

Preparation and Characterization of 1,2-Dialkyl Compounds of Dimolybdenum and Ditungsten of Formula $M_2R_2(NMe_2)_4$ ($M \equiv M$)

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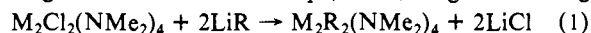
Abstract: 1,2- $M_2Cl_2(NMe_2)_4$ compounds, where $M = Mo$ and W , and alkyllithium reagents react in hydrocarbon solvents to give 1,2- $M_2R_2(NMe_2)_4$ compounds ($M \equiv M$), where $R = -CH_2CH_3$, $-CH_2CD_3$, $-CD_2CH_3$, $-CH_2CH_2CH_2CH_3$, $-CH(CH_3)_2$, $-CH(CH_3)(C_2H_5)$, $-CH_2C(CH_3)_3$, $-CH_2Si(CH_3)_3$, and $-C(CH_3)_3$. These new compounds have been characterized by a combination of physicochemical studies, which include elemental analyses, mass spectroscopy, infrared spectroscopy, and NMR spectroscopy. The molybdenum compounds where $R = CH_2CH_3$ and $-CH(CH_3)_2$ have been examined by single-crystal X-ray diffraction studies. The characterization data establish that all compounds have a staggered ethanelike $M_2N_4C_2$ core. In solution, NMR studies reveal the existence of a mixture of anti and gauche rotamers: as the bulkiness of the alkyl group increases, the gauche rotamer becomes increasingly favored. In the crystalline state, a gauche $Mo_2(C_2H_5)_2(NMe_2)_4$ molecule has been fully characterized by X-ray studies. The molecule has a virtual C_2 axis of symmetry with the following important structural parameters: $Mo-Mo = 2.203$ (1) Å, $Mo-N = 1.96$ (1) Å (average), $M-C = 2.16$ (1) Å (average), $\angle Mo-Mo-N = 104$ (1)° (average), and $\angle Mo-Mo-C = 100.5$ (7)° (average). There are planar $Mo-NC_2$ units which lead to four proximal and four distal N -methyl groups. On the NMR time scale, rotations about $Mo-N$ bonds are fast above +70 °C at 100 MHz, but anti \rightleftharpoons gauche isomerization is slow. An X-ray study on crystalline samples of $Mo_2[CH(CH_3)_2]_2(NMe_2)_4$ revealed disordered $Mo_2N_4C_2$ units: it was not possible to distinguish NMe_2 and $CH(CH_3)_2$ groups. 1H NMR studies revealed that the anti rotamer of $Mo_2[CH(CH_3)_2]_2(NMe_2)_4$ showed frozen out conformers at low temperatures arising from restricted rotations about the $Mo-C$ bonds. The isolation of the isopropyl, *sec*- and *tert*-butyl, and labeled ethyl compounds ($R = CD_2CH_3$ and CH_2CD_3) demonstrates that β -hydrogen elimination does not occur readily in these compounds. The origin of the barrier to β -hydrogen elimination is discussed and these results are compared and contrasted with previous findings for mononuclear transition metal alkyl compounds. The crystal data for $Mo_2(C_2H_5)_2(NMe_2)_4$ are: space group = $P\bar{1}$, $a = 11.730$ (2) Å, $b = 8.402$ (1) Å, $c = 9.840$ (1) Å, $\alpha = 98.09$ (0)°, $\beta = 98.43$ (1)°, $\gamma = 82.74$ (0)°, with $Z = 2$.

Both historically and commercially, σ -alkyl complexes have played a prominent role in the development of mononuclear organotransition metal chemistry.¹⁻³ For many years, it was thought that the σ -alkyl-to-metal bond was inherently weak⁴ and that stability associated with compounds containing π -acceptor ligands such as carbon monoxide and tertiary phosphines could be related to ligand-field effects.⁵ Subsequently, it was recognized that kinetic factors were particularly important and could, in certain cases, block decomposition pathways.⁶ Probably the most common and facile pathway for decomposition of a dialkyl complex involves an initial β -hydrogen elimination (abstraction by the metal) which, though often reversible, is accompanied by a competitive and irreversible reductive elimination of hydrocarbon from the metal center. The latter process involves the formation of a carbon-hydrogen bond. When σ -alkyl groups lack β -hydrogen atoms, then α - or γ -hydrogen-elimination processes may occur. The α -hydrogen-abstraction reaction has been well-documented by Schrock and his co-workers in their pioneering studies of early transition-metal alkyl-alkylidene complexes.⁷ The γ -hydrogen-elimination pathway is seen in the thermal decomposition of *cis*- $Pt(CH_2CMe_3)_2(PEt_3)_2$ which gives the 3,3-dimethylplatinacyclobutane compound *cis*- $Pt[(CH_2)_2CMe_2](PEt_3)_2$ and neopentane.⁸ Rather interestingly, whether by intra- or intermolecular pathways, reductive elimination by carbon-hydrogen bond formation generally appears more favorable than that by carbon-carbon bond formation.⁹

At this time, little is known of the reactivity patterns of σ -alkyl groups coordinated to polynuclear metal centers. These reactions would clearly be important in metal-cluster catalysis and the many varied bonding modes of unsaturated hydrocarbon fragments to polymetallic centers suggest that additional modes of reactivity may be found for alkyl groups attached to polynuclear complexes.¹⁰ As a part of our program in dinuclear transition-metal chemistry,¹¹ we embarked upon a study of the reactions between 1,2- $M_2Cl_2(NMe_2)_4$ ($M \equiv M$) compounds,¹² where $M = Mo$ and W , and organolithium reagents.¹³ Studies of these reactions allow investigation of the reactivity of alkyl groups coordinated to the simplest of polymetallic systems, namely dimetal centers. In this paper, we describe in detail our syntheses and characterizations of an extensive series of 1,2-dialkyl compounds of general formula $Mo_2R_2(NMe_2)_4$ ($M \equiv M$). These compounds show remarkable thermal stability toward decomposition by α -, β - and γ -hydrogen abstraction, particularly in view of the fact that the σ -alkyl groups are coordinated to unsaturated metal centers. In the following paper,¹⁴ we describe studies of reactions of these compounds wherein reductive elimination from the dimetal center is observed.

Results and Discussion

Synthesis. The 1,2-dialkyldimetal compounds were prepared from the general reaction shown in eq 1, below, using the following



$M = Mo$ and W ; $R = Me, Et, CH_2CD_3, CD_2CH_3, n-Bu,$

sec- Bu, i - $Pr, CH_2CMe_3, CH_2SiMe_3,$ and *t*- Bu

common procedure. A suspension of $M_2Cl_2(NMe_2)_4$ in a hydrocarbon solvent, either hexane or toluene,¹⁵ was allowed to react

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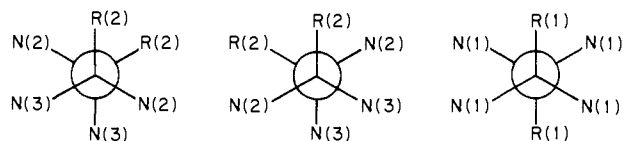
Table I. Analytical Data and Other Characterization Data for 1,2- $M_2R_2(NMe_2)_4$ Compounds

compound	anal. (calcd)			found			color	sublimation temp, °C (at 10^{-4} mmHg)
	C	H	N	C	H	N		
$Mo_2(C_2H_5)_2(NMe_2)_4$	33.8	8.04	13.1	33.6	7.98	13.0	golden yellow	80
$W_2(C_2H_5)_2(NMe_2)_4$	24.0	5.71	9.33	23.9	5.68	9.43	orange red	80
$Mo_2(i-C_3H_7)_2(NMe_2)_4$	37.0	8.37	12.3	36.9	8.25	12.3	yellow	80
$W_2(i-C_3H_7)_2(NMe_2)_4$	26.7	6.03	8.89	26.6	5.98	8.71	red	90
$W_2(n-C_4H_9)_2(NMe_2)_4$	29.2	6.43	8.51	29.3	6.48	8.34	orange	130 distills
$Mo_2[(CH_3)_3CCH_2]_2(NMe_2)_4$	42.4	9.02	10.6	42.5	8.87	10.8	golden yellow	85
$W_2[(CH_3)_3CCH_2]_2(NMe_2)_4$	31.6	6.73	7.76	31.7	6.61	8.04	orange yellow	85
$Mo_2[(CH_3)_3SiCH_2]_2(NMe_2)_4$	35.4	8.48	10.3	39.8	8.48	9.12	yellow	100 distills
$Mo_2(sec-C_4H_9)_2(NMe_2)_4$	39.8	8.71	11.6	39.5	8.66	11.8	golden yellow	80

