J. Am. Chem. Soc. **1982**, *104*, 2138-2146

orbital density in many metal systems is conducive to activating only one or a few localized vibrations in the molecule. The vibrational structure may also be observed for removal of a delocalized electron if the molecule has appropriate symmetry, since it appears that a totally symmetric mode progression will dominate.[19] If the ionization is to a degenerate electronic state, it is helpful if the spin-orbit splitting is either very small or very large. Intermediate values of spin-orbit splitting (on the order of the vibrational spacings) can lead to more complicated vibrational patterns.

The vibrational fine structure can give a quantitative indication of the geometric structures of individual positive ion states, and this can provide unique information on the electronic structure, bonding, and stability of the molecule. In this case the bonding nature of the t_{2g} electrons between the metal and the carbonyls is evidenced by (1) the overall width and shape of the ionization bands, (2) the reduction of the ν_2 (a_{1g}) metal-carbon frequencies in the positive ions, (3) the intensity pattern of the ν_2 (a_{1g}) progressions, and (4) the presence of the ν_1 (a_{1g}) carbon-oxygen vibrational progression in the $Mo(CO)_6$ and $W(CO)_6$ spectra.

The interpretation of vibrational structure generally emphasizes only the bonding character of the orbital which is ionized. For transition-metal ionizations, it is important to also consider the charge reorganization of the remaining occupied orbitals in the positive ion.[24] For t_{2g} ionization from the metal hexacarbonyl, the effective increase in oxidation state of the metal center reduces the bonding ability of the remaining t_{2g} electrons. This serves to magnify the increase in metal-carbon bond length that occurs with removal of a single t_{2g} electron.

Acknowledgment. We wish to acknowledge the U.S. Department of Energy, Contract DE-ACOZ-80ER10746, the University of Arizona, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. D.L.L. is an Alfred P. Sloan Fellow, 1979-1981.

Registry No. $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; $Cr(CO)_6$, 13007-92-6.

Reactions of Metal-Metal Multiple Bonds. 8.[1] Forming Mo-Mo Quadruple Bonds by Reductive Elimination (Alkyl Group Disproportionation) in the Reactions of 1,2-$Mo_2R_2(NMe_2)_4$ Compounds ($M\equiv M$) with Carbon Dioxide and 1,3-Diaryltriazines

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Abstract: Addition of CO_2 and 1,3-diaryltriazines to 1,2-$Mo_2R_2(NMe_2)_4$ compounds ($M\equiv M$), where R = CH_3 and $CH_2Si(CH_3)_3$, yields $Mo_2R_2(O_2CNMe_2)_4$ and $Mo_2R_2(NMe_2)_2(ArN_3Ar)_2$ compounds, respectively, with retention of the $Mo\equiv Mo$ bond, whereas related reactions, where R = C_2H_5, $CH(CH_3)_2$, and *n*-, *sec*-, and *t*-C_4H_9, yield Mo-Mo quadruply bonded compounds $Mo_2(O_2CNMe_2)_4$ and $Mo_2(ArN_3Ar)_4$ by reductive elimination (alkyl group disproportionation) of alkene and alkane. Reactions involving the addition of CO_2 to the labeled compounds $Mo_2(CH_2CD_3)_2(NMe_2)_4$ and $Mo_2(CD_2CH_3)_2(NMe_2)_4$ yield CH_2DCD_3 + $CH_2{=}CD_2$ and CHD_2CH_3 + $CH_2{=}CD_2$, respectively. When a mixture of $Mo_2(CH_2CH_3)_2(NMe_2)_4$ and $Mo_2(CH_2CD_3)_2(NMe_2)_4$ and CO_2 reacted in benzene, the only deuterated products detected by ^2H NMR spectroscopy were $CH_2{=}CD_2$ and CH_2DCD_3. When mixtures of $Mo_2(CH_2CH_3)_2(NMe_2)_4$ and $Mo_2R_2(NMe_2)_4$ compounds (R = CH_3 and $CH_2Si(CH_3)_3$) in toluene-d_8 were allowed to react with CO_2 in sealed NMR tubes, only ethane and ethylene were evolved, whereas when mixtures of $Mo_2(CH_2CH_3)_2(NMe_2)_4$, $Mo_2(CH_2CH_3)(R)(NMe_2)_4$, and $Mo_2R_2(NMe_2)_4$ were allowed to react under similar conditions, the eliminated organic products were ethylene, ethane, and RH. These observations establish that reductive elimination occurs by an intramolecular reaction in which a β-hydrogen atom of one ethyl ligand is transferred to the α-carbon of the other ethyl or alkyl group. The insertion of CO_2 into $Mo-NMe_2$ bonds proceeds via an amine-catalyzed sequence: $Me_2NH + CO_2 \rightleftharpoons Me_2NCOOH$; $Mo-NMe_2 + HOOCNMe_2 \rightarrow MoO_2CNMe_2 + HNMe_2$. The replacement of NMe_2 groups by either O_2CNMe_2 or ArN_3Ar ligands involves a protolysis which is common for metal dimethylamides: $M(NMe_2)_x + yLH \rightarrow M(NMe_2)_{x-y}L_y + yMe_2NH$. In the present instance, the reactions involving $Mo_2(CH_2CH_3)_2(NMe_2)_4$ have been shown to proceed through intermediates of formula $Mo_2(CH_2CH_3)_2(NMe_2)_2L_2$, where L = O_2CNMe_2 and ArN_3Ar (Ar = phenyl or *p*-tolyl). The carbamato intermediate has only been detected by ^1H NMR studies, but the *p*-tolyltriazenido compound has been isolated and structurally characterized. Crystal data for $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$: space group $P2_1/a$, $a = 16.503$ (4) Å, $b = 23.116$ (7) Å, $c = 11.318$ (3) Å, $\beta = 88.15$ (1)°, and $Z = 4$. The molecule has virtual, but not crystallographically imposed, C_2 symmetry. The $Mo\equiv Mo$ bond is bridged by *cis*-triazenido ligands, which afford sufficient flexibility to allow a noneclipsed geometry with respect to each half of the molecule. Each molybdenum is coordinated to three nitrogen atoms and a carbon atom which lie roughly in a plane. Pertinent bond distances are Mo-Mo = 2.171 (1) Å, Mo-N (dimethylamide) = 1.95 (1) Å, Mo-C = 2.21 (1) Å, and Mo-N (triazenido) = 2.17 (1) Å and 2.251 (1) Å with the longer bond being trans to the $Mo-NMe_2$ group. Plausible mechanisms for the reductive-elimination sequence are presented and discussed in light of related organometallic reaction sequences.

The preparation[2] of an extensive series of 1,2-$M_2R_2(NMe_2)_4$ compounds ($M\equiv M$), where M = Mo and W and R = Me, Et, *i*-Pr, *n*-Bu, *sec*-Bu, *t*-Bu, CH_2CMe_3, and CH_2SiMe_3, provides the opportunity of studying the reactivity patterns of σ-alkyl groups[3]

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(2) Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046.

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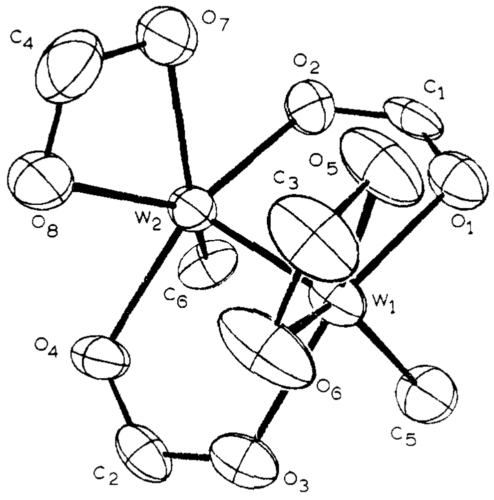
bonded to dimetal centers. Of particular note in the above series are the thermally stable compounds which contain σ-alkyl groups that have β-hydrogen atoms. A common thermal decomposition pathway in mononuclear transition-metal complexes containing such ligands involves the so-called β-hydrogen elimination reaction: M-alkyl → M-H + alkene. For dialkylmetal complexes, this is often the step which precedes reductive elimination by carbon-hydrogen bond formation, leading to the overall reaction shown in eq 1. This may be called reductive alkyl group disproportionation and has been observed and well studied in the thermal decomposition of di-*n*-butyl compounds of platinum(II),[4] cobalt(III),[5] and titanium(IV).[6] It seemed reasonable to suppose that reductive alkyl group disproportionation might also occur for 1,2-dialkyldimetal compounds.

$$L_nM^{x+}R_2 \rightarrow L_nM^{(x-2)+} + \text{alkane} + \text{1-alkene} \qquad (1)$$

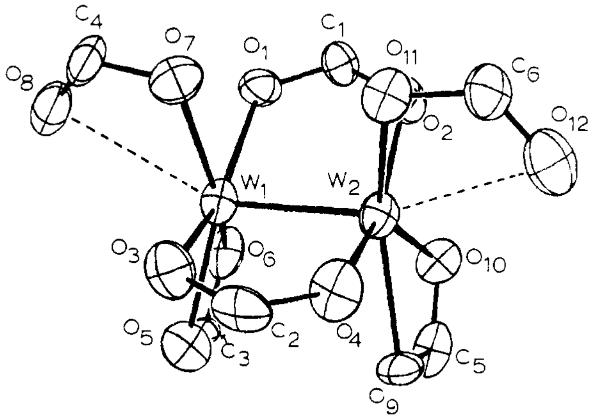
Previously, we suggested that the thermal stability of compounds of the type 1,2-$Mo_2(i\text{-}Pr)_2(NMe_2)_4$ arises from two factors: (i) β-hydrogen elimination is not favored because metal atomic orbitals are not available (or suited) to form C-H-Mo three-center bonds;[7] (ii) reductive elimination would generate a coordinatively unsaturated and presumably highly energetic metallic species[8] $(Me_2N)_2MoMo(NMe_2)_2$, Mo-Mo being quadruply bonded. Both of these factors are controllable, in principle, by suitable reactions involving the dimethylamido ligands, and previous work had shown that $W_2Me_2(NEt_2)_4$ and $W_2(NMe_2)_6$ react with carbon dioxide to give $W_2Me_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$, respectively.[9] The structures of these two molecules, which are shown in I and II, led us to believe that the ethyl compound $Mo_2Et_2(O_2CNMe_2)_4$ would be labile to reductive elimination. (1) The carbamato compound $Mo_2(O_2CNMe_2)_4$, formed upon reductive elimination, would be analogous to scores of well-characterized $Mo_2(O_2CR)_4$ (Mo-Mo being quadruply bonded) compounds.[10] (2) The β-hydrogen elimination step would satisfy the 16-18 electron rule,[11] and formation of the Mo-H bond along the Mo-Mo axis would be stereochemically analogous to formation of the axial W-O bonds found in $W_2(O_2CNMe_2)_6$. We report here the details of our studies which were prompted by these lines of reasoning. A preliminary report of some aspects of this work has appeared.[12]

