strument Grant (Grant No. 28233) which allowed the purchase of the automated diffractometer. We are indebted to Mr. Clifford Feldman for the magnetic susceptibility data and to Dr. Laurence Hoard for additional consultation on the crystal structure.

Registry No. Aluminum zirconium chloride, 74231-09-7.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Tris(*N*,*N'*-dimethylethylenediamido)dimolybdenum (M≡M). A Metallopropellane with a Near-Eclipsed Central Mo_2N_6 Moiety

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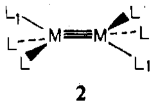
Albright and Hoffmann[2] recently made the provocative claim "triple-bonded ethane-like M_2L_6 transition metal complexes should be eclipsed". The compounds in question are of the general type **1** and **2**, in which the triple bond ($\sigma^2\pi^4$)

1

M = Mo, W
L = CH_2SiMe_3, NMe_2, OR



2

M = Mo, W
L = NMe_2, L_1 = halide or alkyl

is formed by the interaction of metal valence atomic orbitals of a and e symmetry.[3] The rationale for the preference for the eclipsed geometry rests on Albright and Hoffmann's calculation that overlap of the π-type atomic orbitals is favored in that configuration relative to the structurally observed staggered geometries. A test of this prediction by the synthesis of a $L_3M{\equiv}ML_3$ molecule with small monodentate ligands will probably not be forthcoming since, as the steric bulkiness of L decreases, polymeric ML_3 compounds are formed.[4] We wish here to report the synthesis of a new d^3–d^3 M≡M dimer which, by the use of three bridging *N*,*N'*-dimethylethylenediamido ligands, has a virtually eclipsed Mo_2N_6 skeleton. A structural comparison between a staggered and an eclipsed ethane-like M_2L_6 (M≡M) compound is now possible.

The reaction between 1,2-$Mo_2Cl_2(NMe_2)_4$ and 2 equiv of the monolithiated *N*,*N'*-dimethylethylenediamine leads, in the presence of excess free diamine, to the formation of $Mo_2(MeNCH_2CH_2NMe)_3$. The reaction is carried out in hexane at −78 °C, and the title compound is purified by vacuum sublimation (98 °C, 10^{-4} torr) followed by crystallization from hexane.[5] $Mo_2(MeNCH_2CH_2NMe)_3$ shows a strong molecular ion in the mass spectrometer and has a simple two-line ^1H NMR spectrum which is indicative of a bridged and time-averaged eclipsed structure. The *N*-methyl and *N*-CH_2 signals are shifted upfield and downfield, respectively, from positions they would otherwise have had in the absence of the magnetic anisotropy associated with the Mo-to-Mo triple bond.[6]

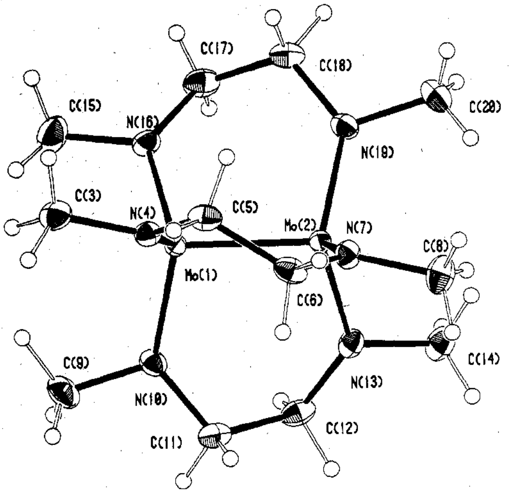


Figure 1. An ORTEP view of the $Mo_2(MeNCH_2CH_2NMe)_3$ molecule showing the atomic numbering scheme used in Tables I and II. Atoms are represented by thermal ellipsoids drawn at the 50% probability level.

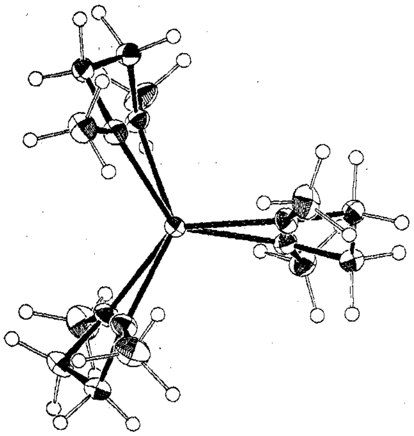


Figure 2. An ORTEP view of the $Mo_2(MeNCH_2CH_2NMe)_3$ molecule viewed down the Mo≡Mo bond emphasizing the near-eclipsed geometry of the Mo_2N_6 moiety. The deviation from the eclipsed conformation is given by the torsional angles listed in Table II.

