

Syntheses and characterization of phenyldiazenido and mixed phenyldiazenido–isocyanide complexes of rhenium. Crystal structure of $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]$

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The complex $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]\text{Br}$ **1**, prepared by bromination of $[\text{ReCl}(\text{NNPh})_2(\text{PPh}_3)_2]$, was reduced, in thf or acetone, to the paramagnetic phenyldiazenido-complex $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]$ **2** and its acetone solvate $2 \cdot \text{Me}_2\text{CO}$ (formed in the presence of $\text{HSC}_6\text{H}_2\text{Pr}^1\text{-2,4,6}$ or CNMe), and converted spontaneously (*via* a conceivable nucleophilic displacement at phenyldiazenide) into $[\text{ReBr}_3(\text{NNPh})(\text{PPh}_3)_2]$ **3** from which **2** can also be derived. The molecular structure of **2** has been determined by X-ray diffraction analysis which indicates that one of the diazenide ligands is doubly bent and the other singly bent, each being *trans* to a bromide ligand and exerting a significant *trans* influence. Complexes **1–3** react with isocyanides to give the reduced mixed diazenido–isocyanide complexes $[\text{ReBr}_2(\text{NNPh})(\text{CNR})(\text{PPh}_3)_2]$ ($\text{R} = \text{Me}$ **4** or $\text{C}_6\text{H}_4\text{Cl-4}$ **5**), $[\text{ReBr}_2(\text{NNPh})(\text{CNMe})_2(\text{PPh}_3)]$ **6** or $[\text{ReBr}(\text{NNPh})(\text{CNMe})_2(\text{PPh}_3)_2]$ **7**.

The co-ordination chemistry of organodiazenides is a matter of current and growing interest^{1,2} with well established importance in fields such as nitrogen fixation^{3,4} and with recognized potential significance⁵ in radiopharmaceutical development. However, in spite of their versatile binding ability which allows them to exhibit different co-ordination geometries and to donate different numbers of electrons to the metal centre,^{1,2} paramagnetic complexes with such ligands are still almost unknown.^{6,7} Also only very rare examples have been reported⁸ of organodiazenido-complexes with isocyanides which are quite versatile co-ordination reagents⁹ and known¹⁰ substrates of nitrogenases.

Within our interest on extending to higher metal oxidation states our studies¹¹ on the activation, by electron-rich transition-metal centres (typically Re^I , Mo^0 , W^0 or Fe^{II}), of biologically significant small molecules with unsaturated nitrogen or carbon, we have also investigated the reactions of isocyanides with organodiazenido-complexes such as $[\text{ReCl}_2(\text{NNCOPh})(\text{PPh}_3)_x\{\text{P}(\text{OR})_3\}_{3-x}]$ ($x = 0$ or 1 , $\text{R} = \text{Me}$ or Et)^{12,13} in the presence of MeOH , and $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]\text{Br}$ **1**.⁷ In the former cases a variety of low-oxidation-state rhenium isocyanide products, *i.e.* $[\text{ReCl}(\text{N}_2)(\text{CNR})(\text{PPh}_3)_x\{\text{P}(\text{OR})_3\}_{3-x}]$ ¹² or $[\text{ReCl}(\text{CNR})_3\{\text{P}(\text{OMe})_3\}_2]$,¹³ were obtained with loss of the organodiazenide ligand which decomposed to N_2 and PhCO_2Me *via* nucleophilic attack by methoxide ion. On attempted reaction of $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]\text{Br}$ **1** with CNMe in thf or acetone the mono(organodiazenido) complex $[\text{ReBr}_3(\text{NNPh})(\text{PPh}_3)_2]$ was isolated and structurally characterized, as quoted⁷ in a preliminary communication.

We now report this reaction in detail and a further investigation of the conversion of $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]\text{Br}$ **1** into other organodiazenido-complexes and of their reactions with isocyanides to form mixed organodiazenido–isocyanide products. Some of the diazenido-complexes obtained are paramagnetic with the rhenium in an unusual oxidation state.

Results and Discussion

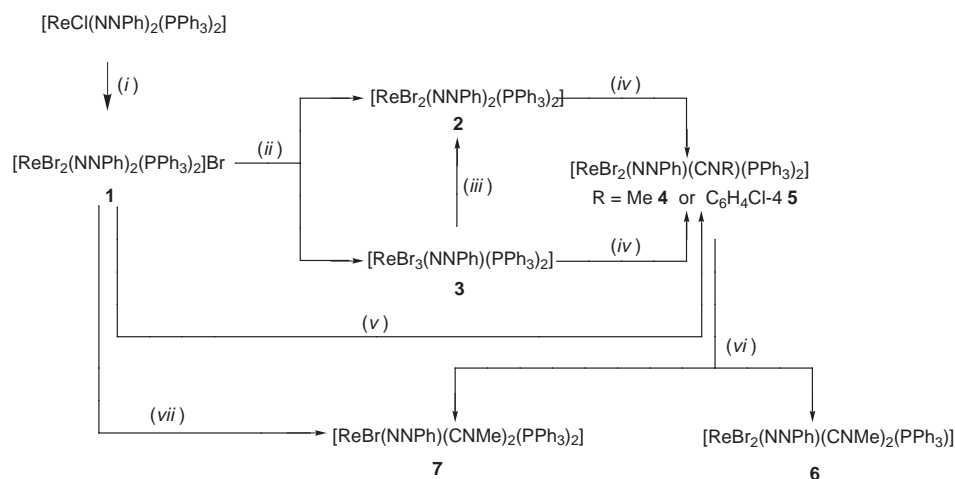
Phenyldiazenido-complexes

As an entry to the study of diazenido-complexes of rhenium in medium/high oxidation states we have selected the bis-(diazenido)-complex $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]\text{Br}$ **1** which we found to be conveniently prepared (isolated as a green solid in *ca.* 85% yield) by bromination in CH_2Cl_2 (*ca.* 15 min) of $[\text{ReCl}(\text{NNPh})_2(\text{PPh}_3)_2]$, a known¹⁴ compound. This last complex, which has low solubility possibly due to polymeric structure, would not be expected to be a promising starting material. It was obtained in a high yield (*ca.* 85%) by adapting a method taken from the literature¹⁴ for related aryldiazenide complexes, *i.e.* by refluxing a suspension of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ in MeOH with PhNHNH_2 and PPh_3 .