Results and Discussion

Reactions with Carbon Dioxide. $Mo_2Me_2(NMe_2)_4$ reacts with CO_2 in hydrocarbon solvents to give a finely divided yellow crystalline solid which is only sparingly soluble in hydrocarbon solvents. The compound shows a molecular ion, $Mo_2Me_2(O_2CNMe_2)_4^+$, in the mass spectrometer which, together with other spectroscopic and analytical data, lead us to believe it is analogous to the tungsten compound $W_2Me_2(O_2CNEt_2)_4$, which was structurally characterized and shown to have a metal-to-metal triple bond.[9] Similarly, $Mo_2(CH_2SiMe_3)_2(NMe_2)_4$ reacts with CO_2 to give $Mo_2(CH_2SiMe_3)_2(O_2CNMe_2)_4$.



I, central skeleton of the $W_2Me_2(O_2CNEt_2)_4$ molecule



II, central skeleton of the $W_2(O_2CNMe_2)_6$ molecule; dotted lines indicate the long, quasi-axial W-O bonds

In contrast to the above, the 1,2-dialkyldimolybdenum compounds $Mo_2R_2(NMe_2)_4$, where the alkyl group contains β-hydrogen atoms, react according to eq 2.

$$Mo_2R_2(NMe_2)_4 + CO_2\ (\text{excess}) \rightarrow Mo_2(O_2CNMe_2)_4 + \text{alkane} + \text{alkene} \qquad (2)$$

The compound $Mo_2(O_2CNMe_2)_4$ is formed as a finely divided, yellow, microcrystalline solid which is virtually insoluble in hydrocarbon solvents and only very sparingly soluble in polar solvents, such as pyridine. The ^1H NMR spectrum shows only one resonance, and the infrared spectrum shows bands associated with the O_2CNMe_2 ligands.[13] In the mass spectrum, the most intense ion was the ion of highest mass, $Mo_2(O_2CNMe_2)_4^+$; there was also an intense doubly charged ion corresponding to $Mo_2(O_2CNMe_2)_4^{2+}$. There is therefore little doubt that $Mo_2(O_2CNMe_2)_4$ is closely related to scores of other well-characterized compounds of general formula $Mo_2(O_2CR)_4$, which contain metal-to-metal quadruple bonds.[10]

Studies of reaction 2 were carried out in sealed NMR tubes, and the reaction course was followed by NMR spectroscopy. Within the limits of detection by the NMR method, reaction 2 is stoichiometric: equimolar quantities of alkane and alkene are liberated. At room temperatures, the reaction is generally rapid and essentially complete within 30 min (see Mechanism of CO_2 Insertion). Reactions involving R = *n*-Bu gave 1-butene and *n*-butane (no 2-butenes were detected); for R = *sec*-Bu, *n*-butane, 1-butene, and a trace of 2-butenes were evolved, while for R = *t*-Bu, the eliminated hydrocarbons were isobutylene and isobutane. These observations are consistent with an irreversible β-hydrogen atom to metal transfer reaction. This was further supported by the studies of the reactions between CO_2 and each of the labeled ethyl compounds $Mo_2(CH_2CD_3)_2(NMe_2)_4$ and $Mo_2(CD_2CH_3)_2$-

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(3) σ-Alkyl groups bonded to transition metals are important in a large number of catalytic and stoichiometric reactions. For example, see: Kochi, J. K. In "Organometallic Mechanisms and Catalysis", Academic Press: New York, 1978.

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

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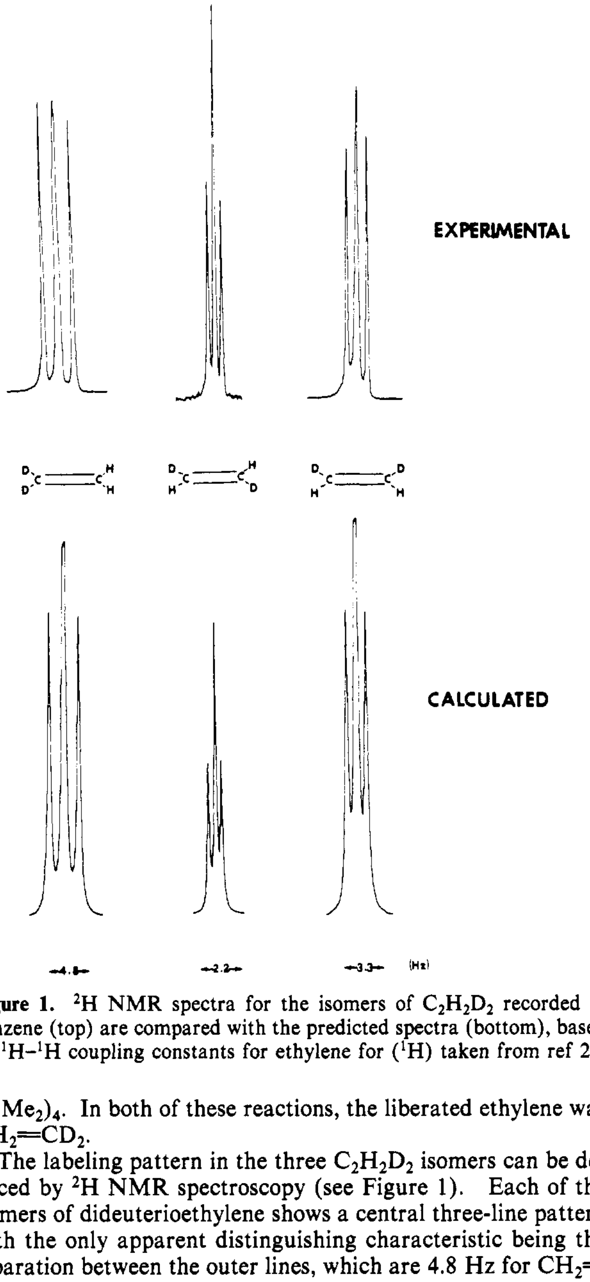


Figure 1. ^{2}H NMR spectra for the isomers of $C_2H_2D_2$ recorded in benzene (top) are compared with the predicted spectra (bottom), based on ^{1}H–^{1}H coupling constants for ethylene for (^{1}H) taken from ref 24.

$(NMe_2)_4$. In both of these reactions, the liberated ethylene was $CH_2{=}CD_2$.

The labeling pattern in the three $C_2H_2D_2$ isomers can be deduced by ^{2}H NMR spectroscopy (see Figure 1). Each of the isomers of dideuterioethylene shows a central three-line pattern with the only apparent distinguishing characteristic being the separation between the outer lines, which are 4.8 Hz for $CH_2{=}CD_2$, 3.3 Hz for *cis*-CHD=CHD, and 2.2 Hz for *trans*-CHD=CHD.

The ethane liberated in these reactions is either CH_2DCD_3 when R = CH_2CD_3 or CHD_2CH_3 when R = CD_2CH_3. The ^{2}H NMR spectra of the evolved ethanes are compared with the spectra obtained for commercially available samples of the specifically labeled ethanes in Figure 2. In a separate experiment, an equimolar mixture of $Mo_2(CH_2CH_3)_2(NMe_2)_4$ and $Mo_2(CH_2CD_3)_2(NMe_2)_4$ was allowed to react with CO_2 in an NMR tube. The ^{2}H NMR spectrum of the liberated ethane was indistinguishable from that shown in Figure 2 for CH_2DCD_3. We conclude that, within the limits of detection by NMR spectroscopy, the elimination of ethane occurs by an intramolecular process: an intermolecular process would generate CH_3CH_2D and CH_3CD_3 along with CH_2DCD_3 and C_2H_6.

One might question how good a probe ^{2}H NMR spectroscopy is for the detection of small quantities of CH_3CH_2D and CH_3CD_3 which might have been formed by a competing bimolecular reaction, given that the majority of the deuterated ethane is CH_2DCD_3, arising from an intramolecular process. This point concerned both referees of this paper. A more reliable estimate of the deuterium distribution in the ethanes liberated from the reaction between CO_2 and a mixture of $Mo_2(CH_2CD_3)_2(NMe_2)_4$ and $Mo_2(CH_2CH_3)_2(NMe_2)_4$ could have been sought by careful GC–MS analysis. However, this procedure is not without its own limitations and uncertainties, and so we proceeded to carry out the following reactions.

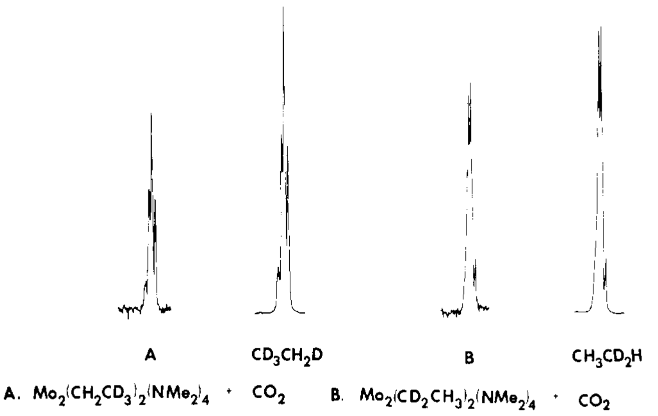


Figure 2. ^{2}H NMR spectra of the ethanes liberated in the reactions between $Mo_2(CH_2CD_3)_2(NMe_2)_4$ and CO_2 (A) and $Mo_2(CD_2CH_3)_2(NMe_2)_4$ and CO_2 (B) are compared with spectra associated with commercially supplied samples of CD_3CH_2D and CH_3CD_2H, respectively.