with the alkylolithium reagent at -78 °C. The solution was then slowly warmed to room temperature and the solvent was stripped. Hexane was then added and lithium chloride and other insoluble species were removed by Schlenk filtration. The hexane-soluble filtrate was collected and the solvent was again stripped. The $M_2R_2(NMe_2)_4$ compounds were isolated as crystalline solids or viscous liquids by vacuum sublimation or distillation. Analytical data and other characterization data are given in Table I. The yields of 1,2-dialkyldimetal compounds (based on eq 1) range from 80% for $R = Me$ ¹⁶ to ca. 20% for $R = i-Pr$ and ca. 5% for $R = t-Bu$. The lower yield associated with the bulky secondary and tertiary alkyl groups does not appear to be indicative of the thermal instability of the pure compound since once isolated, the compounds can be repeatedly sublimed with little decomposition. The low yield in the isolation of these compounds appears to be associated with decomposition during the reactions between $Mo_2Cl_2(NMe_2)_4$ and the organolithium reagents, i.e., reactions leading to decomposition compete with the alkyl-for-chloride group exchange reaction.

Physicochemical Properties. All of the compounds are diamagnetic crystalline solids or viscous liquids at ca. 25 °C. They are thermally quite stable and may be sublimed or distilled in vacuo with little decomposition. In the mass spectrometer, they show clean molecular ions, $M_2R_2(NMe_2)_4^+$; the observed vs. calculated m/e distribution for the $W_2(i-Pr)_2(NMe_2)_4^+$ ion is shown in Figure 1. The compounds are extremely air sensitive and must be handled in rigorously dry and oxygen-free atmospheres. They are extremely soluble in aliphatic and aromatic hydrocarbons, but react with many common organic solvents including alcohols and ketones and partially or totally chlorinated solvents ($CHCl_3$, CH_2Cl_2 , and CCl_4).

NMR Properties. The NMR spectra of the $M_2R_2(NMe_2)_4$ compounds are temperature dependent, but are interpretable upon the assumption that in solution they exist as an equilibrium mixture of anti and gauche 1,2-disubstituted ethanelike dimers. [See the Newman projections shown below.] Anti \rightleftharpoons gauche isomerization is not rapid on the NMR time scale below $+100$ °C.¹⁷ Thus, there are always two types of alkyl ligands, R(1) and R(2), and three types of dimethylamido ligands, denoted by N(1), N(2) and N(3), in the projections shown below. Rotations about M-N



bonds occur with activation energies in the range 11 to 15 kcal mol⁻¹, which depend on R and differ for N(1), N(2), and N(3)

(15) Toluene was not used in reactions involving extremely "hot" alkylolithiums such as $t-BuLi$, since formation of $PhCH_2Li$ occurs.

(16) anti- $Mo_2(CH_3)_2(NMe_2)_4$ has been previously prepared and structurally characterized: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1978**, *17*, 2338.

(17) The energy of activation for anti \rightleftharpoons gauche isomerization has been determined previously for $W_2Me_2(NMe_2)_4$ and $W_2(CH_2SiMe_2)_2(NMe_2)_4$ and falls in the range 22–24 kcal mol⁻¹: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Millar, M.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2244. Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Millar, M.; Stults, B. R. *Ibid.* **1977**, *16*, 3201.

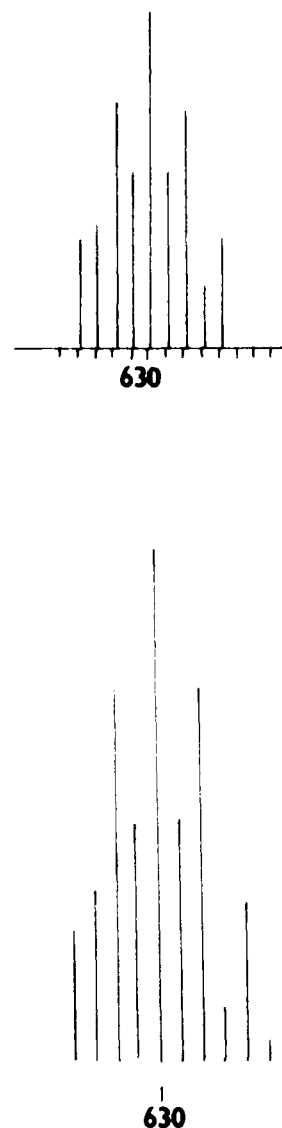


Figure 1. Observed (top) vs. computer simulated (bottom) m/e distribution for the $W_2(i-C_3H_7)_2(NMe_2)_4^+$ ion.

for a given R group. In all cases, rotations are frozen out on the NMR time scale at -60 °C, 270 MHz. Statistically, the gauche-to-anti rotamer concentration ratio is 2 to 1. We find that the [gauche]:[anti] ratios vary with R from ca. 4:1 for $R = Me$ to ca. 20:1 for $R = CH_2CMe_3$ and CH_2SiMe_3 . Qualitatively, these observations may be rationalized by considerations of steric repulsive interactions across the $M\equiv M$ bond, assuming a repulsive interaction order $[NMe_2-NMe_2] > [NMe_2-R] > [R-R]$ with $2[NMe_2-R] > [NMe_2-NMe_2] + [R-R]$.¹⁸

(18) This matter will be discussed further in connection with 1,2- $Mo_2(NMe_2)_2R_4$ compounds: Chisholm, M. H.; Rothwell, I. P., results to be published.

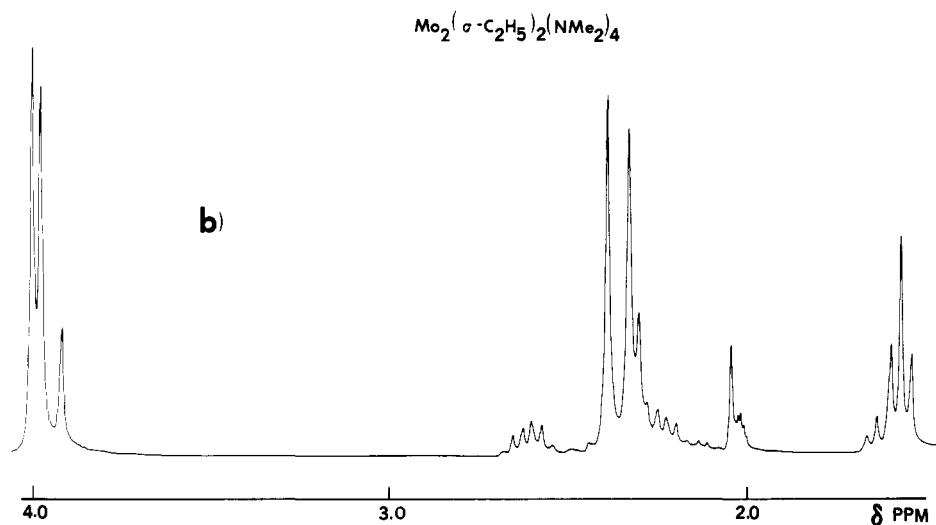


Figure 2. ^1H NMR spectrum of a mixture of anti and gauche $1,2\text{-Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$ in toluene- d_8 at -70°C , 270 MHz. The singlet at δ 2.03 arises from a protiotoluene impurity.

