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Preliminary communication

THE STEREOCHEMISTRY OF *N*-METHYLHYDRAZIDO(2–)-*N*′ LIGANDS COORDINATED TO GROUP VIa METALS. THE STRUCTURAL CHARACTERISATION OF THE BIS(1, 2-BIS(DIPHENYLPHOSPHINO)ETHANE)-BROMO-*N*-METHYLHYDRAZIDO(2–)-*N*′-TUNGSTEN(IV) AND *N*-ETHYL-*N*-PHENYLHYDRAZIDO(2—)-*N*′-TRIS-(*N,N*-PENTAMETHYLENEDITHIOCARBAMATO)MOLYBDENUM(VI) CATIONS

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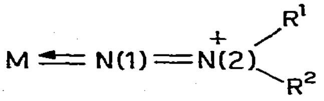
Summary

The structure analyses of two substituted hydrazido(2–) complexes has revealed the detailed stereochemistry of the uncoordinated nitrogen atom; the ligand electron density in several rhenium, tungsten and molybdenum complexes is commented upon in the light of the results.

The study of diazo ligands coordinated to Group VIa and VIIa metals is of interest because their stereochemistry and reactivity may provide some insight into the mechanism of metal-catalysed reduction of dinitrogen. The structure of a phenyldiazenato complex of Re^{III} [1] and a protonated (hydrazido(2—)) derivative [2] indicate that the latter is best represented by I (R^1 = H, R^2 = phenyl), whereas the N_2H_2 ligand in the W^{IV} complex cation [WCl(N—NH_2)(diphos)$_2$]$^+$[**] has a significantly longer N—N bond [3] (Table 1) and the formulation II ($R^1 = R^2$ = H) was, therefore, thought closer. Much clarification of this point could, as we suggested earlier, become available from a characterisation of the planar-pyramidal character of N(2) and this we can now examine.



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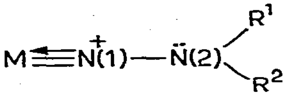

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[**] diphos = 1,2-bis(diphenylphosphino)ethane.

TABLE 1

COMPARISON OF IMPORTANT BOND LENGTHS AND ANGLES IN SOME DIAZENATO AND HYDRAZIDO(2–) COMPLEXES

Compound	M—N(1) (Å)	N(1)—N(2) (Å)	M—N(1)—N(2) (°)
$[ReCl_2(N_2Ph)(PMe_2Ph)_3]$ [1]	1.77(2)	1.23(2)	173(2)
$[ReCl_2(N_2COPh)(PMe_2Ph)_3]$ [1]	1.74(2)	1.22(3)	170(2)
$[ReCl_2(NH_3)(N_2HPh)(PMe_2Ph)_2]^+$	1.75(1)	1.28(2)	172(1)
$[WCl(N_2H_2)(diphos)_2]^+$ [2]	1.73(1)	1.37(2)	171(1)
$[WBr(N_2HCH_3)(diphos)_2]^+$	1.768(14)	1.32(2)	174(1)
$[Mo(N_2EtPh)\{S_2CN(CH_2)_5\}_3]^+$	1.715(16)	1.37(2)	170(2)

Crystals of $[WBr(N—NHCH_3)(diphos)_2]^+Br^-$ are monoclinic with $a = 13.463(2)$ $b = 21.090(3)$, $c = 18.933(3)$ Å, β 93.93(1)°, space group $P2_1/c$, $Z = 4$. The structure was solved by conventional heavy atom techniques using 4001 diffractometer determined intensities (Mo-K_α radiation, $I_0 \geqslant 3\sigma(I_0)$). The structure has been refined by full matrix least squares methods to give a conventional $R = 0.062$, the W, Br, P and Cl atoms being allowed anisotropic thermal motions. A general view of the cation is given in Fig. 1.

