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The syntheses, crystal, molecular and electronic structures of two polymorphs of [$ReCl_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2$] and [$ReCl_2(N_2COPh)(py)(PPh_3)_2$] complexes

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Abstract

The [$ReCl_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2$] complex reacts with pyridine and pyrazole to give [$ReCl_2(N_2COPh)(py)(PPh_3)_2$] and [$ReCl_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2$], respectively. Two monoclinic polymers of [$ReCl_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2$] and [$ReCl_2(N_2COPh)(py)(PPh_3)_2$] have been characterized by IR, UV–Vis, ^1H NMR, magnetic measurements and X-ray structure.

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

1. Introduction

Organodiazenido ligands, as well as other ligands which form metal–nitrogen multiple bonds, have been of great interest in recent years because of their amphoteric nature and close relationship to dinitrogen and nitrosyl ligands. Similarly 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].

The [$ReCl_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2$] complex is a precursor to a variety of organodiazenido and dinitrogen complexes. [$ReCl_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2$] reacts with neutral donor ligands L, such as acetonitrile and pyridine in benzene, giving organodiazenido species [$ReCl_2(N_2COPh)L(PPh_3)_2$] [4], whereas refluxing of [$ReCl_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2$] with phosphine and arsine ligands in boiling methanol leads to the neutral dinitrogen rhenium complexes [5,6].

Considering that the pyrazole-type ligands are an important group in organometallic chemistry, and pyrazolate or pyrazole metal complexes have attracted substantial interest considering their catalytic activity, we have decided to investigate the reactivity of [$ReCl_2(\eta^2\text{-}N_2COPh\text{–}N',O)(PPh_3)_2$] towards pyrazole. In this paper, we report the synthesis, spectroscopic characterization and structural determination of two polymorphs of [$ReCl_2(N_2COPh)(C_3N_2H_4)(PPh_3)_2$] (**1** and **2**). In order to compare [$ReCl_2(N_2COPh)(py)(PPh_3)_2$] (**3**) with the pyrazole complexes, we have determined its X-ray and electronic structure.

2. Experimental

2.1. General procedure

The syntheses were carried out under argon atmosphere. All solvents were of reagent grade and were used as received. Ammonium perrhenate, triphenylphosphine and pyrazole were purchased from Aldrich and used as

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received. The [ReCl$_2$(η^2-N$_2$COPh–N$'$,O)(PPh$_3$)$_2$] and [ReCl$_2$(N$_2$COPh)(py)(PPh$_3$)$_2$] (**3**) complexes were prepared according to the literature methods [4].

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 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 800–220 nm in deoxygenated dichloromethane solution. The magnetic susceptibility was determined using a superconducting quantum interference device (SQUID, Quantum Design) magnetometer.

*2.2. Preparation of (**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 ml) and the reaction mixture was refluxed for 48 h. The green crystalline precipitate of **1** 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 HNMR (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 of **1** (KBr, cm^{-1}) 3338 (s), 3066 (m), 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.* Calc. for $C_{46}H_{39}N_4OCl_2P_2Re$ (**1**): C 56.21; H 4.00; Cl 7.21; N 5.70; O 1.63; P 6.30; Re 18.94. Found: C 56.5; H 4.0; N 5.55%.

*2.3. Preparation of (**2**)*

A solution of pyrazole (0.25 g, 3.6 mmol) in acetone (10 ml) was added to [ReCl$_2$(η^2-N$_2$COPh–N$'$,O)(PPh$_3$)$_2$] (0.5 g, 0.55 mmol) suspended in acetone (30 ml) and stirred at room temperature for 48 h. The green precipitate of **2** was filtered and crystals suitable for X-ray structure determination were obtained by recrystallization from a mixture of chloroform and methanol.

