Reactions of Ketones with Molybdenum Nitrosyl Complexes: *X*-Ray Crystal Structures of $[\{Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I\}_2O]$, a Complex having a Bent Mo–O–Mo Bond, and of a Bicyclic Salt, $[C_6H_3Me_5N_2(OH)][I_{\frac{1}{2}}(I_3)_{\frac{1}{2}}]$†

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Summary Reaction of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2]$ with refluxing acetone or diacetone alcohol led to C–C bond cleavage and formation, in low yield, of $[\{Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I\}_2(\mu\text{-}O)]$ and the bicyclic cation $[C_6H_3Me_5N_2(OH)]^+$ (isolated as the I^- or mixed I^-/I_3^- salt); the structures of the last two were determined crystallographically, the μ-oxo species having a slightly bent Mo–O–Mo bond.

WE have shown that the co-ordinatively unsaturated complex $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2]$ (**1**) $\{HB(3,5\text{-}Me_2C_3HN_2)_3$ = tris-(3,5-dimethylpyrazolyl)borate$\}$ reacts[1,2] with hot alcohols affording air- and moisture-stable crystalline green mono- and pink bis-alkoxides, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(OR)]$ (**2**) and $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(OR)_2]$. We have now observed, unexpectedly, that (**1**) also reacts with ketones affording mixtures containing green

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† $HB(3,5\text{-}Me_2C_3HN_2)_3$ = tris-(3,5-dimethylpyrazolyl)borate; $C_6H_3Me_5N_2(OH)^+$ = 6-hydroxy-2,4,6,8,8-pentamethyl-1,5-diazabicyclo-[3.3.0]octa-1,3-dien-1-onium.

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compounds apparently related to (**2**). This surprising observation has prompted a detailed examination of the reactions of (**1**) with acetone and 4-hydroxy-4-methylpentan-2-one (diacetone alcohol).

$[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2]$

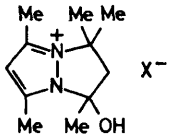
(**1**)

$[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(I)(OR)]$

(**2**) [(A), R = Et]

$[\{Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(I)\}_2(\mu\text{-}O)]$

(**3**)



(**4**) X = I

(**5**) $X = I_{\frac{1}{2}}(I_3)_{\frac{1}{2}}$

After refluxing (**1**) in degassed ethanol-free acetone for 3 days, three solids could be obtained: a light green complex (A) (*ca.* 7—10%), an olive green compound (**3**) (*ca.* 20%), and a white organic salt (**4**) (20—22%).§ The volatile organic products were identified, by g.l.c.–m.s. techniques, as acetone (*ca.* 60%), mesityl and isomesityl oxide (*ca.* 35%), and diacetone alcohol (*ca.* 5%); while water was present at the end of the reaction, methanol or ethanol were not detected. When (**1**) was refluxed in degassed ethanol-free diacetone alcohol for 2 days, (A), (**3**), (**4**), and a red organic salt (**5**) were obtained. The volatile organic components of the system consisted of diacetone alcohol (*ca.* 25%), and mesityl and isomesityl oxide (*ca.* 75%); again water was detected together with traces of acetone, but no ethanol was present at the end of the reaction.

The complex (A) was readily identified spectroscopically and by elemental analysis as $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(OEt)]$, *i.e.* (**2**; R = Et). The formation of ethoxide from acetone, albeit in low yield, is remarkable in that it involves the cleavage of a C–C bond under relatively mild conditions. That this is likely to occur at the metal seems probable from our failure to detect ethanol in the solvent mixture either before or after the reaction. The nature of (**3**) (Figure 1) was established primarily by *X*-ray methods. Olive green crystals were obtained from dichloromethane.

Crystal data: $C_{30}H_{44}B_2I_2N_{14}Mo_2O_3\cdot\frac{1}{2}CH_2Cl_2$, $M = 1158·6$ (1116·1 excluding solvent), triclinic, $a = 12·220(6)$, $b = 13·352(10)$, $c = 14·094(5)$ Å, $\alpha = 96·38(5)$, $\beta = 93·12(4)$, $\gamma = 96·78(5)$°, $U = 2264(2)$ Å^3; $D_m = 1·62$, $D_c = 1·70$ g cm^{-3}, $Z = 2$; $F(000) = 1117$, space group $P\bar{1}$ (No. 2, C_i); Mo-K_α radiation ($\bar{\lambda} = 0·71069$ Å) with graphite monochromator.

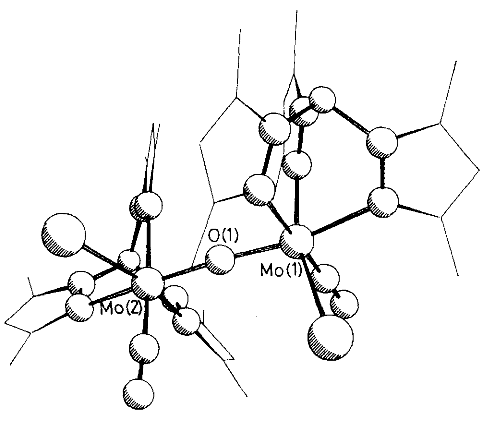


FIGURE 1. Structure of $[\{Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I\}_2(\mu\text{-}O)]$ (**3**) Mo(1)–O, 1·86(2); Mo(2)–O, 1·92(2) Å; Mo(1)–O–Mo(2) 171·0(15)°.

