102979-19-1; **11**, 102979-20-4; **12**, 102979-32-8; (*E*)-**13** (M = Si), 102979-27-1; (*Z*)-**13** (M = Ge), 102979-28-2; (*Z*)-**13** (M = Sn), 102979-29-3; **14**, 102979-31-7; **15**, 39836-21-0; **16** (R = Pr-i, R′ = H), 102979-36-2; **17**, 52755-38-1; (*E*)-**18**, 102979-22-6; (*Z*)-**18**, 102979-23-7; **19**, 102979-41-9; **20**, 102979-35-1; **21**, 102979-39-5; **22**, 102979-40-8; CH_2Br, 74-95-3; $Ph_2MeSiCl$, 144-79-6; $Ph_2MeSiCH_2Br$, 102979-03-3; $PhMe_2SiCH_2Br$, 102979-04-4; $PhMe_2SiCl$, 768-33-2; $PhCH_2Br$, 100-39-0; *n*-$C_8H_{17}I$, 629-27-6; 1,1-dibromo-1-(methyldiphenylsilyl)propane, 102979-05-5; 4,4-dibromo-4-(methyldiphenylsilyl)-1-butene, 102979-06-6; 1,1-dibromo-1-(methyldiphenylsilyl)pentane, 102979-07-7; 1,1-dibromo-1-(methyldiphenylsilyl)tridecane, 102979-08-8; iodoethane, 75-03-6; 3-bromopropene, 106-95-6; 1-iodobutane, 542-69-8; 1-iodododecane, 4292-19-7; 1,1-dibromo-1-(dimethylphenylsilyl)propane, 102979-09-9; 1,1-dibromo-1-(dimethylphenylsilyl)-2-phenylethane, 103002-63-7; (*E*)-1-(methyldiphenylsilyl)-2-pentene, 102979-24-8; (*E*)-3-(methyldiphenylsilyl)-2-heptene, 102979-25-9; (*E*)-3-(methyldiphenylsilyl)-2-tridecene, 102979-26-0; (*E*)-1-(methyldiphenylsilyl)-1-tridecene, 102979-30-6; 1-iodododecane, 2050-77-3; 3-(methyldiphenylsilyl)-2-pentene, 102979-33-9; [(*Z*)-1-(methyldiphenylsilyl)-2-methyl-1-propenyl]magnesium bromide, 102979-34-0; (*Z*)-1-(1-propenyl)cyclohexanol, 102979-38-5; 1-phenyl-1,2-butadiene, 2327-98-2; (*E*)-2-(methyldiphenylsilyl)-2-butene, 102979-21-5; 4,4-dibromo-4-(dimethylphenylsilyl)-1-butene, 102979-10-2; (*E*)-1-[1-(methyldiphenylsilyl)-1-propenyl]cyclohexanol, 102979-37-3.

Metal–Metal Multiple Bonds. 18. Addition Reactions of Diazoalkanes with the $Mo{\equiv}Mo$ Triple Bond in $R_2Mo_2(CO)_4$ ($R = C_5H_5, C_5H_4Me, C_5Me_5$)