In compound **1** the bromide counter ion can easily be replaced by tetraphenylborate, as expected, and the corresponding species $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2][\text{BPh}_4]$ **1'** (greyish green) was obtained upon treatment of a CH_2Cl_2 solution of **1** with $\text{Na}[\text{BPh}_4]$, thus confirming the cationic nature of the complex **1**. The perchlorate salt has previously been reported,¹⁵ although without indication of the preparative method or of any characterization data apart from IR $\nu(\text{NN})$ frequencies. In the IR spectra (KBr disc) of complexes **1** or **1'** (see Experimental section), the bands assigned to $\nu(\text{NN})$ of the diazenide ligands are observed in the $1845\text{--}1565\text{ cm}^{-1}$ range, *i.e.* at values which are higher than those exhibited by $[\text{ReCl}(\text{NNPh})_2(\text{PPh}_3)_2]$ (1540 and 1510 cm^{-1}), in accord with the higher metal oxidation state in the cationic complexes with a resulting lower π -electron releasing ability of the metal.

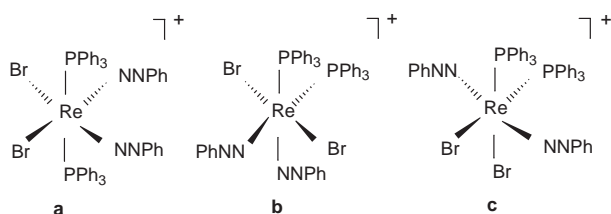
In solution, compounds **1** and **1'** appear to occur as a mixture of three isomers (one of them predominating over the others), as suggested by the detection, in the $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR spectra (CDCl_3) (see Experimental section) of three singlet resonances [the main one at δ *ca.* 148 and the other two at δ *ca.* 144 and 153 relative to $\text{P}(\text{OMe})_3$] which are maintained even after repeated recrystallizations of the sample. This can be accounted for by considering the possibility of occurrence of

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Scheme 1 (i) CH_2Cl_2 , Br_2 , 15 min; (ii) thf, heat, Htipt, 4 h (for **2**); thf (3–4 d) or acetone (2 d) (for **3**); acetone, CNMe (2 h) (for **2**·Me₂CO + **3**); (iii) thf, heat, $\text{PPhCPh}=\text{CPh}$, 2 d; (iv) thf, CNR (3:1), 1 d; (v) thf (for **4**) or acetone (for **5**), CNR (3:1), 1 d; (vi) thf, CNMe (3:1), 18 h; (vii) thf or acetone, CNMe (6:1), 3 d

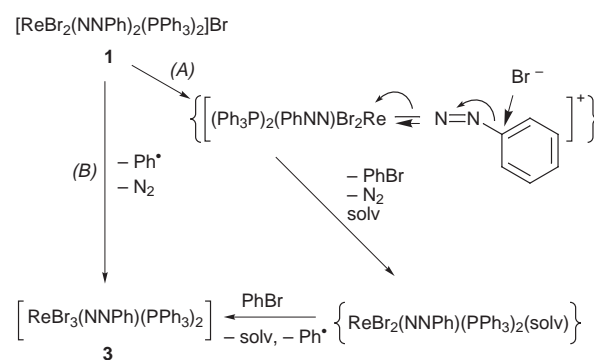
three geometrical isomers, two of them with the diazenide ligands mutually *cis* (each of them *trans* to a bromide or to a phosphine, forms **a** or **b**, respectively) and the other one (form **c**) with the diazenide ligands in *trans* positions. However, the presence of isomers with different relative conformations of the phenyldiazenide ligands cannot be ruled out, as suggested¹⁶ for $[\text{TcCl}(\text{NNC}_6\text{H}_4\text{OMe-4})_2(\text{PPh}_3)_2]$ the ¹H NMR spectrum of which displays three resonances assigned to the methoxide protons.²



For compounds **1** and **1'** the ¹H NMR resonances (see Experimental section) of the phenyl protons of the phenyldiazenide ligands are observed as the expected multiplets at higher fields than those of free PPh_3 and BPh_4^- (the latter species in the case of **1'**).

Complex **1** can act as a good starting material for a variety of other phenyldiazenido-complexes, as shown in Scheme 1 which summarizes the reactions we have investigated. Complex **1** is reduced by a thiol, $\text{HSC}_6\text{H}_2\text{Pr}^{\text{t-2,4,6}}$ (Htipt), to form, after heating in thf under reflux for 4 h [see reactions (ii), Scheme 1], the corresponding paramagnetic neutral complex $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]$ **2** (isolated as a red crystalline solid in ca. 20% yield) [$\nu(\text{NN})$ (KBr pellet) 1625m, 1585w and 1560s cm^{-1}] the crystal structure of which was determined by X-ray diffraction analysis (see below).