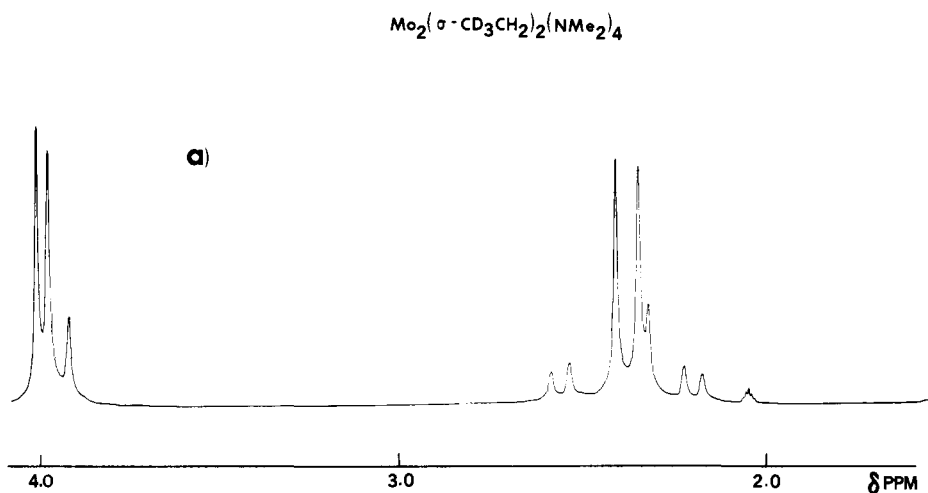


Figure 3. ^1H NMR spectrum of a mixture of anti and gauche $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$ in toluene- d_8 , recorded at -70°C , 270 MHz.

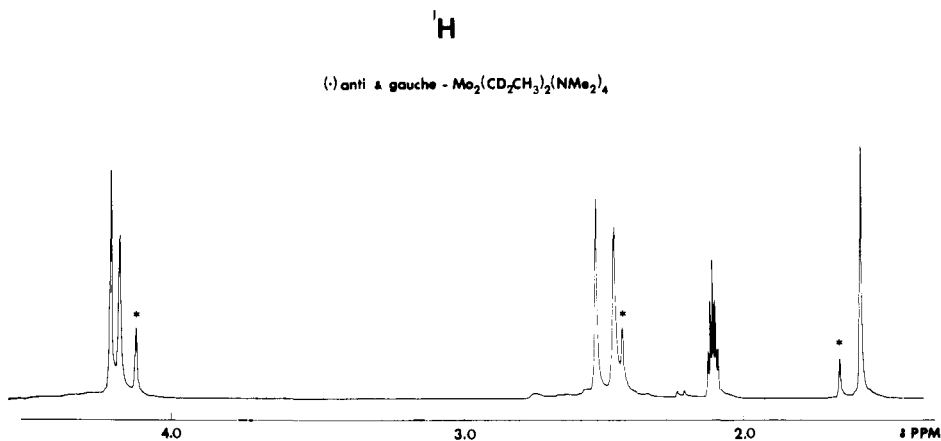


Figure 4. ^1H NMR spectrum of a mixture of anti and gauche $\text{Mo}_2(\text{CD}_2\text{CH}_3)_2(\text{NMe}_2)_4$ in toluene- d_8 , recorded at -70°C , 270 MHz.

The ^1H NMR spectral properties of all the compounds are well illustrated by the following detailed consideration of those associated with $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$ and the ^2H -labeled compounds, $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$ and $\text{Mo}_2(\text{CD}_2\text{CH}_3)_2(\text{NMe}_2)_4$, which are shown at the low-temperature limit in Figures 2, 3, and 4, respectively. The downfield single resonances are assignable¹⁹

to proximal *N*-methyl groups, those lying over the $\text{M}\equiv\text{M}$ bond, and the high-field singlets are assignable to distal *N*-methyl groups, those directed away from the $\text{M}\equiv\text{M}$ bonds. The assignment of anti and gauche isomers follows from the integral ratios predicted by the Newman projections [$\text{N}(2) = \text{N}(3) \neq \text{N}(1)$] and is internally consistent with the ratios of the isomers determined from a consideration of the ethyl resonances. The anti rotamer has a plane of symmetry that contains the methylene carbon atoms of the σ -ethyl ligands, and at 270 MHz, the chemical shifts of the α - and β -hydrogens are sufficiently well separated to allow for

(19) For a discussion of the diamagnetic anisotropy associated with the $\text{Mo}\equiv\text{Mo}$ bond, see: Chisholm, M. H.; Cotton, F. A.; Frenz, B. A.; Shive, L. W.; Stults, B. R.; Reichert, W. W. *J. Am. Chem. Soc.* **1976**, *98*, 4469.

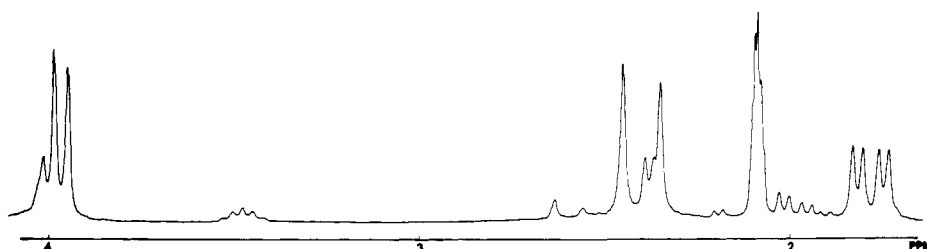
anti & gauche - Mo₂(i-C₃H₇)₂(NMe₂)₄

Figure 5. ^1H NMR spectrum of a mixture of anti and gauche $\text{Mo}_2(i\text{-C}_3\text{H}_7)_2(\text{NMe}_2)_4$, recorded in $\text{toluene-}d_8$ at -75°C , 270 MHz. See text for a discussion of the signals arising from the anti rotamer.

the appearance of a triplet (CH_3) and a quartet (CH_2). The gauche rotamer, which has a C_2 axis of symmetry, has diastereotopic methylene protons, Ha, Hb, and thus, the ethyl group gives rise, at 270 MHz, to an ABX_3 spectrum. The low-temperature-limiting ^1H NMR spectrum, shown in Figure 2, is entirely consistent with these expectations. The spectra shown in Figures 3 and 4, corresponding to the labeled compounds, where $\text{R} = \text{CH}_2\text{CD}_3$ and CD_2CH_3 , respectively, provide unequivocal support for the above assignments. Since the two-bond ^1H - ^1H coupling is very small, the methyl resonances for $\text{R} = \text{CD}_2\text{CH}_3$ appear as singlets, while for the gauche rotamer, where $\text{R} = \text{CH}_2\text{CD}_3$, an apparent AB quartet is seen. The compounds where $\text{R} = \text{CH}_2\text{CMe}_3$ and CH_2SiMe_3 , for which the three-bond ^1H - ^1H couplings are insignificant, give similarly singlets for the methyl resonances and singlets and AB quartets for the methylene proton resonances of anti and gauche rotamers, respectively. The spectra shown in Figures 3 and 4 also show that hydrogen-deuterium scrambling between α - and β -carbon atoms of the ethyl ligand does not occur to any significant extent in these compounds.

The ^1H NMR spectra of the compounds where $\text{R} = n\text{-Bu}$ are similar to those described in detail above for $\text{R} = \text{Et}$, but are further complicated by ^1H - ^1H couplings associated with the n -butyl ligand. For $\text{R} = \text{sec-Bu}$, additional isomers must be present because of the introduction of (+) and (-) carbon atoms directly bonded to the $\text{Mo}_2(\text{NMe}_2)_4$ moiety which also exists as an enantiomeric pair for the gauche rotamer. However, these have not been distinguished. Only the spectra of the compounds where $\text{R} = i\text{-Pr}$ are worthy of additional comment.