Yield 75%: ^{1}H HNMR (CD$_2$Cl$_2$ 293 K): 13.2 (1H, s N–H) 6.8–7.7 (m, 38H, CH of ArH and CH in pyrazole) ^{31}P NMR: −4.38 ppm. IR of **2** (KBr, cm^{-1}) 3338 (s), 3066 (m), 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.* Calc. for $C_{46}H_{39}N_4OCl_2P_2Re$ (**1**): C 56.21; H 4.00; Cl 7.21; N 5.70; O 1.63; P 6.30; Re 18.94%. Found: C 56.5; H 4.0; N 5.5%

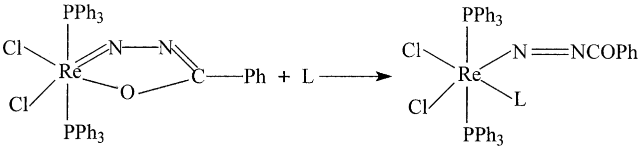
2.4. Crystal structure determination and refinement

The three-dimensional X-ray intensity data were collected on a Kuma KM-4 diffractometer with the ω–2θ scan mode (compounds **1** and **2**) and on a KM-4-CCD automatic diffractometer equipped with a CCD detector and with the ω scan mode (compound **3**). For compound (**3**) 49 s exposure time was used, all of Ewald sphere was collected up to $2\theta = 50.21°$ and the unit cell parameters were determined from least-squares refinement of the setting angles of the 2297 strongest reflections. Graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used and the measurements were carried out at room temperature 293.0(2) K. Details concerning crystal data and refinement for **1**, **2** and **3** are given in Table 1.

Lorentz, polarization, decay and absorption corrections were applied for the determined compounds (empirical absorption [7] for **1**, **2** and numerical absorption [8] for **3**). The structures were solved by the Patterson superposition method and subsequently completed by difference Fourier synthesis. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. The hydrogen atom positions were found from difference Fourier syntheses, and they were treated as "riding" on the adjacent atom and refined with as individual isotropic temperature factor equal 1.2 times the value of the equivalent temperature factor of the parent atom. SHELXS97 [9], SHELXL97 [10] and SHELXTL [11] programs were used for all the calculations. Atomic scattering factors were incorporated in the computer programs.

3. Results and discussion

The reaction of [ReCl$_2$(η^2-N$_2$COPh–N$'$,O)(PPh$_3$)$_2$] with pyrazole and pyridine results in the opening of the chelate ring through displacement of the coordinated carbonyl group by the N donar ligand (Eq. (1)) and leads to the [ReCl$_2$(C$_3$N$_2$H$_4$)(N$_2$COPh)(PPh$_3$)$_2$] and [ReCl$_2$(py)(N$_2$COPh)(PPh$_3$)$_2$] complexes, respectively.



L = pyrazole, pyridine

(1)

Refluxing of [ReCl$_2$(η^2-N$_2$COPh–N$'$,O)(PPh$_3$)$_2$] with pyrazole in methanol leads to the polymorph **1**, whereas the reaction of [ReCl$_2$(N$_2$COPh)(PPh$_3$)$_2$] with pyrazole in acetone at room temperature gives the polymorph **2**. The overall molecular geometry of **2** is similar to that of **1**. The weighted r.m.s. (root mean square) deviation for all atoms of superpositioned molecules is 1.280 Å. The main difference between the polymorphs is the arrangement of

Table 1
Crystal data and structure refinement details for **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{46}H_{39}N_4OCl_2P_2Re$	$C_{46}H_{39}N_4OCl_2P_2Re$	$C_{48}H_{40}Cl_2N_3OP_2Re$
Formula weight	982.85	982.85	993.87
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions			
a (Å)	11.756(2)	12.754(3)	11.2949(9)
b (Å)	12.292(2)	17.249(3)	13.4638(12)
c (Å)	29.219(6)	19.318(4)	14.9011(14)
α (°)	90	90	84.435(7)
β (°)	100.87(3)	99.90	88.809(7
γ (°)	90	90	71.828(8)
Volume (Å^3)	4146.5(13)	4186.6(15)	2142.8(3)
Z	4	4	2
Density (calc., Mg/m^3)	1.574	1.559	1.540
Absorption coefficient (mm^{-1})	3.178	3.147	3.075
$F(000)$	1960	1960	992
Crystal dimensions (mm)	0.13 × 0.13 × 0.05	0.16 × 0.16 × 0.39	0.28 × 0.07 × 0.01
θ range for data collection (°)	1.42–23.51	2.01–25.05	3.32–25.10
Index ranges	$-12 \leqslant h \leqslant 13$	$0 \leqslant h \leqslant 15$	$-13 \leqslant h \leqslant 13$
	$0 \leqslant k \leqslant 13$	$-20 \leqslant k \leqslant 0$	$-16 \leqslant k \leqslant 16$
	$-31 \leqslant l \leqslant 0$	$-22 \leqslant l \leqslant 22$	$-17 \leqslant l \leqslant 17$
Reflections collected	5955	7763	24434
Completeness to 2θ (%)	89.9	96.1	99.8
Absorption correction	empirical	empirical	numerical
Maximum and minimum transmission	0.8573 and 0.6828	0.6329 and 0.3733	0.9582 and 0.4819
Independent reflections	5817 ($R_{int} = 0.0428$)	7391 ($R_{int} = 0.0302$)	7610 ($R_{int} = 0.0874$)
Data/restraints/parameters	5817/0/506	7391/0/505	7610/0/514
Goodness-of-fit on F^2	1.079	1.215	1.153
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0601$	$R_1 = 0.0488$	$R_1 = 0.0582$
	$wR_2 = 0.1306$	$wR_2 = 0.1023$	$wR_2 = 0.1096$
R indices (all data)	$R1 = 0.1096$	$R_1 = 0.0798$	$R_1 = 0.0672$
	$wR_2 = 0.1749$	$wR_2 = 0.1289$	$wR_2 = 0.1139$
Largest difference peak and hole (e Å^{-3})	1.941 and −0.981	0.733 and −1.558	1.570 and −0.821