Complex **2** was also obtained as one of the products from the attempted reaction of **1** with the phosphirene $\text{PPhCPh}=\text{CPh}$, in thf under reflux. Its acetone solvate **2**·Me₂CO was isolated (ca. 20% yield) upon reduction of **1** by CNMe in acetone (for ca. 2 h at ambient temperature), with concomitant formation of another paramagnetic complex, $[\text{ReBr}_3(\text{NNPh})(\text{PPh}_3)_2]$ **3** [$\nu(\text{NN})$ (KBr disc) 1700ms and 1575s cm^{-1}] (isolated as a green solid in ca. 50% yield). Complex **3** can be obtained, in a more convenient way, by the spontaneous conversion of **1** in thf or acetone, for extended periods (typically 3 to 4 d in thf, ca. 85% yield), at ambient temperature and without requiring the addition of any other reagent. The molecular structure of **3**, with a singly bent diazenide ligand, has already been reported by us,⁷ although without any details of its remarkable formation,



Scheme 2 (A), Nucleophilic displacement; (B), CN bond homolysis

which involves the extensive overall conversion of a bis- into a mono-phenyldiazenido-complex.

The extent of conversion of complex **1** into **3** follows the Lewis basicity of the solvent,¹⁷ *i.e.* thf > acetone > CH_2Cl_2 (no reaction), thus pointing towards the involvement of solvent coordination. The presence of the Br^- counter ion is also relevant, since no reaction was observed for **1'**, but the replacement of one of the diazenides by Br^- is not expected in view of their inertness to displacement, and since the association of the two ions (the cationic complex and Br^-) to form an ion pair should be faster¹⁸ in a solvent of low relative permittivity such as CH_2Cl_2 .

The direct nucleophilic attack of Br^- at the *ipso*-carbon of NNPh forming PhBr [route (A), Scheme 2] would be a conceivable step in view of the high $\nu(\text{NN})$ frequencies in **1** indicating a weak π -electron acceptance of the organodiazenides, as observed¹⁹ in the reactions of $[\text{M}(\eta^5\text{-ZC}_5\text{H}_4)(\text{NNR})(\text{CO})_2]^+$ [$\text{M} = \text{Mn}$ or Re , $\text{Z} = \text{H}$ or Me , $\text{R} =$ substituted phenyl; $\nu(\text{NN}) \geq 1750 \text{ cm}^{-1}$] with a nucleophile (X^-) such as a halide or a pseudo-halide, to form the corresponding N_2 complexes and RX . This process, assisted by replacement of the generated N_2 ligand (the rhenium oxidation state would not be sufficiently low to bind N_2)²⁰ by solvent (solv) would lead to the postulated intermediate $[\text{ReBr}_2(\text{NNPh})(\text{PPh}_3)_2(\text{solv})]$. This is strongly corroborated by the fact that the acetonitrile complex $[\text{ReBr}_2(\text{NNPh})(\text{PPh}_3)_2(\text{NCMe})]$ was observed²¹ to react with PhBr to give **3**. Moreover, metal halogenation by organohalides with homolysis of the carbon–halogen bond is a known²² reaction that could account for the formation of **3** from that intermediate.

The alternative route (B) (Scheme 2), involving the homolysis of a C–N bond, is less favoured. It has been reported⁴ for $[\text{Re}(\eta^5\text{-ZC}_5\text{H}_4)\text{L}(\text{L}')(\text{NNC}_6\text{H}_4\text{OMe-4})]^+$ [$\text{Z} = \text{H}$ or Me ; L and/

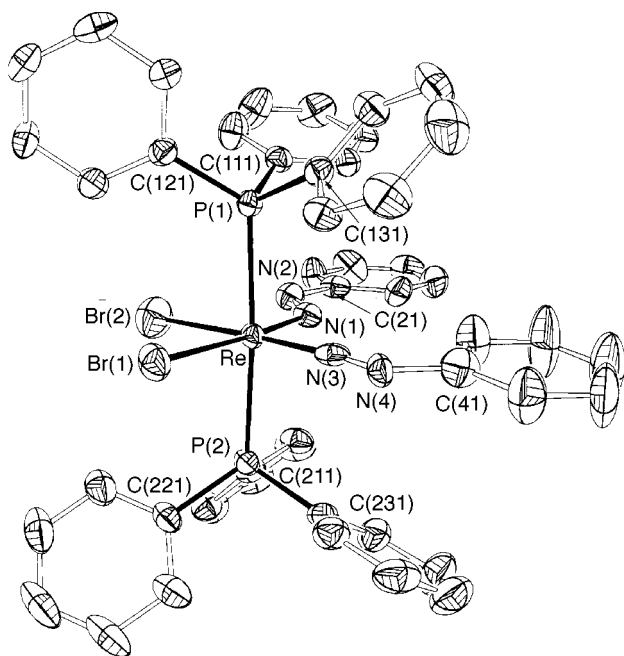


Fig. 1 Molecular structure of $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]$ **2** with numbering scheme

Table 1 Selected bond lengths (Å) and angles (°) for $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]$ **2**

Re–Br(1)	2.596(1)	P–C(average)	1.83
Re–Br(2)	2.563(2)	N(1)–N(2)	1.304(10)
Re–P(1)	2.481(2)	N(3)–N(4)	1.120(10)
Re–P(2)	2.487(2)	N(2)–C(21)	1.430(12)
Re–N(1)	1.908(7)	N(4)–C(41)	1.428(14)
Re–N(3)	1.827(9)		
Br(1)–Re–Br(2)	90.15(4)	Re–N(3)–N(4)	171.2(7)
P(1)–Re–P(2)	176.34(8)	N(1)–N(2)–C(21)	120.3(8)
N(1)–Re–N(3)	94.0(3)	N(3)–N(4)–C(41)	120.9(9)
Re–N(1)–N(2)	130.6(6)		

or $L' = \text{CO}$, PMe_3 or $\text{P}(\text{OMe})_3$ but only *after* reduction of the metal to the +2 oxidation state which conceivably is lower than that of **1**. In contrast with the expected promotion of that homolysis by reduction, **2** (the reduced form of **1**) does not convert into **3**.

No evidence has been found for the involvement of phenylation of the metal which was reported²³ for the synthesis of some arylgold(I) complexes derived from arylhydrazine. This would lead, upon reductive elimination of PhBr , to a less brominated product than the tribromo complex **3**.

