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# Synthesis and X-ray structure of $[ReBr_3(NNPh)(PPh_3)_2]$, a paramagnetic organodiazenido complex

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**Abstract**

The paramagnetic organodiazenido complex $[ReBr_3(NNPh)(PPh_3)_2]$ has been prepared from $[ReBr_2(NNPh)_2(PPh_3)_2]Br$, in THF or acetone, and its molecular structure has been authenticated by an X-ray analysis which indicates the singly bent geometry for the diazenido ligand with an unusual significant *trans* influence on the bromide ligand.

Organodiazenido compounds are recognized intermediates in the chemical reduction of dinitrogen complexes [1] and present a versatile coordination chemistry, in particular behaving formally as monoanionic ligands with singly or doubly bent geometry differing in the number of electrons donated in diamagnetic complexes [2]. However, paramagnetic complexes with organodiazenido ligands are almost unknown [3].

On attempting to extend to higher metal oxidation states our research on the activation, by electron-rich metal sites, of unsaturated nitrogen or carbon species with biological significance [4], we have embarked upon the synthesis and investigation of the reactivity of organodiazenido complexes of Re(V), in particular $[ReBr_2(NNPh)_2(PPh_3)_2]Br$ (**1**), and obtained a derived paramagnetic species, $[ReBr_3(NNPh)(PPh_3)_2]$ (**2**), which, to our knowledge, is the first paramagnetic organodiazenido complex to be structurally characterized using X-ray crystallography.

Complex **1** was obtained by the reaction with bromine of a $CH_2Cl_2$ solution of $[ReCl(NNPh)_2(PPh_3)_2]$. The latter was prepared by refluxing a methanol suspension of $[ReOCl_3(PPh_3)_2]$ with an excess of $PhNHNH_2$ and $PPh_3$ (thus adapting and improving a method taken from the literature [5] for related diazenido complexes).

It was isolated as a green solid with a strong and broad band in the IR spectrum (KBr pellet) at 1760 $cm^{-1}$ (with a shoulder at 1845 $cm^{-1}$), assigned mainly to $\nu$(NN) of the diazenido ligand; in the $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$), a singlet is observed at $\delta$ −148.37 ppm relative to $P(OMe)_3$.

Attempted reaction of **1** with CNMe in THF or acetone resulted in the formation (*c.* 85% yield) of **2** which is also obtained in high yields in the absence of the isocyanide.

Complex **2** was isolated as a green solid with $\nu$(NN) as a strong band at 1700 $cm^{-1}$. No NMR data collection was possible in view of the paramagnetism of the complex.

The molecular structure of complex **2** was authenticated by a single crystal X-ray diffraction analysis and is depicted in Fig. 1, whereas crystallographic data are summarized in Table 1. Data were collected on a Enraf-Nonius CAD4 diffractometer at 291 K. **2** crystallizes with one molecule of acetone, in the orthorhombic system, space group *Pbcn*, with $a = 20.564(2)$, $b = 19.093(3)$ and $c = 21.989(7)$ Å. The structure could

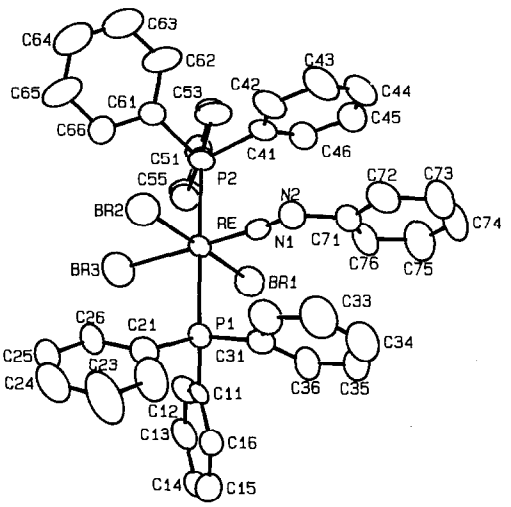


Fig. 1. The molecular structure of $[ReBr_3(NNPh)(PPh_3)_2]$. Selected bond lengths and angles: Re–N1, 1.79(1); N1–N2, 1.20(1); N2–C71, 1.43(2); Re–Br1, 2.492(2); Re–Br2, 2.479(2); Re–Br3, 2.564(2); Re–P1, 2.516(3); Re–P2, 2.513(3) Å; Re–N1–N2, 170(1); N1–N2–C71, 126(1); Br3–Re–N1, 178.5(3); Br1–Re–Br2, 177.49(6); P1–Re–P2, 178.4(1)°.