(1) A mixture of roughly equimolar quantities of $Mo_2Et_2(NMe_2)_4$ and $Mo_2Me_2(NMe_2)_4$ was dissolved in toluene-d_8 and placed in an NMR tube. CO_2 was added by use of a calibrated vacuum manifold, and the NMR tube was sealed with a torch. By ^{1}H NMR spectroscopy, only ethylene and ethane (1:1) were formed. No methane was detected. The insertion of CO_2 proceeded extremely slowly in this reaction, taking 2 days to go to completion. During the course of this reaction, the formation of new ^{1}H signals assignable to $Mo_2Me_2(NMe_2)_2(O_2CNMe_2)_2$ and $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$ were clearly identifiable (see later). The insertion of CO_2 proceeded at essentially the same rate for the ethyl and methyl compounds.

(2) A similar reaction was carried out by using roughly equimolar quantities of $Mo_2Et_2(NMe_2)_4$ and $Mo_2(CH_2SiMe_3)_2(NMe_2)_4$. Again, only ethylene and ethane were evolved. No Me_4Si signal was detected. Note in this reaction an intermolecular transfer of H to give Me_4Si would result in a single resonance equivalent to 12 H.

(3) $Mo_2Cl_2(NMe_2)_4$ and equimolar quantities of MeLi and EtLi were allowed to react in hexane. After workup (see Experimental Section), a yellow product was obtained, which by ^{1}H NMR spectroscopy could reliably be identified as a mixture of the compounds $Mo_2Me_2(NMe_2)_4$, $Mo_2(Me)(Et)(NMe_2)_4$, and $Mo_2Et_2(NMe_2)_4$. Upon addition of CO_2 in the manner described in (1), ethylene, ethane, and methane are evolved.

(4) $Mo_2Cl_2(NMe_2)_4$ was allowed to react with equimolar quantities of EtLi and Me_3SiCH_2Li in hexane. After workup, a yellow solid was isolated, which, by ^{1}H NMR spectroscopy, could reliably be identified as a mixture of $Mo_2Et_2(NMe_2)_4$, $Mo_2Et(CH_2SiMe_3)(NMe_2)_4$, and $Mo_2(CH_2SiMe_3)_2(NMe_2)_4$. Upon addition of CO_2 to this mixture, ethylene, ethane, and Me_4Si were evolved.

Reactions 1 and 2 above show that alkyl group scrambling between molybdenum compounds does not occur to any significant extent in toluene-d_8 and that the reductive elimination process is intramolecular: an intermolecular process would have yielded CH_4 and Me_4Si in reactions 1 and 2, respectively, along with ethylene and ethane. Reactions 3 and 4 show that elimination of methane and Me_4Si does occur in the reactions between $Mo_2(Et)(R)(NMe_2)_4$ compounds when R = Me and CH_2SiMe_3, respectively. We conclude that in these reactions reductive elimination requires the presence of β-hydrogen atoms on at least one alkyl group and that the reaction is intramolecular. Any contribution from an intermolecular reductive-elimination pathway escapes our detection by ^{1}H NMR spectroscopy and must be very small, if indeed such an alternate pathway competes with the intramolecular reaction at all.

Mechanism of CO_2 Insertion. As stated earlier, reactions between $Mo_2R_2(NMe_2)_4$ compounds and CO_2 in hydrocarbon

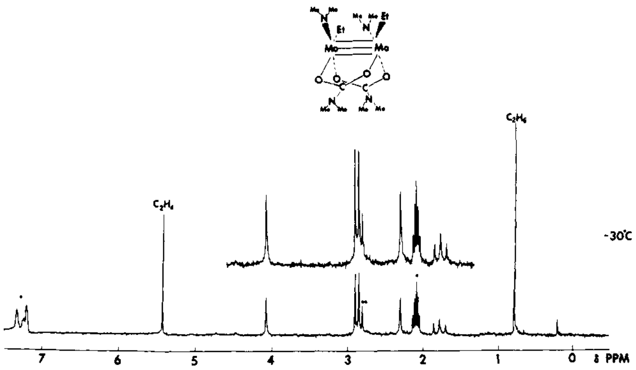
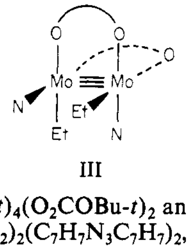


Figure 3. ^1H NMR spectra showing the formation of $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$ at 100 MHz in the reaction between $Mo_2Et_2(NMe_2)_4$ and CO_2 in toluene-d_8 at −30 °C. The signals denoted by * correspond to the protio impurities in toluene-d_8. The signal denoted by ** corresponds to the methyl resonance of $Mo_2(O_2CNMe_2)_4$ which, because of its low solubility, is precipitated as it is formed.

solvents generally proceed rapidly at room temperature and in the presence of excess CO_2 are essentially complete within ca. 30 min. However, as also noted previously, in one reaction between a mixture of $Mo_2Me_2(NMe_2)_4$, $Mo_2Et_2(NMe_2)_4$, and CO_2, the reaction proceeded very slowly, taking over 2 days to reach completion. When reactions are carried out at low temperature, −30 °C, the rate of insertion becomes sufficiently slow that it may be monitored by ^1H NMR spectroscopy, and in general, the reactions require several hours to go to completion. Even when concentrations of $Mo_2Et_2(NMe_2)_4$ and CO_2 were kept virtually constant, the rate of the reaction at −30 °C was found to vary significantly from sample to sample. These observations parallel those of earlier studies of the reactions between $W(NMe_2)_6$, $W_2Me_2(NEt_2)_4$, and CO_2, which were shown to require the presence of trace amounts of free amine.[14] We have no reason to believe that these molybdenum dimethylamides react differently from their tungsten analogues with respect to CO_2 insertion. The presence of dimethylamine allows for a catalytic insertion reaction: $HNMe_2 + CO_2 \rightleftharpoons Me_2NCOOH$; $M{-}NMe_2 + HOOCNMe_2 \rightarrow M(O_2CNMe_2) + HNMe_2$. The actual replacement of NMe_2 groups by O_2CNMe_2 involves the attack of the weak acid, Me_2NCOOH, on a coordinated amide ligand. This appears to be a general reaction for all early transition-metal dimethylamides.

$Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$. The reaction between $Mo_2Et_2(NMe_2)_4$ and CO_2 in toluene-d_8 at −30 °C was followed with time by ^1H NMR spectroscopy. Certain significant observations arose from these studies. (1) The ratio of ethylene and ethane remained constant throughout the course of the reaction. Ethylene and ethane are formed at apparently the same rate, and it is not possible to determine which is eliminated first. (2) No signal, which might have been assigned to a metal hydride, was detected in the range −20 to +30 ppm (none would be expected, given (1)). (3) In all reactions, the buildup in concentration of a reactive intermediate was seen. The ^1H NMR spectrum of this intermediate is shown in Figure 3 and is consistent with that expected for $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$, providing that the molecule has virtual C_2 symmetry. A plausible structure is shown schematically in III. This proposed structure is similar to that found[15] for $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ and that reported in this paper for $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$, where C_7H_7 = p-tolyl. Note in Figure 3 that there are two resonances of equal intensity at $\delta \sim 2.9$. These are assignable to the O_2CNMe_2 signals. At −30 °C, rotations about the central C–N bond are frozen out and the six nonhydrogen atoms of the O_2CNMe_2 are expected to lie in a plane. This is seen in all carbamato structures and perhaps most pertinently in the structures of $W_2(O_2CNMe_2)_6$ and $W_2Me_2(O_2CNEt_2)_4$. In $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$, there are two Me groups trans to Mo–Et ligands and two Me groups trans to Mo–NMe_2 ligands. At −30 °C, rotations about Mo–NMe_2 bonds are frozen out on the NMR time scale and the two signals of equal intensity at ca. δ 2.2 and 4.1 are readily assignable to distal and proximal N-methyl groups, respectively. The 2 ppm chemical shift separation results from the magnetic influence of the $Mo{\equiv}Mo$ bond. Since the molecule has C_2 symmetry, the ethyl groups should appear as an ABX_3 spectrum. The methyl group is clearly visible at $\delta \sim 1.8$, but the methylene resonances are obscured by the signals associated with the O_2CNMe_2 ligands. A related compound, $Mo_2(CH_2SiMe_3)_2(NMe_2)_2(O_2CNMe_2)_2$, has been isolated from the reaction between $Mo_2(CH_2SiMe_3)_2(NMe_2)_4$ and CO_2 and has been shown to be an intermediate in the formation of $Mo_2(CH_2SiMe_3)_2(O_2CNMe_2)_4$ (see Experimental Section).



III

The rate-determining step must involve a reaction of $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$, but we have not been able to determine the nature of this step. It seemed reasonable to suppose that other reactions, in which dimethylamido ligands were replaced by bidentate ligands, would show similar facility in inducing reductive elimination of alkane and alkene, particularly when the bidentate ligand could bridge the metal–metal bond.

Reactions with 1,3-Diaryltriazenes. Previously, we have shown that $Mo_2(NMe_2)_6$ and $Mo_2Me_2(NMe_2)_4$ react with 1,3-diaryltriazenes according to eq 3[16] and 4,[17] respectively.

$$Mo_2(NMe_2)_6 + ArNNNHAr\ (excess) \rightarrow Mo_2(NMe_2)_4(ArN_3Ar)_2 + 2HNMe_2 \quad (3)$$

$$Mo_2Me_2(NMe_2)_4 + ArNNNHAr\ (excess) \rightarrow Mo_2Me_2(NMe_2)_2(ArN_3Ar)_2 + 2HNMe_2 \quad (4)$$

Reactions 3 and 4 appear quantitative and irreversible. Even in the presence of excess triazene, only two dimethylamido groups are substituted. Single-crystal X-ray studies revealed that, in both compounds, the triazenido ligands are bidentate: in $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$,[17] they bridge the $Mo{\equiv}Mo$ bond, while in $Mo_2(NMe_2)_4(C_6H_5N_3C_6H_5)_2$,[16] there is an unbridged $Mo{\equiv}Mo$ bond.

