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Preliminary communication

ORGANIC AZO COMPLEXES OF MOLYBDENUM AND THEIR REACTIONS WITH ELECTROPHILES

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Summary

Organic azo(1—) and *N,N*-disubstituted hydrazido-*N*′(2—) complexes of molybdenum have been prepared by the reactions of certain molybdenum-oxo complexes with hydrazines.

The majority of transition metal azo complexes have been obtained by the reaction of diazonium salts with transition metal complexes. However, a few rhenium [1] and tungsten [2] azo complexes have been derived from organic hydrazines, and alkyltriazenes have been used to prepare platinum and rhodium phenylazo complexes [3]. The study of multiply-bonded nitrogen systems attached to molybdenum may throw some light on the mechanism of reduction of dinitrogen in nitrogenase, and we have prepared a number of new organic azo and related complexes of molybdenum for this purpose.

Generally oxygen is not completely removed from molybdenum by hydrazines to form complexes of simple nitrogen ligands, however we find that the complexes $[MoO_2(S_2CNR_2)_2]$ (R = CH_3, Et, Ph etc.) in refluxing methanol, with phenylhydrazine and NaS_2CNR_2 give an 80% yield of the brown air-stable crystalline phenylazo complexes $[Ph{-}N{=}N{-}Mo(S_2CNR_2)_3]$. The same products are isolated, but in lower yield, without additional dithiocarbamate. Methylazo and benzoylazo complexes are obtained analogously. However the oxine complex $[MoO_2(C_9H_6NO)_2]$ and phenylhydrazine gives the bis(phenylazo) complex $[Mo(N_2Ph)_2(C_9H_6NO)_2]$ as an air-stable crystalline complex.

1,1-Dimethylhydrazine reacts with MoO_2L_2 (L = oxime or dithiocarbamate) to give the *N,N*-dimethylhydrazido-*N*′(2—)oxo complexes $[MoO(NNMe_2)L_2]$, which have $\nu(Mo{=}O)$ at about 890 cm^{-1}.

The ^1H NMR spectra of the dimethyldithiocarbamato-azo complexes in nitrobenzene at room temperature show a pair of doublets in integrated ratio 2/1.

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This suggests that they have the same pentagonal bipyramidal structure in solution as the related nitrosyls $[Mo(NO)(S_2CNR_2)_3]$ [4] and that the azo ligands are linear. The azo complexes $[R'{-}N{=}N{-}Mo(S_2CNR_2)_3]$ ($R' = Me$ or Ph) react with alkylating reagents (MeI, $[Et_3O][BF_4]$ etc. to give the cationic complexes $[Mo(N_2R'R'')(S_2CNR_2)_3]^+$ ($R' = R'' =$ alkyl*). The ^1H NMR spectrum of the complex with $R' = R'' = Me$ shows that the methyl groups of the hydrazido-ligand are equivalent and therefore both are on the terminal nitrogen atom.

The methyl- and phenylazo complexes react with hydrogen chloride to give the non-electrolytes, $[MoCl(N_2HR')(S_2CNR_2)_3]$, whereas fluoroboric acid gives salts $[Mo(N_2HR')(S_2CNR_2)_3]^+BF_4^-$.

In the latter the N_2HR' ligands probably have a linear metal—N—N system with a short metal—nitrogen bond as found in the isoelectronic complex $[WCl(N_2H_2)(dpe)_2]^+$ (dpe = $Ph_2CH_2CH_2PPh_2$) [5]. Thus the metal would achieve an 18-electron configuration with the hydrazido ligand providing 4 electrons for bonding to the metal i.e., ($Mo\overset{\leftarrow}{=}N{-}NHR$). However in the eight coordinate complexes the $Mo{-}N{=}N$ system is unlikely to be linear as this would involve the formation of a 19-electron complex. The alternative 18-electron forms (A) and (B) involving protonation at the different nitrogen atoms would both be bent at the nitrogen adjacent to the metal. Since we have been unable to detect the ^1H NMR resonance of the N-proton, we have been unable to assign its position, but the two forms (A) and (B) are probably tautomeric.

$$[MoCl(\leftarrow NH{=}NR')(S_2CNR_2)_3] \qquad [MoCl({=}N{-}NHR')(S_2CNR_2)_3]$$

(A) (B)

The benzoylazo complexes are not alkylated or protonated analogously. They react with dry hydrogen chloride to evolve dinitrogen and form $[MoCl(S_2CNR_2)_3]$, isolated as somewhat air-sensitive greenish-yellow crystalline solids. The chloride ligand is readily replaced by the 1- or 3-electron ligands. Thus lithium bromide and sodium thiocyanate give $[MoX(S_2CNR_2)_3]$ (X = Br or NCS) and azides and sodium nitrite yield the derivatives with X = N or NO respectively.

References

1 V.F. Duckworth, P.G. Douglas, R. Mason and B.L. Shaw, Chem. Commun., (1970) 1083.
2 M.L.H. Green, J.R. Sanders and R.N. Whiteley, Z. Naturforsch. B, 23 (1968) 106.
3 K.R. Laing, S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton, (1973) 2713 and ref. therein.
4 B.F.G. Johnson, K.H. Al-Obaidi and J.A. McCleverty, J. Chem. Soc. A, (1969) 1668.
5 G.A. Heath, R. Mason and K.M. Thomas, J. Amer. Chem. Soc., 96 (1974) 259.
6 F. March and R. Mason, personal communication.

**Note added in proof.* An X-ray structure determination of $[Mo(N_2PhEt)(S_2CN(CH_2)_5)_3]BPh_4$ has confirmed that alkylation occurs on the terminal nitrogen atom [6].