A Molybdenum Nitrosyl Complex containing a Dihapto Phenylhydrazine Ligand: X-Ray Analysis of the Structure of $[(\eta^5\text{-}C_5H_5)Mo(NO)I(NH_2NHPh)][BF_4]$

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Summary Protonation of $[(\eta^5\text{-}C_5H_5)Mo(NO)I(N_2H_xPh)]_n$ with HBF_4 afforded $[(\eta^5\text{-}C_5H_5)Mo(NO)I(NH_2NHPh)][BF_4]$, and an X-ray crystallographic analysis of the salt showed that the compound contained $PhNHNH_2$ (H fully refined) bidentate with respect to the Mo atom; the neutral precursor was reformulated with $x = 2$.

IN a previous communication it was reported[1] that $PhNHNH_2$ reacted with $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$ giving the adduct $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2(NH_2NHPh)]$ and an apparently binuclear hydrazide ($-$2H) species $[(\eta^5\text{-}C_5H_5)Mo(NO)I(NNHPh)]_2$ (I). During further studies of this system we obtained another hydrazide, $[\{(\eta^5\text{-}C_5H_5)Mo(NO)I\}_2NNHPh]$, which is clearly analogous to $[\{(\eta^5\text{-}C_5H_5)Mo(NO)I\}_2NNMe_2]$, the structure of which is known (Figure 1)[1].

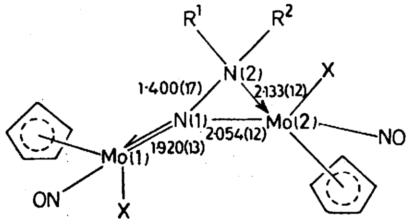


FIGURE 1. Structure of $[\{(\eta^5\text{-}C_5H_5)Mo(NO)I\}_2NNHPh]$ (from ref. 1; distances in Å).

We were unable to obtain crystals of (I) suitable for X-ray analysis and were therefore unable to confirm the proposed structure [ref. 1, Figure B (b)]. We observed, however, that the compound could be protonated in HBF_4–CH_2Cl_2 thereby affording a crystalline salt (II). Believing initially that this compound might be $[(\eta^5\text{-}C_5H_5)Mo(NO)I(N_2H_2Ph)]_2[BF_4]_2$, we carried out a full X-ray structural analysis hoping to use the result to deduce the nature of the precursor (I).

Crystals of (II), from ethanol, were triclinic, $a = 10{\cdot}737(5)$, $b = 10{\cdot}818(5)$, $c = 7{\cdot}451(2)$ Å, $\alpha = 85{\cdot}014(4)$, $\beta = 110{\cdot}272(13)$, $\gamma = 100{\cdot}581(6)°$, $U = 797{\cdot}8(6)$ Å^3, $D_m = 2{\cdot}125$ g ml^{-1}, $M = 513$, $Z = 2$ ($M = 1024$, $Z = 1$ for the postulated structure); space group $P\bar{1}$ (assumed and proved). The X-ray intensities were obtained using a STOE STADI-2 diffractometer with graphite-monochromated Mo-K_α radiation. The structure was solved by Patterson and Fourier techniques and refined using block-diagonal least-squares to $R = 0{\cdot}029$ for 3100 reflections.

The molecule (II) (Figure 2) is a monomer, having a planar η^5-C_5H_5 ring, an almost linear Mo–N–O bond system, and a terminal iodine atom. Most significantly, it contains a phenylhydrazine group in which *both* nitrogen atoms are bonded to the molybdenum and appear to be essentially sp^3 hybridised. This structure appears to be the first in which the presence of a hydrazine ligand bidentate with respect to one metal atom has been confirmed. Whilst all 13 H atoms in the molecule were located and included in the structure-factor calculation, the positions of the three hydrogen atoms attached to the N atoms were allowed to refine. The conformation about the N–N bond is eclipsed, the dihedral angle defined by the planes C(1)–N(1)–N(2)–H(3) and H(1)–N(1)–N(2)–H(2) being 127°. The N(1)–N(2) bond length is 1·430(5) Å which is consistent with a bond order of unity; it is comparable to that found in the cation of $[N_2H_5][N_3]$,[2] but is somewhat longer than the N(1)–N(2) distance in $[\{(\eta^5\text{-}C_5H_5)Mo(NO)I\}_2NNMe_2]$ and is significantly longer than the value of 1·235(10) Å found[3] in $[Pt(PEt_3)_2(HN\text{:}NC_6H_4F)Cl][ClO_4]$. The Mo–N distances are comparable with that of the formal single bond between Mo(2) and N(2) in Figure 1. Hydrogen bonding occurs between the BF_4^- anion and the hydrogen atoms of the hydrazine, giving rise to weak polymerisation parallel to the *z*-axis.

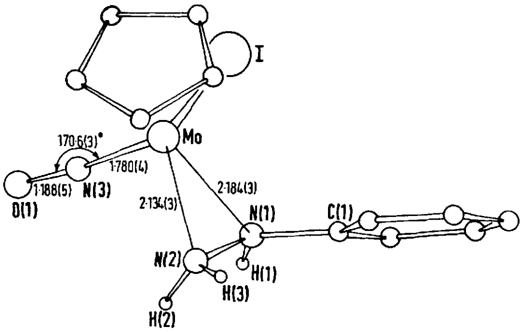
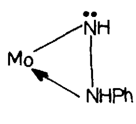
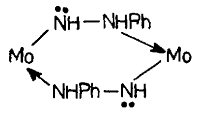


FIGURE 2. Structure of compound (II); distances in Å.

The solution of the structure of (II) raised doubts about the formulation of (I) as containing $\{NNHPh\}^{2-}$. Accordingly a detailed ^1H Fourier transform n.m.r. spectral examination revealed that (I) contained two protons bound to different N atoms (one resonance is broad). Thus (I) must be reformulated as $[(\eta^5\text{-}C_5H_5)Mo(NO)I(NHNHPh)]_n$, thereby making it formally similar to $[(\eta^5\text{-}C_5H_5)Mo(NO)I(NHNMe_2)]$.[1] In view of the insolubility and apparent thermal instability (decomposition to $[\{(\eta^5\text{-}C_5H_5)Mo(NO)I\}_2\text{-}NNHPh]$) of (I), the value of *n* cannot be directly determined. However, in view of its protonation to give (II) (in *ca.* 20% yield), (I) might contain the groups (A) or (B); neither arrangement would be inconsistent with the other properties of the compound or with the ^{13}C n.m.r. spectral data reported earlier.[1]



(A)



(B)

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