The low-temperature-limiting ^1H NMR spectrum for $\text{Mo}_2(i\text{-Pr})_2(\text{NMe}_2)_4$ is shown in Figure 5. The predominant rotamer is again the gauche rotamer and resonances are readily assignable to two proximal N -methyl groups, two distal N -methyl groups, a septet for the methyne proton, and a pair of doublets for the isopropyl methyl groups. The latter arise because a C_2 axis of symmetry generates a pair of diastereotopic methyl groups. A number of other signals are observed. We believe that these are associated with the anti rotamer which may exist in a variety of conformers determined by the positioning of the $\text{Mo-CH}(\text{CH}_3)_2$ groups between the Mo-NC_2 blades. There may be, for each $\text{Mo-CH}(\text{CH}_3)_2$ group, two distal methyl groups, one distal and one proximal methyl group, or two proximal methyl groups which could lead to the presence of a number of diastereomers and enantiomers. By irradiation experiments at low temperature, we have found a methyne signal at δ 2.40, which belongs to an isopropyl group having two methyl signals at δ 2.20 and 1.91. The methyne resonance is markedly upfield relative to the methyne proton resonance of the gauche $\text{Mo}_2(i\text{-Pr})_2(\text{NMe}_2)_4$ molecule (δ 3.48) which suggests that the methyne proton in this conformer of the anti rotamer is not directed over the Mo=Mo bond. Furthermore, the presence of two distinct methyl resonances for this isopropyl group implies the presence of proximal and distal methyl groups. Little more can be said concerning the structures of the isopropyl derivatives, but the apparent disordering of the methyl groups of the isopropyl ligands with respect to the Mo=Mo

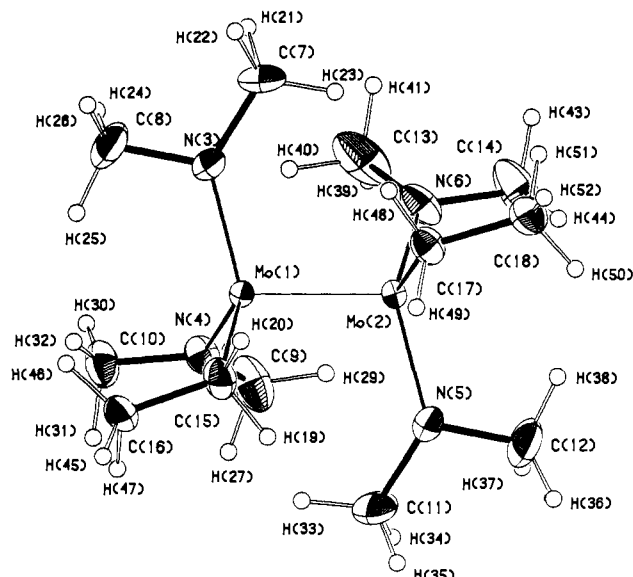


Figure 6. An ORTEP view of the gauche $\text{Mo}_2(\text{C}_2\text{H}_5)_2(\text{NMe}_2)_4$ molecule showing the atom numbering scheme used in the tables.

bond found in solution at low temperatures by ^1H NMR studies is also supported by the X-ray studies described below.

^1H NMR data for the $\text{M}_2\text{R}_2(\text{NMe}_2)_4$ compounds are given in the Experimental Section.

Solid-State Structures. The previous single-crystal X-ray characterizations of the compounds $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_4$ ¹⁶ and $\text{W}_2\text{Me}_2(\text{NET}_2)_4$ ¹⁷ taken together with the ^1H NMR spectra of the compounds, left no doubt concerning the gross structural features of the other 1,2-dialkyl compounds. However, the detailed arrangements of the alkyl groups and the various possibilities for C-H...Mo three-center, 2-electron bonding interactions prompted us to determine the structure of either an ethyl or an isopropyl compound. Our efforts were severely impeded by the air sensitivity of the compounds and also by their extremely high solubility in pentane and hexane. Growing crystals from either of these solvents yields extremely large crystals which had to be cut to yield smaller crystals of suitable size for X-ray work. Crystals of $\text{Mo}_2(i\text{-Pr})_2(\text{NMe}_2)_4$ were first examined and yielded an interesting disordered structure from which it was not possible to distinguish $i\text{-Pr}$ and NMe_2 groups. This does suggest that the isopropyl methyl groups are arranged in a variety of conformers as was inferred from the low-temperature ^1H NMR spectra. Crystals of $\text{Mo}_2(\text{Et})_2(\text{NMe}_2)_4$ grown by slow vacuum sublimation in sealed tubes were of a good size for X-ray work. However, once again a disorder problem was encountered. Finally, a small crystal of $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$, cleaved from a large one, proved to be satisfactory for the detailed study required.

gauche-Mo₂(CH₂CH₃)₂(NMe₂)₄. An ORTEP view of the gauche- $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$ molecule found in the crystal

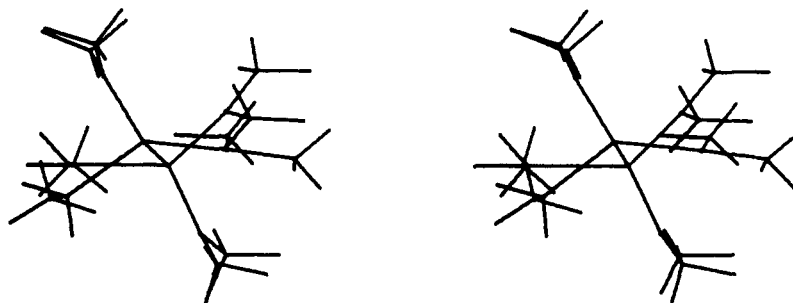


Figure 7. Stereoview of the gauche $\text{Mo}_2(\text{C}_2\text{H}_5)_2(\text{NMe}_2)_4$ molecule viewed down the Mo-Mo axis showing the orientations of the C-H bonds.

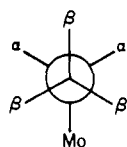
is shown in Figure 6. The molecule has a virtual, but not crystallographically imposed, C_2 axis of symmetry. The view shown in Figure 6 clearly shows how this relates the diastereotopic methylene protons in a pair-wise manner: $\text{H}(19) \rightleftharpoons \text{H}(48)$, $\text{H}(20) \rightleftharpoons \text{H}(49)$. The view shown in Figure 6 also reveals the planar hybridization at nitrogen and the presence of the two types of proximal and distal *N*-methyl groups.

Final atomic positional parameters are given in Table II. Anisotropic thermal parameters are given in Table III and listings of bond distances and bond angles are given in Tables IV and V, respectively. Complete listings of bonded and nonbonded distances to 3.3 Å and a number of dihedral angles between planes are given in the Supplementary Material. Pertinent nonbonding Mo-to-H distances are given in Table VI.

The Mo-Mo distance (2.203 (1) Å), the Mo-N distances (1.95 Å, averaged), the Mo-C distances (2.165 (6) Å, averaged), and the angles associated with the $\text{Mo}_2\text{N}_4\text{C}_2$ skeleton are all as might have been anticipated from previous structural work. This is, however, the first gauche ethanelike dimer to be structurally characterized, though this apparently has little effect on the distances and angles associated with the $\text{M}_2\text{N}_4\text{C}_2$ skeleton other than the obvious changes associated with gauche and anti rotamers.

As is seen in Figure 6, the methyl groups of the ethyl ligands are distal from the $\text{Mo}=\text{Mo}$ bond. The Mo-Mo-C-C torsional angles are 163 and 166°; the Mo-Mo-N-C torsional angles are $180 \pm 5^\circ$, i.e., as in other $\text{M}_2\text{X}_2(\text{NMe}_2)_4$ structures, the NC_2 blades are aligned along the Mo-Mo axis.

A stereoview of the $\text{Mo}_2(\text{C}_2\text{H}_5)_2(\text{NMe}_2)_4$ molecule is shown in Figure 7 which includes the hydrogen atoms and shows the rotational conformation about the C-C bond of the ethyl groups. Within the limits of experimental error, the perfectly staggered conformation is found. As is shown below in a Newman pro-



jection, this brings two of the β -hydrogen atoms equally close to the molybdenum atom to which the ethyl group is bonded.

The Mo(1) to H(46) and H(47) distances are 3.16 (5) and 3.25 (5) Å, and the Mo(2) to H(50) and H(51) distances are 3.15 (5) and 3.22 (5) Å, respectively. These distances are too long to suggest the possibility of any incipient β -CH...Mo bond formation. Indeed, these distances, together with the staggered rotational conformation about the C-C bond, indicate no significant metal-to- β -hydrogen interaction occurs in the ground state. The shortest Mo-to-H distances are to hydrogen atoms on dimethylamido groups. The C-H bonds of each dimethylamido group are arranged in the manner shown below.