the PPh_3 substituents. Molecule 2, in comparison to **1**, has rotated PPh_3 substituents around the P–Re bond by about 41° and 16° for $P(1)$ and $P(2)$, respectively, thus weighted r.m.s. deviation for all atoms of superpositioned molecules except Ph substituents is 0.205 Å.

The r.m.s deviation of the superpositioned Re environment is 0.093 Å, which suggests that differences in structure are caused rather by packing effects than electronic properties. The unit cell parameters, crystal data and details concerning the refinement of structures **1**, **2** and **3** are given in Table 1. The perspective view of **1** and **2** together with the atom numbering scheme is shown in Figs. 1 and 2 presents the perspective drawing of **3**. The structures of **1**, **2** and **3** are stabilized by multiple weak intramolecular hydrogen bonds whose geometries are given in Table 2. The intramolecular hydrogen bonding scheme, as expected, is different in every structure. In each structure one intermolecular weak C–H···Cl hydrogen bond can be found [12–14] (C···Cl distance in the range 3.24–3.74 Å and C–H···Cl angle 123.6°–1154.5°) but in **1** it links C(32)···Cl(2# $-x, y-1/2, -z+1/2$) atoms, in **2** C(45)···Cl(2# $x-1, y, z$) atoms and in **3** C(45)···Cl(2# $-x, -y, -z$) which creates infinite hydrogen bonded chains with zig-zag geometry along y-axis in **1**, linear geometry along the x-axis in **2** and hydrogen bonded dimers in **3**. The packing diagrams of **1**, **2** and **3** are depicted in Figs. 3–5, respectively.

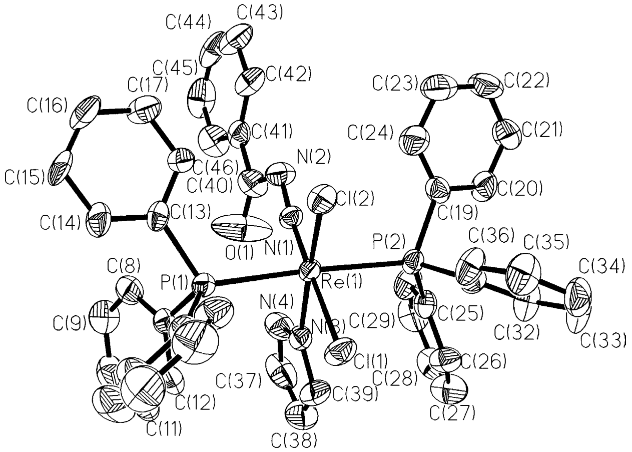


Fig. 1. ORTEP view of the structure of **1** and **2** showing 50% thermal ellipsoids.