The conversion of $[\text{ReBr}_3(\text{NNPh})(\text{PPh}_3)_2]$ **3** into $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]$ **2** involves a formal replacement of a bromide by a diazenide ligand and could occur *via* the formation of diazenide and bromide bridges between two rhenium metal centres, but the overall yield in this reaction is low and the mechanism may be very complex.

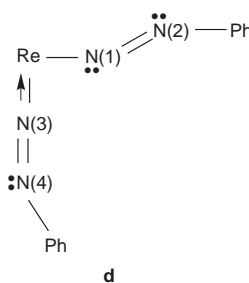
Crystal structure of $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]$ **2**

The crystal structure of $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]$ **2** was authenticated by single-crystal X-ray diffraction analysis (Fig. 1), and selected bond distances and angles are given in Table 1. It presents an octahedral-type geometry with the two phosphines in *trans* positions and the four charged ligands in the equatorial sites, the phenyldiazenides being mutually *cis* and each of them *trans* to a bromide ligand. One of the phenyldiazenide ligands has a *trans* doubly bent geometry (1e donor) whereas the other one is singly bent (three-electron donor), thus providing the complex with a formal 17-electron configuration. The

phenyldiazenide ligands are essentially coplanar, suggesting an extensive π -electron delocalization over the $\text{Ph}-\text{N}(2)=\text{N}(1)=\text{Re}=\text{N}(3)=\text{N}(4)-\text{Ph}$ system.

The doubly bent diazenide ligand in **2** has $\text{Re}-\text{N}(1)-\text{N}(2)$ and $\text{N}(1)-\text{N}(2)-\text{C}(21)$ angles of $130.6(6)$ and $120.3(8)^\circ$, whereas the $\text{Re}-\text{N}(1)$ and $\text{N}(1)-\text{N}(2)$ bond lengths are $1.908(7)$ and $1.304(10)$ Å, respectively. This doubly bent geometry is much less common than the singly bent one,² and in our complexes the angles fall in the expected range (115 – 135°) for sp^2 hybridization,² in spite of being significantly greater (*i.e.* the diazenide ligand is less bent at both N atoms) than the corresponding ones for other complexes such as $[\text{RhCl}(\text{NNPh})\{\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}][\text{PF}_6]$ [$125.1(6)$ and $118.9(8)^\circ$, respectively].²⁴

The singly bent diazenide exhibits a bending angle, $120.9(9)^\circ$, at the β -N atom, $\text{N}(3)-\text{N}(4)-\text{C}(41)$, which is similar to that observed for the doubly-bent ligand, whereas the $\text{Re}-\text{N}(3)-\text{N}(4)$ angle is $171.2(7)^\circ$, showing the approach to linearity of this ligand at the α -N atom. In comparison with the doubly bent ligand, the $\text{Re}-\text{N}$ distance in the singly bent diazenide [$\text{Re}-\text{N}(3)$ $1.827(9)$ Å] is significantly shorter, consistent with the expected multiple $\text{Re}-\text{N}$ bond character for the singly bent ligand (three-electron donor) and single $\text{Re}-\text{N}$ bond character for the doubly bent diazenide (one-electron donor) (see the valence bond resonance form **d**). A lengthening of the $\text{M}-\text{N}$ distance as a result of bending at this N atom is commonly observed.²



The $\text{N}-\text{N}$ bond length for the singly bent diazenide, $\text{N}(3)-\text{N}(4)$ $1.120(10)$ Å, is shorter than for the doubly bent one, $\text{N}(1)-\text{N}(2)$ $1.304(10)$ Å, in contrast to the usual² behaviour. Although theoretical calculations²⁵ indicate that a bending at N_α would commonly lead to a weakening of the $\text{N}-\text{N}$ bond, in the $\text{M}-\text{N}-\text{N}$ 135 – 115° range (in which our complexes fall) the effect cannot be clearly established.

The $\text{Re}-\text{Br}$ bond lengths, in the $2.563(2)$ – $2.596(1)$ Å range, are comparable with that, $2.564(2)$ Å, which we have observed⁷ in the isoelectronic complex $[\text{ReBr}_3(\text{NNPh})(\text{PPh}_3)_2]$ **3** for the bromide ligand *trans* to the singly bent phenyldiazenide which presents a significant *trans* influence. Hence, in complex **2**, both the singly and the doubly bent diazenides also appear to exhibit an appreciable *trans* influence on the bromide ligand. Interestingly, in **2** both diazenides, although having different geometries, exert approximately the same *trans* influence. The *trans* influence of the singly bent species {with a rather limited number of exceptions for some thiolate complexes^{14b,26} such as $[\text{HNEt}_3][\text{Re}_2(\text{NNPh})_2(\text{SPh})_7]$ } is usually small, although quite a perceptible *trans* influence has been recognized²⁷ for the doubly bent geometry, *e.g.* in $[\text{IrCl}_2(\text{NNC}_6\text{H}_4\text{NO}_2)_2(\text{CO})(\text{PPh}_3)_2]$.

The average $\text{Re}-\text{P}$ bond distance, $2.484(2)$ Å, is close to that for complex **3**, $2.514(3)$ Å,⁷ and identical to the reported²⁸ average value for triphenylphosphine complexes of rhenium(IV), -(V) and -(VII).

It is also noteworthy to mention that the structural data for complex **2** are quite similar to those reported^{14a} for the related diazenido-hydrazide complex $[\text{ReBr}_2(\text{NNPh})(\text{NNHPh})(\text{PPh}_3)_2]$, indicating that the presence of the hydrogen atom at the β -N of the hydrazide ligand does not result in a significant structural alteration. The absence of such an H atom in **2**, *i.e.* the presence of the doubly bent diazenide NNPh rather than

the hydrazide(2-) NNHPh ligand, is consistent with the paramagnetism of the complex (as clearly indicated by EPR and ^1H NMR) and with the failure to detect it by X-rays and by ^1H NMR (the resonance at δ 12.3 assigned 14a to NNHPh was not observed for **2**).