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The $Mo{\equiv}Mo$ triple bond in $R_2Mo_2(CO)_4$ ($R = C_5H_5, C_5H_4Me, C_5Me_5$) (1) reacts with diazoalkanes to give 1:1 adducts whose bonding modes depend markedly on the substituents, R, as well as on the diazoalkane. Diaryldiazomethanes form an adduct in which the terminal N atom asymmetrically bridges a Mo–Mo single bond. Bond distances suggest the N atom is doubly bonded to one Mo atom and singly bonded to the other. These adducts (R = Cp) lose N_2 upon photolysis or thermolysis via an intramolecular 1,3-dipolar cycloadduct to give μ-diarylmethylene complexes. Me_2CN_2 reacts to give a mixture of isomers, one similar to the diaryldiazomethane adducts and the other contains a μ-η^1,η^2-diazoalkane bridge with the terminal nitrogen bonded to both Mo atoms and the central N atom bonded to only one. Ethyl diazoacetate forms an adduct with the latter structure when $R = C_5Me_5$. Diethyl diazomalonate or α-keto diazoalkanes react with 1 to give adducts in which the carboxyl or ketone oxygen forms a chelate ring to one Mo atom and the metal–metal bond is broken entirely. ^1H and ^{13}C NMR spectra for these complexes are reported. The crystal structures of $Cp_2Mo_2(CO)_4(\mu\text{-}N_2CPh_2)$ (2), $Cp_2Mo_2(CO)_4[N_2C(CO_2Et)_2]$ (4A), and $(C_5Me_5)_2Mo_2(CO)_4(N_2CHCO_2Et)$ (6) were determined. For 2: $a = 11.847$ (4) Å, $b = 10.407$ (3) Å, $c = 20.572$ (6) Å; $\beta = 97.81$ (2)°; $V = 2513$ (1) Å^3; $Z = 4$, $\rho = 1.64$ g/mL; space group $P2_1/n$ (no. 14); $R_1 = 0.048$, $R_2 = 0.059$. Some pertinent bond distances (Å): Mo1–Mo2 = 2.987 (4), Mo1–N1 = 1.914 (8), Mo2–N1 = 2.083 (8), N1–N2 = 1.35 (1), N2–C15 = 1.28 (1). For 4A: $a = 11.144$ (2) Å, $b = 7.497$ (1) Å, $c = 28.939$ (7); $\beta = 95.13$ (2)°; $V = 2408.2$ (9) Å^3; $Z = 4$; $\rho_{calcd} = 1.71$ g/mL; space group $P2_1/c$ (no. 14); $R_1 = 0.048$, $R_2 = 0.061$. Selected distances (Å): Mo1–N1 = 1.86 (1), N1–N2 = 1.24 (1), N2–C15 = 1.42 (1), C15–C16 = 1.41 (2), C16–O5 = 1.26 (1), O5–Mo2 = 2.14 (1), Mo2–N2 = 2.21 (1). For 6: $a = 10.515$ (3) Å, $b = 18.868$ (6) Å, $c = 15.334$ (4) Å; $\beta = 104.43$ (2)°; $V = 2946$ (1) Å^3; $Z = 4$, $\rho_{calcd} = 1.55$ g/mL; space group $P2_1/n$ (no. 14); $R_1 = 0.034$, $R_2 = 0.035$. Selected distances (Å): Mo1–Mo2 = 3.040 (1), Mo1–N1 = 2.105 (4), Mo2–N1 = 2.109 (4), Mo2–N2 = 2.108 (5), N1–N2 = 1.336 (6), N2–C5 = 1.288 (7).

Introduction

Diazoalkanes, R_2CN_2, are reactive carbenoid synthons with wide applications in preparative organic chemistry,[3] particularly in the conversion of olefinic functional groups to cyclopropanes. Carbenoid transfer to unsaturated organic substrates is usually catalyzed by small amounts of transition-metal salts such as those of copper. The intermediate in carbenoid transfer is presumed to be a metal alkylidene derived from attack of the metal salt on the diazoalkane α-carbon and loss of dinitrogen.

The fact that transition-metal compounds are effective catalysts for diazoalkane decomposition has limited study of the coordination chemistry of these molecules. In principle, diazoalkanes should exhibit a variety of coordination modes in mononuclear and dinuclear complexes because of the possibilities for C- or N-terminal coordination, C=N or N=N side-on coordination, or even metallacyclic structures with both diazoalkane ends coordinated. Examples of several of these have been synthesized,[4] either by direct addition of the diazoalkane to an organometallic reactant or by condensation reactions of ketones or dihalomethanes with transition-metal hydrazide or dinitrogen complexes. In general, the interest in the

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[1] Present address: Department of Chemistry, University of Iowa, Iowa City, IA 52242.

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[3] (a) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971. (b) Patai, S., Ed. *The Chemistry of Diazonium and Diazo Groups*; Wiley: New York, 1978.