In contrast to the above, 1,3-diaryltriazenes react with $Mo_2R_2(NMe_2)_4$ compounds, where R = Et and i-Pr, in hydrocarbon solvents according to eq 5.

$$Mo_2R_2(NMe_2)_4 + ArNNNHAr\ (excess) \rightarrow Mo_2(ArN_3Ar)_4 + 4HNMe_2 + alkane + alkene \quad (5)$$

The compound $Mo_2(C_6H_5N_3C_6H_5)_4$ has been synthesized previously and shown by Cotton and co-workers[18] to have a Mo-to-Mo quadruple bond.

We were unable to obtain satisfactory elemental analyses for our compounds; indeed, analytical data varied in a seemingly erratic manner. Thus, crystals of the compound $Mo_2(C_7H_7N_3C_7H_7)_4$, grown from toluene/hexane solution, were studied by X-ray diffraction. This yielded a solution[19] having a structure

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[14] Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 802.

[15] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 1727.

[16] Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1981**, *20*, 171.

[17] Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1981**, *20*, 2211.

[18] Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1143.

[19] Crystal data for $Mo_2(C_7H_7N_3C_7H_7)_4(toluene)_x$: cell dimensions at −142 °C from 32 reflections, a = 10.443 (7) Å, b = 17.159 (8) Å, c = 19.771 (13) Å, β = 108.08 (2)°, Z = 4, d_{calcd} = 1.674 g cm^{-3}, and space group = $P2_1/n$. A total of 5168 reflections were collected, 4426 of which were unique; the number with $F > 2.33\ \sigma(F)$ was 3425. The final residuals are $R(F)$ = 0.0951 and $R_w(F)$ = 0.0948. For the last cycle, the goodness of fit was 1.450 and the maximum Δ/σ = 0.05. The Mo–Mo distance, 2.090 (2) Å, the Mo–N distances, 2.14 (2) Å (averaged), and the Mo–Mo–N angles, 91.5 (5) Å (averaged), are all essentially the same as those reported by Cotton et al. (ref 18) for the phenyl analogue.

Table I. Fractional Coordinates for the $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ Molecule[a,b]

atom	10^4x	10^4y	10^4z	$10B_{iso}$
Mo(1)	4878.8 (4)	2293.1 (3)	8199 (1)	14
Mo(2)	5997.0 (4)	2268.3 (3)	9156 (1)	14
N(3)	4518 (4)	1480 (3)	9174 (5)	15
N(4)	4876 (4)	1306 (3)	10097 (5)	17
N(5)	5510 (3)	1619 (2)	10368 (5)	14
N(6)	6281 (3)	1435 (3)	8195 (5)	15
N(7)	5909 (3)	1278 (3)	7267 (5)	15
N(8)	5306 (3)	1622 (3)	7006 (5)	15
N(9)	4848 (3)	3014 (3)	7310 (5)	16
C(10)	5389 (5)	3512 (3)	7144 (7)	23
C(11)	4063 (4)	3132 (3)	6769 (7)	22
C(12)	3959 (4)	2579 (3)	9529 (6)	20
C(13)	3990 (5)	2485 (4)	10891 (7)	25
N(14)	6089 (3)	3001 (3)	9998 (5)	18
C(15)	5582 (5)	3523 (3)	10109 (7)	23
C(16)	6894 (5)	3108 (4)	10505 (7)	24
C(17)	6941 (4)	2516 (4)	7807 (6)	19
C(18)	6902 (5)	2406 (4)	6469 (7)	29
C(19)	3826 (4)	1141 (3)	8886 (6)	15
C(20)	3400 (4)	1312 (3)	7913 (7)	20
C(21)	2714 (5)	992 (3)	7564 (7)	24
C(22)	2466 (5)	510 (3)	8205 (7)	23
C(23)	1741 (5)	147 (4)	7812 (8)	29
C(24)	2906 (5)	340 (4)	9197 (7)	27
C(25)	3588 (5)	653 (3)	9529 (7)	22
C(26)	5880 (4)	1409 (3)	11391 (6)	18
C(27)	5872 (4)	828 (3)	11714 (7)	22
C(28)	6243 (5)	653 (4)	12750 (7)	27
C(29)	6649 (5)	1046 (4)	13468 (7)	28
C(30)	7027 (5)	840 (4)	14583 (7)	34
C(31)	6665 (5)	1619 (4)	13130 (7)	30
C(32)	6294 (5)	1811 (4)	12084 (7)	25
C(33)	6974 (4)	1086 (3)	8417 (6)	16
C(34)	7456 (5)	1245 (3)	9353 (7)	21
C(35)	8185 (5)	947 (3)	9580 (7)	20
C(36)	7456 (5)	1245 (3)	9353 (7)	21
C(35)	8185 (5)	947 (3)	9580 (7)	20
C(36)	8417 (5)	493 (3)	8864 (7)	22
C(37)	9208 (5)	175 (4)	9082 (8)	28
C(38)	7911 (5)	315 (4)	7949 (7)	25
C(39)	7193 (5)	607 (3)	7731 (7)	21
C(40)	4911 (4)	1435 (3)	5961 (6)	17
C(41)	4659 (5)	1860 (4)	5177 (7)	24
C(42)	4269 (5)	1701 (4)	4138 (7)	28
C(43)	4102 (5)	1119 (4)	3910 (7)	26
C(44)	3692 (5)	944 (4)	2789 (7)	31
C(45)	4350 (5)	698 (4)	4714 (7)	26
C(46)	4748 (4)	858 (4)	5738 (7)	22
C(47)	−753 (8)	1307 (7)	3265 (10)	74
C(48)	85 (7)	1215 (5)	3654 (8)	45
C(49)	625 (7)	1672 (5)	3635 (8)	52
C(50)	1425 (8)	1588 (8)	3991 (9)	78
C(51)	1681 (8)	1022 (9)	4366 (10)	83
C(52)	1108 (11)	588 (8)	4355 (11)	98
C(53)	322 (9)	683 (5)	4015 (9)	65

[a] The isotropic thermal parameters listed for those atoms refined anisotropically are the isotropic equivalent. [b] Numbers in parentheses in this and all following tables refer to the error in the least significant digits.

essentially identical with that reported by Cotton et al.[18] for the $Mo_2(PhN_3Ph)_4$. The problem associated with obtaining good elemental analytical results probably arises from the partial solvation observed in the crystals. The blades of the aryl groups are packed in such a way as to generate channels and holes. In the crystal that we examined, toluene molecules were located and refined in the channels, but a large hole, ca. 12 Å in diameter, was apparently partially occupied by some molecule of inclusion. Full structural details are given in the supplementary material. The characterization of $Mo_2(C_7H_7N_3C_7H_7)_4$ is not pertinent to the thrust of this paper beyond establishing that, in reaction 5, the metal-to-metal bond order changes from three to four.

By the careful addition of 2 equiv of 1,3-di-*p*-tolyltriazene to a hydrocarbon solution of $Mo_2Et_2(NMe_2)_4$, we have been able to isolate $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ as an orange crystalline compound. In the solid state, it is quite stable and like $Mo_2Me_2(NMe_2)_2(ArN_3Ar)_2$ and $Mo_2(NMe_2)_4(ArN_3Ar)_2$ compounds may be exposed to the atmosphere for short periods of time without significant decomposition. (This contrasts with the high reactivity of $Mo_2Et_2(NMe_2)_4$, which smolders when exposed to the atmosphere.) On the other hand, $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ *slowly* decomposes in solution at room temperature and eliminates ethane (no ethylene is evolved). Significantly, *the addition of either* $C_7H_7NNNHC_7H_7$ *or* CO_2 *causes a more rapid evolution of ethane and ethylene.* Addition of $C_7H_7NNNHC_7H_7$ yields $Mo_2(C_7H_7N_3C_7H_7)_4$; reaction with CO_2 presumably generates $Mo_2(C_7H_7N_3C_7H_7)_2(O_2CNMe_2)_2$, but this remains to be established.

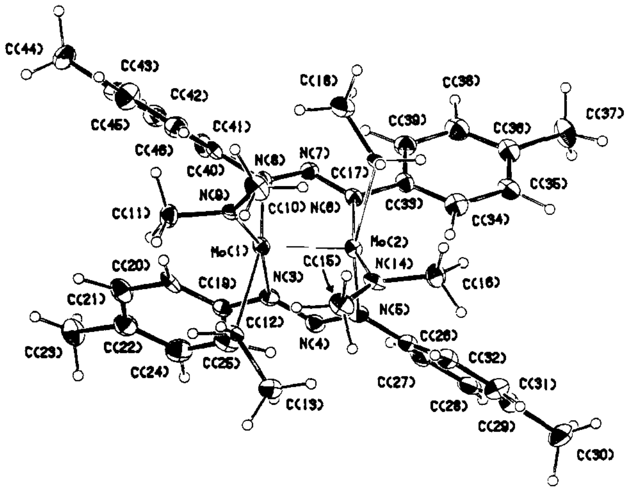

Figure 4. An ORTEP view of the $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ molecule showing the atom numbering scheme used in the tables.

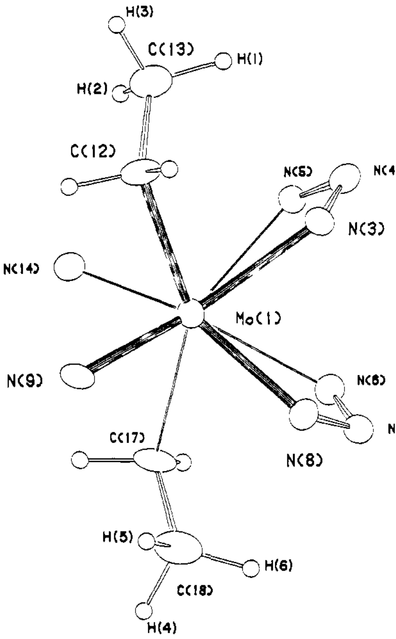

Figure 5. An ORTEP view of the central skeleton of the $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ molecule viewed down the Mo≡Mo bond showing the arrangement of the ethyl groups.

