)]$.

Band position [cm^{-1}]	ε [$M^{-1} cm^{-1}$]	Assignment
$[ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2]$		
13 224	70	$^1A_1 \rightarrow {}^3T_1$
14 302	116	$^1A_1 \rightarrow {}^3T_2$
26 178	9421	$^1A_1 \rightarrow {}^3T_1$, $5d \rightarrow \pi^*_{pyrazole}$, $5d \rightarrow \pi^*_{N=N–C}$
37 202	40 256	$^1A_1 \rightarrow {}^1T_2$, $\pi \rightarrow \pi^*_{C_6H_5CON}$
43 821	65 543	$\pi^b{}_{C_6H_5} \rightarrow 3d(P)$, $\pi \rightarrow \pi^*_{pyrazole}$
$[ReBr_2(N_2COPh)(bpy)(PPh_3)]$		
14 633	1890	$^1A_1 \rightarrow {}^3T_1$, $5d \rightarrow bpy(N-1)(\pi^*)$
19 164	3620	$^1A_1 \rightarrow {}^3T_2$, $5d \rightarrow bpy(N-2)(\pi^*)$
24 594	8060	$^1A_1 \rightarrow {}^1T_1$, $5d \rightarrow \pi^*_{–N=C}$
34 495	36 960	$^1A_1 \rightarrow {}^1T_2$, $\pi \rightarrow \pi^*_{=N=N}$
43 706	75 050	$\pi \rightarrow \pi^b{}_{by}$, $\pi^b{}_{C_6H_4} \rightarrow 3d_P$
46 685	64 150	$\pi \rightarrow \pi^*_{N_2COPh}$

ε = molar absorption coefficient.

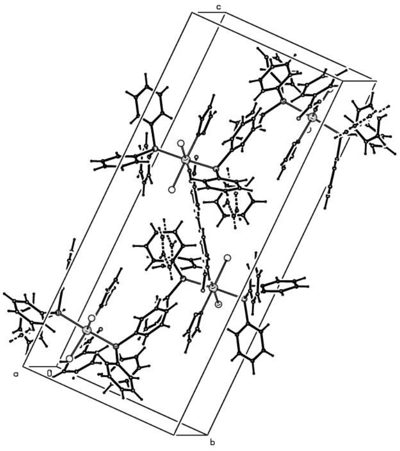


Figure 3. The packing diagram of 1.

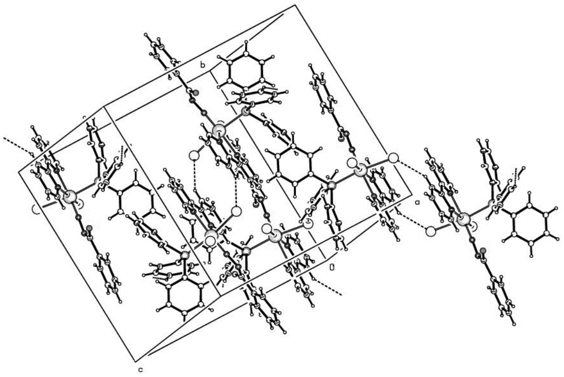


Figure 4. The packing diagram of 2.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, on request, quoting the CCDC deposition numbers 226252 for $[ReBr_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2]$ and 242459 for $[ReBr_2(N_2COPh)(bpy)(PPh_3)]$.

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