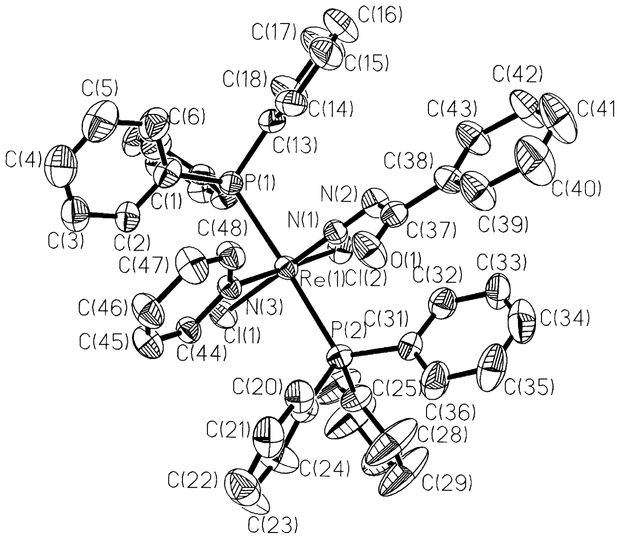


Fig. 2. ORTEP view of the structure **3** showing 50% thermal ellipsoids.

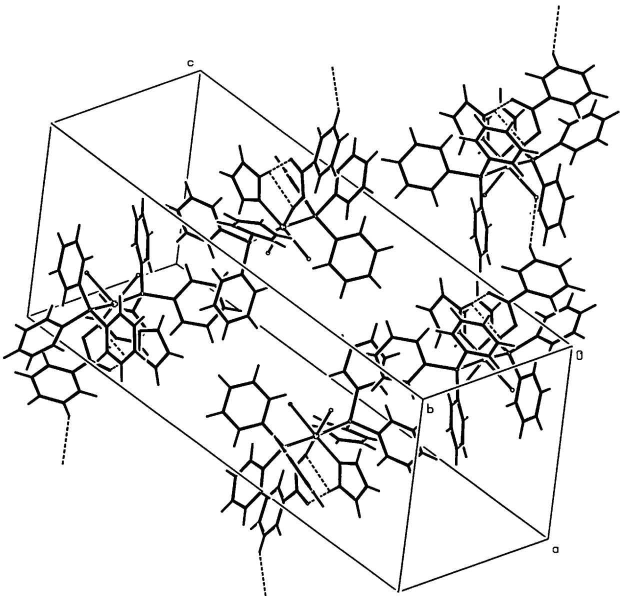


Fig. 3. The packing diagram of **1**.

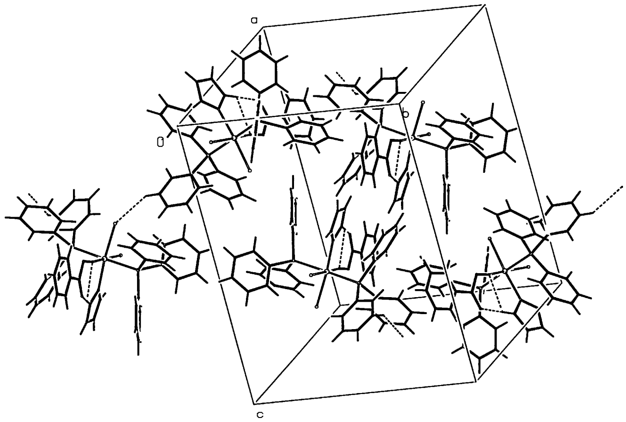


Fig. 4. The packing diagram of **2**.

The coordination geometry about the rhenium centre in **1**, **2** and **3** exhibits mutually *trans* triphenylphosphine molecules, minimizing steric congestion, and chloride donors *trans* to the monodentate organodiazenido ligand and to the pyrazole or pyridine molecule which has displaced the carbonyl oxygen of the diazenido substituent. The selected bond lengths and angles for **1**, **2** and **3** are summarized in Table 3. The angular distortions from an ideal octahedron in **1**, **2** and **3** are caused by the presence of the multiply bonding ligand (–NNR) in the *cis* position to the N-heterocycle ring. The Re(1)–N(1)–N(2) angles are essentially linear and the N(1)–N(2)–C(40) are near 120°, indicating that **1**, **2** and **3** are 'singly bent' benzoyldiazenido complexes. The bond valences were computed as $v_{ij} = \exp[(R_{ij} - d_{ij})/B]$ [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]. The $R_{\text{Re–N}}$, $R_{\text{Re–P}}$, $R_{\text{Re–Cl}}$ values were taken as 2.06, 2.46 and 2.23 [15] respectively and the value of B was taken as 0.37 [16]. The computed bond valences of the rhenium $v_{\text{Re-j}}$ are gathered in Table 4. The total valence of Re(1) is 6.36, 6.44 and 6.24 v.u. (valence units), respectively for compounds **1**, **2** and **3**, which means that rhenium substituents in compound **1** are more weakly bonded than in compound **2** and more strongly bonded than in compound **3**. The short Re–N(1) and N(1)–N(2) distances