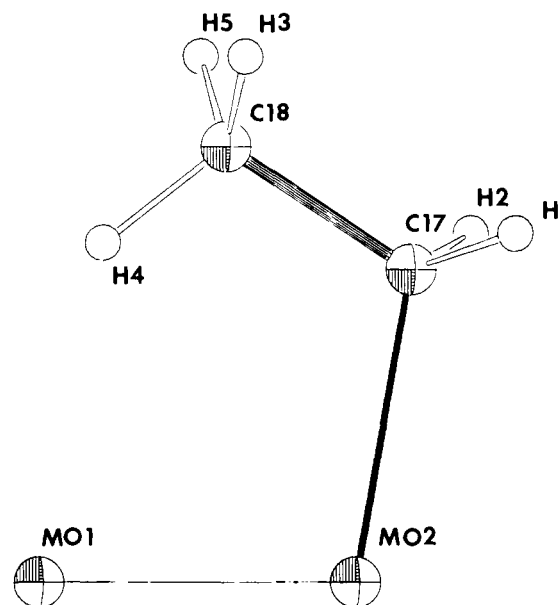
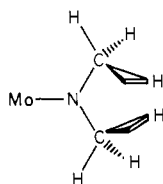
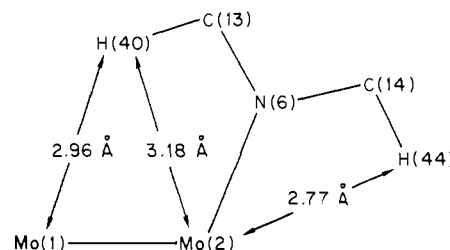


Figure 8. ORTEP view of the $\text{Mo}_2\text{-C}_2\text{H}_5$ fragment showing the closest CH...Mo distance which arises allowing for rotations about Mo-C and C-C bonds.

One C-H bond of each methyl group is contained in the Mo- NC_2 plane. This is typically observed for transition-metal dimethylamido structures.^{20,21} The four short Mo...H distances of this type are 2.67 (4) Å (C(8) methyl), 2.71 (5) Å (C(10) methyl), 2.78 (5) Å (C(17) methyl), and 2.77 (5) Å (C(14) methyl); note—the hydrogen atoms are on the four distal *N*-methyl carbons. Though these distances are short, β -hydrogen elimination with M-H and $\text{CH}_2=\text{NMe}$ formation is not a commonly observed decomposition pathway for early transition-metal dimethylamides.²⁰ Rather interestingly, the proximal *N*-methyl hydrogen-to-molybdenum distances are shorter by ca. 0.2 Å across the $\text{Mo}=\text{Mo}$ bond as is illustrated below.



This observation raises an interesting question: what is the shortest possible M...H distance to a β -hydrogen on an alkyl group in one of these ethanelike $\text{M}_2\text{R}_2(\text{NMe}_2)_4$ compounds? If we maintain the coordinates of the $\text{Mo}_2\text{N}_4\text{C}_2$ skeleton and merely perform rotations about the Mo-C and C-C bonds, this question

(20) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* 1977, 9, 276.

(21) This arrangement of hydrogen atoms is also observed in isobutylene: Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* 1973, 95, 4121.

Table II. Fractional Coordinates for the $Mo_2Et_2(NMe_2)_4$ Molecule^{a-c}

atom	10 ⁴ x	10 ⁴ y	10 ⁴ z	10B _{Iso}
Mo(1)	7398.6 (2)	6859.1 (3)	1415.3 (3)	14
Mo(2)	7624.9 (2)	7353.4 (3)	3691.7 (3)	15
N(3)	5724 (3)	7035 (5)	882 (3)	27
N(4)	8341 (3)	8342 (4)	838 (3)	22
N(5)	9295 (3)	7030 (5)	4236 (3)	27
N(6)	6783 (3)	9485 (4)	4053 (4)	29
C(7)	4738 (4)	7540 (9)	1645 (6)	44
C(8)	5352 (5)	6896 (9)	-611 (5)	45
C(9)	8934 (5)	9671 (6)	1587 (5)	36
C(10)	8340 (4)	8300 (6)	-661 (4)	30
C(11)	10282 (4)	6684 (10)	3471 (6)	45
C(12)	9700 (5)	7457 (11)	5697 (5)	53
C(13)	6283 (6)	10686 (6)	3144 (7)	48
C(14)	6792 (6)	10175 (7)	5505 (6)	48
C(15)	8140 (4)	4369 (5)	1122 (4)	24
C(16)	8424 (4)	3853 (6)	-351 (4)	27
C(17)	6784 (4)	5392 (5)	4188 (4)	22
C(18)	6533 (4)	5613 (6)	5687 (5)	29

atom	10 ³ x	10 ³ y	10 ³ z	10B _{Iso}
H(19)	880 (4)	418 (6)	174 (5)	39 (11)
H(20)	763 (4)	368 (6)	140 (4)	35 (11)
H(21)	426 (5)	852 (7)	143 (6)	46 (13)
H(22)	415 (4)	700 (5)	131 (4)	24 (9)
H(23)	499 (5)	781 (7)	264 (6)	57 (14)
H(24)	509 (5)	792 (7)	-78 (6)	49 (15)
H(25)	609 (4)	660 (5)	-105 (4)	26 (9)
H(26)	485 (5)	628 (6)	914 (5)	40 (12)
H(27)	970 (4)	958 (5)	127 (4)	25 (9)
H(28)	865 (4)	1075 (5)	128 (4)	21 (8)
H(29)	889 (4)	970 (6)	244 (5)	34 (10)
H(30)	800 (4)	935 (6)	-88 (5)	33 (11)
H(31)	925 (6)	804 (8)	-78 (6)	67 (16)
H(32)	802 (5)	756 (7)	-96 (5)	43 (13)
H(33)	1008 (4)	639 (5)	243 (5)	31 (10)
H(34)	1070 (5)	746 (7)	368 (6)	40 (14)
H(35)	1080 (6)	587 (7)	377 (6)	60 (16)
H(36)	1025 (6)	671 (7)	609 (6)	58 (16)
H(37)	1009 (6)	836 (7)	567 (6)	55 (14)
H(38)	912 (4)	762 (5)	604 (4)	22 (10)
H(39)	667 (4)	1167 (6)	323 (4)	32 (10)
H(40)	628 (3)	1023 (5)	215 (4)	17 (7)
H(41)	562 (6)	1108 (8)	326 (6)	61 (16)
H(42)	726 (5)	1097 (7)	565 (5)	45 (13)
H(43)	605 (5)	1064 (6)	566 (5)	41 (13)
H(44)	705 (5)	926 (7)	608 (5)	49 (12)
H(45)	875 (4)	276 (5)	-57 (4)	22 (9)
H(46)	786 (5)	411 (6)	895 (6)	45 (13)
H(47)	909 (4)	431 (6)	-39 (5)	37 (11)
H(48)	609 (4)	509 (6)	366 (5)	30 (10)
H(49)	734 (4)	450 (6)	406 (5)	39 (11)
H(50)	713 (5)	581 (6)	625 (5)	34 (12)
H(51)	602 (5)	643 (7)	579 (6)	47 (14)
H(52)	618 (4)	457 (6)	592 (5)	41 (11)

^a The isotropic thermal parameter listed for those atoms refined anisotropically is the isotropic equivalent. ^b Numbers in parentheses in this and all following tables refer to the error in the least significant digits. ^c Estimated standard deviations greater than 29 are not statistically significant, but are left "unrounded", since the tables are all produced automatically by the X-TEL interactive programs.

is easily answered. In Figure 8, we show a computer-simulated ORTEP of the ethyldimolybdenum fragment concerned. The shortest metal-hydrogen distance is 2.36 Å to the molybdenum atom to which the ethyl group is not directly coordinated. The β -carbon of the ethyl ligand to Mo(2) is the γ -carbon with respect to Mo(1). When reductive elimination from this dinuclear center occurs with the formation of ethylene and ethane,^{13,14} mechanisms which involve this type of interaction must be considered. For the isopropyl and *tert*-butyl compounds, there must be short M---HC distances across the M≡M bond in the ground-state structures since all the methyl groups cannot be distal to the M≡M bond as is found for $Mo_2Et_2(NMe_2)_4$.

Finally, we note that this Mo-to-H-C distance of 2.36 Å is little longer than those found by Cotton and co-workers²²⁻²⁴ for a series of $Et_2B(\text{pyrazolyl})_2Mo$ compounds where a 3-center, 2-electron bond from one of the methylene protons of the $Et_2B(\text{pyrazolyl})_2^-$ ligand allows the molybdenum atoms to achieve a formal 18-electron valence-shell configuration.

