process and that the chemical oxidation procedure described herein offers a method for the production of metallic conducting materials from otherwise stoichiometric and nonconducting systems.

Acknowledgment. Work at Argonne National Laboratory is sponsored by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-109-ENG-38. K.L.K., M.A.F., and K.S.W. are student research participants coordinated by the Argonne Division of Educational Programs from the University of Wisconsin, River Falls, WI, Indiana University, Indiana, PA, and St. Michael's College, Winooski, VT, respectively. Research at North Carolina State University was in part supported by DOE, Office of Basic Sciences, Division of Materials Sciences, under Grant DE-FG05-86ER45259. M.-H.W. is a participant in the Faculty Research Program, sponsored by Argonne Division of Educational Programs with funding provided by DOE. The authors express their appreciation for computing time on the ER-Cray X-MP computer, made available by DOE.

Registry No. ET, 66946-48-3; $(ET)_2(I_3)(I_5)$, 107798-36-7; $(ET)(I_3)(TlI_4)$, 107798-35-6.

Supplementary Material Available: Tables of the refined anisotropic thermal parameters for all non-hydrogen atoms of ζ-$(ET)_2(I_3)(I_5)$, ϵ-$(ET)_2(I_3)(I_8)_{0.5}$, and $(ET)_2(I_3)(TlI_4)$ (Tables IX, XIII, and XIV) and listings of experimental parameters for the X-ray diffraction study and final positional and thermal parameters for ϵ-$(ET)_2(I_3)(I_8)_{0.5}$ (Tables XI and XII) (5 pages); lists of observed and calculated structure factors for ζ-$(ET)_2(I_3)(I_5)$ and $(ET)_2(I_3)(TlI_4)$ (Tables X and XV) (48 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Molecular Structure Center,
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Tris(*N*,*N*′-dimethylethylenediaminato)dimolybdenum and Tris(*N*,*N*′-dimethylethylenediaminato)ditungsten. A Comparison of Eclipsed and Staggered Triple Bonds, $\sigma^2\pi^4$, between Molybdenum and Tungsten Atoms in $X_3M{\equiv}MX_3$ Compounds

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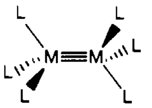
Received September 10, 1986

The compounds $M_2(MeNCH_2CH_2NMe)_3$ have been prepared by metathetic reactions involving $1,2\text{-}M_2Cl_2(NMe_2)_4$ and $Li_2[MeNCH_2CH_2NMe]$ compounds for M = Mo and W. Addition of the diamine $Me(H)NCH_2CH_2N(H)Me$ (>3 equiv) to hydrocarbon solutions of either $M_2(O\text{-}t\text{-}Bu)_6$ or $M_2(NMe_2)_6$ in the presence of a trace amount of HBr also gives $M_2(MeNCH_2CH_2NMe)_3$ compounds. The latter compounds have been characterized by a variety of physical techniques including single-crystal X-ray studies. The diaminato ligands span the M≡M bond such that the central M_2N_6 moiety is nearly eclipsed, having N-M-M-N torsion angles in the range 10-14°. The M-M distances are 2.190 (1) Å (M = Mo) and 2.264 (1) Å (M = W), shorter by 0.02 and 0.03 Å than the M-M distances in the related $M_2(NMe_2)_6$ compounds. The origin of this shortening is discussed and attributed to the presence of the bridging ligands rather than to differences in the electronic nature of the M≡M bond as a function of the eclipsed vs. staggered conformation of the central M_2N_6 unit. Cell dimensions at -175 °C for $Mo_2(MeNCH_2CH_2NMe)_3$: $a = 12.036$ (3) Å, $b = 9.480$ (3) Å, $c = 8.783$ (2) Å, $\alpha = 107.94$ (3)°, $\beta = 100.56$ (2)°, $\gamma = 100.65$ (2)°, cell volume = 905.55 (9) Å^3, $Z = 2$, $d_{calcd} = 1.651$ g cm^{-3}, $R(F) = 0.0247$, $R_w(F) = 0.0408$, space group $P\bar{1}$. Cell dimensions for $W_2(MeNCH_2CH_2NMe)_3$ at -161 °C: $a = 11.869$ (3) Å, $b = 9.477$ (2) Å, $c = 8.841$ (2) Å, $\alpha = 107.92$ (1)°, $\beta = 99.61$ (1)°, $\gamma = 98.99$ (1)°, cell volume = 909.76 (10) Å^3, $Z = 2$, $d_{calcd} = 2.286$ g cm^{-3}, $R(F) = 0.0475$, $R_w(F) = 0.0494$, space group $P\bar{1}$.

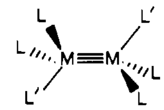
Introduction

Compounds of types **1** and **2** have proven to be quite extensive.[1] These compounds contain metal-metal triple bonds unsupported by bridging ligands, where the triple bond is viewed as being composed of one σ and two equivalent π components $[\sigma(d_{z^2}\text{-}d_{z^2}), \pi(d_{xz},d_{yz}\text{-}d_{xz},d_{yz})]$.[2] In all structural studies to date, M_2L_6 and $M_2L'_2L_4$ compounds adopt staggered, D_{3d}, ethane-like core conformations. In all of the early work this geometry was assumed to arise because of steric constraints since a metal-metal triple bond of configuration $\sigma^2\pi^4$ should be cylindrical for any molecule having a C_3 axis of symmetry coincident with the M-M bond.



1

L = NR_2,[1a] OR,[1b] R,[1c] SAr[1d]



2

L = NR_2; L′ = alkyl,[1e] aryl,[1f] Cl,[1g], OR[1h]
L = OR; L′ = OR[1h]
L = OR; L = R[1i]
L = R; L′ = OR, NR_2, Br[1k]

Albright and Hoffmann's[3] provocative claim that these M_2L_6 (M≡M) dimers "should prefer the eclipsed conformation" has

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(2) Electronic description via SCF-Xα and photoelectron spectra: (a) Cotton, F. A.; Stanley, G. G.; Kalbacher, B. J.; Green, J. C.; Seddon, E.; Chisholm, M. H. *Proc. Natl. Acad. Sci. USA* **1977**, *74*, 3109. (b) Bursten, B. E.; Cotton, F. A.; Green, J. C.; Seddon, E. A.; Stanley, G. G. *J. Am. Chem. Soc.* **1980**, *102*, 4579.