Table 2
Hydrogen-bonding geometry for **1**, **2** and **3** (Å, °)

1				**2**				**3**			
D–H···A	H···A	D···A	D–H···A	D–H···A	H···A	D···A	D–H···A	D–H···A	H···A	D···A	D–H···A
N4–H4A···O1	1.81	2.707(15)	172.0	N4–H4N···O1	1.74	2.700(13)	177.7	C8–H8A···C12	2.61	3.463(9)	152.1
N4–H4A···N1	2.56	2.977(15)	109.2	N4–H4N···N1	2.62	3.035(10)	106.8	C26–H26A···C11	2.77	3.512(11)	137.3
C2–H2B···C11	2.66	3.481(15)	144.4	C2–H2A···C12	2.75	3.630(11)	152.2	C48–H37A···Ol	2.60	3.152(10)	118.9
C8–H8A···N3	2.60	3.173(19)	118.9	C18–H18A···N1	2.49	3.274(12)	138.6	C48–H37A···N1	2.55	3.039(9)	113.1
C8–H8A···N4	2.55	3.41(2)	148.2	C18–H18A···N2	2.52	3.336(13)	142.8	C44–H41A···Cll	2.57	3.169(7)	122.6
C24–H24A···C12	2.85	3.74(3)	154.5	C24–H24A···C12	2.72	3.554(11)	146.3	C43–H48A···N2	2.46	2.788(10)	100.7
C36–H36A···C11	2.79	3.418(14)	123.6	C33–H33A···C12	2.70	3.534(10)	145.1				
C36–H36A···C12	2.75	3.474(15)	132.4	C36–H36A···C12	2.62	3.502(10)	153.2				
C39–H39A···C11	1.76	3.244(16)	112.3	C39–H39A···C11	2.70	3.170(12)	153.2				
C45–H45A···C12	2.82	3.632(14)	143.0								

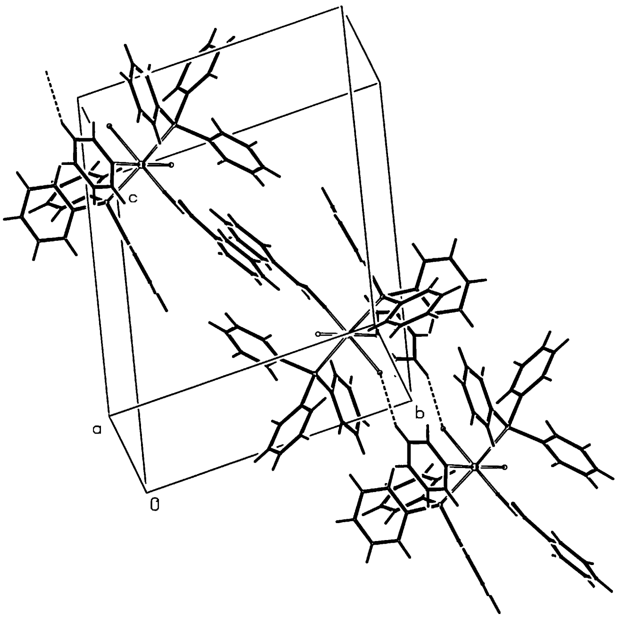


Fig. 5. The packing diagram of **3**.