Concluding Remarks

It now seems that dialkylamido ligands in mixed alkyl-dialkylamido compounds have the ability to inhibit the common decomposition pathways associated with alkyl ligands. This is seen in the following: (1) the preparation by Burger and Neese²⁵ of a series of Ti^{4+} compounds of formula $(R_2N)_3TiR'$, where R = Me or Et and R' = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, and *t*-Bu (the thermal decompositions of these compounds, which occur at >120 °C, yield alkanes R'H and polymeric titanium(IV) compounds: the carbon-hydrogen bond formed upon elimination of R'H arises from a hydrogen atom of either the *N*-methyl or *N*-methylene groups of the NR_2 ligands);²⁶ (2) Anderson's²⁷ preparations of the thermally stable (<100 °C) compounds $RM(NSi_2Me_6)_3$ (M = Zr, Hf) and $Et_2Zr(NSi_2Me_6)_2$; and (3) in the present syntheses and characterizations of 1,2- $M_2R_2(NMe_2)_4$ compounds.

We propose that the stabilizing influence of the NR_2 ligands arises primarily²⁸ from their ability to act as strong π -donor ligands. Acting as four-electron donor ligands ($\sigma^2 + \pi^2$), the NMe_2 ligands bond to metal atomic orbitals which would otherwise be available for CH---Mo interactions. Indeed, each metal atom in the $M_2R_2(NMe_2)_4$ compounds (M = Mo, W) attains a 16 valence shell of electrons as a result of forming the M≡M bond, three metal-ligand σ bonds, and two nitrogen-to-metal π bonds (delocalized over the three Mo-N bonds). Only the p_z atomic orbital of molybdenum is not used in bonding: the M-M σ bond is predominantly formed by d_{z^2} - d_{z^2} interactions.²⁹ In principle then, the p_z atomic orbitals are available for use in the β -hydrogen-elimination process and since the organometallic chemistry of molybdenum and tungsten generally adheres to the EAN rule,³⁰ one might anticipate a significant CH---M interaction of the type noted by Cotton and coworkers.²²⁻²⁴ Yet, no such interaction is seen in the ground state and the thermal stability of these compounds shows that the energy barrier to β -hydrogen elimination must be greater than ca. 30 kcal mol⁻¹. One is left to wonder and speculate why this is so. Perhaps the answer lies in the fact that forming a bond along the M-M axis would weaken the M-M σ bond. It is an empirical observation that the preferred coordination geometries about the $(M\equiv M)^{6+}$ unit avoid the use of axial ligand binding.³¹ Only in the compound $W_2(O_2CNMe_2)_6$, in which each tungsten atom is coordinated to six oxygen atoms, is there any evidence of axial ligand binding and this is relatively weak since the W-O distances to the axial oxygen atoms are 2.67 Å (averaged).³² The other oxygen atoms coordinate to the tungsten atoms in a pentagonal plane. In compounds of the type $X_4M\equiv MX_4$, the X_4 ligand atoms lie in a square plane, e.g., as

(22) Cotton, F. A.; Day, V. W. *J. Chem. Soc., Chem. Commun.* **1974**, 415.

(23) Cotton, F. A.; LaCour, T.; Stanislawski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 754. In this paper, the authors concluded "the CH---Mo distance appears to be not more than 2.27 (8) Å".

(24) Cotton, F. A.; Stanislawski, A. G. *J. Am. Chem. Soc.* **1976**, *96*, 5074. In this paper, the authors determined, from NMR studies, an energy of activation of 14 kcal mol⁻¹ for the CH_a ---Mo \rightleftharpoons CH_b ---Mo exchange.

(25) Burger, H.; Neese, H. J. *J. Organomet. Chem.* **1969**, *20*, 129.

(26) Burger, H.; Neese, H. J. *J. Organomet. Chem.* **1970**, *21*, 381.

(27) Anderson, R. A. *Inorg. Chem.* **1979**, *18*, 1724, 2928; *J. Organomet. Chem.* **1980**, *192*, 183.

(28) This is in addition to stability which may arise from the bulkiness of the group. The $M_2R_2(NMe_2)_4$ are not sterically congested: they will undergo a large number of associative reactions leading to an increase in the coordination number of the metal atoms.

(29) For a detailed discussion of the bonding in these compounds, see: Bursten, B. E.; Cotton, F. A.; Green, J. C.; Seddon, E. A.; Stanley, G. G. *J. Am. Chem. Soc.* **1980**, *102*, 4579.

(30) Cotton, F. A.; Wilkinson, F. "Advanced Inorganic Chemistry"; Wiley-Interscience: New York, 1980; 4th ed.

(31) Chisholm, M. H. *Faraday Soc. Symp.*, No. 14 **1980**, 194.

(32) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Inorg. Chem.* **1977**, *16*, 603.

Table III. Anisotropic Thermal Parameters for the $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ Molecule^a

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	150 (2)	230 (2)	137 (2)	-22 (1)	13 (1)	27 (1)
Mo(2)	180 (2)	224 (2)	141 (2)	-6 (1)	30 (1)	5 (1)
N(3)	199 (17)	588 (23)	245 (17)	-33 (16)	-10 (14)	79 (16)
N(4)	314 (18)	267 (16)	279 (17)	-94 (14)	96 (14)	57 (13)
N(5)	263 (18)	531 (22)	213 (16)	-17 (16)	-9 (13)	84 (15)
N(6)	429 (21)	266 (17)	399 (20)	39 (15)	210 (17)	-23 (15)
C(7)	159 (22)	953 (46)	519 (32)	45 (25)	34 (21)	107 (30)
C(8)	364 (29)	1025 (49)	301 (25)	-170 (29)	-114 (21)	133 (28)
C(9)	679 (34)	374 (25)	390 (26)	-216 (24)	235 (24)	-13 (21)
C(10)	460 (28)	466 (27)	251 (21)	-146 (22)	95 (19)	52 (19)
C(11)	194 (23)	1069 (51)	463 (31)	-68 (25)	27 (21)	208 (31)
C(12)	412 (32)	1310 (63)	266 (25)	-254 (36)	-92 (22)	57 (30)
C(13)	813 (42)	315 (26)	757 (40)	265 (27)	453 (34)	199 (26)
C(14)	920 (47)	385 (28)	572 (34)	-115 (30)	418 (34)	-180 (25)
C(15)	403 (24)	243 (19)	234 (19)	-6 (17)	60 (17)	-26 (15)
C(16)	294 (22)	431 (25)	268 (21)	-16 (19)	84 (17)	-73 (18)
C(17)	318 (22)	270 (19)	266 (19)	-44 (17)	94 (17)	72 (16)
C(18)	323 (23)	476 (26)	327 (23)	-32 (20)	94 (18)	115 (20)

^a The form of the exponent is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}lc^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}klb^{*}c^{*})]$.

Table IV. Bond Distances in Angstroms for the $\text{Mo}_2(\text{C}_2\text{H}_5)_2(\text{NMe}_2)_4$ Molecule^a

A	B	distance	A	B	distance
Mo(1)	Mo(2)	2.203 (1)	C(10)	H(30)	0.96 (5)
Mo(1)	N(3)	1.950 (3)	C(10)	H(31)	1.08 (6)
Mo(1)	N(4)	1.956 (3)	C(10)	H(32)	0.77 (6)
Mo(1)	C(15)	2.159 (4)	C(11)	H(33)	1.02 (5)
Mo(2)	N(5)	1.948 (3)	C(11)	H(34)	0.84 (5)
Mo(2)	N(6)	1.946 (3)	C(11)	H(35)	0.91 (6)
Mo(2)	C(17)	2.169 (4)	C(12)	H(36)	0.92 (6)
N(3)	C(7)	1.456 (6)	C(12)	H(37)	0.94 (6)
N(3)	C(8)	1.463 (6)	C(12)	H(38)	0.79 (4)
N(4)	C(9)	1.446 (6)	C(13)	H(39)	0.98 (5)
N(4)	C(10)	1.471 (5)	C(13)	H(40)	1.00 (4)
N(5)	C(11)	1.450 (6)	C(13)	H(41)	0.82 (6)
N(5)	C(12)	1.456 (6)	C(14)	H(42)	0.90 (6)
N(6)	C(13)	1.453 (6)	C(14)	H(43)	0.93 (5)
N(6)	C(14)	1.464 (6)	C(14)	H(44)	1.01 (6)
C(15)	C(16)	1.525 (5)	C(15)	H(19)	0.92 (5)
C(17)	C(18)	1.528 (6)	C(15)	H(20)	0.97 (5)
C(7)	H(21)	0.96 (6)	C(16)	H(45)	0.95 (4)
C(7)	H(22)	0.87 (4)	C(16)	H(46)	0.91 (6)
C(7)	H(23)	0.98 (6)	C(16)	H(47)	0.92 (5)
C(8)	H(24)	0.91 (6)	C(17)	H(48)	0.95 (5)
C(8)	H(25)	1.01 (5)	C(17)	H(49)	0.94 (5)
C(8)	H(26)	0.82 (5)	C(18)	H(50)	0.85 (5)
C(9)	H(27)	0.99 (4)	C(18)	H(51)	0.86 (6)
C(9)	H(28)	1.00 (4)	C(18)	H(52)	1.08 (5)
C(9)	H(29)	0.85 (5)			

^a Nonbonding distances to 3.0 Å are given in the supplementary data.

in $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{py})_2$.³¹ Thus, the $(\text{M}\equiv\text{M})^{6+}$ unit ($\text{M} = \text{Mo}, \text{W}$) appears to have rather rigorous coordination preferences for a given coordination number.