Solid-State Structure of $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$. An ORTEP view of the molecule giving the atom numbering scheme is shown in Figure 4. A view down the Mo–Mo bond is shown in Figure 5. Final atomic coordinates and thermal parameters are given in Tables I and II, respectively. Complete listings of bond distances and bond angles are given in Tables III and IV, respectively.

The molecule has virtual, but not crystallographically imposed, C_2 symmetry and is, in this and most other respects, analogous

Table II. Anisotropic Thermal Parameters for the $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ Molecule[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	15.6 (4)	15.7 (4)	20.9 (4)	0.8 (3)	0.4 (3)	1.1 (3)
Mo(2)	15.4 (4)	16.2 (4)	21.3 (4)	0.2 (3)	−0.1 (3)	−0.6 (3)
N(3)	20 (4)	18 (4)	20 (4)	−1 (3)	3 (3)	1 (3)
N(4)	20 (4)	22 (4)	22 (4)	3 (3)	3 (3)	−2 (3)
N(5)	21 (4)	15 (3)	18 (3)	1 (3)	2 (3)	2 (3)
N(6)	16 (3)	19 (4)	23 (4)	3 (3)	1 (3)	0 (3)
N(7)	21 (4)	19 (4)	17 (3)	−2 (3)	0 (3)	−0 (3)
N(8)	18 (3)	19 (4)	21 (4)	1 (3)	−1 (3)	−1 (3)
N(9)	18 (4)	26 (4)	17 (3)	0 (3)	4 (3)	5 (3)
C(10)	28 (5)	14 (4)	44 (5)	−7 (4)	2 (4)	0 (4)
C(11)	24 (4)	30 (5)	28 (5)	4 (4)	−6 (4)	6 (4)
C(12)	15 (4)	37 (5)	23 (4)	2 (4)	7 (3)	−3 (4)
C(13)	30 (5)	39 (5)	25 (5)	4 (4)	4 (4)	−0 (4)
N(14)	18 (4)	22 (4)	27 (4)	−2 (3)	9 (3)	−3 (3)
C(15)	31 (5)	20 (5)	36 (5)	7 (4)	4 (4)	−5 (4)
C(16)	22 (4)	37 (5)	32 (5)	−11 (4)	−4 (4)	−1 (4)
C(17)	13 (4)	39 (5)	19 (4)	−3 (4)	6 (3)	6 (4)
C(18)	29 (5)	50 (6)	31 (5)	2 (4)	6 (4)	8 (5)
C(19)	19 (4)	15 (4)	21 (4)	3 (3)	3 (3)	−1 (3)
C(20)	11 (4)	26 (5)	37 (5)	1 (3)	6 (4)	−1 (4)
C(21)	23 (5)	27 (5)	42 (5)	6 (4)	2 (4)	−5 (4)
C(22)	27 (5)	26 (5)	33 (5)	3 (4)	4 (4)	−4 (4)
C(23)	26 (5)	41 (6)	44 (6)	−19 (4)	−3 (4)	−4 (4)
C(24)	39 (5)	30 (5)	32 (5)	0 (4)	4 (4)	−5 (4)
C(25)	27 (5)	24 (5)	32 (5)	−3 (4)	8 (4)	−4 (4)
C(26)	20 (4)	28 (5)	19 (4)	3 (4)	3 (3)	0 (4)
C(27)	17 (4)	33 (5)	35 (5)	7 (4)	3 (4)	9 (4)
C(28)	25 (5)	49 (6)	29 (5)	10 (4)	11 (4)	7 (4)
C(29)	23 (5)	54 (7)	28 (5)	9 (4)	2 (4)	3 (5)
C(30)	43 (6)	63 (7)	24 (5)	14 (5)	−1 (4)	11 (5)
C(31)	40 (6)	51 (7)	23 (5)	1 (5)	0 (4)	3 (4)
C(32)	25 (5)	41 (5)	27 (5)	4 (4)	4 (4)	3 (4)
C(33)	17 (4)	19 (4)	25 (4)	−1 (3)	1 (3)	4 (4)
C(34)	30 (5)	17 (4)	33 (5)	−3 (4)	1 (4)	12 (4)
C(35)	24 (5)	20 (5)	32 (5)	3 (4)	5 (4)	12 (4)
C(36)	25 (5)	22 (5)	36 (5)	−0 (4)	1 (4)	12 (4)
C(37)	27 (5)	28 (5)	53 (6)	14 (4)	−3 (4)	5 (4)
C(38)	31 (5)	28 (5)	35 (5)	2 (4)	5 (4)	7 (4)
C(39)	26 (5)	27 (5)	26 (5)	1 (4)	3 (4)	3 (4)
C(40)	11 (4)	30 (5)	24 (4)	−2 (3)	3 (3)	1 (4)
C(41)	29 (5)	32 (5)	28 (4)	−4 (4)	3 (4)	3 (4)
C(42)	40 (5)	30 (5)	37 (5)	−7 (4)	−6 (4)	−5 (4)
C(43)	31 (5)	45 (6)	22 (4)	−3 (4)	6 (4)	5 (4)
C(44)	35 (5)	56 (6)	25 (5)	−8 (4)	−6 (4)	−8 (4)
C(45)	25 (5)	40 (5)	32 (5)	0 (4)	3 (4)	−15 (4)
C(46)	18 (4)	32 (5)	34 (5)	2 (4)	−3 (4)	−7 (4)
C(47)	88 (10)	139 (13)	55 (8)	−30 (9)	−7 (7)	6 (8)
C(48)	77 (8)	63 (8)	30 (6)	−18 (7)	7 (5)	−3 (5)
C(49)	87 (9)	84 (9)	27 (6)	−27 (7)	15 (6)	−15 (5)
C(50)	79 (10)	187 (18)	28 (7)	−26 (11)	24 (7)	−25 (9)
C(51)	68 (10)	215 (21)	30 (7)	29 (12)	9 (7)	−15 (10)
C(52)	143 (17)	181 (19)	45 (8)	57 (15)	21 (11)	−33 (10)
C(53)	147 (14)	68 (10)	29 (6)	13 (9)	15 (7)	−6 (6)

[a] The form of the exponent is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}lc^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] All Us are $\times 10^3$.

to that observed in $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$. The Mo–C bond distance, 2.21 (1) Å (average), is longer than that in the methyl analogue, 2.193 (4) Å, and that in the parent compound, $Mo_2Et_2(NMe_2)_4$, which is 2.16 (1) Å (averaged).[2] Also, unlike in $Mo_2Et_2(NMe_2)_4$, the ethyl groups are directed over the Mo≡Mo bond. As we predicted for this situation, the Mo–β-H distances across the Mo≡Mo bond are shorter than are those to the molybdenum atoms to which the ethyl group is directly bonded (see Table V). However, in the present case, no significant C–H- - -Mo interaction is seen in the ground state. The orientation of the ethyl group over the Mo≡Mo moiety can readily be understood in terms of steric considerations. The tolyl groups effectively block the axial positioning of the methyl groups and direct them inward. The obtuse Mo–C–C angles (126.1 (5)° and 125.7 (5)°), which may be compared with Mo–C–C = 112.0 (3)° and 113.0 (3)° found in $Mo_2Et_2(NMe_2)_4$, reflect the internal crowding of the molecule. This may also be the cause of the lengthening of the Mo–C(ethyl) bond distances.[20]

Concluding Remarks. Addition of either CO_2 or 1,3-diaryltriazines to 1,2-$Mo_2R_2(NMe_2)_4$ compounds promotes reductive elimination from the dimetal center by alkyl group disproportionation with a concomitant metal–metal bond order change from three to four when R = an alkyl group having β-hydrogen atoms. Both reactions proceed through intermediates of the form 1,2-$Mo_2R_2(NMe_2)_2$(chelate)$_2$. The elimination of alkane and alkene is intramolecular and has a formal analogy with that found in mononuclear chemistry, namely β-hydrogen elimination followed by reductive elimination by carbon–hydrogen bond formation. The detailed pathway leading to this is, however, uncertain.

The presence of the dimetal center introduces additional possibilities. For example, the H–Mo bond could be formed across

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[20] For a discussion of the lengthening of the Co–C bond distances in cobaloximes as a function of steric and conformational factors, see: Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 6754; **1980**, *102*, 7372.

Table III. Bond Distances for the $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ Molecule

A	B	distance, Å	A	B	distance, Å
Mo(1)	Mo(2)	2.171 (1)	C(26)	C(27)	1.393 (11)
Mo(1)	N(3)	2.251 (6)	C(26)	C(32)	1.406 (11)
Mo(1)	N(8)	2.160 (6)	C(27)	C(28)	1.400 (11)
Mo(1)	N(9)	1.949 (6)	C(28)	C(29)	1.403 (12)
Mo(1)	C(12)	2.205 (7)	C(29)	C(30)	1.502 (11)
Mo(2)	N(5)	2.171 (6)	C(29)	C(31)	1.380 (12)
Mo(2)	N(6)	2.253 (6)	C(31)	C(32)	1.421 (11)
Mo(2)	N(14)	1.952 (6)	C(33)	C(34)	1.395 (10)
Mo(2)	C(17)	2.221 (7)	C(33)	C(39)	1.394 (10)
N(3)	N(4)	1.281 (8)	C(34)	C(35)	1.417 (10)
N(3)	C(19)	1.431 (9)	C(35)	C(36)	1.372 (11)
N(4)	N(5)	1.316 (8)	C(36)	C(37)	1.526 (10)
N(5)	C(26)	1.412 (9)	C(36)	C(38)	1.413 (11)
N(6)	N(7)	1.286 (8)	C(38)	C(39)	1.391 (11)
N(6)	C(33)	1.428 (9)	C(40)	C(41)	1.397 (10)
N(7)	N(8)	1.314 (8)	C(40)	C(46)	1.384 (11)
N(8)	C(40)	1.437 (9)	C(41)	C(42)	1.407 (11)
N(9)	C(10)	1.464 (9)	C(42)	C(43)	1.400 (12)
N(9)	C(11)	1.476 (9)	C(43)	C(44)	1.511 (11)
N(14)	C(15)	1.471 (9)	C(43)	C(45)	1.402 (11)
N(14)	C(16)	1.484 (9)	C(45)	C(46)	1.400 (11)
C(12)	C(13)	1.559 (10)	C(47)	C(48)	1.479 (16)
C(17)	C(18)	1.539 (11)	C(48)	C(49)	1.382 (14)
C(19)	C(20)	1.384 (10)	C(48)	C(53)	1.358 (16)
C(19)	C(25)	1.393 (10)	C(49)	C(50)	1.407 (16)
C(20)	C(21)	1.420 (11)	C(50)	C(51)	1.445 (21)
C(21)	C(22)	1.384 (11)	C(51)	C(52)	1.379 (22)
C(22)	C(23)	1.540 (11)	C(52)	C(53)	1.383 (19)
C(22)	C(24)	1.411 (11)			
C(24)	C(25)	1.400 (11)			