Table 3
The selected bond lengths (Å) and angles (°) for **1**, **2** and **3**

	1	**2**	**3**
Bond lengths			
Re(1)–Cl(1)	2.416(3)	2.397(2)	2.4268(18)
Re(1)–Cl(2)	2.426(3)	2.424(2)	2.4457(19)
Re(1)–P(1)	2.475(3)	2.465(2)	2.4800(19)
Re(1)–P(2)	2.461(4)	2.484(2)	2.4873(19)
Re(1)–N(1)	1.725(11)	1.717(6)	1.735(6)
Re(1)–N(3)	2.150(10)	2.159(7)	2.174(5)
Bond angles			
N(1)–Re(1)–N(3)	92.7(4)	94.0(3)	92.9(2)
N(1)–Re(1)–Cl(1)	178.3(4)	177.5(2)	178.77(19)
N(3)–Re(1)–Cl(1)	85.6(3)	84.1(2)	88.30(15)
N(1)–Re(1)–Cl(2)	89.4(4)	94.2(2)	90.14(19)
N(3)–Re(1)–Cl(2)	177.3(3)	171.6(2)	176.69(15)
Cl(1)–Re(1)–Cl(2)	92.28(13)	87.70(8)	88.63(7)
N(1)–Re(1)–P(1)	94.5(4)	92.6(2)	92.9(2)
N(3)–Re(1)–P(1)	91.7(3)	90.10(19)	88.34(16)
Cl(1)–Re(1)–P(1)	85.28(12)	89.15(8)	87.25(7)
Cl(2)–Re(1)–P(1)	89.70(12)	87.89(8)	90.27(7)
N(1)–Re(1)–P(2)	93.4(4)	91.7(2)	90.0(2)
N(3)–Re(1)–P(2)	88.3(3)	89.67(19)	91.53(16)
Cl(1)–Re(1)–P(2)	86.84(12)	86.60(8)	89.93(7)
Cl(2)–Re(1)–P(2)	90.02(14)	87.88(8)	89.71(7)
P(1)–Re(1)–P(2)	172.10(13)	175.75(7)	177.18(7)
N(2)–N(1)–Re(1)	168.3(9)	171.6(6)	170.7(5)
C(39)–N(3)–Re(1)	134.7(10)	133.1(7)	
N(4)–N(3)–Re(1)	120.5(8)	132.2(7)	

Table 4
Rhenium bond valences $\nu_{\text{Re-j}}$ (v.u.)

Bond	**1**	**2**	**3**
Re(1)–Cl(1)	0.60	0.64	0.56
Re(1)–Cl(2)	0.59	0.59	0.56
Re(1)–P(1)	0.96	0.99	0.95
Re(1)–P(2)	0.96	0.94	0.97
Re(1)–N(1)	2.47	2.52	2.41
Re(1)–N(3)	0.78	0.76	0.79

suggest extensive delocalization and multiple bonding throughout the N_2COPh unit. This observation is confirmed by virtual planarity of the entire Re–N–NCOPh grouping, by linearity of Re–N–N unit and by the value of the valence parameter being larger than 2 for the Re(1)–N(1) bond. These groups are the stronger bonded Re substituents. The Re–N(1), N(1)–N(2) and N(2)–C bond lengths and N(1)–N(2)–C(37), M–N(1)–N(2) angles in **1**, **2** and **3** are in good accordance with values found by others for 'singly bent' organodiazenido complexes, which are shown in Table 5. The Re–Cl(1) adn Re–Cl(2) bond lengths of **1**, **2** and **3** are considerable longer in comparison with the Re–Cl distances of *trans*-[$ReCl_4(PPh_3)_2$] [2.3203(8) and 2.3300(8) Å] [25] The significant lengthening of Re–Cl results from the *trans* location of chloride donors to the strongly π-interacting benzoyldiazenido group and pyrazole or pyridine ligand. The Re–Cl(1) distance *trans* to the NNR ligand is shorter than the Re–Cl(2) distance in the *trans* position to the pyrazole or pyridine molecule, which indicates the stronger *trans* influence of the heterocycle molecules in comparison with the benzoyldiazenido group in **1**, **2** and **3**. According to the calculated valences, the Re–Cl bonds are the weakest in the Re coordination sphere. the Re–N(3) bond lengths in **1**, **2** and **3** (2.068–2.151 Å) are in good accordance with appropriate values found previously in similar rhenium compounds containing coordinated pyrazole and pyridine [19,20], and these bonds are slightly stronger than Re–Cl bonds. The Re–P bonds are also unexceptional, and from a formal point of view may be consider as single bonds, weaker than Re(1)–N(1), and stronger than the other bonds.