An interesting analogy emerges with the chemistry of mononuclear square-planar d^8 transition-metal complexes such as those of Pt^{2+} and Au^{3+} . Here, the metal atoms have 16 valence shell electrons and facile β -hydrogen elimination could be anticipated based on considerations of the 16-18-electron rule.³³ But, as Whitesides et al.³⁴ have shown for the thermal decomposition of *cis*-Pt-*n*-Bu₂(PPh₃)₂ and as Kochi and Tamaki³⁵ found for the isomerization reaction *t*-BuAu(Me)₂(PPh₃) → *i*-BuAu(Me)₂(PPh₃), the β -hydrogen-elimination process proceeds most readily by a prior Lewis base dissociation reaction: the β -hydrogen elimination occurs from a 14 valence shell electron-metal center. It can reasonably be assumed that in both of the aforementioned

(33) Tolman, C. A. *Chem. Rev.* **1972**, *1*, 337.

(34) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.

(35) Kochi, J. K.; Tamaki, A. *J. Chem. Soc., Chem. Commun.* **1973**, 423.

Table V. Angles in Degrees for the $\text{Mo}_2(\text{C}_2\text{H}_5)_2(\text{NMe}_2)_4$ Molecule^a

A	B	C	angle
Mo(2)	Mo(1)	N(3)	104.6 (1)
Mo(2)	Mo(1)	N(4)	104.3 (1)
Mo(2)	Mo(1)	C(15)	101.0 (1)
N(3)	Mo(1)	N(4)	120.8 (1)
N(3)	Mo(1)	C(15)	110.8 (2)
N(4)	Mo(1)	C(15)	112.8 (2)
Mo(1)	Mo(2)	N(5)	104.7 (1)
Mo(1)	Mo(2)	N(6)	103.6 (1)
Mo(1)	Mo(2)	C(17)	100.1 (1)
N(5)	Mo(2)	N(6)	120.1 (2)
N(5)	Mo(2)	C(17)	111.0 (2)
N(6)	Mo(2)	C(17)	114.4 (1)
Mo(1)	N(3)	C(7)	133.6 (3)
Mo(1)	N(3)	C(8)	114.8 (3)
C(7)	N(3)	C(8)	110.7 (4)
Mo(1)	N(4)	C(9)	132.4 (3)
Mo(1)	N(4)	C(10)	116.5 (3)
C(9)	N(4)	C(10)	110.5 (3)
Mo(2)	N(5)	C(11)	133.7 (3)
Mo(2)	N(5)	C(12)	116.2 (3)
C(11)	N(5)	C(12)	109.2 (4)
Mo(2)	N(6)	C(13)	131.8 (3)
Mo(2)	N(6)	C(14)	116.7 (3)
C(13)	N(6)	C(14)	110.6 (4)
Mo(1)	C(15)	C(16)	112.0 (3)
Mo(2)	C(17)	C(18)	113.2 (3)

^a Angles involving hydrogen atoms are given in the supplementary data.

Table VI. Pertinent Molybdenum-to-Hydrogen Nonbonding Distances, in Angstroms, in the $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ Molecule

atom	atom	distance	atom	atom	distance
Mo(1)	H(25)	2.67 (4)	Mo(2)	H(38)	2.69 (4)
Mo(1)	H(32)	2.71 (5)	Mo(2)	H(44)	2.77 (5)
Mo(1)	H(46)	3.16 (5)	Mo(2)	H(50)	3.15 (5)
Mo(1)	H(47)	3.25 (5)	Mo(2)	H(51)	3.22 (5)
Mo(1)	H(19)	2.64 (5)	Mo(2)	H(48)	2.78 (5)
Mo(1)	H(20)	2.65 (5)	Mo(2)	H(49)	2.54 (5)
Mo(1)	H(48)	3.46 (5)	Mo(2)	H(19)	3.33 (5)
Mo(1)	H(49)	3.50 (5)	Mo(2)	H(20)	3.56 (5)
Mo(1)	H(23)	3.20 (6)	Mo(2)	H(33)	3.27 (5)
Mo(1)	H(29)	3.11 (5)	Mo(2)	H(40)	3.16 (4)
Mo(1)	H(33)	3.15 (5)	Mo(2)	H(23)	3.10 (6)
Mo(1)	H(40)	3.00 (4)	Mo(2)	H(29)	3.09 (5)

reactions, the hydride ligand is formed within the square plane of the metal center. Similarly, it has been demonstrated that the site for C-H activation in cyclopaladation reactions lies within the square plane of the Pd(II) complex: axial Pd---H distances as short as 2.09 Å have to be nonbonding and ineffective in yielding

metallation.^{36,37} Thus, we conclude that despite numerous short CH---M distances in $M_2R_2(NMe_2)_4$ compounds, C-H activation does not occur readily because the metal atomic orbitals are either tied up in bonding ($M\equiv M$, $M-C$, and $M=N$ ($\sigma + \pi$)) or apparently are not suited for receiving an electron pair, as is the case for the p_z atomic orbital which lies along the M-M axis.

Experimental Section

General Procedures. Throughout, care was taken to maintain dry and oxygen-free atmospheres (nitrogen) and solvents. Standard Schlenk procedures³⁸ were coupled with the use of Vacuum Atmospheres Company Dri-Lab Systems.

1H , ^{13}C , and 2H NMR spectra were recorded by using either a Varian HR-220 or a Bruker HX270 spectrometer³⁹ equipped with variable-temperature accessories. Infrared spectra were obtained from Nujol mulls between CsI plates with the use of a Perkin-Elmer 283 spectrophotometer and data were calibrated with polystyrene. Mass spectra were obtained, courtesy of Mr. Peter Cook, by the method of direct insertion, using an AEI MS902 spectrometer. Elemental analyses were performed by Alfred Bernhardt Analytical Laboratories, West Germany, using dry box sampling techniques.

Chemicals. The compounds $M_2Cl_2(NMe_2)_4$ were made by the published¹² route involving the reaction between $M_2(NMe_2)_6$ and Me_3SiCl (2 equiv).

Alkylolithium reagents were purchased (*i*-PrLi, Orgmetallics Inc.; *t*-BuLi, ROC/RIC; *n*-BuLi, Alfa Ventron; *sec*-BuLi, Aldrich Chemical Co.) or synthesized according to published procedures⁴⁰ (EtLi, Me_3CCH_2Li , and Me_3SiCH_2Li). The deuterated ethyllithium reagents, CD_3CH_2Li and CH_3CD_2Li , were synthesized from respective deuterated bromoethanes which were purchased from Merck, Sharp and Dohme.

Preparations of $M_2R_2(NMe_2)_4$ compounds followed the general procedure outlined in the text of this paper and were as given in detail below for the preparation of $1,2-Mo_2Et_2(NMe_2)_4$.

$Mo_2Et_2(NMe_2)_4$. $Mo_2Cl_2(NMe_2)_4$ (1.25 g, 2.85 mmol) and EtLi (0.26 g, 7.12 mmol) were placed in a round-bottomed 100-mL flask equipped with a N_2 inlet adapter and a Teflon-coated magnetic spin-bar. To the dry components, toluene (60 mL) was added at $-78^\circ C$. The solution was stirred at $-78^\circ C$ for 0.5 h and then the reaction mixture was allowed to warm slowly to room temperature. The solution was stirred for a further 3 h at which time the toluene was stripped off in vacuo and the resulting solids thoroughly dried. Hexane (ca. 70 mL) was added and the mixture was filtered, using a fine frit. The filtrate was collected and the hexane stripped off to yield orange solids. These were transferred to a high-vacuum line and upon heating to $80^\circ C$ at 10^{-4} torr yielded $Mo_2Et_2(NMe_2)_4$ as a golden microcrystalline sublimate (0.97 g, 80% yield based on Mo).

