Dithiocarbamato Derivatives of Allyl Molybdenum Nitrosyls

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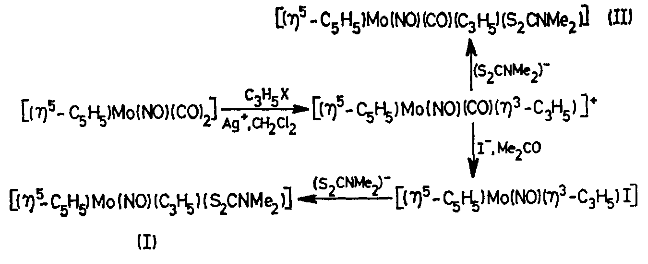
Summary $[(\eta^5\text{-}C_5H_5)Mo(NO)(CO)_2]$ treated with C_3H_5Br–$AgPF_6$ gave $[(\eta^5\text{-}C_5H_5)Mo(NO)(CO)(\eta^3\text{-}C_3H_5)][PF_6]$ which then gave with I^-, BH_4^-, and $(S_2CNMe_2)^-$, $[(\eta^5\text{-}C_5H_5)Mo(NO)(\eta^3\text{-}C_3H_5)I]$, $[(\eta^5\text{-}C_5H_5)Mo(NO)(CO)(H_2C:CHMe)]$ and $[(\eta^5\text{-}C_5H_5)Mo(NO)(CO)\text{-}\{\eta^2\text{-}H_2C:CHCH_2SC(:S)NMe_2\}]$ respectively; the structures of the latter and of $[(\eta^5\text{-}C_5H_5)Mo(NO)(H_2CCH:CH_2)(\eta^2\text{-}S_2CNMe_2)]$, obtained from $[(\eta^5\text{-}C_5H_5)Mo(NO)(\eta^3\text{-}C_3H_5)I]$ and $(S_2CNMe_2)^-$, were established by *X*-ray crystallography.

DURING studies of fluxional cyclopentadienyl nitrosyl molybdenum dithiocarbamates and related complexes,[1] we have prepared $[(\eta^5\text{-}C_5H_5)Mo(NO)(C_3H_5)(S_2CNMe_2)]$, (I) and $[(\eta^5\text{-}C_5H_5)Mo(NO)(CO)(C_3H_5)(S_2CNMe_2)]$, (II). These complexes are of interest because they contain potentially trihapto allylic and bihapto sulphur ligands, and these may confer on the metal unusual electronic and structural configurations.



SCHEME

The synthetic routes are outlined in the Scheme. The carbonyl nitrosyl cation, and its iodinated derivative, exist as isomers (^1H n.m.r. spectra) which arise from the orientation of the η-allylic group with respect to the $[(\eta^5\text{-}C_5H_5)Mo(NO)X]$ unit (*cf.* $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)]^2$).

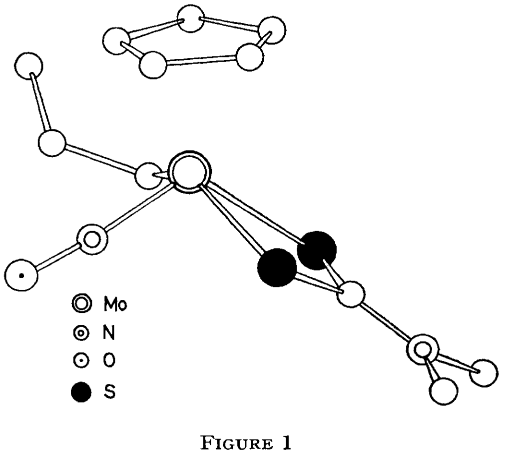


FIGURE 1

Unambiguous assignment of the structure of (I) could not be made on the basis of ^1H n.m.r. spectra (in particular, the methyl resonances appeared as a singlet implying that the molecule contained a plane of symmetry bisecting the MoS_2CNMe_2 system, or that there was rapid free rotation about the S_2C–NMe_2 bond, or that the methyl proton resonances were accidentally degenerate). The ^{13}C n.m.r. spectrum of (I) indicated that the allylic group was σ-bonded[3] [δ (ref. Me_4Si) in $CDCl_3$, 32·8, 38·3 and 38·8 ($\overset{\cdots}{-}CH_2$ and $-NMe_2$), 102·8 (C_5H_5), 106·1 ($\overset{\cdots}{-}CH_2$), 144·9 ($\overset{\cdots}{-}CH\overset{\cdots}{-}$) and 202·9 p.p.m. (CS)] and that the sulphur ligand was probably bidentate (the methyl resonances probably occur as a doublet).