The crystal structure of the acetone-solvated complex **2**·Me₂CO was also determined, by single-crystal X-ray diffraction. Probably as a result of solvation, it crystallizes in a different crystal system from that of the unsolvated compound **2**: monoclinic, space group $P2_1/c$ (no. 14) with $a = 10.401(1)$, $b = 23.639(3)$ and $c = 19.379(3)$ Å, $\beta = 96.35(2)^\circ$. The molecular structure of the complex with acetone as solvate is similar to that of **2**, but the lower quality of the crystallographic data ($R = 0.089$), as well as a disorder in the linear phenyldiazenide ligand, precluded an accurate comparison.

Phenyldiazenido-isocyanide complexes

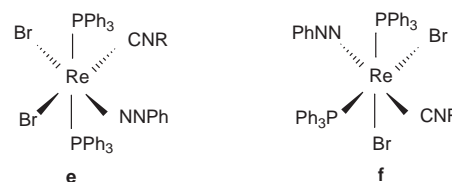
As indicated above, [ReBr₂(NNPh)₂(PPh₃)₂]Br **1**, in acetone or thf, is reduced by CNMe (3:1) to give [ReBr₂(NNPh)₂(PPh₃)₂] **2**, isolated after *ca.* 2 h reaction (complex **3** also formed in the absence of the isocyanide). However, extending the reaction time leads to the formation of the isocyanide complex [ReBr₂(NNPh)(CNMe)(PPh₃)₂] **4** [reaction (v), Scheme 1] which was isolated after 1 d (*ca.* 55% yield) as a red solid. The analogous aryl isocyanide complex [ReBr₂(NNPh)(CNC₆H₄Cl-4)-(PPh₃)₂] **5** was obtained in a similar way, by using CNC₆H₄Cl-4 instead of CNMe, and was isolated also as a red crystalline solid (*ca.* 60% yield).

Complex **4** can also be obtained from [ReBr₂(NNPh)₂(PPh₃)₂] **2** or [ReBr₃(NNPh)(PPh₃)₂] **3** [route (iv), Scheme 1], under similar experimental conditions to those used in the reaction of **1** with the isocyanide for 1 d. However, it was isolated in a lower yield (*ca.* 30%) and the diisocyanide complex [ReBr(NNPh)(CNMe)₂(PPh₃)₂] **7** was also an isolated product formed upon further reaction of **4** with CNMe. In fact **7** was also isolated (*ca.* 30%) from the reaction of **4** with CNMe (3:1), in thf, a process in which another diisocyanide complex, [ReBr₂(NNPh)(CNMe)₂(PPh₃)] **6**, was also obtained (orange solid, *ca.* 20% yield). The latter complex of Re^{III} was formed by simple replacement of PPh₃ in **4** by CNMe [route (vi), Scheme 1]. A better method [route (vii), Scheme 1] for the synthesis of the diisocyanide complex [ReBr(NNPh)(CNMe)₂(PPh₃)₂] **7** is the direct treatment of [ReBr₂(NNPh)₂(PPh₃)₂]Br **1**, in thf or acetone, with a higher excess of CNMe (6:1) for a prolonged period (**7** was isolated after 3 d as a green solid, *ca.* 40% yield). In the formation of **4** or **5**, **6** and **7** from **1**, complexes **2** and/or **3** are detected intermediates and the reduction of Re is in accord with the reducing ability of the isocyanide. In their IR spectra (KBr discs) the isocyanide complexes exhibit medium/strong intensity bands in the 2220–2110 cm⁻¹ range, assigned to $\nu(\text{C}\equiv\text{N})$, whereas $\nu(\text{NN})$ of the phenyldiazenide ligand occurs as two strong bands at *ca.* 1650 and *ca.* 1560 cm⁻¹.

The complexes [ReBr₂(NNPh)(CNMe)(PPh₃)₂] **4** and [ReBr₂(NNPh)(CNMe)₂(PPh₃)] **6**, which differ only on the relative numbers of CNMe and PPh₃ ligands, display a common $\nu(\text{C}\equiv\text{N})$ value, 2170 cm⁻¹. This suggests that CNMe and PPh₃ present similar electron donor/acceptor abilities as those metal centres which are not strong π -electron releasers as indicated by the relatively high $\nu(\text{C}\equiv\text{N})$ frequency (slightly above that shown by the free isocyanide, 2150 cm⁻¹). The CNMe and PPh₃ ligands exhibit then comparable electrochemical P_1 values (−0.43 and −0.35 V, respectively),²⁹ *i.e.* behave as similar net electron donor/acceptors. The higher $\nu(\text{C}\equiv\text{N})$ value for [ReBr(NNPh)(CNMe)₂(PPh₃)₂] **7** (2220 cm⁻¹) results from the replacement, relatively to **4** and **6**, of a bromide ligand (a very strong net electron donor, P_1 *ca.* −1.2 V)²⁹ by an isocyanide or a phosphine ligand, a much weaker net electron donor, with a resulting decrease of the π -electron releasing ability of the metal centre to the isocyanide ligands. The observation of a single

$\nu(\text{C}\equiv\text{N})$ band for the diisocyanide complexes **6** and **7** suggests a *trans* arrangement of the two CNMe ligands.

Proton and $^{31}\text{P}\{-^1\text{H}\}$ NMR data were collected (in CDCl₃) for the diamagnetic complexes **4**, **5** and **6** (see Experimental section). Each of them exhibits a singlet resonance in its $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum [δ −150.93, −154.01 or −136.34 relative to P(OMe)₃, respectively], thus showing, in the cases of the diphosphine complexes **4** and **5**, the equivalency of the two PPh₃ ligands which therefore should be either mutually *trans* or each of them in the *trans* position to a bromide ligand (forms **e** or **f**, respectively).