(3) Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7736.

0020-1669/87/1326-1920$01.50/0

stimulated several theoretical appraisals of this system.[2b,4–6] The rationale put forth by Albright and Hoffmann for the preference for the eclipsed geometry rests on their calculation that the overlap of the π-type orbitals is maximized in the eclipsed conformation rather than in the staggered one.[3] Theoretical approaches utilized by others, i.e. GMO–CI, single determinant STO–3G and Hartree–Fock–Slater transition state methods have suggested (i) no geometric preference based upon electronics,[4b] (ii) a preference for staggered or eclipsed conformations as a function of the ligand type,[5] and (iii) a definite favoring of a staggered geometry.[6] From these calculations two common observations can be made: (1) The orbitals involved in the metal–metal triple bond are all primarily metal based with the π bonds exhibiting nearly pure $d\pi$ character. (2) Any determined rotational barriers are overwhelmingly the result of the steric requirements of the ligands.

The difference between these calculational methods arises primarily from the amount of δ and π orbital mixing. In the EHMO approach the dimer M_2L_6 is constructed from ML_3 hybrid orbitals.[7] If each metal were to use essentially octahedral hybrid orbitals, then the M_2L_6 molecule could be viewed as a confacial bioctahedron lacking the common face. This would clearly favor the eclipsed conformation.

A test of these theoretical predictions based on the synthesis of a M_2L_6 compound for which the uninegative ligands L are sufficiently small that steric repulsive interactions could be ignored, e.g. L = H, Cl, or CH_3, seems most unlikely since oligomerization would then occur.[8]

This leads to the frustrating situation in which a theoretical prediction cannot reasonably be tested experimentally. We reasoned that by choice of a suitable chelating dinegative ligand we could prepare a $M_2(L\text{-}L)_3$ compound that would be electronically and sterically related to a M_2L_6 compound in all ways except in conformation, with the $M_2(L\text{-}L)_3$ molecule having an eclipsed and the M_2L_6 molecule the staggered conformation. We describe here our preparation and characterization of $M_2(Me_2NCH_2CH_2NMe)_3$ compounds and a comparison with the $M_2(NMe_2)_6$ compounds (M = Mo and W). A preliminary report of some of this work has appeared.[9]

Experimental Section

Physical Techniques. The physical techniques used have been described previously.[1]

Synthesis. $Mo_2Cl_2(NMe_2)_4$,[1a] $W_2Cl_2(NMe_2)_4$,[1a] $Mo_2(O\text{-}t\text{-}Bu)_6$,[1b] $Mo_2(O\text{-}i\text{-}Pr)_6$,[1b] $Mo_2(NMe_2)_6$[1a] were prepared by the literature methods. *N,N'*-Dimethylethylenediamine and *N*-ethyl-*N'*-methylethylenediamine were purchased from Ames Laboratories, Inc. These diamines were placed over molecular sieves and purged with nitrogen prior to use. Anhydrous pinacol was obtained from Matheson Coleman and Bell and was used as received. *n*-BuLi, 2.4 M, was purchased from Alfa.

$Li_2[MeNCH_2CH_2NMe]$ and $Li_2[EtNCH_2CH_2NMe]$. The synthesis of dilithium *N,N'*-dimethylethylenediaminate illustrates the mode of preparation of these dilithium diaminate salts. $MeN(H)CH_2CH_2N(H)Me$ (2.64 g, 30.0 mmol) was added via syringe to a hexane solution, 2.4 M, of *n*-butyllithium (60.0 mmol) that had been frozen at liquid-nitrogen temperature, −196 °C. The flask containing this reaction mixture was brought slowly to room temperature over $1^1/_2$ h. Shortly after the hexane was thawed, a rather vigorous reaction occurs liberating butane. The solution changes from a clear yellowish color to give a white flocculent product. After room temperature was attained, the solvent was removed in vacuo leaving the $Li_2[MeNCH_2CH_2NMe]$ behind as a fluffy white powder.[10] The dilithiated diaminates are marginally soluble in hexane. Therefore, due to this limited solubility in hexane they are utilized as a solid in all subsequent reactions.

$Mo_2(EtNCH_2CH_2NMe)_3$. $Mo_2(O\text{-}t\text{-}Bu)_6$ (600 mg, 0.95 mmol) was dissolved in toluene (25 mL) in a 50-mL round-bottomed Schlenk flask. $Li_2[MeNCH_2CH_2NEt]$ (326 mg, 2.86 mmol) was added as a solid over 2 h with stirring via a side-arm addition tube. The reaction was allowed to stir for 8 h at room temperature after which it was filtered and placed in the refrigerator at −30 °C. The reaction mixture was filtered again to remove $LiO\text{-}t\text{-}Bu$. The filtrate was placed back in the refrigerator. This sequence was repeated two more times. Finally, the solvent was removed in vacuo, leaving behind a brown-yellow oil. By ^1H NMR no starting material remained but the product, $Mo_2(EtNCH_2CH_2NMe)_3$, is contaminated with some $LiO\text{-}t\text{-}Bu$.

^1H NMR (toluene-d_8, 220 MHz): $CH_3\mathit{NCH_2CH_2}NCH_2CH_3$, δ 3.70 (singlet); $CH_3NCH_2CH_2N\mathit{CH_2}CH_3$, δ 3.02 (complex); $\mathit{CH_3}NCH_2CH_2NCH_2CH_3$, δ 2.88 (singlet, isomer 1), δ 2.84 (singlet, 6 H, isomer 2), δ 2.79 (singlet, 3 H, isomer 2); $CH_3NCH_2CH_2NCH_2\mathit{CH_3}$, δ 1.05 (triplet, 6 Hz).

$W_2(MeNCH_2CH_2NMe)_3$. $W_2Cl_2(NMe_2)_4$ (750 mg, 1.22 mmol) was dissolved in toluene (40 mL) in a 100-mL pear-shaped Schlenk flask. By the use of a side-arm addition tube, $Li_2[MeNCH_2CH_2NMe]$ (367 mg, 3.67 mmol) was added as a solid over a 3-h period while the reaction mixture was stirred. After the mixture was stirred at room temperature for 6 h, the toluene was removed in vacuo and the residue was dissolved in hexane. The resulting hexane solution was filtered, and the filtrate was placed in the refrigerator at −30 °C. After 3 days pale yellow crystals of $W_2(MeNCH_2CH_2NMe)_3$ formed and were filtered and dried in vacuo. Three crops of crystals were harvested, giving a recrystallized yield of 490 mg (64%).