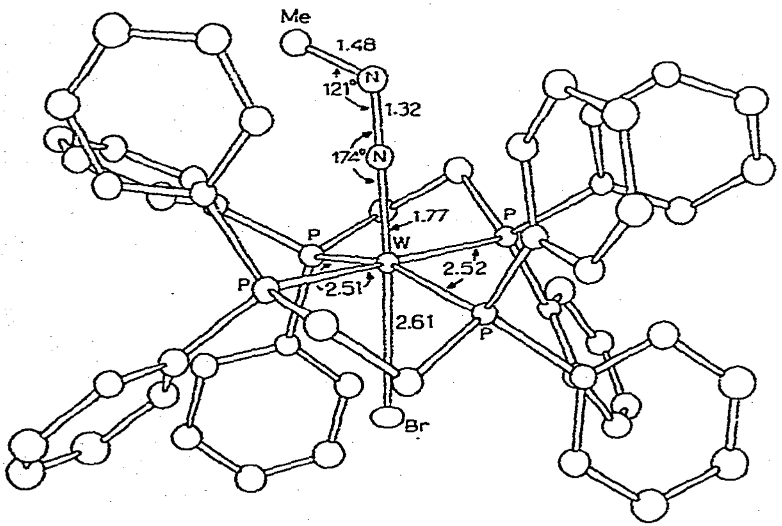

Fig. 1. Structure and important bond lengths and angles in $[WBr(N—NHCH_3)(diphos)_2]^+$.

The metal has a distorted octahedral configuration; distances and angles around the metal ion are in sensible agreement with those found for $[WCl(N—NH_2)(diphos)_2]^+$ [3] and intra-ligand parameters are summarised in Table 1 and Fig.1.

Crystals of $[Mo\{S_2CN(CH_2)_5\}_3\{N—NEt(phenyl)\}]^+ BPh_4^-$ [4] are monoclinic, $a = 15.467(2)$, $b = 13.131(2)$, $c = 12.895(2)$ Å, β 103.55(5)°, space group $P2_1$, $Z = 2$. The conditions for data collection and structure solution were identical to those outlined above. The structure has been refined using 1946 observed reflexions to give $R = 0.063$ with the Mo, S, N and ethyl-carbon atoms assigned anisotropic thermal motions. The cation is represented in Fig. 2, the coordination around the metal being a distorted pentagonal bipyramid with the main distortional feature reflecting, obviously, the S(21)—Mo—S(22) bite angle.

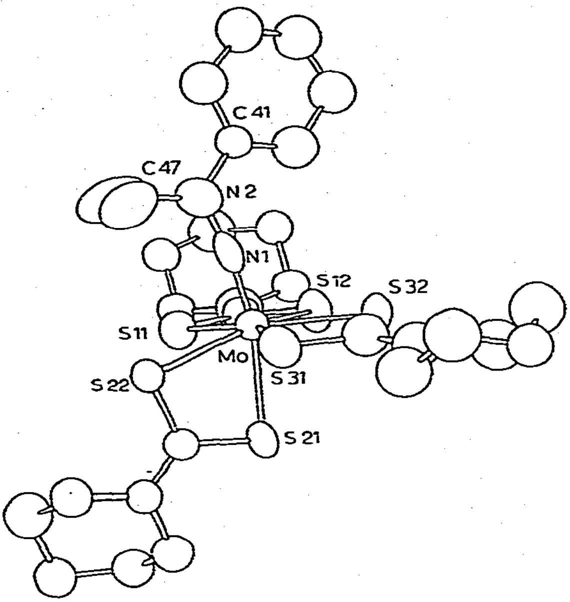

Fig. 2. Structure of $[\mathrm{Mo}\{S_2CN(CH_2)_5\}_3\{N{-}NEt(phenyl)\}]^+$. N(1)—N(2) = 1.37, Mo—N(1) = 1.72, Mo—S(11) = 2.50, Mo—S(12) = 2.50, Mo—S(21) = 2.55, Mo—S(22) = 2.48, Mo—S(31) = 2.51, Mo—S(32) = 2.50 Å, angle N(1)N(2)C(41) 118°, angle N(1)N(2)C(47) 116°, angle C(41)N(2)C(47) 123°.

Variation of the substituents on the coordinated hydrazido(2−) ligands has little effect on the M—N bond lengths but a trend can be discerned in which a decrease in the metal—nitrogen bond length provides, as expected, for a lengthening of the N(1)—N(2) bond. The M—N and N—N distances in the W(N—NH_2) and Mo(N—NEtPh) moieties are very similar despite the change in metal, and its formal oxidation state and coordination number, but apparently different from those in the W(N—$NHCH_3$) fragment; we do not, however, place high significance on this result.

The geometry of N(2) is revealed unambiguously in the molybdenum complex and is significantly non-planar, N(2) being displaced 0.16 Å from the plane formed by the atoms N(1), C(41) and C(47). This result parallels the longer N—N bond length found in this and in the W^{IV} complexes and contrasts with its planarity in the rhenium complexes. There is a smooth transition between the two valence forms, I and II, in a way which relates obviously to the metal electron density and the Lewis basicities of the remaining ligands in the coordination sphere.

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