The equivalency of the two CNMe ligands in complex **6** (as suggested by IR spectroscopy, see above) was confirmed by the detection in its ^1H NMR spectrum of a single resonance assigned to the methyl protons (singlet at δ 3.56). For complex **4** the resonances due to the phenyl protons of the diazenide ligand are clearly detected with the expected patterns at higher fields than those of PPh₃.

The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of complex **7** are broad and the former spread along an extended δ range, thus clearly indicating its expected paramagnetism. The formulation was confirmed by its FAB MS spectrum in which the molecular ion (m/z 977) was very clearly observed with the expected isotopic pattern.

Conclusion

This study shows that [ReBr₂(NNPh)₂(PPh₃)₂]Br can act as a convenient starting material for a variety of diazenido- and mixed diazenido-isocyanide complexes, a number of them being paramagnetic. The susceptibility of the rhenium metal to ready reduction by a reagent such as a thiol or an isocyanide is evident, as is the versatility of the phenyldiazenide ligand towards formal displacement by bromide or isocyanide (its loss being interpreted, in the former case, in terms of a nucleophilic displacement of the phenyl group) or transfer to another metal. The potential synthetic interest of these unusual types of reactions of organodiazenides should be explored, as well as the establishment of the conditions to induce their reactions with isocyanides.

Experimental

The solvents were dried and degassed by using standard techniques. All reactions were performed under an inert atmosphere (N₂). Phenylhydrazine and HBr were commercially available and used without further purification. The compounds HSC₆H₂Pr₃-2,4,6,³⁰ CNMe³¹ and [ReOCl₃(PPh₃)₂]³² were prepared according to published methods, and [ReCl(NNPh)₂(PPh₃)₂] by adapting a method taken from the literature¹⁴ for related aryldiazenido-complexes. All of the equipment used is that existing at the Instituto Superior Técnico.

Infrared spectra were run with a Perkin-Elmer 683 spectrophotometer and NMR spectra on a Varian Unity 300 spectrometer; δ values are in ppm relative to SiMe₄ (^1H) or to P(OMe)₃ (^{31}P); the dominant ^{31}P resonance for mixtures of isomers is given in italics. The FAB MS spectrometric measurements were performed on a Trio 2000 spectrometer, positive-ion spectra being obtained by bombarding 3-nitrobenzyl alcohol matrices of the samples with 8 keV (*ca.* 1.28×10^{-15} J) Xe atoms.

Syntheses

[ReCl(NNPh)₂(PPh₃)₂]. Phenylhydrazine (2.0 cm³, 20.3 mmol) was added to a stirred suspension of [ReOCl₃(PPh₃)₂] (2.0 g, 2.4 mmol) and PPh₃ (1.0 g, 3.8 mmol) in MeOH (10 cm³) and the system refluxed for 2 h. The dark orange product was filtered off, washed with MeOH–Et₂O and CH₂Cl₂ and dried *in vacuo* (ca. 85% yield) (Found: C, 58.8; H, 4.4; N, 5.7. Calc. for C₄₈H₄₀ClN₄P₂Re·0.5CH₂Cl₂: C, 58.3; H, 4.1; N, 5.6%). IR (KBr disc): 1540s and 1510s cm⁻¹ [ν(NN)]. ¹H NMR (CDCl₃): δ 7.73–6.99 (m, 30 H, PPh₃) and 6.88–6.44 (m, 10 H, NNPh). ³¹P-{¹H} NMR (CDCl₃): δ -127.30 (s) and -130.24 (s).

[ReBr₂(NNPh)₂(PPh₃)₂]Br 1. To a stirred suspension of [ReCl(NNPh)₂(PPh₃)₂] (2.0 g, 2.1 mmol) in CH₂Cl₂ (10 cm³) was added a 0.5 M Br₂ solution in CH₂Cl₂ (16.8 cm³, 8.4 mmol Br₂). After 15 min the dark green solution was taken to dryness *in vacuo*. Methanol was then added and the residual green solid (complex **1**) was filtered off, washed with MeOH–Et₂O and dried *in vacuo* (ca. 85% yield) (Found: C, 50.4; H, 3.5; N, 4.7. Calc. for C₄₈H₄₀Br₃N₄P₂Re: C, 49.7; H, 3.5; N, 4.8%). IR (KBr pellet): 1845 (sh), 1755ms (br), 1575m and 1565m cm⁻¹ [ν(NN)]. ¹H NMR (CDCl₃): δ 7.90–7.77 (m, 12 H, *o*-H of PPh₃), 7.35–7.27 (m, 18 H, *m,p*-H of PPh₃), 7.18–7.08 (m, 6 H, *m,p*-H of NNPh) and 6.75 [t, *J*(HH) = 7.1 Hz, 4 H, *o*-H of NNPh]. ³¹P-{¹H} NMR (CDCl₃): δ -143.80 (s), -148.40 (s) and -152.98 (s).

[ReBr₂(NNPh)₂(PPh₃)₂][BPh₄]⁻ 1'. The salt Na[BPh₄]⁻ (160 mg, 0.47 mmol) was added to a CH₂Cl₂ solution (20 cm³) of [ReBr₂(NNPh)₂(PPh₃)₂]Br **1** (0.50 g, 0.43 mmol) and the system was stirred for 1 h. Filtration followed by concentration of the solution and addition of methanol resulted in the precipitation of **1'** as a greyish green solid (ca. 70% yield) (Found: C, 61.4; H, 3.9; N, 4.3. Calc. for C₇₂H₉₀BBr₂N₄P₂Re: C, 61.8; H, 4.0; N, 4.3%). IR (KBr disc): ν(NN) as for **1**. ¹H NMR (CDCl₃): δ 7.77–6.96 (m, 49 H, PPh₃, BPh₄⁻), 6.83 [t, *J*(HH) = 7.14, 6 H, *m,p*-H of NNPh] and 6.35 [d, *J*(HH) = 7.14 Hz, 4 H, *o*-H of NNPh]. ³¹P-{¹H} NMR: δ -142.74 (s), -147.41 (s) and -152.28 (s).