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TABLE 1. Crystal data and data collection parameters for $2 \cdot OC(CH_3)_2$

| | |
|---|---|
| Formula | $ReBr_3P_2ON_2C_{45}H_{41}$ |
| Formula weight | 1113.72 |
| Crystal system | orthorhombic |
| Space group | *Pbcn* |
| $a$ (Å) | 20.564(2) |
| $b$ (Å) | 19.093(3) |
| $c$ (Å) | 21.989(7) |
| $V$ (Å$^3$) | 8633 |
| $Z$ | 8 |
| $D_{calc}$ (g/cm$^3$) | 1.701 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 57.1 |
| Wavelength (Å) | 0.71073 |
| Crystal size (mm) | $0.4 \times 0.5 \times 0.3$ |
| No. reflections for lattice parameters | 25 |
| $\theta$ Range for lattice parameters (°) | $2 \leqslant \theta \leqslant 25$ |
| Temperature (K) | 291 |
| Diffractometer | Enraf-Nonius CAD 4 |
| Absorption correction | empirical |
| Collection method | $\omega$–$2\theta$ |
| Maximum $\theta$ (°) | 25 |
| No. reflections measured | 9915 |
| No. independent reflections | 7591 |
| No. observed reflections with $I \geqslant 1.5\sigma(I)$ | 5214 |
| No. parameters refined | 467 |
| No. reflections used in refinement | 5214 |
| $R$ | 0.058 |
| $R_w$ | 0.073 |
| $w$ | $(\sigma(F)^2 + 0.0004F^2 + 1)^{-1}$ |

be refined to $R = 0.058$. Its presents an octahedral type geometry with the two phosphines in *trans* positions and the four charged ligands in the equatorial sites. The phenyldiazenido ligand displays the singly bent geometry with Re–N–N and N–N–Ph angles of 170(1) and 126(1)°, respectively; the Re–N and the N–N bond lengths are 1.79(1) and 1.20(1) Å, respectively. These values are close to the limits of the usual ranges known [2, 6, 7] for this geometry.

A significant structural *trans* influence of the diazenide on the *trans* bromide ligand is evident, with a considerable lengthening of the corresponding Re–Br bond length (2.564(2) Å) relative to the *cis* Re–Br distances (2.492(2) and 2.479(2) Å). This contrasts with the commonly negligible *trans* influence of singly bent organodiazenides [2], and only one previous case has been reported for the thiolate-bridged species $[HNEt_3][Re_2(NNPh)_2(SPh)_7]$ [7]. Doubly bent diazenido ligands however frequently exert significant a *trans* influence as in $[IrCl_2(NNC_6H_4NO_2\text{-}2)(CO)(PPh_3)_2]$ [8].

Complex **2** reacts with dialkyldithiocarbamates or isocyanides, undergoing bromide or phosphine replacement, to give rhenium(III) products, such as $[ReBr(S_2CNMe_2)(NNPh)(PPh_3)_2]$ or $[ReBr_2(NNPh)(CNMe)_2(PPh_3)]$.

Further investigation of these reactions is under way, as well as of the formation of complex **2** from **1** which involves, *inter alia*, formal replacement of one diazenide by one bromide ligand, a noteworthy process in view of the still rather poor current knowledge of the substitution chemistry of diazenido ligands.

## Supplementary material

Tables of atomic coordinates, bond lengths, interbond angles, thermal parameters and structural factors are available from the authors on request.

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