

inner end. A third 1.5-mm hole, for the quenching solution, enters the tube at a point 5 cm from the two reactant holes. The holes are connected to glass tubes on the outside of the rod; these are connected through glass and Teflon needle valves to siphon tubes inserted into three separate bottles. The bottles can be simultaneously pressurized with nitrogen gas at a regulated pressure from a cylinder. Before each run, the needle valves are adjusted so that the flow rates of the three solutions are equal. The reaction tube is mounted vertically, and the quenched product is collected in a beaker placed beneath the open end of the tube.

Wang and Jolly² have shown that, in methanol-water solution at -78° , the borohydride ion reacts very rapidly with strong acid to form H_2OBH_3 . This species hydrolyzes under these conditions with a half-life of about 300 sec, but it can be deprotonated to form the relatively stable BH_3OH^- ion, which has a half-life of several hours at room temperature. An estimated effective activation energy for the H_2OBH_3 hydrolysis of 12 kcal/mol³ corresponds to a half-life of about 20 msec at 0° . Thus, it seemed reasonable to attempt the synthesis of BH_3OH^- using the quenched flow reactor with aqueous solutions initially at 0° and with a reaction time (time between the initial mixing of H^+ and BH_4^- and the quenching with OH^-) of the order of 20 msec or less. Our experimental data are given in Table I. The

relatively stable in alkaline solutions.⁴⁻⁷ The literature procedure for the synthesis of peroxyxynitrite involves the mixing of an acidic peroxide solution with a nitrite solution, immediately followed by treatment with excess base. Yields of 45–50% have been reported.⁵ We have carried out this synthesis with our quenched flow reactor, using equal flow rates of the following solutions at 0° : 0.6 M KNO_2 , a solution 0.6 M in HCl and 0.7 M in H_2O_2 , and 3 M NaOH. The product solution was analyzed spectrophotometrically.⁵ The reaction times (msec) and corresponding percentage yields follow: 44, 44%; 88, 67%; 88, 68%; 230, 77%; 280, 72%; 450, 82%. The relatively low yield obtained for the shortest reaction time (44 msec) was probably a consequence of incomplete reaction of the nitrous acid with the hydrogen peroxide.

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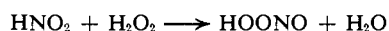
Table I. Data for BH_3OH^- Syntheses

Reaction time, msec	Reagent concn, M			Product temp, ^a °C	Yield of BH_3OH^- , ^b %
	BH_4^-	H^+	OH^-		
26	0.3	0.45	0.6	6	75
21	0.3	0.45	0.6	6	87
16	0.3	0.45	0.6	6	94
10	0.3	0.45	0.6	6	86
10	1.0	2.5	3.0	16	65
10	3.0	4.5	6.0	37	51

^a Temperature of BH_3OH^- solution. Reagent solutions cooled to 0° . ^b Determined from amount of H_2 evolved upon complete hydrolysis.

change in the percentage yield of BH_3OH^- with change in reaction time was qualitatively as expected. Relatively high yields, essentially independent of reaction time, were obtained for reaction times of 10–21 msec; the yield dropped off for a reaction time of 26 msec. The decrease in the percentage yield with increasing concentration of the solutions may be due to the corresponding increase in the reaction temperature caused by the increased heat of reaction.

The reaction of nitrous acid with hydrogen peroxide in acidic solution yields peroxyxynitrous acid.



This acid decomposes to nitric acid with a half-time of 7 sec at 0° , but the conjugate base, peroxyxynitrite ion, is

(2) F. T. Wang and W. L. Jolly, *Inorg. Chem.*, **11**, 1933 (1972).

(3) This is admittedly an optimistically low estimate of the activation energy. At -78° the acid-independent hydrolysis of H_2OBH_3 has a rate comparable to that of the acid-dependent hydrolysis.² The former reaction would be expected to have an activation energy near 20 kcal/mol, thus making the hydrolysis too rapid for a quenched flow reactor operated near room temperature. We have no explanation for the discrepancy.