[ReBr₂(NNPh)₂(PPh₃)₂] 2. This complex was obtained upon reduction of [ReBr₂(NNPh)₂(PPh₃)₂]Br **1** by HSC₆H₂Prⁱ₃-2,4,6 (Htipt) in thf or from the attempted reaction of [ReBr₃(NNPh)(PPh₃)₂] **3** (see below) with $\overline{\text{PPhCPh=CPh}}$ in thf.

First method. The compound Htipt (0.13 cm³, 0.52 mmol) was added to a suspension of complex **1** (0.15 g, 0.13 mmol) in thf (20 cm³) and the system left under reflux for 4 h. Concentration of the red solution *in vacuo* followed by addition of Et₂O led to the precipitation of **2** as a red microcrystalline solid which was filtered off, washed with Et₂O and dried *in vacuo* (ca. 20% yield).

Second method. A suspension of [ReBr₃(NNPh)(PPh₃)₂] **3** (see below) (0.20 g, 0.19 mmol) in thf (60 cm³), in the presence of $\overline{\text{PPhCPh=CPh}}$ (60 mg, 0.21 mmol), was refluxed for 2 d. Concentration *in vacuo* and addition of pentane led to the formation of an orange solid which was filtered off. Concentration of the mother-liquor and addition of pentane resulted in the precipitation of **2** as a red crystalline solid which was filtered off, washed with Et₂O and dried *in vacuo* (ca. 15% yield). One of the crystals was analysed by X-ray diffraction (Found: C, 53.7; H, 3.6; N, 5.0. Calc. for C₄₈H₄₀Br₂N₄P₂Re: C, 53.3; H, 3.7; N, 5.2%). IR (KBr pellet): 1625m, 1585w and 1560s cm⁻¹ [ν(NN)].

[ReBr₂(NNPh)₂(PPh₃)₂]·Me₂CO 2·Me₂CO. This acetone solvate was obtained with [ReBr₃(NNPh)(PPh₃)₂] **3** (see below) in the following way. To a suspension of complex **1** (0.50 g, 0.43 mmol) in acetone (60 cm³) was added CNMe (56 μl, 1.1 mmol) and the system stirred for 2 h to give a clear green solution. This was concentrated *in vacuo* to give a green precipitate of **3** (see

below) (ca. 50% yield) which was filtered off. Concentration of the mother-liquor led to the formation of 2·Me₂CO as a red crystalline solid (ca. 20% yield). One of the crystals was analysed by X-ray diffraction.

[ReBr₃(NNPh)(PPh₃)₂] 3. Although this complex could be obtained from [ReBr₂(NNPh)₂(PPh₃)₂] **1** in acetone, either in the presence (see above preparation of 2·Me₂CO) or in the absence of CNMe (other experimental conditions as for the preparation of 2·Me₂CO, but extending the reaction time to 2 d), a better route (with a higher yield) involves the use of thf as the solvent, in the following way. A suspension of [ReBr₂(NNPh)₂(PPh₃)₂]Br **1** (2.0 g, 1.7 mmol) in thf (100 cm³) was stirred until a clear dark green solution formed (ca. 3 to 4 d) which was then concentrated *in vacuo* to give **3** as a green crystalline solid. This was filtered off, washed with pentane and dried *in vacuo*. Further crops could be obtained from the mother-liquor upon concentration and addition of pentane (yield ca. 85%) [Found (when prepared in acetone): C, 48.4; H, 3.7; N, 2.5. Calc. for C₄₂H₃₅Br₃N₂P₂Re·OCMe₂: C, 48.5; H, 3.7; N, 2.5%]. IR (KBr pellet): 1700ms and 1575s cm⁻¹ [ν(NN)].

[ReBr₂(NNPh)(CNMe)(PPh₃)₂] 4. A suspension of [ReBr₂(NNPh)₂(PPh₃)₂]Br **1** (0.15 g, 0.13 mmol) in thf (40 cm³), in the presence of CNMe (20 μl, 0.39 mmol), was stirred for 1 d. Concentration of the solution followed by addition of pentane resulted in the precipitation of **4** as a red solid. A further crop was obtained from the mother-liquor, upon concentration and addition of pentane. These fractions were recrystallized together from CH₂Cl₂–Et₂O, and the resulting solid was filtered off, washed with Et₂O and dried *in vacuo* (ca. 55% yield). Complex **4** could also be obtained, although in lower yield (ca. 30%) and with concomitant formation of [ReBr(NNPh)(CNMe)₂(PPh₃)₂] **7** (see below), by using [ReBr₂(NNPh)₂(PPh₃)₂] **2** or [ReBr₃(NNPh)(PPh₃)₂] **3** instead of **1**, under similar experimental conditions (Found: C, 52.8; H, 4.3; N, 3.9. Calc. for C₄₄H₃₈Br₂N₃P₂Re·Et₂O: C, 52.9; H, 4.4; N, 3.9%). IR (KBr pellet): 2170ms [ν(C≡N)], 1630s and 1560s cm⁻¹ [ν(NN)]. ¹H NMR (CDCl₃): δ 7.81–6.20 (m, 30 H, PPh₃), 6.97 [t, *J*(HH) = 7.3, 2 H, *m*-H of NNPh], 6.77 [t, *J*(HH) = 7.3, 1 H, *p*-H of NNPh], 6.49 [d, *J*(HH) = 7.3 Hz, 2 H, *o*-H of NNPh] and 3.14 (s, 3 H, CNCH₃). ³¹P-{¹H} NMR (CDCl₃): δ -150.93 (s).

