The Synthesis and Structural Characterization of $[ReCl_2(PPh_3)_2(NNHCOPh)(NHNHCO-Ph)]\cdot\frac{1}{2}Et_2O$, a Complex exhibiting Linear Hydrazido(2−) Ligation and End-on Hydrazido(1−) Ligation

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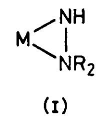
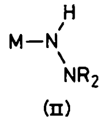
The title compound was prepared by treating $[ReCl_2(PPh_3)_2(NNCOPh)]$ with excess of benzoylhydrazine in methanol solution: *X*-ray crystallography reveals a unique example of monohapto-co-ordination by a hydrazido(1−) grouping, -NHNHR, and an unusual instance of mixed hydrazido(2−) and hydrazido(1−) co-ordination to a metal site.

Hydrazido(1−) complexes are of considerable interest as possible intermediates in the chemistry of co-ordinated dinitrogen. The relatively few structurally characterized cases of hydrazido(1−) complexes reveal that the side-on configuration (I) is adopted[1] unless steric features intervene to produce the end-on geometry, (II) or (III).[2] In an effort to elucidate the course of the protic degradation of co-ordinated nitrogenous ligands, we have been investigating the protonation of metal–diazenido complexes as precursors to co-ordinated hydrazido(2−) and hydrazido(1−) units.



(I)



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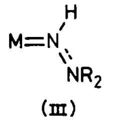
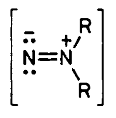
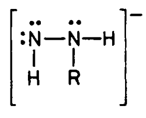


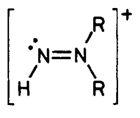
(III)



(A)



(B)



(C)

The complex $[ReCl_2(PPh_3)_2(NNCOPh)]$ (**1**) exhibits six-co-ordinate geometry as a consequence of chelate ring formation *via* the nitrogen and carbonyl oxygen of the benzoyldiazenido ligand. The rhenium–oxygen bond is relatively weak, and reaction with a variety of ligands yields benzoylazo-rhenium compounds of the type $[ReCl_2(PPh_3)_2(NNCOPh)L]$, where L has displaced the oxygen donor.[3] Hence, complex (**1**) provides a useful synthetic precursor both for ligand substitution reactions and for protonation studies. Reaction of (**1**) with excess of benzoylhydrazine in methanol solution yields grey-green crystals analysing as $[ReCl_2(PPh_3)_2(NNHCOPh)(NHNHCOPh)]$ (**2**). The i.r. spectrum of (**2**) shows bands in the 3150—3230 and 1540—1600 cm^{-1} regions characteristic of ν(NH) and ν(NN), respectively. Since ^{1}H n.m.r. spectroscopy failed to confirm the location or number of nitrogen-bound protons, an *X*-ray crystallographic study was undertaken.

$[ReCl_2(PPh_3)_2(NNCOPh)]$
(**1**)

$[ReCl_2(PPh_3)_2(NNHCOPh)(NHNHCOPh)]$
(**2**)

Crystal data: $C_{50}H_{43}Cl_2N_4O_2P_2Re\cdot\frac{1}{2}(CH_3CH_2)_2O$, M = 1087.2, triclinic space group $P\bar{1}$, a = 12.276(2), b = 14.147(2), c = 15.284(2) Å, α = 86.33(1), β = 72.04(1), γ = 83.10(1)°, U = 2405.7(12) Å^3, Z = 2, D_c = 1.44 g/cm^3; 4995 reflections were used of 6874 collected (Mo-K_α radiation, final R value 4.3%, error of fit 1.20). The structure is shown in Figure 1, together with relevant bond lengths and angles.†