Hexakis(dimethylamino)- and Hexakis(*tert*-butoxy)dimolybdenum(III)

Sir:

We wish to report the preparation and characterization of Mo_2L_6 where $\text{L} = \text{NMe}_2$ and *O-t*-Bu. These compounds provide¹ (i) the first examples of dialkylamides and alkoxides of tervalent molybdenum, (ii) the first example of oligomerization by metal-metal bond formation in the chemistry of metal-alkoxides and dialkylamides, (iii) synthetically useful starting materials for the synthesis of other metalloorganic compounds of molybdenum(III), and (iv) a unique opportunity for the study of strong homonuclear interactions in the structurally related series $\text{L}_3\text{Mo}\equiv\text{MoL}_3$ where $\text{L} = \text{CH}_2\text{-SiMe}_3$,² NMe_2 , and *O-t*-Bu.

The addition of MoCl_3 to an ice-cooled, magnetically stirred solution of LiNMe_2 (3 mol equiv in 50:50 THF-hexane) gave a dark brown solution. The reaction mixture was stirred for 12 hr at 0° under an atmosphere of dry, oxygen-free nitrogen. Solvent was then removed by vacuum distillation and the residue dried under high vacuum at 60° . Subsequent extraction with pentane yielded a dark, red-brown solution which, on removal of pentane, gave a dark brown solid containing crude $\text{Mo}_2(\text{NMe}_2)_6$. Analytically pure samples of the yellow crystalline solid of $\text{Mo}_2(\text{NMe}_2)_6$ were obtained by vacuum sublimation (100° (10^{-6} cm)) from the crude product.

Addition of *t*-BuOH (>6 mol equiv) to a solution of $\text{Mo}_2(\text{NMe}_2)_6$ in a hydrocarbon solvent led to quantita-

(1) (a) D. C. Bradley, *Advan. Inorg. Chem. Radiochem.*, **15**, 259 (1972); (b) D. C. Bradley and K. Fisher, *MTP (Med. Tech. Publ.) Int. Rev. Sci.*, **5**, 65 (1972).

(2) (a) G. Wilkinson, *et al.*, *J. Chem. Soc., Dalton Trans.*, 533 (1973); (b) G. Wilkinson, *et al.*, *Chem. Commun.*, 1079 (1971).

tive formation of $\text{Mo}_2(\text{O}-t\text{-Bu})_6$ with the liberation of HNMe_2 . Vacuum sublimation at 100° (10^{-6} cm) or crystallization from either pentane or toluene at -78° gave analytically pure $\text{Mo}_2(\text{O}-t\text{-Bu})_6$ as an orange crystalline solid.

Both $\text{Mo}_2(\text{NMe}_2)_6$ and $\text{Mo}_2(\text{O}-t\text{-Bu})_6$ are moisture- and oxygen-sensitive diamagnetic compounds. Cryoscopic molecular weight determinations in benzene and mass spectral data show that these compounds are dimeric (*i.e.*, Mo_2L_6) in solution and in the vapor state. The mass spectra show strong parent ions, Mo_2L_6^+ , and several other Mo_2 -containing species. Indeed the virtual absence of ions containing only one molybdenum is very striking. The volatility and thermal stability of Mo_2L_6 contrast with those observed for the CrL_3 series³ ($\text{L} = \beta$ -elimination stabilized alkyl, tertiary alkoxide, or dialkylamide). The latter are thermally unstable *in vacuo* and readily disproportionate (or are oxidized) to give the volatile CrL_4 compounds.³ The color of Mo_2L_6 is derived from uv absorption which tails into the visible region; no d-d transitions are observed. The Raman spectra of $\text{Mo}_2(\text{O}-t\text{-Bu})_6$ and $\text{Mo}_2(\text{NMe}_2)_6$ show intense bands at 240 and 230 cm^{-1} , respectively. These bands are associated, at least in part, with Mo-Mo symmetric stretching vibrations. Other Mo-L stretching vibrations in the infrared and Raman spectra are consistent with local C_{3v} symmetry about molybdenum. Variable temperature ^1H nmr spectra (100 MHz) of Mo_2L_6 in toluene- d_8 indicate the presence of only terminally bonded ligands. For $\text{Mo}_2(\text{O}-t\text{-Bu})_6$ a single proton resonance occurs at δ 1.42 ppm from hexamethyldisiloxane in the temperature range $+90$ to -90° . The variable temperature nmr spectrum of $\text{Mo}_2(\text{NMe}_2)_6$ in toluene- d_8 warrants specific comment. At 20° and above, a single sharp resonance occurs at δ 3.28 ppm from hexamethyldisiloxane. On cooling the sample this resonance broadens until at -20° there is essentially complete loss of signal. Below -20° two new resonances appear at δ 2.41 and 4.13 ppm from hexamethyldisiloxane. These integrate in the ratio 1:1. The nmr spectrum is independent of concentration and is unaffected by the presence of added HNMe_2 . These observations are incompatible with a fluxional dimeric species having a ground-state structure involving bridging dimethylamido ligands; *cf.*⁴ $[\text{Ti}(\text{NMe}_2)_3]_2$. A closer consideration of the bonding and stereochemistry of $\text{Mo}_2(\text{NMe}_2)_6$ is required to appreciate our observations.