[ReBr₂(NNPh)(CNC₆H₄Cl-4)(PPh₃)₂] 5. A suspension of [ReBr₂(NNPh)₂(PPh₃)₂]Br **1** (0.15 g, 0.13 mmol) in acetone (30 cm³) in the presence of CNC₆H₄Cl-4 (54 mg, 0.39 mmol) was stirred for 1 d. Concentration of the solution followed by addition of Et₂O resulted in the precipitation of **5** as a red solid. Further crops could be obtained from the mother-liquor upon concentration and addition of Et₂O. Recrystallization from CH₂Cl₂–Et₂O formed a red crystalline solid of **5** which was filtered off, washed with Et₂O and dried *in vacuo* (ca. 60% yield) (Found: C, 53.8; H, 3.6; N, 3.8. Calc. for C₄₉H₃₉Br₂ClN₃P₂Re: C, 52.9; H, 3.5; N, 3.8%). IR (KBr pellet): 2110ms [ν(C≡N)], 1650s and 1565s cm⁻¹ [ν(NN)]. ¹H NMR (CDCl₃): δ 7.51–6.94 (m, C₆H₅ and C₆H₄). ³¹P-{¹H} NMR (CDCl₃): δ -154.01 (s).

[ReBr₂(NNPh)(CNMe)₂(PPh₃)₂] 6. The compound CNMe (31 μl, 0.60 mmol) was added to a thf solution (60 cm³) of [ReBr₂(NNPh)(CNMe)(PPh₃)₂] **4** (0.20 g, 0.20 mmol) and the solution was stirred for 18 h. Filtration followed by concentration *in vacuo* and addition of pentane resulted in the precipitation of a green solid (complex **7**, see below, ca. 30% yield) which was filtered off and dried *in vacuo*. Concentration of the remaining filtered solution followed by addition of pentane led to the precipitation of **6** as an orange crystalline solid which was filtered off, washed with pentane and dried *in vacuo* (ca. 20% yield) (Found: C, 53.5; H, 3.9; N, 5.2. Calc. for C₂₈H₂₆Br₂N₃PRe: C, 53.9; H, 4.0; N, 5.5%). IR (KBr pellet): 2170ms [ν(C≡N)], 1645s and 1570m cm⁻¹ [ν(NN)]. ¹H NMR

(CDCl₃): δ 7.65–6.95 (m, 20 H, C₆H₅) and 3.56 (s, 6 H, CNCH₃). ³¹P-{¹H} NMR (CDCl₃): δ -136.34 (s).

[ReBr(NNPh)(CNMe)₂(PPh₃)₂] **7**. Although this complex could also be obtained (*ca.* 30% yield) in the above procedure for **6**, its direct synthesis from [ReBr₂(NNPh)₂(PPh₃)₂]**1** constitutes a better method, as follows. The compound CNMe (40 μ l, 0.78 mmol) was added to a suspension of **1** (0.15 g, 0.13 mmol) in thf or acetone (30 cm³) which was then stirred for 3 d. The green solid of **7** was filtered off, washed with thf (or acetone)-Et₂O and dried *in vacuo*. A further crop was obtained upon concentration of the mother-liquor and addition of pentane. Recrystallization from CH₂Cl₂-Et₂O gave **7** as a green microcrystalline solid which was filtered off, washed with Et₂O and dried *in vacuo* (*ca.* 40% yield) (Found: C, 53.1; H, 4.2; N, 4.6. Calc. for C₄₆H₄₁BrN₃P₂Re·CH₂Cl₂: C, 53.2; H, 4.1; N, 5.3%). IR (KBr pellet): 2220 cm⁻¹ [v(C≡N)], 1630s and 1560 cm⁻¹ [v(NN)]. FAB mass spectrum: *m/z* 977 (M⁺).

Crystallography

Crystal data. C₄₈H₄₀Br₂N₄P₂Re **2**, *M_r* = 1080.83, triclinic, *a* = 12.334(2), *b* = 12.146(2), *c* = 17.844(3) Å, α = 62.02(1), β = 91.99(1), γ = 71.55(1)°, *U* = 2185.1(7) Å³, *T* = 293 K, space group *P*1̄ (no. 2), *Z* = 2, *D_c* = 1.64 g cm⁻³, μ (Mo-K α) = 4.69 mm⁻¹, specimen 0.4 × 0.5 × 0.3 mm, 5987 reflections measured, 5581 unique (*R_{int}* = 0.0185), 5418 (*F*² > 0) which were used in all calculations. The final *wR*(*F*²) was 0.113, *R*1 = 0.042.

The unit cell and orientation matrix were obtained by least-squares refinement of 25 automatically centred reflections 14 < θ < 18°, in an Enraf-Nonius TURBO CAD4 diffractometer equipped with a rotating anode, using graphite-monochromated radiation. Three standard reflections were monitored during data collection (1.5 < θ < 25°), but no decay or instrumental instability was detected. Using the CAD4 software, data were corrected for Lorentz-polarization effects and empirically for absorption. 5418 Reflections were used in structure solution and refinement of 554 parameters. The position of the Re atom was obtained by a three-dimensional Patterson synthesis, and all the other non-hydrogen atoms were located in subsequent Fourier-difference maps and refined with anisotropic thermal motion parameters. The hydrogen atoms were inserted in calculated positions and refined isotropically with fixed distances to the parent carbon atom. The program SHELXS 86³³ was used in the structure solution and SHELXL 93³⁴ in the refinement of the crystal structure; the illustration was drawn with ORTEP II.³⁵ The atomic scattering factors and anomalous scattering terms were taken from ref. 36.

CCDC reference number 186/995.

See <http://www.rsc.org/suppdata/dt/1998/2405/> for crystallographic files in .cif format.

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