the $Mo\equiv Mo$ bond. This would be akin to a cyclometalation reaction involving a 5-membered ring,[21] and the structure of $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ clearly shows the geometric plausibility of this reaction pathway. The observation that excess $C_7H_7NNNHC_7H_7$ promotes a reaction with $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$, but not with $Mo_2R_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ compounds, where R = CH_3 or CH_2CMe_3, could be correlated with a reversible protonation of a Mo–NMe_2 nitrogen lone pair. In the $Mo_2R_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ compounds, the NMe_2 ligands are clearly strong π donors to one of the five in-plane molybdenum atomic orbitals (s, p_x, p_y, d_{xy}, $d_{x^2-y^2}$). Upon protonation of the amide lone pair, one of these orbitals would be freed to form a CH–Mo 3-center, 2-electron bond. The structure of $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ suggests that the β-hydrogens of the ethyl ligands are poised for such an opportunity. Alternatively, a 1,2- to 1,1-$Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ isomerization reaction, involving an alkyl group transfer across the $Mo\equiv Mo$ bond, may be required, and promoted in the association reaction between 1,2-$Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ and excess triazine, prior to β-hydrogen elimination. For a 1,1-$Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ molecule, one molybdenum atom would have one in-plane atomic orbital available for β-hydrogen elimination in the more conventional sense of this terminology (i.e., mononuclear). Within this context, it should be noted that (i) there is a high kinetic barrier to 1,1 and 1,2 isomerization of $Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ compounds,[22] and (ii) Bergman et al.[23] have proposed, with good experimental evidence, that reductive elimination of acetone from 1,2-$Cp_2Co_2Me_2(CO)_2$ proceeds via an initial methyl group transfer from one cobalt atom to the other.

Finally, it should be recognized that it is not necessary to invoke the formation of an intermediate metal hydride in these reactions. The β-hydrogen atom of an ethyl ligand could be transferred to the α-carbon of the other ethyl ligand through the agency of one of the nitrogen atoms, which could be either a triazenido or dimethylamido ligand. In a formal sense this would have analogy with E2 reactions of substituted alkanes. These, and other possibilities, provide us with the stimulus for further studies of reductive eliminations of hydrocarbons from dinuclear metal centers.

Experimental Section

General procedures, including the preparations of 1,2-$Mo_2R_2(NMe_2)_4$ compounds, have been described previously.[2] Note the use of dry and oxygen-free solvents and atmospheres.

^1H and ^2H NMR spectra were recorded on a Varian HR220 MHz spectrometer equipped with a variable temperature probe. Infrared spectra were recorded on a PE-283 spectrophotometer. Mass spectra were obtained on a Varian MS-902 by the method of direct insertion, courtesy of Peter Cook, Queen Mary College, London.

Preparation of $Mo_2Me_2(O_2CNMe_2)_4$. To a 50-mL round-bottomed flask equipped with a stir-bar and N_2 inlet was added $Mo_2Me_2(NMe_2)_4$ (199 mg, 0.5 mmol) followed by hexane (20 mL) to give a clear yellow solution. The solution was cooled to liquid N_2 temperature, and the flask was attached to a calibrated vacuum manifold containing bone-dry CO_2 gas. The solution was slowly warmed to room temperature under 1 atm of CO_2. As CO_2 was taken into the solution, more CO_2 was introduced into the vacuum manifold to maintain close to 1-atm pressure. After 2 h, no further uptake of CO_2 occurred, and a yellow precipitate that had formed was collected by filtration and recrystallized from a large volume of hot toluene (ca. 100 mL): $Mo_2Me_2(O_2CNMe_2)_4$ (145 mg, ca. 50% yield based on Mo). Anal. Calcd for $Mo_2Me_2(O_2CNMe_2)_4$: C, 29.3; H, 5.23; N, 9.75. Found: C, 29.5; H, 5.14; N, 9.65.

The mass spectrum obtained at 90 °C showed a molecular ion, M^+, followed by successive loss of CH_3, $(M - 15)^+$ and $(M - 30)^+$ and loss of 44 (either NMe_2 or CO_2) and 88 (O_2CNMe_2). IR (KBr plates, Nujol mull) 1675 (w), 1560 (vs, br), 1490 (s), 1405 (vs), 1261 (vs), 1234 (s), 1093 (s), 1025 (s), 945 (m), 795 (s), 655 (m), 636 (m) cm^{-1}. $Mo_2Me_2(O_2CNMe_2)_4$ is insufficiently soluble in toluene-d_8 or benzene-d_6 to yield reliable characterization by ^1H NMR spectroscopy.

Preparation of $Mo_2(O_2CNMe_2)_4$. To a 25-mL flask equipped with a stir bar and N_2 inlet was added 0.100 g (0.23 mmol) of $Mo_2Et_2(NMe_2)_4$ in 15 mL of toluene. The flask was attached to a calibrated manifold and evacuated at liquid N_2 temperature, and 6 equiv of CO_2 was added. As the flask gradually warmed to room temperature, the color changed from a golden yellow to orange with the precipitation of a pale yellow powder. The solution above the powder was virtually colorless at the completion of the reaction. Infrared spectra of the pale yellow powder using Nujol mull and CsI plates gave a strong absorption at 1560 cm^{-1} (ν_{NCO_2} of bridging carbamate). The yellow powder was extremely insoluble in most solvents; however, a sufficient quantity was soluble in pyridine-d^5 to record its NMR spectrum, which showed a singlet at 2.93 ppm relative to Me_4Si corresponding to O_2CNMe_2. Anal. Calcd: C, 33.79; H, 8.04; N, 13.15. Found: C, 33.55; H, 7.89; N, 12.99.

Preparation of $Mo_2(CH_2SiMe_3)_2(NMe_2)_2(O_2CNMe_2)_2$. In a manner analogous to that described above, $Mo_2(CH_2SiMe_3)_2(NMe_2)_4$ (543 mg, 1 mmol) was dissolved in hexane (30 mL). The solution was allowed to react with CO_2 until no further absorption of CO_2 occurred. A light brown precipitate which had formed was collected by filtration and dried in vacuo (10^{-4} torr, 5 h, room temperature): $Mo_2(CH_2SiMe_3)_2(NMe_2)_2(O_2CNMe_2)_2$, 480 mg (76% yield based on Mo). Anal. Calcd for $Mo_2(CH_2SiMe_3)_2(NMe_2)_2(O_2CNMe_2)_2$: C, 34.3; H, 7.35; N, 8.88. Found: C, 34.4; H, 7.29; N, 8.93.

IR (KBr, Nujol mull) 1550 (vs, br), 1500 (sh), 1403 (s), 1265 (s), 1040 (w), 1020 (w), 900 (w), 855 (sh), 838 (m), 788 (w), 745 (m), 715 (w), 640 (m), 612 (w) cm^{-1}; ^1H NMR (toluene-d_8, 16 °C, 220 MHz) δ (Mo–NMe_2) 4.05 (proximal, 6 H) and 2.61 (distal, 6 H); (O_2CNMe_2) 2.84, 2.75 (6 H, 6 H); (CH_2SiMe_3) 2.03 AB quartet partially obscured by toluene-d_8 methyl impurity signal (4 H); (CH_2SiMe_3) 0.09 (18 H) (δ in ppm relative to Me_4Si). The O_2CNMe_2 resonances are slightly broadened at 16 °C but sharpen at lower temperatures.

Preparation of $Mo_2(CH_2SiMe_3)_2(O_2CNMe_2)_4$. $Mo_2(CH_2SiMe_3)_2(NMe_2)_2(O_2CNMe_2)_2$ (315 mg, 0.5 mmol) was dissolved in hexane (30 mL), and the solution was placed in a small pressure bottle. The solution was frozen at liquid N_2 temperature, and by use of a calibrated vacuum manifold, CO_2 (3 mmol) was added to the vessel to give an initial pressure of 6 atm. A yellow-brown precipitate formed as the solution was allowed to warm to room temperature. The solution was maintained at room temperature for 1 h, after which time the excess CO_2 was released and the supernatant hexane solution was decanted and discarded. The precipitate was washed with hexane (10 mL) twice and dried under vacuum, yielding $Mo_2(CH_2SiMe_3)_2(O_2CNMe_2)_4$ (324 mg, ca. 90% yield based on Mo). Anal. Calcd for $Mo_2(CH_2SiMe_3)_2(O_2CNMe_2)_4$: C, 33.4; H, 6.45; N, 7.80. Found: C, 33.5; H, 6.29; N, 8.12.

IR (KBr plates, Nujol mull) 1720 (m), 1545 (vs, br), 1405 (vs), 1258 (vs), 1090 (s), 1024 (s), 945 (w), 925 (w), 900 (vw), 855 (sh), 793 (s), 740 (w), 637 (m) cm^{-1}.

