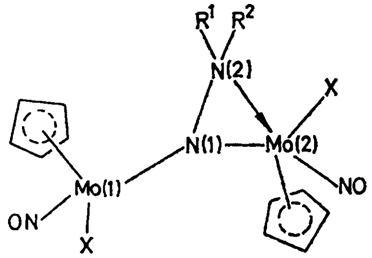
Molybdenum Nitrosyl Complexes Containing Bridging Hydrazido-groups: *X*-Ray Analysis of the Structure of $\{(\pi\text{-}C_5H_5)Mo(NO)I\}_2(\mu\text{-}NNMe_2)$.

By W. GEORGE KITA, JON A. MCCLEVERTY,* BRIAN E. MANN, and DUNCAN SEDDON
(*University of Sheffield, Sheffield* S3 7HF)
and GEORGE A. SIM* and DAVID I. WOODHOUSE
(*University of Glasgow, Glasgow* G12 8QQ)

Summary $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ reacted with $R^1R^2NNH_2$ ($R^1 = R^2 = Me$; X = Cl, Br, or I; $R^1 = H$, $R^2 = Ph$, X = Cl or Br; $R^1 = Me$, $R^2 = Ph$, X = Cl or Br) giving $[\{(\pi\text{-}C_5H_5)Mo(NO)X\}_2NNR^1R^2]$ (A) and an *X*-ray cystallographic analysis showed that when, for (A), X = I, $R^1 = R^2 = Me$, the molecule contained an asymmetric hydrazide group bridging two $\{(\pi\text{-}C_5H_5)Mo(NO)I\}$ units; Mo(1) is bound to the terminal N atom and Mo(2) to both N atoms of the hydrazido ligand; the symmetrically bridged hydrazide $[(\pi\text{-}C_5H_5)Mo(NO)I(NNHPh)]_2$ (B) was also prepared.

THE dimers $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ (X = Cl, Br or I) react with Lewis bases ($L = PR_3$, AsR_3, CNR, pyridine, *etc.*) giving monomeric adducts $[(\pi\text{-}C_5H_5)Mo(NO)X_2L]$ and $[(\pi\text{-}C_5H_5)Mo(NO)XL_2]^+$.[1] When the dimers are treated with hydrazines, $R^1R^2NNH_2$ ($R^1 = R^2 = Me$, Et; $R^1 = Me$, $R^2 = Ph$; X = Cl, Br, or I), however, the novel hydrazide complexes $[\{(\pi\text{-}C_5H_5)Mo(NO)X\}_2(N_2R^1R^2)]$ (A) are produced.



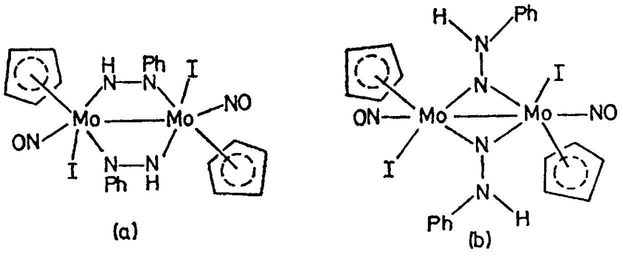
(A)

Mo(1)–N(1) 1·920(13), Mo(2)–N(1) 2·054(12), Mo(2)–N(2) 2·133(12), Mo(1)–NO 1·765(12), Mo(1)–I 2·733(2), Mo(2)–NO 1·763(12), Mo(2)–I 2·767(2), N(1)–N(2) 1·400(17) Å. ∠Mo(1)–N(1)–N(2) 135(0·9)°, Mo(2)–N(1)–N(2) 74(0·7)°, Mo(1)–N(1)–Mo(2) 151(0·7)°.

The ^1H and ^{13}C n.m.r. spectra indicated that when $R^1 = R^2$, the hydrazido-substituents, and the $\pi\text{-}C_5H_5$ rings, are inequivalent; there was no n.m.r. or i.r. spectroscopic evidence for NH groups.

The detailed molecular structure of complex (A; $R^1 = R^2 = Me$; X = I) was elucidated by single-crystal *X*-ray diffraction. The dimensions of the monoclinic cell are $a = 14{\cdot}673(2)$, $b = 7{\cdot}732(1)$, $c = 16{\cdot}867(2)$ Å, $\beta = 102°\ 18(1)'$, the space group is $P2_1/c$, and $Z = 4$. The *X*-ray intensities were obtained on a four-circle diffractometer with Mo-K_α radiation, and the atomic co-ordinates derived by Fourier and least-squares calculations. The analysis is currently at $R = 0{\cdot}069$ over 3837 reflections.