We suggest⁵ that in the ground state (i) the Mo_2N_6 moiety is staggered⁶ (*i.e.*, the Mo_2N_6 unit has D_{3d} symmetry) and (ii) the Mo- NC_2 units are planar.⁷ Two extreme conformations should then be recognized—that in which (a) the Mo- NC_2 planes are all colinear with the Mo-Mo axis and (b) the Mo- NC_2 planes are perpendicular to the Mo-Mo axis. For both (a) and (b) the Mo_2 -

$(\text{NC}_2)_6$ unit has D_{3d} symmetry, but the transformational properties of the nitrogen p orbitals differ with the conformation. Conformation b permits maximum ligand p to metal dp π -bonding and thereby allows molybdenum to attain an 18-electron valence shell. However, (b) also leads to maximum steric repulsion on each $\text{Mo}(\text{NMe}_2)_3$ unit. Consequently the adoption of a propeller arrangement of Mo- NC_2 planes about each $\text{Mo}(\text{NMe}_2)_3$ group provides a compromise of opposing steric and electronic factors. This situation has been observed for monomeric compounds $\text{M}(\text{NR}_2)_3$, *e.g.*,⁸ $\text{Cr}(\text{N}-i\text{-Pr})_3$. Propeller arrangements of the Mo- NC_2 planes generate a chiral axis coincident with the Mo-Mo axis thus leading to a pair of enantiomers of D_3 symmetry and a meso diastereomer of S_6 symmetry. In all three isomers, however, six methyl groups are directed toward (proximal), and six methyl groups are directed away from (distal), the metal-metal triple bond.

The observed nmr spectrum is interpreted as follows. At 20° and above intramolecular motions (see later) lead to the equivalence of all 12 methyl groups on the nmr time scale; below -20° intramolecular motions are restricted which leads to the freezing out of six proximal and six distal methyl groups. The large chemical shift difference (*ca.* 2.0 ppm) between proximal and distal methyl protons arises from the diamagnetic anisotropy induced by the molybdenum-molybdenum triple bond.⁹ Methyl groups associated with the enantiomers of D_3 symmetry are magnetically equivalent but differ from those of the meso isomer of S_6 symmetry. Our low temperature spectra show only two sharp resonances even at -90° . This must arise from (i) the freezing out of a preferred isomer in the ground state, D_3 or S_6 , (ii) accidental magnetic degeneracy of the S_6 and D_3 isomers, or (iii) the rapid interconversion of S_6 and D_3 isomers even at low temperatures.¹⁰