IR: 2770 (sh), 2680 (w), 1290 (s), 1246 (w), 1190 (s), 1150 (w), 1090 (s), 1060 (m), 1008 (s), 943 (s), 890 (s), 550 (w), 500 (m), 300 (w) cm^{-1}. ^1H NMR (toluene-d_8, 220 MHz): $CH_2N\mathit{CH_2CH_2}NCH_3$, δ 3.52 (singlet, 4 H); $\mathit{CH_3}NCH_2CH_2N\mathit{CH_3}$, δ 2.86 (singlet, 6 H). Anal. Found (calcd): C, 22.95 (23.01); N, 13.38 (13.42); H, 4.70 (4.79). In the mass spectrometer a parent ion, *m/e* 626, corresponding to $W_2(MeNCH_2CH_2NMe)_3^+$ was observed.

$Mo_2(MeNCH_2CH_2NMe)_3$. $Mo_2Cl_2(NMe_2)_4$ (800 mg, 1.82 mmol) was placed in a 100-mL pear-shaped Schlenk flask and dissolved in toluene (35 mL). To this solution was added $Li_2[MeNCH_2CH_2NMe]$ (547 mg, 5.47 mmol) as a solid, via a side-arm addition tube over a period of 2 h with stirring. The reaction mixture was allowed to stir at room temperature for 8 h, after which time the toluene was removed in vacuo. The residue was dissolved in hexane and filtered. The volume of the filtrate was then reduced and the filtrate subsequently placed in the refrigerator at −30 °C. Within 1 day pale yellow-tan crystals of $Mo_2(MeNCH_2CH_2NMe)_3$ were formed. The crystals were filtered and dried in vacuo. The process was repeated to yield 540 mg (66%) of $Mo_2(MeNCH_2CH_2NMe)_3$. The product may also be obtained in a pure state via sublimation (105 °C, 10^{-4} Torr) from the crude reaction mixture obtained upon removal of the solvent.

IR: 2800 (sh), 2760 (s), 1280 (w), 1236 (s), 1175 (w), 1148 (s), 1119 (m), 1090 (w), 1059 (w), 1047 (m), 1009 (m), 959 (vs), 944 (vs), 890 (m), 552 (vs), 510 (w), 356 (m). ^1H NMR (toluene-d_8, 220 MHz): $CH_3N\mathit{CH_2CH_2}NCH_3$, δ 3.80 (singlet, 4 H); $\mathit{CH_3}NCH_2CH_2N\mathit{CH_3}$, δ 2.87 (singlet, 6 H). Anal. Found (calcd): C, 31.86 (31.9); N, 18.66 (18.67); H, 6.65 (6.67). In the mass spectrometer a strong molecular ion corresponding to $Mo_2(MeNCH_2CH_2NMe)_3^+$ was observed.

$Mo_2(MeNCH_2CH_2NMe)_3$ via $Mo_2(O\text{-}t\text{-}Bu)_6$ or $Mo_2(NMe_2)_6$ + $Li_2[MeNCH_2CH_2NMe]$. The standard procedure for the synthesis of $Mo_2(MeNCH_2CH_2NMe)_3$ by this method is illustrated in the reaction using $Mo_2(NMe_2)_6$. $Mo_2(NMe_2)_6$ (500 mg, 1.10 mmol) was dissolved in toluene (25 mL) in a 50-mL round-bottomed Schlenk flask. While this solution was being stirred, $Li_2[MeNCH_2CH_2NMe]$ (330 mg, 3.30 mmol) was added as a solid via a side-arm addition tube over 2 h at room temperature. The reaction mixture was allowed to stir for 6 h at room temperature. Subsequent workup procedures were identical with those stated previously for isolation of $Mo_2(MeNCH_2CH_2NMe)_3$. When $Mo_2(O\text{-}t\text{-}Bu)_6$ is the starting material, the product, $Mo_2(MeNCH_2CH_2NMe)_3$, must be sublimed to be made free of $LiO\text{-}t\text{-}Bu$. Yields of ca. 60% based on molybdenum were repeatedly obtained.

$Mo_2(MeNCH_2CH_2NMe)_3$ via $Mo_2(NMe_2)_6$ or $Mo_2(O\text{-}t\text{-}Bu)_6$ + $MeN(H)CH_2CH_2N(H)Me$ Catalyzed by HBr. The standard preparation of $Mo_2(MeNCH_2CH_2NMe)_3$ by this method is illustrated by using $Mo_2(NMe_2)_6$. $Mo_2(NMe_2)_6$ (600 mg, 1.32 mmol) was dissolved in toluene (40 mL) in a 100-mL pear-shaped Schlenk flask. The diamine $MeN(H)CH_2CH_2N(H)Me$ (349 mg, 3.96 mmol) was added via microsyringe. The resulting solution was frozen with liquid nitrogen. The HBr (0.05 mmol) was added by using a calibrated gas line. The reaction mixture was brought to room temperature and subsequently stirred at room temperature for 6 h. Workup procedures were as stated before.

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(10) The dilithiated nature of this compound was verified by a titration with a solution of 2-propanol/benzene of known molarity with 1,10-phenanthroline as an indicator.

Table I. Summary of Crystal Data[a]

	I	II
empirical formula	$Mo_2N_6C_{12}H_{30}$	$W_2C_{12}N_6H_{30}$
color of cryst	yellow	yellow
cryst dimens, mm	0.4 × 0.4 × 0.2	0.11 × 0.12 × 0.12
space group	$P\bar{1}$	$P\bar{1}$
cell dimens		
temp, °C	−175	−161
a, Å	12.036 (3)	11.869 (3)
b, Å	9.480 (3)	9.477 (2)
c, Å	8.783 (2)	8.841 (2)
α, deg	107.94 (3)	107.92 (1)
β, deg	100.56 (2)	99.61 (1)
γ, deg	100.65 (2)	98.99 (1)
Z, molecules/cell	2	2
V, Å^3	905.55 (9)	909.76 (10)
d_{calcd}, g/cm^3	1.651	2.286
wavelength, Å	0.71069	0.71069
M_r	450.29	626.11
linear abs coeff, cm^{-1}	13.545	129.105
detector–sample dist, cm	22.5	22.5
sample–source dist, cm	23.5	23.5
av ω-scan width at half-height	0.25	0.25
scan speed, deg/min	4.0	4.0
scan width (+dispersion), deg	2.2	1.8
individual bkgd, s	5	5
aperture size, mm	2.5 × 3.5	3.0 × 4.0
2θ range, deg	4–50	5–50
tot. no. of reflcns collcd		
no. of unique intens	3215	3310
no. with $F > 0.0$	3180	3226
no. with $F > \sigma(F)$	3142	2998
no. with $F > 2.33\sigma(F)$	3088	2896
$R(F)$[b]	0.0247	0.0475
$R_w(F)$[b]	0.0408	0.0494
goodness of fit for the last cycle[c]	1.115	1.824
max Δ/σ for last cycle	0.05	0.05