In contrast to the starting [$ReCl_2$ (η^2-N_2COPh–N′,O) ($PPh_2)_3$] complex, the infrared spectra of **1**, **2** and **3** show several bands in the range of 1550–1650 cm^{-1} range. These bands are assigned to ν(N=N), ν(C=N) and ν(C=O), confirming the opening of the chelate ligand and the presence of a pyrazole or pyridine molecule [3]. All the complexes contain triphenylphosphine ligands and thus they show the charecteristics pair of bands at approximately 1430 and 1480 cm^{-1}, and typically the lower frequency band is the more intensive one. The strong band at 3338 cm^{-1} for **1** and **2** assignable to N–H vibrations, and the ^{1}H NMR specturm for **1** and **2** exhibiting a singlet at 13.2 ppm, confirm the presence of a terminal pyrazole molecule in the coordination spheres of these compounds [23,24]. **1** and **2** dissolved in dichloromethane give identical UV–Vis spectra, So the electronic structures of both polymorphs are the same. Table 6 presents the positions, molar absorption coefficients of electronic bands and the electronic transitions assigned to the bands of **1** and **3**.

Considering the diamagnetism of complexes **1** and **3** and the linear Re=N=N—Ph bond systems, it may be

Table 5
Bond distances and angles for complexes with 'singly bent' organodiazenido ligands

Complex	M–N (Å)	N–N (Å)	N–C (Å)	N–N–C (Å)	M–N–N (Å)	Ref.
$[ReCl_2(N_2COPh)(PPhMe_2)_3]$	1.74(2)	1.22(3)	1.42(1)	124(2)	170(2)	[21]
$[ReCl_2(PPh_3)_2(N_2COPh)(NCCH_3)]$	1.756(7)	1.25(1)	1.40(1)	120.5(7)	172.1(6)	[3]
$[ReCl_2(PPh_3)_2(NNCO_2CH_3)(C_6H_5N)]$	1.72(2)	1.28(2)	1.44(2)	123.8(11)	166.9(12)	[3]
$[ReCl_2(PPh_3)_2(NNC_6H_{4-}$-*o*-Br$)(NH_3)]$	1.755(7)	1.25(1)	1.40(1)	119.9(6)	167.1(12)	[3]
$[MoCl_2(N_2COPh)(dpe)_2]$	1.813(7)	1.255(10)	1.369(12)	116.7(7)	172.1(6)	[22]

Table 6
Positions, molar absorption coefficients of electronic bands and the electronic transitions assigned to the bands for **1** and **3**

2			**3**		
Band position (cm^{-1})	ε	Assignment	Band position (cm^{-1})	ε	Assignment
16 299	199	$^1A_1 \rightarrow {}^3T_1$	16 299	199	$5d \rightarrow \pi^*_{pyridine}$
26 990	10 205	$^1A_1 \rightarrow {}^1T_1$ $5d \rightarrow \pi^*_{pyrazole}$	26 990	10 205	$^1A_1 \rightarrow {}^1T_1$ $5d \rightarrow \pi^*_{N=N-C}$ $5d \rightarrow \pi^*_{pyridine}$
26 212	8734	$5d \rightarrow \pi^*_{N=N-C}$ $5d \rightarrow \pi^*_{pyrazole}$	26 212	8734	$^1A_1 \rightarrow {}^1T_2$ $\pi \rightarrow \pi^*_{C_6H_5-N}$
36 231	33 984	$^1A_1 \rightarrow {}^1T_2$ $\pi \rightarrow \pi^*_{pyrazole}$ $\pi \rightarrow \pi^*_{C_6H_5-N}$	36 231	33 984	$\pi \rightarrow \pi^*_{pyridine}$
42 918	54 107	$\pi^b_{C_6H_5-N} \rightarrow 3d$ $\pi \rightarrow \pi^*_{pyrazole}$	42 918	54 107	$\pi^b_{C_6H_5-N} \rightarrow 3d$

assumed that the N=N–Ph ligand is a donor of four electrons, and the central ion has a d^6 electron configuration [1]. Taking into consideration the possible d–d transitions in the pseudo-octahedral ligand field, the transition connected with charge transfer and internal electron transitions in the ligands, in spite of superimposing of these bands, were attributed qualitatively, according to the literature data. Charge transfer transitions may only be MLCT ones (d^6), and pyridine has a higher π-acceptor ability than pyrazole, because pyridine weakens the Re–Cl bond in the *trans* position to a higher degree than pyrazole.

4. Supplementary data

Supplementary data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk), quoting the depositions numbers: 208205 $[ReCl_2(N_2COPH)(C_3N_2\ H_4)(PPh_3)_2]$ polymorph 1, 2082206 $[ReCl_2(N_2COPH)(C_3N_2\ H_4)(PPh_3)_2]$. polymorph 2, 208207 $[ReCl_2(N_2COPH)(py)(PPh_3)_2]$.

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