$Mo_2(CH_2SiMe_3)_2(O_2CNMe_2)_4$ is only very sparingly soluble in tolu-

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Table IV. Bond Angles for the $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ Molecule

A	B	C	angle, deg
Mo(2)	Mo(1)	N(3)	87.1 (2)
Mo(2)	Mo(1)	N(8)	91.6 (2)
Mo(2)	Mo(1)	N(9)	108.5 (2)
Mo(2)	Mo(1)	C(12)	104.2 (2)
N(3)	Mo(1)	N(8)	77.4 (2)
N(3)	Mo(1)	N(9)	163.1 (2)
N(3)	Mo(1)	C(12)	75.5 (3)
N(8)	Mo(1)	N(9)	107.8 (2)
N(8)	Mo(1)	C(12)	147.8 (3)
N(9)	Mo(1)	C(12)	93.9 (3)
Mo(1)	Mo(2)	N(5)	91.7 (2)
Mo(1)	Mo(2)	N(6)	87.1 (1)
Mo(1)	Mo(2)	N(14)	107.5 (2)
Mo(1)	Mo(2)	C(17)	103.8 (2)
N(5)	Mo(2)	N(6)	77.4 (2)
N(5)	Mo(2)	N(14)	109.0 (2)
N(5)	Mo(2)	C(17)	148.2 (3)
N(6)	Mo(2)	N(14)	163.5 (2)
N(6)	Mo(2)	C(17)	76.0 (3)
N(14)	Mo(2)	C(17)	92.8 (3)
Mo(1)	N(3)	N(4)	122.7 (5)
Mo(1)	N(3)	C(19)	123.1 (5)
N(4)	N(3)	C(19)	114.0 (6)
N(3)	N(4)	N(5)	114.1 (6)
Mo(2)	N(5)	N(4)	120.9 (4)
Mo(2)	N(5)	C(26)	126.4 (5)
N(4)	N(5)	C(26)	111.8 (6)
Mo(2)	N(6)	N(7)	122.6 (4)
Mo(2)	N(6)	C(33)	123.6 (5)
N(7)	N(6)	C(33)	113.0 (6)
N(6)	N(7)	N(8)	113.4 (6)
Mo(1)	N(8)	N(7)	121.9 (4)
Mo(1)	N(8)	C(40)	125.7 (5)
N(7)	N(8)	C(40)	111.7 (6)
Mo(1)	N(9)	C(10)	135.4 (5)
Mo(1)	N(9)	C(11)	114.2 (4)
C(10)	N(9)	C(11)	110.0 (6)
Mo(2)	N(14)	C(15)	134.5 (5)
Mo(2)	N(14)	C(16)	114.7 (5)
C(15)	N(14)	C(16)	110.1 (6)
Mo(1)	C(12)	C(13)	126.1 (5)
Mo(2)	C(17)	C(18)	125.7 (5)
N(3)	C(19)	C(20)	117.0 (6)
N(3)	C(19)	C(25)	122.6 (7)
C(20)	C(19)	C(25)	120.4 (7)
C(19)	C(20)	C(21)	120.1 (7)
C(20)	C(21)	C(22)	119.9 (8)
C(21)	C(22)	C(23)	120.4 (7)
C(21)	C(22)	C(24)	119.4 (8)
C(23)	C(22)	C(24)	120.1 (8)
C(22)	C(24)	C(25)	120.6 (8)
C(19)	C(25)	C(24)	119.6 (8)
N(5)	C(26)	C(27)	123.0 (7)
N(5)	C(26)	C(32)	117.5 (7)
C(27)	C(26)	C(32)	119.4 (7)
C(26)	C(27)	C(28)	119.9 (8)
C(27)	C(28)	C(29)	121.9 (8)
C(28)	C(29)	C(30)	120.1 (8)
C(28)	C(29)	C(31)	117.8 (8)
C(30)	C(29)	C(31)	122.1 (8)
C(29)	C(31)	C(32)	121.7 (8)
C(26)	C(32)	C(31)	119.3 (8)
N(6)	C(33)	C(34)	117.7 (7)
N(6)	C(33)	C(39)	123.1 (7)
C(34)	C(33)	C(39)	119.2 (7)
C(33)	C(34)	C(35)	121.2 (8)
C(34)	C(35)	C(36)	119.2 (7)
C(35)	C(36)	C(37)	119.8 (7)
C(35)	C(36)	C(38)	119.7 (7)
C(37)	C(36)	C(38)	120.5 (7)
C(36)	C(38)	C(39)	121.0 (8)
C(33)	C(39)	C(38)	119.6 (7)
N(8)	C(40)	C(41)	117.6 (7)
N(8)	C(40)	C(46)	122.4 (7)
C(41)	C(40)	C(46)	119.9 (7)
C(40)	C(41)	C(42)	120.0 (7)
C(41)	C(42)	C(43)	120.3 (8)
C(42)	C(43)	C(44)	120.6 (8)
C(42)	C(43)	C(45)	118.9 (8)
C(44)	C(43)	C(45)	120.5 (8)
C(43)	C(45)	C(46)	120.6 (8)
C(40)	C(46)	C(45)	120.3 (8)
C(47)	C(48)	C(49)	119.6 (11)
C(47)	C(48)	C(53)	120.0 (12)
C(49)	C(48)	C(53)	120.4 (12)
C(48)	C(49)	C(50)	120.1 (13)
C(49)	C(50)	C(51)	119.7 (13)
C(50)	C(51)	C(52)	116.8 (13)
C(51)	C(52)	C(53)	122.4 (17)
C(48)	C(53)	C(52)	120.7 (14)

Table V. Distances from β-Hydrogens of the Ethyl Ligands to the Molybdenum Atoms in the $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ Molecule, As Located in the Difference Map

atom[b]	atom[b]	distance,[a] Å
Mo(1)	H(1)	3.5 (1)
Mo(1)	H(2)	3.6 (1)
Mo(1)	H(3)	4.2 (1)
Mo(2)	H(4)	3.5 (1)
Mo(2)	H(5)	3.7 (1)
Mo(2)	H(6)	4.1 (1)
Mo(1)	H(4)	3.4 (1)
Mo(1)	H(5)	4.2 (1)
Mo(1)	H(6)	4.7 (1)
Mo(2)	H(1)	3.4 (1)
Mo(2)	H(2)	4.0 (1)
Mo(2)	H(3)	4.8 (1)

[a] Errors are estimated based on the internal consistancy of the C-H distances and angles, as located in the difference synthesis.
[b] The numbering scheme for the hydrogen atoms is given in Figure 5.

ene-d_8 and benzene-d_6 and, at 220 MHz, 16 °C, shows only a sharp singlet at δ 0.07 assignable to CH_2SiMe_3 protons and a broad resonance at δ 2.9 assignable to O_2CNMe_2 protons.

Preparation of the Mixture $Mo_2Me_nEt_{n-2}(NMe_2)_4$ (n = 0, 1, and 2). $Mo_2Cl_2(NMe_2)_4$ (217 mg, 0.49 mmol) was added to a mixture of solid MeLi (11 mg, 0.5 mmol) and EtLi (18 mg, 0.5 mmol) in a drybox. To this mixture was added hexane (20 mL), giving an orange solution and suspended solids. The reaction mixture was magnetically stirred for 12 h and filtered through Celite and a fine frit to remove LiCl and any unreacted or other solid materials, and the filtrate was collected and stripped in vacuo to yield an orange solid. A yellow-orange sublimate was collected by sublimation at 70–80 °C (10^{-4} torr). The ^1H NMR spectrum of this material was complex. However, in addition to the resonances of the compounds $Mo_2Me_2(NMe_2)_4$ and $Mo_2Et_2(NMe_2)_4$, which exist in anti and gauche rotamers and have temperature-dependent NMe_2 resonances due to restricted rotation about Mo–N bonds, new resonances which could reasonably be assigned to the mixed alkyl compound $Mo_2(Me)(Et)(NMe_2)_4$ were observed. In particular, a new Mo–CH_3 resonance at δ 1.18 was observed in a relatively clear portion of the spectrum. Superimposed on the ABX_3 and A_2X_3 triplets for CH_2CH_3 groups of the gauche and anti rotamers of $Mo_2Et_2(NMe_2)_4$ (δ 1.57 and 1.65, respectively), another triplet for the CH_2CH_3 group of the gauche $Mo_2(Me)(Et)(NMe_2)_4$ molecule was observed at δ 1.59. The compounds $Mo_2Me_2(NMe_2)_4$, $Mo_2(Me)(Et)(NMe_2)_4$, and $Mo_2Et_2(NMe_2)_4$ appeared to be in the ratio 1:2:3, respectively.

Preparation of the Mixture $Mo_2Et_n(CH_2SiMe_3)_{2-n}(NMe_2)_4$ (where n = 0, 1, and 2). $Mo_2Cl_2(NMe_2)_4$ (439 mg, 1 mmol) was added to solid $LiCH_2SiMe_3$ (94 mg, 1 mmol) in a Schlenk apparatus. The mixture of solids was cooled to liquid N_2 temperature and EtLi in hexane (2.5 mL of a 0.4 M solution) was added, followed by hexane (30 mL). The frozen solution was allowed to warm to room temperature slowly and was then stirred for 12 h. The solution was filtered by using Celite and a fine frit. The orange filtrate was collected, the solvent was stripped in vacuo, and the orange solids thus obtained were sublimed slowly at 80 °C (10^{-4} torr). The ^1H NMR spectrum of the orange sublimate indicated the presence of a mixture of $Mo_2Et_2(NMe_2)_4$, $Mo_2(Et)(CH_2SiMe_3)(NMe_2)_4$, and $Mo_2(CH_2SiMe_3)_2(NMe_2)_4$ in close to the statistical ratio 1:2:1. A resonance at δ 0.27 is assigned to the CH_2SiMe_3 protons of *gauche*-$Mo_2(Et)(CH_2SiMe_3)(NMe_2)_4$. Other resonances aside from those found for

$Mo_2Et_2(NMe_2)_4$ and $Mo_2(CH_2SiMe_2)_2(NMe_2)_4$ could be ascribed to the mixed alkyl.