Table I. Bond Distances (Angstroms)

A	B	dist	A	B	dist
Mo(1)	Mo(2)	2.190 (1)	N(10)	C(9)	1.467 (4)
Mo(1)	N(4)	1.969 (2)	N(10)	C(11)	1.452 (4)
Mo(1)	N(10)	1.964 (2)	N(13)	C(12)	1.456 (4)
Mo(1)	N(16)	1.961 (2)	N(13)	C(14)	1.458 (4)
Mo(2)	N(7)	1.967 (2)	N(16)	C(15)	1.458 (4)
Mo(2)	N(13)	1.967 (2)	N(16)	C(17)	1.459 (4)
Mo(2)	N(19)	1.971 (2)	N(19)	C(18)	1.456 (4)
N(4)	C(3)	1.463 (4)	N(19)	C(20)	1.444 (4)
N(4)	C(5)	1.447 (4)	C(5)	C(6)	1.518 (4)
N(7)	C(6)	1.458 (4)	C(11)	C(12)	1.512 (4)
N(7)	C(8)	1.456 (4)	C(17)	C(18)	1.512 (4)

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[1] Camille and Henry Dreyfus Teacher-Scholar, 1979–1984.

[2] Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7736. See also: Dedien, A; Albright, T. A.; Hoffmann, R. *Ibid.* **1979**, *101*, 3141. Calculations by others have implied little or no conformational preference for these molecules: Hall, M. B. *Ibid.* **1980**, *102*, 2104. Bursten, B. E.; Cotton, F. A.; Green, J. C.; Seddon, E. A.; Stanley, G. G. *Ibid.* **1980**, *102*, 4579.

[3] (a) For a recent review of the chemistry of these compounds, see: Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356. (b) The detailed electronic structures have been reviewed: Cotton, F. A. *Ibid.* **1978**, *11*, 225.

[4] Successive replacement of Me_2N ligands by Cl ligands leads to polymeric $MoCl_3$: Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407.

[5] All operations were carried out by using dry and oxygen-free solvents and atmospheres.

[6] ^1H NMR data obtained in toluene-d_8 solution at 220 MHz: $\delta(CH_3)$ = 2.87, $\delta(CH_2)$ = 3.80; δ in ppm relative to $(CH_3)_4Si$. For a discussion of the diamagnetic anisotropy associated with the triple bond, see the discussion in ref 8.

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Table II

Angles (Deg)

A	B	C	angle
Mo(2)	Mo(1)	N(4)	101.8 (1)
Mo(2)	Mo(1)	N(10)	102.1 (1)
Mo(2)	Mo(1)	N(16)	102.1 (1)
N(4)	Mo(1)	N(10)	116.5 (1)
N(4)	Mo(1)	N(16)	114.7 (1)
N(10)	Mo(1)	N(16)	116.1 (1)
Mo(1)	Mo(2)	N(7)	102.2 (1)
Mo(1)	Mo(2)	N(13)	101.8 (1)
Mo(1)	Mo(2)	N(19)	101.5 (1)
N(7)	Mo(2)	N(13)	115.5 (1)
N(7)	Mo(2)	N(19)	114.0 (1)
N(13)	Mo(2)	N(19)	118.3 (1)
Mo(1)	N(4)	C(3)	115.5 (2)
Mo(1)	N(4)	C(5)	131.0 (2)
C(3)	N(4)	C(5)	111.4 (2)
Mo(2)	N(7)	C(6)	130.8 (2)
Mo(2)	N(7)	C(8)	115.6 (2)
C(6)	N(7)	C(8)	111.4 (2)
Mo(1)	N(10)	C(9)	114.7 (2)
Mo(1)	N(10)	C(11)	132.3 (2)
C(9)	N(10)	C(11)	110.7 (2)
Mo(2)	N(13)	C(12)	131.8 (2)
Mo(2)	N(13)	C(14)	115.8 (2)
C(12)	N(13)	C(14)	110.9 (2)
Mo(1)	N(16)	C(15)	115.7 (2)
Mo(1)	N(16)	C(17)	132.8 (2)
C(15)	N(16)	C(17)	110.4 (2)
Mo(2)	N(19)	C(18)	129.4 (2)
Mo(2)	N(19)	C(20)	116.1 (2)
C(18)	N(19)	C(20)	111.5 (2)
N(4)	C(5)	C(6)	115.1 (2)
N(7)	C(6)	C(5)	114.2 (2)
N(10)	C(11)	C(12)	115.2 (2)
N(13)	C(12)	C(11)	116.1 (2)
N(16)	C(17)	C(18)	114.7 (2)
N(19)	C(18)	C(17)	115.0 (2)