[a] I = $Mo_2(MeNCH_2CH_2NMe)_3$; II = $W_2(MeNCH_2CH_2NMe)_3$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Yields are generally lower by this method, ca. 40% recrystallized yield.

Crystallographic Studies. General operating procedures and listings of programs have been given.[11] A summary of crystal data is given in Table I.

$Mo_2(MeNCH_2CH_2NMe)_3$. The structure was solved by a combination of direct methods and Fourier techniques. The two Mo atoms were located in the *E* map; the remainder of the non-hydrogen atoms were located in a difference Fourier synthesis based on the refined Mo atoms. All hydrogen atoms were subsequently located in chemically reasonable positions. Before the final least-squares refinements the hydrogen atom coordinates were reset so that the C–H distance was 1.08 Å along the C–H vector and the methyl group hydrogen atoms were idealized. All hydrogen atom parameters were subsequently refined to the final positions given in Table II.

$W_2(MeNCH_2CH_2NMe)_3$. A suitable sample was cleaved from a large, poorly defined crystal and fractured until it was nearly spherical. It was not possible to obtain well-defined faces while cleaving. The sample was transferred to the goniostat and cooled to −161 °C by using standard inert-gas handling techniques employed by the Indiana University Molecular Structure Center.

Preliminary examination indicated the sample to be isomorphous with the molybdenum complex examined earlier, and the same cell was chosen.

While location of most of the hydrogen atoms was possible, several would not properly refine, so fixed atom contributions for the hydrogen atoms were made on the basis of idealized coordinates whose initial positions were obtained from the molybdenum structure.

ψ-Scans of several strong reflections indicated less than 10% variance in intensity. Since the crystal was nearly spherical, no absorption correction was performed.

The final difference Fourier synthesis was featureless with the exception of four peaks of intensity 1.35–2.20 e/Å^3 located within 1.0 Å of the two tungsten atoms.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for $Mo_2(MeNCH_2CH_2NMe_2)_3$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	2683.8 (2)	2375.9 (2)	6128.1 (3)	10
Mo(2)	2728.4 (2)	4793.9 (2)	6593.0 (2)	10
C(3)	1161 (3)	182 (3)	7043 (4)	22
N(4)	1594 (2)	1826 (3)	7397 (3)	14
C(5)	903 (2)	2696 (3)	8299 (4)	16
C(6)	1532 (2)	4356 (3)	9341 (3)	17
N(7)	1944 (2)	5273 (3)	8396 (3)	14
C(8)	2054 (3)	6896 (3)	9239 (4)	18
C(9)	4544 (3)	1075 (4)	7225 (4)	24
N(10)	4333 (2)	2480 (3)	6994 (3)	15
C(11)	5358 (2)	3762 (3)	7860 (4)	18
C(12)	5423 (3)	5095 (4)	7250 (4)	20
N(13)	4420 (2)	5749 (3)	7220 (3)	15
C(14)	4756 (3)	7345 (4)	7337 (5)	24
C(15)	2282 (3)	−32 (3)	2937 (4)	20
N(16)	2067 (2)	1455 (2)	3715 (3)	14
C(17)	1620 (2)	2065 (3)	2460 (3)	16
C(18)	1048 (2)	3351 (3)	3061 (3)	17
N(19)	1794 (2)	4686 (3)	4449 (3)	14
C(20)	1496 (3)	6080 (4)	4398 (4)	22
H(1)	39 (3)	−24 (4)	640 (5)	27 (8)
H(2)	155 (3)	−22 (4)	643 (4)	233 (8)
H(3)	116 (3)	1 (4)	808 (5)	27 (8)
H(4)	22 (3)	256 (4)	747 (5)	29 (8)
H(5)	60 (3)	224 (3)	900 (4)	10 (6)
H(6)	103 (3)	481 (4)	991 (4)	14 (6)
H(7)	217 (2)	425 (3)	1014 (3)	8 (5)
H(8)	256 (3)	725 (4)	1029 (4)	18 (7)
H(9)	231 (4)	759 (5)	863 (5)	42 (10)
H(10)	127 (2)	715 (3)	923 (3)	8 (5)
H(11)	386 (4)	31 (5)	685 (6)	46 (11)
H(12)	513 (3)	82 (4)	662 (4)	24 (7)
H(13)	469 (3)	107 (4)	841 (5)	28 (8)
H(14)	547 (3)	415 (4)	894 (5)	26 (8)
H(15)	610 (3)	334 (4)	781 (4)	17 (6)
H(16)	603 (4)	573 (4)	796 (5)	30 (8)
H(17)	555 (4)	488 (5)	618 (6)	39 (10)
H(18)	529 (3)	796 (4)	843 (5)	26 (7)
H(19)	514 (3)	743 (3)	644 (4)	10 (6)
H(20)	422 (4)	783 (5)	729 (5)	32 (9)
H(21)	153 (3)	−80 (3)	233 (4)	12 (5)
H(22)	290 (3)	3 (4)	245 (4)	19 (7)
H(23)	257 (3)	−35 (4)	389 (5)	31 (8)
H(24)	216 (3)	242 (3)	203 (4)	15 (6)
H(25)	102 (3)	126 (4)	147 (4)	12 (6)
H(26)	82 (3)	369 (4)	209 (4)	15 (6)
H(27)	42 (2)	297 (3)	329 (3)	6 (5)
H(28)	207 (4)	700 (5)	541 (6)	44 (10)
H(29)	160 (3)	617 (4)	354 (4)	22 (8)
H(30)	67 (3)	606 (4)	439 (4)	25 (8)

Results and Discussion

Synthesis of $M_2(MeNCH_2CH_2NMe)_3$ (M = Mo, W). The best syntheses of these compounds were achieved by metathetic reactions employing the $M_2Cl_2(NMe_2)_4$ compound and slightly greater than 3 equiv of $Li_2[MeNCH_2CH_2NMe]$. Crystalline yields of ca. 60–65% were typically obtained. Other methods were also found for the synthesis of $Mo_2(MeNCH_2CH_2NMe)_3$ as shown in Scheme I. It seems likely that the ditungsten compound can be similarly prepared by a variety of routes, though this has not been experimentally determined.