Reaction of a Mixture of $Mo_2Me_2(NMe_2)_4$ and $Mo_2Et_2(NMe_2)_4$ with CO_2. $Mo_2Me_2(NMe_2)_4$ (29 mg, 0.073 mmol) was placed in an NMR tube in a drybox, and $Mo_2Et_2(NMe_2)_4$ (0.4 mL of a 0.2 M solution in toluene-d_8, 0.08 mmol) was added by syringe. The NMR tube was shaken; $Mo_2Me_2(NMe_2)_4$ dissolved to give a homogeneous yellow solution. The ^1H NMR spectrum was recorded and showed only signals assignable to a mixture of anti and gauche rotamers of $Mo_2Me_2(NMe_2)_4$ and $Mo_2Et_2(NMe_2)_4$; no alkyl scrambling was detected.

The NMR tube was then attached to a calibrated vacuum manifold, the solution was frozen at liquid N_2 temperature, CO_2 (0.8 mmol) was condensed into the tube, and the sample tube was then sealed under vacuum by a torch. The NMR tube was allowed to warm to room temperature behind a safety screen. The ^1H NMR spectrum recorded within 15 min of this operation showed the formation of C_2H_4 (δ 5.24) and C_2H_6 (δ 0.81) together with resonances assignable to the compounds $Mo_2Me_2(NMe_2)_2(O_2CNMe_2)_2$, $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$, $Mo_2Me_2(O_2CNMe_2)_4$, and $Mo_2(O_2CNMe_2)_4$. No signal for CH_4 was observed. With time, the signals associated with thhe intermediates $Mo_2R_2(NMe_2)_2(O_2CNMe_2)_2$ (R = Me and Et) decreased and after 2 days had virtually disappeared, leaving behind signals associated with C_2H_4, C_2H_6, and the sparingly soluble compounds $Mo_2Me_2(O_2CNMe_2)_4$ and $Mo_2(O_2CNMe_2)_4$. These sparingly soluble species were centrifuged to the top of the sealed NMR tube as they precipitated from solution during the course of reaction. No CH_4 signal was detected; the C_2H_4 and C_2H_6 signals were in the ratio 2:3.

Reaction of a Mixture of $Mo_2Et_2(Me_2)_4$ and $Mo_2(CH_2SiMe_3)_2(NMe_2)_4$ with CO_2. An NMR tube reaction was carried out in an analogous manner to that described for $Mo_2Me_2(NMe_2)_4$, $Mo_2Et_2(NMe_2)_4$, and CO_2. No Me_4Si was detected; only C_2H_4 and C_2H_6 were formed along with the sparingly soluble species $Mo_2(O_2CNMe_2)_4$ and $Mo_2(CH_2SiMe_3)_2(O_2CNMe_2)_4$ which were precipitated from solution.

Reaction of the Mixture $Mo_2Me_nEt_{2-n}(NMe_2)_4$ (n = 0, 1, 2) with CO_2. A sample of the titled mixture (25 mg, ca. 0.06 mmol) was placed in an NMR tube and dissolved in toluene-d_8 (0.4 mL). The tube was transferred to a calibrated vacuum manifold; the solution was frozen at liquid N_2 temperature and CO_2 (0.53 mmol) was condensed in. The NMR tube was sealed with a torch and allowed to warm to room temperature behind a safety screen. The ^1H NMR spectrum was then recorded; C_2H_4, C_2H_6, and CH_4 (δ 0.34) were observed.

Reaction of the Mixture $Mo_2Et_n(CH_2SiMe_3)_{2-n}(NMe_2)_4$ (n = 0, 1, 2) with CO_2. A sample of the mixed dialkyl complexes $Mo_2Et_n(CH_2SiMe_3)_{2-n}(NMe_2)_4$ (30 mg) was placed in an NMR tube and dissolved in toluene-d_8 (0.4 mL). The tube was transferred to a vacuum manifold; the solution was frozen at −196 °C and excess CO_2 (0.5 mmol) was added. The NMR tube was sealed with a torch and then allowed to warm to room temperature behind a safety shield. The ^1H NMR spectrum was recorded and showed the formation of C_2H_4, C_2H_6, and Me_4Si.

Reactions Involving $Mo_2R_2(NMe_2)_4$ Compounds with CO_2 (R = C_2H_5, CH_2CD_3, CD_2CH_3, $CH(CH_3)_2$, n-, sec-, t-C_4H_9). Reactions involving $Mo_2R_2(NMe_2)_4$ compounds, where R contained β-hydrogen atoms (or deuterium atoms), with CO_2 were carried out in sealed NMR tubes with toluene-d_8 in precisely the manner described previously. All reactions proceeded to yield a yellow finely divided precipitate of $Mo_2(O_2CNMe_2)_4$ with the liberation of alkene and alkane (1:1 ratio within the limits of NMR detection). The gases liberated were all compared with spectra obtained on authentic samples dissolved in toluene-d_8.

The deuterated gases CD_3CH_2D, 1,1-CD_2CH_2, and CH_3CD_2H were purchased from Merck, Sharp, and Dohme and compared identically with those generated in the reactions given in Figure 2 at 33.77 MHz in benzene. Calculations using $^1H-^1H$ coupling constants given in ref 24 for ethylene and a comparison of the magnetogyric ratios $\gamma(^1H) = 2.675 \times 10^4$ rad/(s·G), $\gamma(^2H) = 4.107 \times 10^3$ rad/(s·G) allowed the simulation of the ^2H NMR at 33.77 MHz of the various dideuterioethylenes shown in Figure 1. The calculated splittings were obtained by using the program entitled NMRCAL, a part of the Nicolet 80 computer system. Having purchased the various dideuterioethylenes, we found the line shapes and splittings observed for the commercial samples to be identical with those predicted by simulation.

Preparation of $Mo_2(C_7H_7N_3C_7H_7)_4(toluene)_x$. A 25-mL round-bottomed flask was charged with 0.25 g (0.58 mmol) of $Mo_2Et_2(NMe_2)_4$ and 0.78 g (3.5 mmol) of di-p-tolyltriazene. Approximately 15 mL of toluene was added at room temperature in a Vacuum Atmospheres Dri Lab. The color was intensely red-orange. Hexanes (5 mL) were added to the flask before placing it in the cool storage refrigerator of the Dri Lab at −35 °C. Dark orange crystals of $Mo_2(C_7H_7N_3C_7H_7)_4$ were prepared in this manner. Satisfactory analysis could not be obtained for this complex, as was the case for many of the p-tolyltriazene derivatives of analogous complexes.[16,17] In all respects, the complex showed properties similar to the unsubstituted aromatic derivative prepared by Cotton et al.[18]

Synthesis of $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$. In a 50-mL round-bottomed flask was placed 0.50 g (1.17 mmol) of $Mo_2Et_2(NMe_2)_4$ and 0.53 g (2.35 mmol) of p-tolyltriazene. To this flask 30 mL of toluene was added in the Dri Lab. The color of the solution was intensely red. After 3 days in the refrigerator of the Dri Lab at −35 °C, red crystals precipitated. Addition of 10 mL of hexane to the reaction flask induced crystallization. A crystal of appropriate dimensions was chosen for X-ray analysis.

X-ray Structural Determination of $Mo_2(NMe_2)_2Et_2(C_7H_7N_3C_7H_7)_2$. A crystal of dimensions 0.20 × 0.20 × 0.40 mm was mounted in a nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off system of the diffractometer.

The cell dimensions obtained from 46 reflections at −175 °C with Mo Kα (λ = 0.71069 Å) were a = 16.503 (4) Å, b = 23.116 (7) Å, c = 11.318 (3) Å, β = 88.15 (1)°, V = 4315.6 (5) Å^3, Z = 4, d_{calcd} = 1.353 g cm^{-3}, and space group $P2_1/a$.

A total of 6970 reflections were collected by using standard moving-crystal, moving-detector techniques with the following values: scan speed = 4.0° min^{-1}, scan width = 1.8° + dispersion, single background time at extremes of scan = 5 s, aperture size = 3.0 × 4.0 mm. Of the 6970 reflections collected, the number with unique amplitudes was 5667 and the number with $F > 2.33\,\sigma(F)$ was 4622. The limits of data collection were $6° < 2\theta < 45°$.

The structure was solved by using a combination of direct methods and Fourier techniques. A molecule of solvent, toluene, was located. All nonhydrogen atoms were refined anisotropically. All hydrogens were located in the difference map but were not refined due to space limitations in the least-squares program. The final residuals were $R(F)$ = 0.057 and $R_w(F)$ = 0.0795. The goodness of fit for the last cycle was 1.795 and the maximum Δ/σ, 0.01.

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Registry No. $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$, 80864-94-4; $Mo_2(C_7H_7N_3C_7H_7)_4(toluene)_x$, 80864-96-6; $Mo_2Me_2(O_2CNMe_2)_4$, 68046-33-3; $Mo_2(O_2CNMe_2)_4$, 68046-32-2; $Mo_2(CH_2SiMe_3)_2(NMe_2)_2(O_2CNMe_2)_2$, 80878-14-4; $Mo_2(CH_2SiMe_3)_2(O_2CNMe_2)_4$, 72335-04-7; $Mo_2MeEt(NMe_2)_4$, 80864-99-9; $Mo_2Et(CH_2SMe_3)(NMe_2)_4$, 80865-00-5; $Mo_2Me_2(NMe_2)_2(O_2CNMe_2)_2$, 80865-01-6; $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$, 80865-02-7; $Mo_2(CH(CH_3)_2)_2(NMe_2)_4$, 72286-60-3; $Mo_2(n\text{-}C_4H_9)_2(NMe_2)_4$, 72286-59-0; $Mo_2(sec\text{-}C_4H_9)_2(NMe_2)_4$, 78274-35-8; $Mo_2(t\text{-}C_4H_9)_2(NMe_2)_4$, 72286-63-6; $Mo_2Me_2(NMe_2)_4$, 67030-82-4; $Mo_2Et_2(NMe_2)_4$, 68046-30-0; $Mo_2(CH_2SiMe_3)_2(NMe_2)_4$, 72286-62-5; $Mo_2Cl_2(NMe_2)_4$, 63301-82-6; CO_2, 124-38-9; C_2H_4, 74-85-1; C_2H_6, 74-84-0; CH_4, 74-82-8; Me_4Si, 75-76-3.

Supplementary Material Available: Observed and calculated structure factor table for $Mo_2Et_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ (35 pages). Ordering information is given on any current masthead page.

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