For the purposes of X-ray analysis, ca. 0.5 g of $Mo_2Et_2(NMe_2)_4$ was dissolved in a minimal amount of pentane (ca. 5 mL) at room temperature. The solution was then placed in a refrigerator at ca. $-40^\circ C$ in a Vacuum Atmospheres Co. Dri-Lab facility. After a few days, golden platelike hexagonal crystals had formed. These were collected by filtration in the Dri-Lab and used in the X-ray crystallographic study.

Infrared spectra of analogous molybdenum and tungsten compounds were virtually identical, as indeed they are for the parent compounds $Mo_2(NMe_2)_6$ ($M = Mo, W$).⁴¹ In general, the IR spectra were not informative with respect to characterization of the compounds as is shown in the data recorded below.

IR data recorded between CsI plates in Nujol mulls in the region 1500–200 cm^{-1} follow.

$Mo_2Et_2(NMe_2)_4$: 1420 (m), 1260 (w), 1242 (m), 1147 (m), 1122 (w), 1041 (m), 947 (vs), 800 (w), 724 (w), 577 (m), 560 (m), 350 (m), 332 (m).

$Mo_2(sec-C_4H_9)_2(NMe_2)_4$: 1420 (m), 1262 (w), 1240 (m), 1147 (m), 1119 (w), 1041 (m), 950 (s), 940 (vs), 720 (m), 563 (m), 335 (mbr).

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$Mo_2(CH_2CMe_3)_2(NMe_2)_4$: 1453 (m), 1415 (w), 1375 (m), 1240 (m), 1143 (m), 1120 (w), 1043 (w), 950 (s), 940 (vs), 739 (w), 721 (w), 566 (w), 335 (mbr).

$Mo_2(CH_2SiMe_3)_2(NMe_2)_4$: 1415 (w), 1250 (w), 1242 (m), 1150 (m), 1120 (w), 1042 (w), 1020 (w), 952 (s), 942 (vs), 895 (m), 850 (s), 825 (m), 737 (w), 720 (w), 569 (w), 340 (mbr).

1H NMR data recorded at 270 MHz in toluene- d_6 (all δ in ppm relative to Me_4Si) follow.

$1,2-Mo_2Et_2(NMe_2)_4$ at $-61^\circ C$: Gauche rotamer: δ ($CH_3CH_2H_b$) 1.64 (t, $^2J_{HH} = 8.3$ Hz), δ ($CH_3CH_2H_a$) 2.33 and 2.69 (m), δ (NMe proximals) 4.06, 4.03 (s); δ (NMe distal) 2.46, 2.40 (s). Anti rotamer: δ (CH_3CH_2) 1.70 (t, $^2J_{HH} = 8.3$ Hz), δ (CH_3CH_2) obscured by other resonances, δ (NMe proximal) 3.98, δ (NMe distal) 2.37 (s).

$1,2-Mo_2(CH_2CD_3)_2(NMe_2)_4$ (gauche rotamer): δ ($CH_2H_aCD_3$) 2.62, 2.25 (d, $J_{HH} = -14.7$ Hz). Other resonances were as for the protio compound.

$1,2-Mo_2(CD_2CH_3)(NMe_2)_4$ (gauche rotamer): δ (CD_2CH_3) 1.62 (s). Anti rotamer: δ (CD_2CH_3) 1.68 (s). Other resonances were as for the protio compound.

$1,2-W_2(CH_2CD_3)_2(NMe_2)_4$ recorded at $-70^\circ C$: Gauche rotamer: δ ($CH_2H_bCD_3$) 2.57, 2.18 (d, $J_{HH} = -16.4$ Hz), δ (NMe proximals) 4.15, 4.08 (s), δ (NMe distals) 2.39, 2.32 (s). Anti rotamer: (CH_2CD_3) obscured, δ (NMe distal) 2.32, δ (NMe proximal) 4.05.

$1,2-Mo_2(CH(CH_3)_2)(NMe_2)_4$ at $-70^\circ C$: Gauche rotamer: δ (isopropylmethyls) 1.75, 1.82 (d, $^2J_{HH} = 7.3$ Hz), δ (isopropylmethyne) 3.48 (septet, $^2J_{HH} = 7.3$ Hz), δ (NMe proximals) 3.90, 4.00 (s), δ (NMe distals) 2.45, 2.35 (s). Anti rotamer: see text.

$1,2-Mo_2(CH_2SiMe_3)(NMe_2)_4$ at $-70^\circ C$: Gauche rotamer: δ ($CH_2H_bSiMe_3$) 1.21, 1.69 (d, $J_{HH} = -12.7$ Hz), δ ($SiMe_3$) 0.29 (s), δ (NMe proximals) 3.99, 3.98 (s), δ (NMe distals) 2.55, 2.50 (s). Anti rotamer: δ (CH_2SiMe_3) 1.31 (s), δ ($SiMe_3$) 0.34 (s), δ (NMe proximal) 3.92, δ (NMe distal) 2.53 (s).

$1,2-W_2(CH_2CMe_3)_2(NMe_2)_4$ at $-70^\circ C$: Gauche rotamer: δ ($CH_2H_bCMe_3$) 3.46, 2.02 (d, $J_{HH} = -15.6$ Hz), δ (CMe_3) 1.16 (s), δ (NMe proximals) 4.18, 4.14 (s), δ (NMe distals) 2.49, 2.48 (s). Anti rotamer: δ (CH_2CMe_3) 2.44 (s), δ (CMe_3) 1.19 (s), δ (NMe proximal) 4.11, δ (NMe distal) 2.44 (s).

$1,2-Mo_2(CH_2CMe_3)_2(NMe_2)_4$ at $-60^\circ C$: Gauche rotamer: δ ($CH_2H_bCMe_3$) 3.50, 2.25 (d, $J_{HH} = -13.8$ Hz), δ (CMe_3) 1.19 (s), δ (NMe proximal) 4.14, 4.04, δ (NMe distal) 2.57, 2.52 (s). Anti rotamer: δ (CH_2CMe_3) obscured, δ (CMe_3) 1.23 (s), δ (NMe proximal) 4.04, δ (NMe distal) 2.51 (s).

X-ray Structural Determination. General procedures were as described previously.⁴²

$Mo_2Et_2(NMe_2)_4$. A yellow crystal of dimensions $0.15 \times 0.17 \times 0.13$ mm was cleaved from a large crystal and transferred to the cold stream of the goniostat under an atmosphere of dry nitrogen. The cell dimensions obtained from 36 reflections at $-172^\circ C$ with $Mo K\alpha(\lambda 0.71069 \text{ \AA})$ were $a = 11.730$ (2) \AA , $b = 8.402$ (1) \AA , $c = 9.840$ (1) \AA , $\alpha = 98.09$ (1) $^\circ$, $\beta = 98.43$ (1) $^\circ$, and $\gamma = 82.74$ (1) $^\circ$, $V = 944.20$ (2) \AA^3 , $Z = 2$, and $d_{\text{calc}} = 1.499$ g cm^{-3} with space group $P1$.

A total number of 3501 reflections were collected using standard moving-crystal moving-detector techniques with the following values: scan speed = 3 deg min^{-1} , scan width = 2.0 + dispersion, single background time at extremes of scan = 10 s, aperture size = 3.0 \times 4.0 mm. The limits of data collection were $5^\circ < 2\theta < 55^\circ$. Of the 3501 reflections collected, 3333 were unique. The number of reflections with $F > 2.33\sigma(F)$ was 3028. The linear absorption coefficient = 12.917 cm^{-1} .

The structure was solved by direct methods and refined by full-matrix techniques, including all hydrogen atoms, to give final residuals: $R(F) = 0.032$ and $R_w(F) = 0.039$. The goodness of fit for the last cycle was 1.024 and the maximum Δ/σ was 0.05.

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Supplementary Material Available: Tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page. The complete structural report, MSC Report No. 8030, is available, in microfiche form only, from the Indiana University Library.

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