

**Addition of Diphenyldiazomethane to Hexa-alkoxydimolybdenum($M \equiv M$)
Compounds: Characterization of $\text{Mo}_2(\text{OPr}^i)_6(\text{N}_2\text{CPh}_2)_2(\text{pyridine})$
by X-Ray Crystallography**

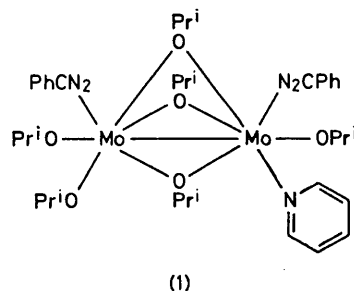
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Summary Addition of diphenyldiazomethane (2 equiv.) to hexane solutions of $\text{Mo}_2(\text{OR})_6$, where R = isopropyl or neopentyl, in the presence of pyridine (py) leads to the formation of the crystalline compounds $\text{Mo}_2(\text{OR})_6(\text{N}_2\text{CPh}_2)_2(\text{py})$, which are shown to contain mixed valence (Mo-Mo)¹⁰⁺ units.

THE addition† of diphenyldiazomethane (2 equiv.) to hexane solutions of $\text{Mo}_2(\text{OR})_6$, where R = isopropyl or neopentyl, in the presence of pyridine (py) at -78°C gives the complexes $\text{Mo}_2(\text{OR})_6(\text{N}_2\text{CPh}_2)_2(\text{py})$ which crystallize from the mother liquor. In the absence of added pyridine, no simple products have been isolated. When only one equivalent of Ph_2CN_2 is added, a mixture of $\text{Mo}_2(\text{OR})_6(\text{N}_2\text{CPh}_2)_2(\text{py})$ and unchanged $\text{Mo}_2(\text{OR})_6$ is obtained. With more than two equivalents of Ph_2CN_2 , further reactions occur to give as yet uncharacterized products.

Though elemental analytical data supported the formula $\text{Mo}_2(\text{OR})_6(\text{N}_2\text{CPh}_2)_2(\text{py})$, spectroscopic data did not allow any obvious formulation of structure. The ^1H n.m.r. spectra (220 MHz) recorded in [$^3\text{H}_8$]toluene at $+16^\circ\text{C}$ indicated six different OR ligands with resonances of equal integral intensity. The methylene protons of the neopentoxide appeared as six AB quartets and the methyl protons

of the isopropoxide as 12 partially overlapping doublets. At higher temperature ($> 70^\circ\text{C}$, 220 MHz), the molecules become fluxional on the n.m.r. time-scale and this leads to scrambling of all six alkoxy-ligands. This process also allows rapid (n.m.r. time-scale) exchange of free and coordinated pyridine.



The solid-state structure‡ of $\text{Mo}_2(\text{OPr}^i)_6(\text{N}_2\text{CPh}_2)_2(\text{py})$ (**1**) revealed that each molybdenum is in a distorted octahedral environment and that the two molybdenum atoms share a face formed by three bridging OPrⁱ ligands (Figure). The molecule has no symmetry and there are indeed six different alkoxy-ligands as indicated by the ^1H n.m.r. spectroscopic studies just mentioned.

† All operations were carried out under nitrogen atmospheres using dried and deoxygenated solvents.

