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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 δ −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

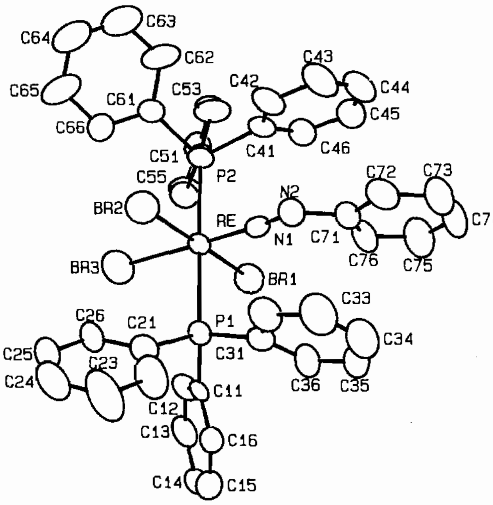

Fig. 1. The molecular structure of $[ReBr_3(NNPh)(PPh_3)_2]$. Selected bond lengths and angles: Re–N1, 1.79(1); N1–N2, 1.20(1); N2–C71, 1.43(2); Re–Br1, 2.492(2); Re–Br2, 2.479(2); Re–Br3, 2.564(2); Re–P1, 2.516(3); Re–P2, 2.513(3) Å; Re–N1–N2, 170(1); N1–N2–C71, 126(1); Br3–Re–N1, 178.5(3); Br1–Re–Br2, 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
μ(Mo Kα) (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
θ Range for lattice parameters (°)	$2 \leqslant \theta \leqslant 25$
Temperature (K)	291
Diffractometer	Enraf-Nonius CAD 4
Absorption correction	empirical
Collection method	ω–2θ
Maximum θ (°)	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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