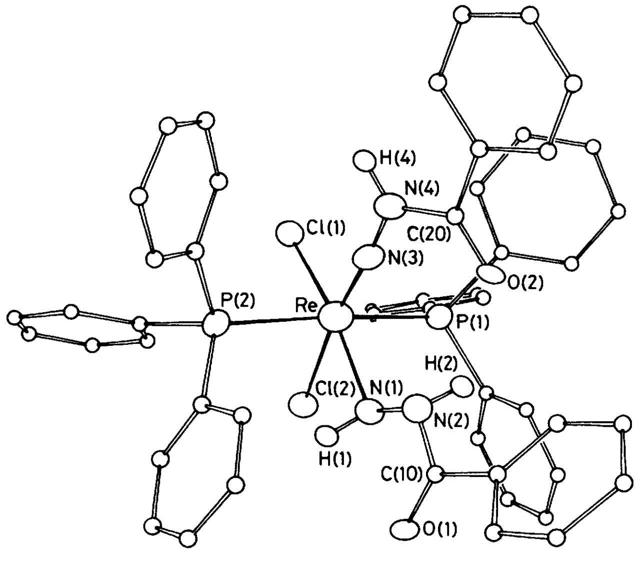


Figure 1. ORTEP representation of $[ReCl_2(PPh_3)_2(NNHCOPh)(NHNHCOPh)]$ (**2**) showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Re–P(1), 2.479(2); Re–P(2), 2.470(2); Re–Cl(1), 2.416(3); Re–Cl(2), 2.427(2); Re–N(1), 2.211(8); Re–N(3), 1.728(7); N(1)–N(2), 1.44(1); N(3)–N(4), 1.27(1); P(1)–Re–P(2), 172.8(1); P(1)–Re–Cl(1), 88.5(1); P(1)–Re–Cl(2), 89.5(1); P(1)–Re–N(1), 89.4(2); P(1)–Re–N(3), 93.2(2); P(2)–Re–Cl(1), 89.6(1); P(2)–Re–Cl(2), 83.8(1); P(2)–Re–N(1), 91.3(2); P(2)–Re–N(3), 93.8(2); Cl(1)–Re–Cl(2), 94.4(1); Cl(1)–Re–N(1), 169.5(2); Cl(1)–Re–N(3), 93.7(3); Cl(2)–Re–N(1), 75.2(2); Cl(2)–Re–N(3), 171.5(2); N(1)–Re–N(3), 96.7(3); Re–N(1)–N(2), 119.7(5); N(1)–N(2)–C(10) 116.1(7); Re–N(3)–N(4), 174.7(7); N(3)–N(4)–C(20), 119.47(7).

The rhenium exhibits pseudo-octahedral co-ordination geometry, with the mutually *trans*-phosphine groups minimizing steric congestion and with the chlorine ligands disposed *trans* to the nitrogen donors of the hydrazido(1−) and hydrazido(2−) units, N(1) and N(3), respectively. The Re–P and Re–Cl distances are unexceptional. The Re–hydrazido(2−) unit, Re–N(3)–N4(H)(COPh), assumes the linear, end-on geometry most commonly encountered for this grouping. The short Re–N(3) and N(3)–N(4) distances are consistent with extensive multiple-bonding throughout the Re–N(3)–N(4) moiety.

In contrast, the Re–N(1) bond length of 2.211(8) Å suggests a rhenium–nitrogen single bond. Furthermore, the N(1)–N(2) distance, 1.44(1) Å, is normal for a nitrogen–nitrogen single

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table 1. Comparison of structural features of co-ordinated isodiazene and hydrazido(1−) units.[a]

Complex	Nitrogenous unit	*r*(M–N)/Å	*r*(N–N)/Å	<(M–N–N)/°	Ref.
$[ReBr_2(NNPh)(NNHPh)(PPh_3)_2]$	–NNHPh, isodiazene	1.922(11)	1.287(15)	131.2(10)	4
$[(cp)_2WH(NNHC_6H_4F\text{-}p)]^+$	–NNHR, isodiazene	1.837(7)	1.315(9)	146.4(5)	5
$[Mo\{HB(Me_2pz)_3\}(NO)(NHNMe_2)]$	$-NHNR_2$, hydrazido(1−)	1.98(2)	1.34(3)	140.3(15)	2
$[ReCl_2(NNHCOPh)(NHNHCOPh)(PPh_3)_2]$, (**2**)	–NHNHR, hydrazido(1−)	2.211(8)	1.44(1)	116.1(7)	This work

[a] cp = cyclopentadienyl; Me_2pz = 3,5-dimethylpyrazol-1-yl.

bond. This evidence, together with the valence angle at N(1) and the appearance of two peaks on the final electron density map attributable to H(N1) and H(N2), confirms that this unit indeed functions as a hydrazido(1−) moiety, –NHNHR. It is instructive to compare the structural parameters of this unit with those reported for bent isodiazene ligands, $-NNR_2$,[4,5] and with the geometry of the only other structurally confirmed instance of an end-on hydrazido(1−) fragment,[7] as illustrated in Table 1. The bent isodiazene unit functions as a two-electron donor, consistent with valence structure (A), whereas the hydrazido(1−) ligand of (**2**), also formally a two-electron donor, is best described by structure (B). In contrast, the structural parameters reported for the $-NHNR_2$ unit of $[Mo\{HB(Me_2pz)_3\}(NO)I(NHNR_2)]$ are suggestive of a formalism based upon a protonated form of the isodiazene structure, as illustrated by structure (C). The –NHNHR moiety of (**2**) represents a unique instance of the hydrazido(1−) limit, structure (B), with structural parameters consistent with sp^3 hybridization at N(1) and N(2), whereas the $-NHNR_2$ unit of the pyrazolylborato-complex is best described by (C), a structural type more closely related to the isodiazenes and retaining sp^2 hybridization at the nitrogen atom (see also ref. 6).

Complex (**2**) exhibits chemistry consistent with the structural assignment. Protonation releases benzoylhydrazine, $H_2NNHCOPh$, whereas treatment with Bu_3N in MeOH appears to deprotonate the complex to give $[Bu_3NH][ReCl_2(NNHPh)_2(PPh_3)_2]$, presumably a mixed hydrazido(2−) isodiazene species.

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