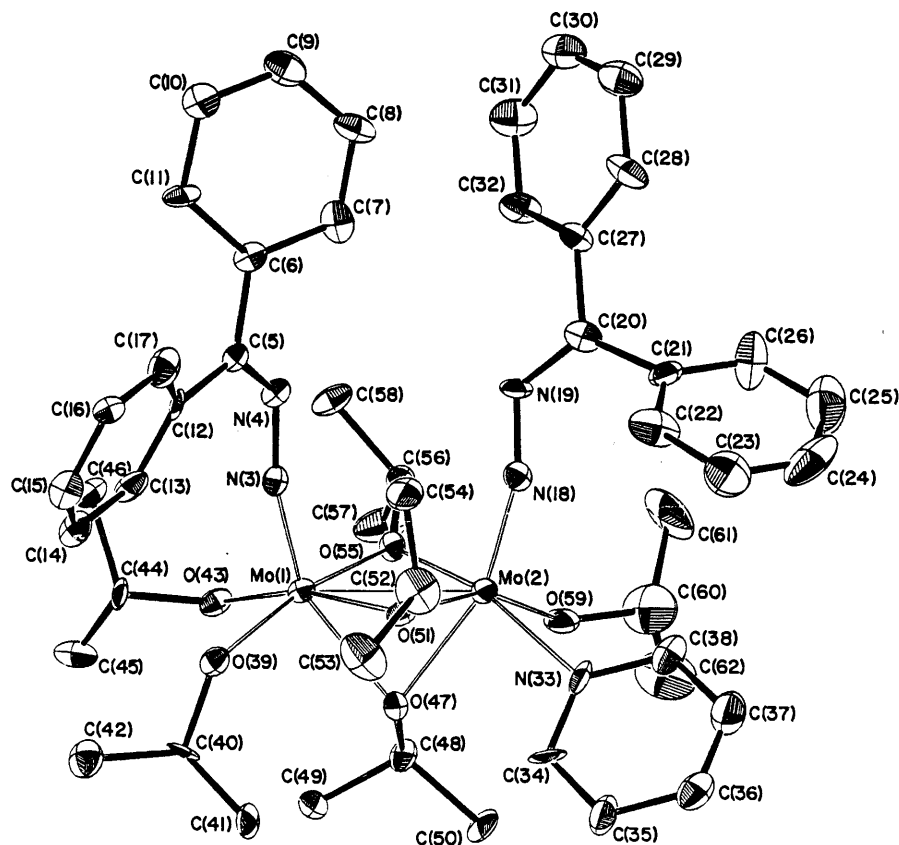


FIGURE. An ORTEP view of the structure of complex (1). Some pertinent distances (Å) and angles (°) are Mo–Mo 2.661(2); Mo(1)–O(39) 1.96(1), –O(43) 1.96(1), –O(47) 2.24(1), –O(51) 2.11(1), –O(55) 2.13(1), –N(3) 1.76(1); Mo(2)–O(47) 2.16(1), –O(51) 2.04(1), –O(55) 2.04(1), –O(59) 1.98(1), –N(18) 1.78(1), –N(33) 2.225(10); N(3)–N(4) 1.30(1); N(4)–C(5) 1.30(2); N(18)–N(19) 1.30(1); N(19)–C(20) 1.31(2); \angle Mo(1)–N(3)–N(4) 164(1); N(3)–N(4)–C(5) 124(1); Mo(2)–N(18)–N(19) 155(1); N(18)–N(19)–C(20) 122(1).

The following points are noteworthy.

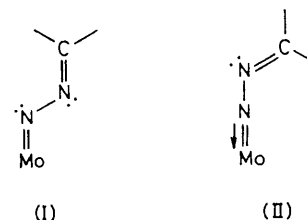
(i) There are terminal, rather than bridging Ph_2CN_2 ligands. This contrasts with the addition of Ph_2CN_2 to $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(M\equiv M)$, which gives $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\mu\text{-N}_2\text{CPh}_2)(M-M)$.²

(ii) The structural parameters associated with the MoNNC units are consistent with a mode of bonding intermediate between the Lewis structures (I) and (II), in which the diazo ligand has been reduced by two electrons upon coordination to molybdenum.³⁻⁵ This form of the ligand has been seen previously in the work of Chatt *et al.*⁶

(iii) The Mo–Mo distance, 2.662 Å, is consistent with the presence of an Mo–Mo single bond for a Mo_2^{10+} unit bridged by three OR groups and may be compared with the Mo–Mo distance of 2.73 Å found in $\text{Mo}_2(\text{OPr}^1)_6\text{X}_4$ compounds (X = Cl or Br), which have edge-shared ($\mu\text{-OR}$) octahedral geometries.⁸

(iv) The compound contains metals in mixed oxidation

states. If oxidation numbers are assigned in the manner –2 for N_2CPh_2 , –1 for terminal OPr^1 ligands, and $-\frac{1}{2}$ for bridging OPr^1 ligands, then Mo(1) is in oxidation state $+5\frac{1}{2}$ and Mo(2) is $+4\frac{1}{2}$. This formal charge imbalance is offset by the formation of asymmetrical bridging Mo–OPr¹ bonds, which have shorter distances to Mo(2) than to Mo(1), and by the different contributions of (I) and (II) as shown by the different Mo–N–N angles.



† Crystal data (at -162°C) for complex (1) $\text{C}_{49}\text{H}_{67}\text{O}_6\text{Mo}_2\text{N}_5$: monoclinic, space group $P2_1$, $a = 12.512(8)$, $b = 14.795(9)$, $c = 14.099(8)$ Å, $\beta = 109.51(2)^\circ$, $D_c = 1.369\text{ g cm}^{-3}$, $Z = 2$. The structure was solved by Patterson and Fourier techniques using 3373 unique intensities collected on an automated diffractometer using Mo- K_α radiation for $6^\circ \leq 2\theta \leq 40^\circ$. Final refinement utilized anisotropic thermal parameters for all atoms and converged to $R = 0.051$ and $R_w = 0.053$. 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.

Finally, it should be noted that the $(\text{Mo}\equiv\text{Mo})^{6+}$ unit in $\text{Mo}_2(\text{OR})_6$ compounds provides a most versatile inorganic functionality. It acts as a Lewis acid toward Lewis bases in the formation of $\text{Mo}_2(\text{OR})_6\text{L}_2$ compounds^{1,9} and as a source of electrons towards oxidizing agents⁸ and π -acids such as CO,¹⁰ alkynes,¹¹ and, as shown here, diazoalkanes.

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