The molecule contains a unique asymmetric bridging hydrazido-ligand. There are two possible descriptions of the bonding: (i) that Mo(1) has a 16-electron configuration, being σ-bonded to N(1), and that Mo(2) has an 18-electron configuration, or (ii) that Mo(1) is σ-bonded to N(1), and that N(1) also contributes its 'lone pair' or 'p_z' electrons to Mo(1) in a π-donor ($p_\pi \rightarrow d_\pi$) bond, thereby giving Mo(1) an 18-electron count, while Mo(2) is σ-bonded to N(1) and receives a σ-lone pair from N(2). We favour the latter description since the Mo(1)–N(1) bond length is substantially shorter than either Mo(2)–N(1), or Mo(2)–N(2); further, the atoms Mo(1)N(1)N(2)Mo(2) are essentially coplanar. It seems likely that the other complexes (A) have a structure like (A; $R^1 = R^2 = Me$; X = I).



(a) (b)

Proposed structures for (B)

Reaction of $(C_5H_5)_2Mo(NO)I$ with Me_2NNH_2 gives two compounds, the orange-red (A; $R^1 = R^2 = Me$; X = I) and an orange-yellow species $[(\pi\text{-}C_5H_5)Mo(NO)I(NHNMe_2)]$. The latter is a σ-hydrazide, and is monomeric in chloroform, but decomposes on heating (60° in $CHCl_3$ or 80° *in vacuo*, releasing, *inter alia* Me_2NNH_2) to give (A; $R^1 = R^2 = Me$; $X = I$).

Treatment of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ (X = Cl or Br) with $PhNHNH_2$ afforded $[\{(\pi\text{-}C_5H_5)Mo(NO)X\}_2NNHPh]$, probably analogous to (A; $R^1 = R^2 = Me$; $X = I$). The ^1H n.m.r. spectra of these compounds clearly showed τ_{NH} [absent in D_2O–$(CD_3)_2SO$], and ν_{NH} was observed in the i.r. spectra. However, reaction of $[(\pi\text{-}C_5H_5)Mo(NO)I_2]_2$ with $PhNHNH_2$ gave, initially, the Lewis base adduct $[(\pi\text{-}C_5H_5)Mo(NO)I_2(NH_2NHPh)]$ and then $[(\pi\text{-}C_5H_5)Mo(NO)I(N_2HPh)]_2$, (B) [also obtained from $(C_5H_5)_2Mo(NO)I$ and phenylhydrazine]. The compound (B) differs from (A; $R^1 = R^2 = Ph$; X = Cl or Br) in that it contains two hydrazide groups per $\{(\pi\text{-}C_5H_5)Mo(NO)X\}_2$ group, and the ^{13}C n.m.r. spectral data obtained from the phenyl groups of (A) and (B) show that these phenyl groups are in different environments in the two species. Thus δ_C (125—127 p.p.m.)† for the *para*-C atom of the phenyl groups in (A) is consistent with co-ordination of the terminal N atom, whereas δ_C (121·1 p.p.m.) for the *para*-C atom in (B) is closer to that of the free amines and hydrazines ($PhNHNH_2$, 119·2 p.p.m.) Accordingly, we propose that, of the two feasible structures for (B) (a) or (b), (b) is the more acceptable, and some support may be gained for this suggestion from the protonation of (B) in HBF_4–CH_2Cl_2 which affords $[(\pi\text{-}C_5H_5)Mo(NO)I(N_2H_2Ph)]_2[BF_4]_4$. Protonation would occur at the uncomplexed N atom in (b) much more readily than in (a).

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† Chemical shifts ± 0·2 p.p.m., at 22·62 MHz with reference to internal Me_4Si in $(CH_3)_2SO$ containing 10% $(CD_3)_2CO$ to provide ^2H lock signal.

[1] T. A. James and J. A. McCleverty, *J. Chem. Soc.* (*A*), 1971, 1596; J. A. McCleverty and D. Seddon, *J.C.S. Dalton*, 1972, 2526; R. B. King, *Inorg. Chem.*, 1967, 6, 30.