Of note in all the preparations of $M_2(MeNCH_2CH_2NMe)_3$ compounds is their high formation tendency. If only 1 equiv of the diamine or its dilithio reagent is employed, only $M_2(MeNCH_2CH_2NMe)_3$ and unreacted M_2X_6 compounds are recovered. These observations indicate a cooperative allosteric effect.[12] The introduction of one diaminate ligand produces an enhanced rate for further substitution.

Two further comments on the reactions shown in Scheme I should be made. (1) The use of HBr as a catalyst finds a parallel

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(11) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

(12) Allosteric effects can be cooperative or inhibitive; see: Jolly, *J. Am. Chem. Soc.* **1979**, *101*, 2443; *Acc. Chem. Res.* **1975**, *8*, 385.

Scheme I. Available Methods for the Synthesis of the $Mo_2(MeNCH_2CH_2NMe)_3$ Compound

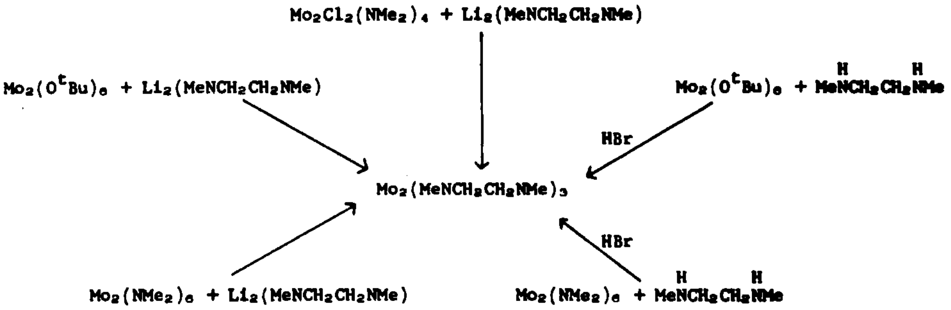

Table III. Fractional Coordinates and Isotropic Thermal Parameters for $W_2(MeNCH_2CH_2NMe)_3$[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$
W(1)	2659.7 (4)	2298 (1)	6133 (1)	10
W(2)	2746.6 (4)	4812 (1)	6654 (1)	9
C(3)	1090 (13)	196 (17)	7092 (19)	24
N(4)	1553 (9)	1823 (11)	7428 (13)	13
C(5)	909 (11)	2737 (15)	8385 (16)	16
C(6)	1560 (11)	4379 (15)	9379 (15)	16
N(7)	1973 (9)	5315 (12)	8463 (12)	13
C(8)	2000 (12)	6893 (15)	9284 (17)	21
C(9)	4487 (12)	867 (15)	7164 (18)	21
N(10)	4298 (9)	2272 (12)	6960 (13)	15
C(11)	5327 (12)	3543 (16)	7791 (17)	19
C(12)	5399 (11)	4840 (16)	7146 (19)	22
N(13)	4453 (9)	5635 (12)	7244 (13)	14
C(14)	4849 (12)	7235 (16)	7556 (21)	26
C(15)	2269 (12)	−25 (15)	2892 (16)	19
N(16)	2064 (9)	1469 (11)	3761 (13)	14
C(17)	1673 (11)	2182 (14)	2580 (15)	17
C(18)	1104 (10)	3497 (15)	3219 (15)	16
N(19)	1854 (9)	4789 (13)	4553 (13)	16
C(20)	1658 (15)	6226 (17)	4455 (18)	26
H(1)	27*	−6*	662*	34
H(2)	147*	−39*	633*	34
H(3)	123*	−2*	807*	34
H(4)	24*	278*	767*	26
H(5)	69*	227*	912*	26
H(6)	105*	486*	997*	26
H(7)	222*	434*	1014*	26
H(8)	256*	727*	1032*	30
H(9)	224*	750*	865*	30
H(10)	126*	701*	947*	30
H(11)	385*	6*	652*	32
H(12)	519*	67*	685*	32
H(13)	457*	97*	828*	32
H(14)	531*	394*	892*	30
H(15)	601*	315*	771*	30
H(16)	612*	556*	774*	31
H(17)	544*	444*	603*	31
H(18)	533*	771*	863*	37
H(19)	531*	737*	679*	37
H(20)	420*	770*	744*	37
H(21)	156*	−65*	218*	31
H(22)	285*	10*	230*	31
H(23)	253*	−48*	367*	31
H(24)	233*	253*	220*	27
H(25)	111*	141*	168*	27
H(26)	85*	384*	235*	26
H(27)	44*	313*	359*	26
H(28)	222*	704*	527*	35
H(29)	172*	627*	341*	35
H(30)	89*	633*	460*	35

[a] Parameters marked by an asterisk were not varied.

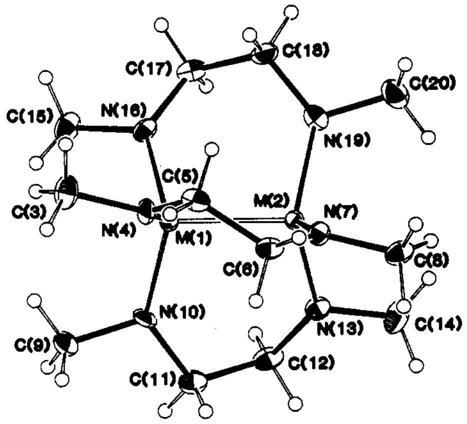

Figure 1. ORTEP view of the $Mo_2(MeNCH_2CH_2NMe)_3$ molecule giving the atom number scheme used for the $M_2(MeNCH_2CH_2NMe)_3$ molecules. This view is looking down one of the pseudo-C_2 axes of symmetry and shows the skew-boat conformation of the six-membered rings.