In order to confirm these findings, a single crystal *X*-ray structural determination of (I) was undertaken. The yellow crystals were monoclinic, of dimensions $a = 15{\cdot}247(4)$, $b = 12{\cdot}419(3)$, $c = 7{\cdot}729(3)$ Å, $\beta = 98{\cdot}71(2)°$, space group $P2_1/c$ and $Z = 4$. The three-dimensional *X*-ray data were obtained on a two-circle Stöe diffractometer using graphite monochromated Mo-K_α radiation. The structure was solved by Fourier and Patterson techniques and refined to $R = 0{\cdot}056$ using 772 reflections of greater than 3σ significance. The essential features of the structure (Figure 1) are a linear (178°) Mo–N–O system, a planar S_2CNMe_2 (RMSD 0·020 Å) group, and a planar pentahapto cyclopentadienyl ring (RMSD 0·016 Å). The Mo atom is 1·952 Å out of the plane defined by the three carbon allyl fragment, and 0·0365 Å out of the plane defined by the dithiocarbamate chelate ring. (I) is structurally analogous to $[(\eta^5\text{-}C_5H_5)Mo(NO)(\eta^1\text{-}C_5H_5)\text{-}(\eta^2\text{-}S_2CNMe_2)]$ in that a polyhapto group has been forced by the S_2CNMe_2 group to adopt a monohapto configuration;[4] (I), however, unlike the biscyclopentadienyl species, is stereochemically rigid over the temperature range −60 to + 110°.

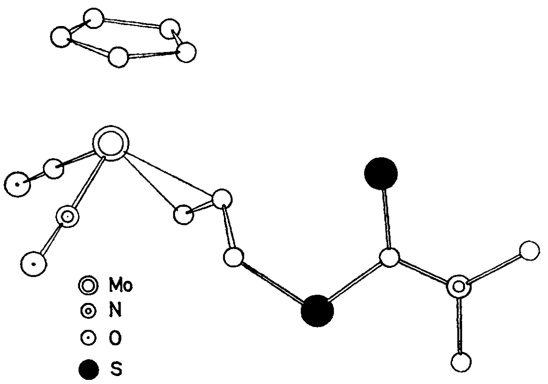


FIGURE 2

The complex (II) was obtained by direct dithiocarbamate attack on $[(\eta^5\text{-}C_5H_5)Mo(NO)(CO)(\eta^3\text{-}C_3H_5)]^+$. It exhibited terminal NO and CO stretching frequencies but ^1H and ^{13}C n.m.r. spectral studies failed to provide unambiguous structural information.

A single crystal *X*-ray structural determination of (II) was carried out (Figure 2). The orange crystals were monoclinic, of dimensions $a = 11{\cdot}634(3)$, $b = 7{\cdot}155(4)$, $c = 19{\cdot}068(4)$ Å, $\beta = 104{\cdot}5(2)$ Å, space group $P2_1/c$ and $Z = 4$. The three-dimensional *X*-ray data were collected photographically by the precession method using Zrfiltered Mo-K_α radiation and the intensities were estimated visually. The structure was solved and refined as before to $R = 0{\cdot}10$ using 1702 independent reflections. In this structure, the NO and CO ligands are both linear with respect to the Mo atom, and are clearly distinguishable by the metal-ligand bond lengths, 1·79 and 1·97 Å respectively. The atoms of the dithiocarbamate ligand, which is bonded to the allylic group rather than to the metal, are essentially coplanar (RMSD = 0·012 Å) and bond length data show that the S–C and C–N bond orders are greater than unity, leading presumably to restricted rotation about these bonds and hence to the observed ^1H and ^{13}C n.m.r. inequivalence of the methyl groups.

It therefore appears that (II) is derived from $[(\eta^5\text{-}C_5H_5)\text{-}Mo(NO)(CO)(\eta^3\text{-}C_3H_5)]^+$ by nucleophilic attack by $(S_2CNMe_2)^-$ at a terminal allylic carbon atom. Although there are several other potential sites for attack, other nucleophiles have a preference for the allylic site. Thus with H^- (as BH_4^-), OMe^-, $C_5H_5^-$ and OAc^-, molybdenum bound propene derivatives are formed. With halide ion, however, CO displacement occurs, giving $[(\eta^5\text{-}C_5H_5)Mo(NO)(\eta^3\text{-}C_3H_5)X]$.

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