Torsion Angles (Deg)

N(4)	Mo(1)	Mo(2)	N(7)	11.8 (2)
N(10)	Mo(1)	Mo(2)	N(13)	10.7 (2)
N(16)	Mo(1)	Mo(2)	N(19)	12.6 (2)

A single-crystal X-ray study[7] confirmed the triply bridged structure, shown in Figure 1. This view of the molecule emphasizes the twist-boat nature of the six-membered ring formed by each $Mo_2N_2C_2$ unit. In Figure 2 the molecule is viewed down the Mo–Mo axis which emphasizes the near-eclipsed geometry of the Mo_2N_6 moiety. Pertinent bond distances and bond angles are given in Tables I and II, respectively.

A comparison between the structures of this new compound and $Mo_2(NMe_2)_6$[8] reveals striking similarities. In both compounds each Mo–NC_2 unit is virtually planar with the planes aligned along the Mo–Mo axis and the Mo–N distances are within the range 1.96–1.98 Å indicative of nitrogen-to-molybdenum π bonding. The close similarity in nitrogen-to-molybdenum bonding is also revealed in a comparison of the Mo–Mo–N and proximal (α) and distal (β) Mo–N–C angles. These are given in Table III. It is reasonable to conclude that ligand-to-metal bonding is virtually identical in the two compounds.

Table III. Summary of Angles (Degrees) Associated with the $Mo_2N_6C_{12}$ Skeletons of the $Mo_2(NMe_2)_6$ and $Mo_2(MeNCH_2CH_2NMe)_3$ Molecules

	Mo_2-$(NMe_2)_6$	Mo_2-$(MeNCH_2CH_2NMe)_3$
Mo-Mo-N	103.7 ± 0.3	101.8 ± 0.4
Mo-N-C (α)	133.4 ± 1.2	131.8 ± 1.0
Mo-N-C (β)	116.3 ± 0.3	115.7 ± 0.2

The unit cell of $Mo_2(NMe_2)_6$ contains two crystallographically independent molecules which yield two Mo-to-Mo distances, 2.211 (2) and 2.217 (2) Å. The Mo-to-Mo distance in $Mo_2(MeNCH_2CH_2NMe)_3$ is 2.190 (1) Å, which is significantly shorter by 0.02 Å. Whether this implies a significantly stronger metal-to-metal bond is a matter for further speculation. The known Mo-to-Mo distances in the staggered ethane-like Mo_2X_6 molecules span the range 2.167–2.222 Å, found for X = CH_2SiMe_3[9] and OCH_2CMe_3,[10] respectively. Our interpretation of the present finding is that the Mo-to-Mo triple bond is not particularly perturbed by the rotational conformation of the Mo_2N_6 skeleton.

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Registry No. $Mo_2(MeNCH_2CH_2NMe)_3$, 74331-59-2; 1,2-$Mo_2Cl_2(NMe_2)_4$, 63301-82-6.

Supplementary Material Available: A table of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page. The complete report, MSC Report 7965, is available upon request in microfiche form only from the Indiana University Chemistry Library.

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(7) Crystal data were collected at −175 ± 2 °C with the use of a gaseous-nitrogen cold stream and locally constructed goniostat system: triclinic, space group $P\bar{1}$ with a = 12.036 (3), b = 9.480 (3), c = 8.783 (2) Å; α = 107.94 (2), β = 100.56 (1), γ = 100.65 (1)°; Z = 2; d_{calcd} = 1.65 g cm^{-3}. Of 3215 unique structure amplitudes, the 3142 having $F > \sigma(F)$ were used in the refinement which included anisotropic thermal parameters for all nonhydrogen atoms. Final residuals were $R(F)$ = 0.025 and $R_w(F)$ = 0.041. All hydrogen atoms were located and refined with isotropic thermal parameters.

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Alkali-Metal-Ion Catalysis of the Electron-Transfer Reaction between 1-Propyl-3-carbamoyl-1,4-dihydropyridine and Hexacyanoferrate(III). A Linear Relationship Involving Catalytic Activity

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The rates of electron-transfer reaction between two ions or complexes have long been known to be influenced by the concentration and identity of supporting electrolytes.[1] Although less sensitive than ion–ion reactions, the reaction between an ion and a neutral molecule is also influenced by metal ions but in an unpredictable manner at present.[2] We are reporting here the electron-transfer reaction of N-propyl-

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