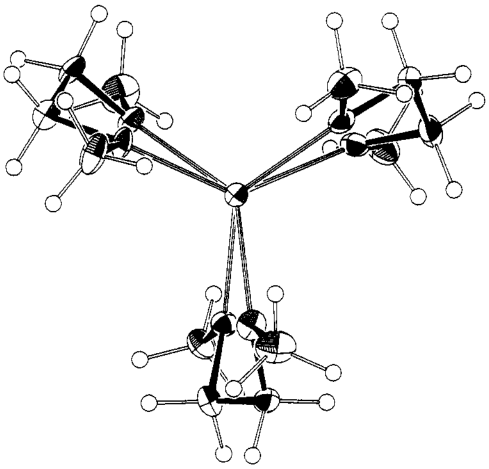

Figure 2. ORTEP view of the $Mo_2(MeNCH_2CH_2NMe)_3$ molecule as viewed down the M–M axis, emphasizing the nearly eclipsed conformation of the molecule.

in the mechanism of chloride for amido substitution in the reactions between $M_2(NMe_2)_6$ and Me_3SiCl compounds.[1g] (2) The displacement of *t*-BuO ligands by the diaminate in the reaction between $Mo_2(O\text{-}t\text{-}Bu)_6$ and $Me(H)NCH_2CH_2N(H)Me$ represents a very rare case in which metal–amide bonds are formed from metal alkoxides. The reverse reaction, in which metal alkoxides are formed by the addition of alcohols to metal amides, is, of course, a commonly employed procedure for the syntheses of certain metal alkoxides. Again we see the high formation tendency of the $M_2(MeNCH_2CH_2NMe)_3$ compounds, which no doubt arises largely from favorable entropic factors.

The new compounds are air-sensitive, volatile, diamagnetic, and yellow or pale-yellow crystalline solids and are soluble in all common hydrocarbon solvents.

Attempts to prepare the related dimetal complexes from the asymmetric diamine $Me(H)NCH_2CH_2N(H)Et$ were much less successful, and no pure crystalline sample was obtained. There is, however, good reason to believe that the compound $Mo_2(MeNCH_2CH_2NEt)_3$ does exist and is formed in at least two isomeric forms as we shall show later.

Solid-State and Molecular Structures. The molybdenum and tungsten compounds are isomorphous and isostructural. Atomic positional parameters are given in Tables II and III. An ORTEP

Table IV. Comparison of Bond Distances (Å) for the $M_2(MeNCH_2CH_2NMe)_3$ Molecules (M = Mo, W)

	M = Mo	M = W		M = Mo	M = W
M(1)–M(2)	2.190 (1)	2.265 (1)	N(10)–C(9)	1.457 (4)	1.444 (16)
M(1)–N(4)	1.969 (2)	1.968 (10)	N(10)–C(11)	1.452 (4)	1.476 (17)
M(1)–N(10)	1.964 (2)	1.966 (10)	N(13)–C(12)	1.456 (4)	1.447 (17)
M(1)–N(16)	1.961 (2)	1.958 (10)	N(13)–C(14)	1.458 (4)	1.440 (17)
M(2)–N(7)	1.967 (2)	1.946 (10)	N(16)–C(15)	1.458 (4)	1.468 (15)
M(2)–N(13)	1.967 (2)	1.971 (10)	N(16)–C(17)	1.459 (4)	1.460 (17)
M(2)–N(19)	1.971 (2)	1.970 (10)	N(19)–C(18)	1.456 (4)	1.450 (17)
N(4)–C(3)	1.463 (4)	1.472 (17)	N(19)–C(20)	1.444 (4)	1.443 (17)
N(4)–C(5)	1.447 (4)	1.422 (17)	C(5)–C(6)	1.518 (4)	1.532 (19)
N(7)–C(6)	1.458 (4)	1.457 (16)	C(11)–C(12)	1.512 (4)	1.502 (18)
N(7)–C(8)	1.456 (4)	1.440 (17)	C(17)–C(18)	1.512 (4)	1.512 (19)

Table V. Comparison of Bond Angles (deg) for the $Mo_2(MeNCH_2CH_2NMe)_3$ Molecules (M = Mo, W)

	M = Mo	M = W		M = Mo	M = W
M(2)–M(1)–N(4)	101.8 (1)	101.4 (3)	M(1)–N(10)–C(9)	114.7 (2)	115.5 (8)
M(2)–M(1)–N(10)	102.1 (1)	102.2 (3)	M(1)–N(10)–C(11)	132.3 (2)	130.1 (8)
M(2)–M(1)–N(16)	102.1 (1)	101.6 (3)	C(9)–N(10)–C(11)	110.7 (2)	112.5 (10)
N(4)–M(1)–N(10)	116.5 (1)	115.7 (4)	M(2)–N(13)–C(12)	131.8 (2)	129.6 (8)
N(4)–M(1)–N(16)	114.7 (1)	115.7 (4)	M(2)–N(13)–C(14)	115.8 (2)	117.2 (9)
N(10)–M(1)–N(16)	116.1 (1)	116.6 (4)	C(12)–N(13)–C(14)	110.9 (2)	112.3 (10)
M(1)–M(2)–N(7)	102.2 (1)	102.0 (3)	M(1)–N(16)–C(15)	115.7 (2)	117.3 (8)
M(1)–M(2)–N(13)	101.8 (1)	101.4 (3)	M(1)–N(16)–C(17)	132.8 (2)	131.7 (8)
M(1)–M(2)–N(19)	101.5 (1)	101.1 (3)	C(15)–N(16)–C(17)	110.4 (2)	109.3 (10)
N(7)–M(2)–N(13)	115.5 (1)	114.9 (4)	M(2)–N(19)–C(18)	129.4 (2)	128.1 (8)
N(7)–M(2)–N(19)	114.0 (1)	115.5 (4)	M(2)–N(19)–C(20)	116.1 (2)	117.0 (9)
N(13)–M(2)–N(19)	118.3 (1)	118.1 (4)	C(18)–N(19)–C(20)	111.5 (2)	112.8 (10)
M(1)–N(4)–C(3)	115.5 (2)	115.8 (8)	N(4)–C(5)–C(6)	115.1 (2)	115.7 (10)
M(1)–N(4)–C(5)	131.0 (2)	131.4 (8)	N(7)–C(6)–C(5)	114.2 (2)	116.7 (10)
C(3)–N(4)–C(5)	111.4 (2)	111.2 (10)	N(10)–C(11)–C(12)	115.2 (2)	115.5 (11)
M(2)–N(7)–C(6)	130.8 (2)	129.6 (8)	N(13)–C(12)–C(11)	116.1 (1)	116.7 (11)
M(2)–N(7)–C(8)	115.6 (2)	118.0 (8)	N(16)–C(17)–C(18)	114.7 (2)	115.1 (10)
C(6)–N(7)–C(8)	111.4 (2)	111.1 (10)	N(19)–C(18)–C(17)	115.0 (2)	115.1 (10)