X-Ray intensity data ($3·5 < 2\theta < 50$°) were collected using a Nicolet R3 four-circle *X*-ray diffractometer in the ω-scan mode, and were corrected for Lorentz and polarisation effects and for pronounced crystal decay which was monitored during data collection. The final data set for which $I/\sigma(I) > 3·0$ comprised 1932 independent reflections. The structure was solved by standard Patterson methods and was refined by block-diagonal least-squares methods to R 0·0756 with allowance for anisotropic thermal vibration of the molybdenum and iodine atoms only. Hydrogen atoms were detected in difference electron density syntheses and inserted (B–H 1·10, C–H 0·95 Å) in predicted positions.¶

Each molybdenum atom exists in the distorted octahedral environment detected in related mono- and bis-alkoxy species.[1,2] Of significance are the Mo–O bond lengths [1·86(2), 1·92(2) Å] which are shorter than might be expected for an Mo–O single bond in systems containing Mo in oxidation states II, III, or IV. Thus a degree of π-bonding between the O and the two metal atoms must occur, as had been reported earlier for the alkoxides analogous to (**2**).[1,2] Also of interest is the occurrence of a slightly but significantly bent Mo–O–Mo angle [171·0(15)°]. The great majority of molybdenum complexes containing a single μ-oxo bridge have a linear array of atoms,[3] and the distortion from linearity here must arise as a result of steric restraints imposed by the proximity of two very bulky $HB(3,5\text{-}Me_2C_3HN_2)_3$ groups. Steric restraint is also responsible for enforcing the inequivalence of all six pyrazolyl rings in the dimer. This inequivalence persists in solution, where ten separate CH_3 signals and six 4-H signals are observed in the ^1H n.m.r. spectrum at 220 MHz.

The nature of the red organic salt (**5**) (Figure 2) was also established by *X*-ray crystallography. Red needles were obtained from dichloromethane.

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§ Substantial decomposition of the Mo-containing compounds occurred, and identification of the fragments generally proved impossible.

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

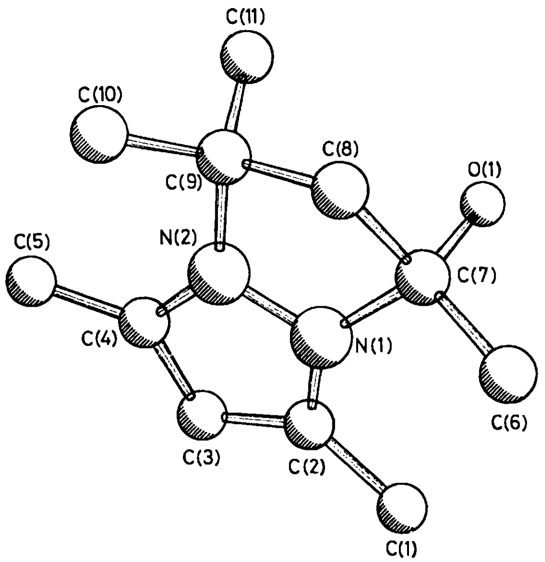

FIGURE 2. Structure of $[C_6H_3Me_5N_2(OH)]^+$: N(1)–N(2) 1·355(13) Å.

Crystal Data: $C_{11}H_{19}I_2N_2O$, M = 449·1; triclinic, a = 7·752(5), b = 9·394(4), c = 11·424(9) Å, α = 91·21(5), β = 93·24(6), γ = 110·26(4)°, U = 778·5(9) $Å^3$; Z = 2; $F(000)$ = 426, space group $P\bar{1}$ (No. 2, C_i); Mo-K_α radiation (λ = 0·71069 Å) with graphite monochromator, μ(Mo-K_α) = 39·79 cm^{-1}.

X-Ray data (with corrections for absorption) were collected (2021 independent reflections) and the structure was solved and refined (R 0·0518) as described for (**2**; R = Et) above; allowance was made for anisotropic thermal vibrations of all non-hydrogen atoms.

The unsaturated five-membered ring is closely planar (r.m.s. deviation 0·0016 Å) whereas the saturated ring adopts an envelope conformation; bond lengths show no unexpected features, the nitrogen–nitrogen bond length being 1·355(13) Å. The oxygen atom exhibits a rather short contact to the free iodide ion (3·43 Å) and the hydrogen atom was detected between the two atoms: the bond length in the centrosymmetric tri-iodide ion is 2·940 Å.¶

This unusual bicyclic compound is derived, formally, by fusing a C_3 fragment, presumably derived from diacetone alcohol or mesityl oxide, across the N–N bond of a 3,5-dimethylpyrazole ring. It is known[4] that pyrazoles undergo addition reactions with $\alpha\beta$-unsaturated carbonyl compounds but, as far as we can ascertain, this particular type of 1,4-addition has not been reported previously. The compound was isolated as the $[(I^-)_{\frac{1}{2}}(I_3^-)_{\frac{1}{2}}]$ salt, and is essentially identical to (**4**), on the basis of spectral and other analytical data, which is obtained as the simple mono-iodide salt.

The mechanisms of formation of (**2**; R = Et) and (**4**)/(**5**) are unknown at present, but it is possible that radical pathways[5] are involved. However, the formation of the salts (**4**)/(**5**) implies that, under certain conditions, trispyrazolylborate ligands may not be as stable as previously imagined.

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