The stereochemical correspondence between many organic and inorganic molecules has only recently been noted explicitly.¹¹ We note here (i) the parallelism between triarylcarbonium ions¹² and the $\text{Mo}(\text{NMe}_2)_3$ moiety and (ii) the stereochemical correspondence of $\text{Mo}_2(\text{NMe}_2)_6$ to hexaphenyldisilane.¹³ Intramolecular motions which interchange proximal and distal methyls in $\text{Mo}_2(\text{NMe}_2)_6$ may be expressed in terms of flip rearrangements.¹¹ For $\text{Mo}_2(\text{NMe}_2)_6$ a six-flip rearrangement (*i.e.*, rotation of the six Mo- NC_2 planes through conformation a) can be ruled out since this does not interconvert proximal and distal methyls. However, in addition to flip rearrangements, a fluxional process in which dimethylamido groups are transferred from one molybdenum to the other could be operative. We cannot distinguish between these mechanisms since they are permutationally indistinguishable. We note, how-

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(9) J. S. Filippo, *Inorg. Chem.*, 11, 3140 (1972).

(10) The only mechanism which interconverts D_3 and S_6 isomers and does not interconvert proximal and distal groups is the three-flip rearrangement. Molecular models suggest that this is unlikely on steric grounds.

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(12) (a) R. J. Kurland, I. I. Schuster, and A. K. Colter, *J. Amer. Chem. Soc.*, 87, 2279 (1965); (b) I. I. Schuster, R. J. Kurland, and A. K. Colter, *ibid.*, 90, 4679 (1968); (c) J. W. Rakshys, S. V. McKinley, and H. H. Freeman, *ibid.*, 92, 3518 (1970).

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(3) (a) G. Wilkinson *et al.*, *J. Chem. Soc., Dalton Trans.*, 770 (1973); (b) J. S. Basl, D. C. Bradley, and M. H. Chisholm, *J. Chem. Soc. A*, 1433 (1971); (c) E. C. Alyea, J. S. Basl, D. C. Bradley, and M. H. Chisholm, *ibid.*, 2330 (1971).

(4) M. F. Lappert and A. R. Sanger, *J. Chem. Soc. A*, 874 (1971).

(5) This suggestion is not crucial to an interpretation of our nmr data which merely requires a temperature-dependent interchange of proximal and distal methyl groups. However, alternative geometries involving an eclipsed Mo_2N_6 unit and pyramidal nitrogens are sterically and electronically unfavorable.

(6) As found for $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$. See ref 2b.

(7) All crystal structures of transition metal dialkylamides to date show planar M- NC_2 units. See ref 1b. This allows maximum ligand to metal π -bonding.

ever, that only a zero-flip rearrangement (in which the six Mo-NC₂ planes rotate through b) and a fluxional process involving a concerted pairwise exchange of dimethylamido ligands allow molybdenum to retain an 18-electron valence shell throughout.

We are currently extending our studies to the synthesis and characterization¹⁴ of the series Mo₂L₆ where L = Ar, PR₂, and SR.

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(14) Single-crystal X-ray diffraction studies are being carried out on Mo₂(O-*t*-Bu)₆, Mo₂(NMe₂)₆, and related compounds by Professor F. A. Cotton and coworkers.

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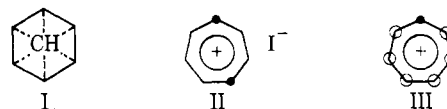
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Rearrangement Ions. V.¹ The C₇H₇⁺ Ion in the Mass Spectrum of Tropylium-1,4-¹³C₂ Iodide

Sir:

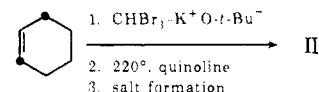
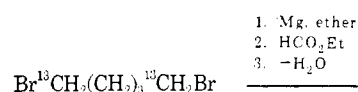
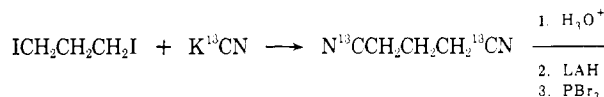
Since Meyerson's earlier discovery that the hydrogen atoms in toluene attain almost complete equivalence in the process leading to the formation of C₇H₇⁺ ions,² several efforts have been directed at examining the electron impact induced skeletal reorganization of toluene and related benzyl systems utilizing ¹³C labeling.³⁻⁵ Thus, a single ¹³C atom in position α,^{2,3} 1,^{3,5} or 2⁴ is nearly lost statistically in the path C₇H₇⁺ → C₅H₅⁺. These results support, although do not prove, Meyerson's original proposal of a tropylium ion structure for the C₇H₇⁺ ion. Whereas a single ¹³C atom may distinguish between a benzyl ion and a tropylium ion structure for the fragmenting C₇H₇⁺ ion, it cannot offer information regarding the mode of formation of the C₇H₇⁺ ion. Rinehart, *et al.*,^{3,5} in examining toluene-α,¹-¹³C₂ found that the label retentions in the C₅H₅⁺ ions indicated that the C₇H₇⁺ ions are not formed solely, if at all, by insertion of the α-carbon atom between C₁ and C₂ of the ring, but rather by a mechanism in which some or all of the carbon atoms have lost positional identity with respect to their toluene origin, *e.g.*, by insertion of the α-carbon atom randomly between adjacent carbon atoms of the ring (I).⁶ A subsequent report⁴ dealing with the mass spectrum of toluene-2,6-¹³C₂, a doubly labeled toluene in which the ¹³C atoms are not adjacent, showed that some unlabeled C₅H₅⁺ ions and some ¹³C₂-H₂⁺ ions were formed. These data suggested a mechanism more complicated than I.

In order to gain more insight into the problem, efforts were directed at examining the mass spectrum of tro-



pylium-1,4-¹³C₂ iodide (II) in order to determine whether scrambling occurs in those C₇H₇⁺ ions which have sufficient energy to form C₅H₅⁺ ions. Synthesis of II proceeded according to Scheme I,⁷ which represents

Scheme I



only minor modifications of procedures described.⁸⁻¹⁰ Mass spectra were recorded on an AEI MS-9 mass spectrometer at a resolution of 16,000 (10% valley definition); data represent averages of 15-20 scans.

Loss of C₂H₂ from a skeletally "intact" C₇H₇⁺ ion derived from II should produce no unlabeled C₅H₅⁺ ions; loss of C₂H₂ from a skeletally rearranged C₇H₇⁺ ion (III) should produce some unlabeled C₅H₅⁺ ions, the precise amount depending on the extent and mode of reorganization. The anticipated relative abundances, as well as the observed data recorded at 70 and 20 eV, are presented in Table I.

Table I. High Resolution Mass Spectral Peaks

m/e	Composition ^a	Relative abundance ^{b-d}			
		70 eV	20 eV	Theory II'	Theory III ^e
65	C ₅ H ₅ ⁺	0.029	0.039	0.000	0.048
66	¹³ CC ₄ H ₅	0.549	0.500	0.571	0.476
67	¹³ C ₂ C ₃ H ₅	0.422	0.461	0.429	0.476

^a Other hydrocarbon ions omitted. ^b Σ65-67 = 1.000 ^c Corrected for naturally abundant ¹³C. ^d Calculated for 100% isotopic enrichment. ^e Sample contained 83.5% doubly labeled, 15.7% singly labeled, and 0.8% unlabeled tropylium iodide. ^f Calculated for unrearranged II. ^g Calculated for a completely scrambled ion (III).

The presence of unlabeled C₅H₅⁺ ions, as well as ¹³C₂H₂ ions beyond that of natural abundance, suggests extensive skeletal reorganization. As anticipated, the extent of reorganization increases at lower ionizing

(7) The disposition of the labels in the cyclohexene was substantiated by comparison of its mass spectrum with cyclohexene and cyclohexene-1-¹³C. Prior nmr evidence (see ref 6) showed no skeletal rearrangement in the dehydration of labeled methylcyclohexanol. The synthesis of several dimethyl-, methylethyl-, and diethyltropylium salts from the appropriate alkyl cyclohexenes by the method described in Scheme I afforded the expected tropylium salts indicating no skeletal rearrangement.

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