Table VI. Comparison of Bond Distances (Å) for $Mo_2(NMe_2)_6$ and $M_2(MeNCH_2CH_2NMe)_3$ Compounds (M = Mo, W)

compd	M–M	M–N(av)	N–C(av)	ref
$Mo_2(NMe_2)_6$	2.214 (3)	1.98 (1)	1.47 (2)	1a
$Mo_2(MeNCH_2CH_2NMe)_3$	2.190 (1)	1.97 (1)	1.46 (1)	*a*
$W_2(NMe_2)_6$	2.294 (1)	1.98 (1)	1.47 (1)	1a
$W_2(MeNCH_2CH_2NMe)_3$	2.265 (1)	1.96 (1)	1.45 (1)	*a*

[a] This work

view for the molybdenum compound is shown in Figure 1 and the number scheme for the atoms is common to both molecules. A view looking down the Mo–Mo bond is given in Figure 2. Listings of bond distances and bond angles are compared for the two compounds in Tables IV and V, respectively.

Particularly pertinent to the objective of this work is a comparison of the structural parameters of the $M_2(MeNCH_2CH_2NMe)_3$ and $M_2(NMe_2)_6$ compounds. A comparison of bond distances is given in Table VI, and a comparison of bond angles is given in Table VII. The torsional angles N–M–M–N for the $M_2(MeNCH_2CH_2NMe)_3$ compounds are also given in Table VII.

Collectively, the data reveal the remarkably similar structural parameters for the staggered $M_2(NMe_2)_6$ and the near-eclipsed $M_2(MeNCH_2CH_2NMe)_3$ compounds. The internal angles M–M–N and the proximal M–N–C (α) and distal M–N–C (β) angles differ by less than 2° within the two sets of compounds. To the extent that small differences are seen, the pattern is understandable in terms of the bridging ligand favoring the smaller angles.

The conformation of the six-membered rings involving the bridging ligands is that of a skew-boat as can be seen from examination of Figure 1. This is presumably preferred to the chair because of the differing lengths of the six bonds in the ring, which span the range 1.46–2.3 Å corresponding to the short N–C and long M–M bonds, respectively. The conformation about the C–C bond allows for staggered C–H bonds.

The only significant differences are the M–M distances, which are 0.02 (Mo)–0.03 A (W) shorter in the diaminato compounds.

^{1}H NMR Studies. The ^{1}H NMR spectra of the $M_2(MeNCH_2CH_2NMe)_3$ compounds are temperature independent in the range −80 to +60 °C in toluene-d_8. There is a single two-line pattern with δ 3.80 (2 H) and 2.87 (3 H) for M = Mo and δ 3.52 (2 H) and 2.86 (3 H) for M = W. From this we must conclude that methylene protons spanning the M≡M bond are equivalent because of facile motions within the six-membered rings. Specifically $\lambda \rightarrow \delta$ interconversions of the ring generate a time-averaged molecule having equivalent methylene protons and an eclipsed M_2N_6 structure (torsional angles N–M–M–N = 0°).

The assignment of the methylene protons and *N*-methyl protons in $M_2(MeNCH_2CH_2NMe)_3$ is, of course, unambiguous since their integral intensity is 2:3, respectively. The observed deshielding of the methylene protons and shielding of the *N*-methyl protons

Table VII. Comparison of Pertinent Angles (deg) (Averaged) for the $M_2(NMe_2)_6$ and $M_2(MeNCH_2CH_2NMe)_3$ Molecules (M = Mo, W)[a]

compd	M–M–N	M–N–C (α)	M–N–C (β)	C–N–C (γ)	ref
$Mo_2(NMe_2)_6$	103.7 (3)	133.4 (12)	116.3 (3)	110.2 (13)	1a
$Mo_2(MeNCH_2CH_2NMe)_3$	102.0 (2)	131.4 (8)	115.6 (5)	111.1 (4)	*b*
$W_2(NMe_2)_6$	103.8 (3)	132.6 (6)	116.5 (5)	111.0 (7)	1a
$W_2(MeNCH_2CH_2NMe)_3$	101.6 (5)	130.1 (14)	116.8 (12)	111.5 (17)	*b*

	torsional angles		
compd	N(4)–M(1)–M(2)–N(7)	N(10)–M(1)–M(2)–N(13)	N(16)–M(1)–M(2)–N(19)
$Mo_2(MeNCH_2CH_2NMe)_3$	11.8 (1)	10.7 (1)	12.6 (1)
$W_2(MeNCH_2CH_2NMe)_3$	12.7 (1)	11.1 (1)	13.9 (1)

[a] Key: α = proximal; β = distal. [b] This work.

is consistent with our previous suggestions for proximal and distal N–Me groups in $M_2(NMe_2)_6$ compounds.[1a] From the chemical shifts of the latter and the known structures, McGlinchey[13] calculated $\chi_{M\equiv M} = -156 \times 10^{-36}$ (M = Mo) and -142×10^{-36} (M = W) M^3/molecule, for the triple bonds in $M_2(NMe_2)_6$ compounds. If we use these values of $\chi_{M\equiv M}$ and determine the average distance of the hydrogen atoms from the M_2 center from the structural data, we can calculate the chemical shift separations of the proximal and distal protons. This gives 1.63 and 1.48 ppm for the tungsten and molybdenum compounds, respectively, which is unmistakably at variance with the observed separations, 0.66 (M = W) and 0.93 ppm (M = Mo). Although some error in the calculations might arise from trying to correlate time-averaged solution properties with ground-state geometries, these differences are too large and the trends for M = Mo and W are in the reverse order for the two sets of compounds. What we may conclude is (1) the triple bonds in $M_2(NMe_2)_6$ and $M_2(MeNCH_2CH_2NMe_2)_3$ are very different in their $\chi_{M\equiv M}$ values or (2) the model used to calculate $\chi_{M\equiv M}$ was insufficiently developed.

We are inclined toward the latter view for two reasons. (1) The observed structural data and spectroscopic data (still to be presented) suggest that the M≡M bonds are at least very similar in both sets of compounds. (2) McGlinchey's calculation of $\chi_{M\equiv M}$ did not take into consideration the magnetic anisotropy of the M=N bonds. For an isolated $M-NMe_2$ moiety with $\alpha = \beta$ this would not be a significant omission. However, for a M_2N_6 moiety, the M–N contributions to the field of the proximal protons are clearly different for staggered and eclipsed forms of the molecule.

The ^1H NMR spectra of the oil assigned to $Mo_2(MeNCH_2CH_2NEt)_3$ are indicative of the presence of two isomers, one having three NMe and three NEt groups at each molybdenum atom (isomer 1) and the other having the 2:1 arrangement of ligands (isomer 2). The methylene protons are degenerate and give rise to a single resonance at δ 3.70; cf. δ 3.80 for $Mo_2(MeNCH_2CH_2NMe)_3$. The fortuitous degeneracy of the methylene protons is also found in the free ligand $MeN(H)CH_2CH_2N(H)Et$ at 220 MHz. The *N*-methyl resonances appear as three singlets, δ 2.88, 2.84, and 2.79 in the integral ratio 2:6:3. The resonance at δ 2.88 is assigned to the more symmetric isomer having all three N-Me groups at one molybdenum. The NCH_2 protons of the N–Et groups appear as three overlapping ABX_3 patterns centered at δ 3.02 while the NCH_2CH_3 protons appear as a triplet, δ 1.05, again indicating a degeneracy. These resonances are unaffected by temperature changes in the range –45 to +60 °C, indicating that interconversion of the two isomers is slow on the NMR time scale. Moreover their relative intensities remain unchanged suggesting that the distribution of isomer 2 to isomer 1, 4:1, may be kinetically controlled in the substitution reaction.

Other Spectroscopic Studies. The infrared spectra of the $M_2(MeNCH_2CH_2NMe)_3$ and $M_2(NMe_2)_6$ compounds are virtually superimposible and the electronic absorption spectra are also extremely similar; cf. λ_{max}, nm (ϵ, M^{-1} cm^{-1}), for $Mo_2(NMe_2)_6$ (326 (12 300), 259 (13 800), 244 (19 600)) and for $Mo_2(MeNCH_2CH_2NMe)_3$ (323 (12 400), 255 (20 000), 237 (28 300)).

The He I and He II PE spectra of the $M_2(MeNCH_2CH_2NMe)_3$ compounds have been examined by Kober and Lichtenberger as part of their general studies of photoionizations of M–M multiple bonds.[14] Assignment of ionizations from Mo–Mo π and σ orbitals to bands centered at 7.23 and 7.55 eV, respectively, may be compared to the similar ionizations in $Mo_2(NMe_2)_6$ at 7.13 and 7.48 eV. Aside from a slight shift to higher binding energy the separation of the σ and π ionizations remains essentially the same for the eclipsed and staggered M_2N_6-containing compounds.

Concluding Remarks. This work has provided a comparison of structural and spectroscopic properties of the compounds $M_2(MeNCH_2CH_2NMe)_3$ and $M_2(NMe_2)_6$. Despite the differing M_2N_6 conformations, the two sets of compounds are remarkably similar in their structural and spectroscopic properties. Only the M–M distance is significantly shorter in the diaminato-bridged compounds. The shortening of the M≡M bond, 0.02 Å for M = Mo and 0.03 Å for M = W, is, however, small within the known range of compounds containing the central $(M\equiv M)^{6+}$ unit.[1,15] It seems unlikely that any significant electronic effect is at work and that the M≡M bond in these compounds is essentially cylindrical.

The observed shortening is well within the range commonly observed for bridged vs. unbridged triple or quadruple bonds in otherwise similar compounds.[15] For example, we recently reported[16] the characterization of two $(W\equiv W)^{6+}$-containing compounds of formula $W_2Et_2(NMe_2)_2(ArN_3Ar)_2$. In both compounds the 1,3-diaryltriazenido ligand was behaving as a bidentate ligand and each tungsten atom formed one W–C and three W–N bonds (one to Me_2N and two to ArN_3Ar ligands). In one compound, where Ar = Ph, there was an unbridged W≡W bond of distance 2.304 (1) Å while in the other, where Ar = *p*-tolyl, there was a pair of cis-bridging triazenido ligands and a W≡W bond of distance 2.267 (1) Å. In solution each compound exists as an equilibrium mixture of bridged and unbridged Ar_2N_3 isomers with the position of the equilibrium being only modestly shifted by Ar = Ph relative to *p*-tolyl. It seems safe to conclude that for M_2X_6 compounds the M≡M bond is little influenced by eclipsed or staggered conformations, but bridging groups that may favor eclipsed geometries will tend to produce slightly shorter M–M distances.

Acknowledgment. We thank the National Science Foundation and the Wrubel Computing Center for support.

Registry No. I, 74331-59-2; II, 107799-69-9; $Li_2[MeNCH_2CH_2NMe]$, 54760-74-6; $Li_2[EtNCH_2CH_2NMe]$, 107819-62-5; $MeN(H)CH_2CH_2N(H)Me$, 110-70-3; BuLi, 109-72-8; $EtN(H)CH_2CH_2N(H)Me$, 111-37-5; $Mo_2(EtNCH_2CH_2NMe)_3$, 107799-68-8; $Mo_2(O\text{-}t\text{-}Bu)_6$, 51956-21-9; $W_2Cl_2(NMe_2)_4$, 63301-81-5; $Mo_2Cl_2(NMe_2)_4$, 63301-82-6; $Mo_2(NMe_2)_6$, 51956-20-8; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Tables of anisotropic thermal parameters and complete listings of bond distances and bond angles for the compounds $M_2(MeNCH_2CH_2NMe)_3$ (6 pages); listings of F_o and F_c for both compounds (35 pages). Ordering information is given on any current masthead page.

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