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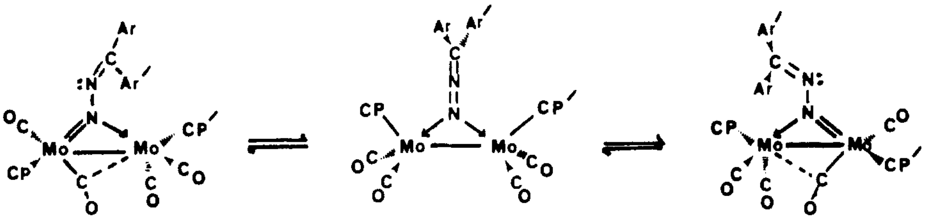
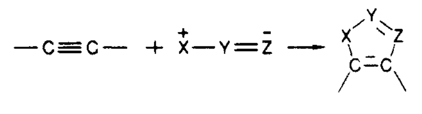
Scheme I



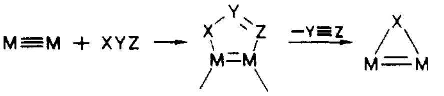
organometallic chemistry of diazoalkanes[5] has centered around the use of diazoalkanes in the synthesis of terminal[6] and bridging[7] alkylidene complexes.

Diazoalkanes are employed in synthetic transformations of carbon–carbon multiple bonds, but no examples of diazoalkane additions to *metal–metal* multiple bonds had been reported when we initiated our studies in this area. We reasoned that formal carbene addition to metal–metal double bonds could afford a new route to dimetallacyclopropanes and that addition to a metal–metal triple bond could generate the first example of a *dimetallacyclopropene*. Since a dimetallacyclopropene might be expected to be more reactive because of the metal–metal bond unsaturation, diazoalkane additions to the metal–metal triple bond in $Cp_2Mo_2(CO)_4$[8] (1) were studied since this molecule exhibits a rich and diverse chemistry[9] associated with the Mo≡Mo bond.

A second reason for studying the reactions of diazoalkanes with metal–metal multiple bonds derives from the fact that a diazoalkane is a prime example of the class of reagents known as 1,3-dipoles. Reactions of C–C multiple bonds with 1,3-dipoles have been extensively studied.[10] With alkynes, for example, the *initial* adduct is usually the five-membered heterocycle shown in eq 1. It is of interest, therefore, to determine whether or not d_π–d_π multiple bonds react in the same fashion to give dimetallaheterocycles (eq 2). Extrusion of a stable molecule, Y≡Z, might then be a general synthetic route to dimetallacyclopropene complexes.



(1)

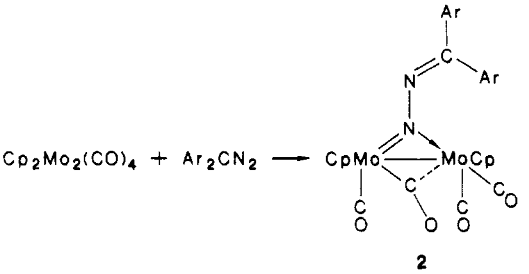


(2)

Preliminary accounts of this work have appeared,[11] and other workers have reported studies of diazoalkane additions to metal–metal double bonds[12] and triple bonds,[13] and unusual reaction and structural diversity have been discovered.

Results

Synthesis and Characterization. The brick-red molybdenum compounds $Cp_2Mo_2(CO)_4$ (Cp = η-C_5H_5, 1) and $Cp'_2Mo_2(CO)_4$ (Cp′ = η-C_5H_4Me) react readily with diaryldiazomethanes such as Ph_2CN_2 or $(p\text{-}MeC_6H_4)_2CN_2$ at room temperature in CH_2Cl_2 to give deep forest green diaryldiazomethane adducts in greater than 90% isolated yields (eq 3). Elemental analysis confirmed that the new complex retained the diazoalkane nitrogen atoms, and an infrared spectrum of the solid showed a weak C=N stretch at 1535 cm^{-1} in addition to one semibridging[14] and three terminal C–O stretches. The nature of the diaryldiazomethane bonding mode, depicted in eq 3, was found by single-crystal X-ray diffraction to be an asymmetric N-terminal bridge of a bonding type which had not been previously observed (vide infra).



(3)

2

The diaryldiazomethane adducts are fluxional on the ^1H and ^{13}C NMR time scales. At low temperatures (see Experimental Section), the spectra are consistent with the solid-state structure and display resonances for two types of aryl groups, two Cp rings and two peaks for the CO carbons. One of the CO resonances, δ 241, is broad at −80°C, indicating residual fluxional motion of the CO groups at this temperature. As the temperature is increased, the Cp resonances coalesce ($\Delta G^\ddagger = 6.3 \pm 0.1$

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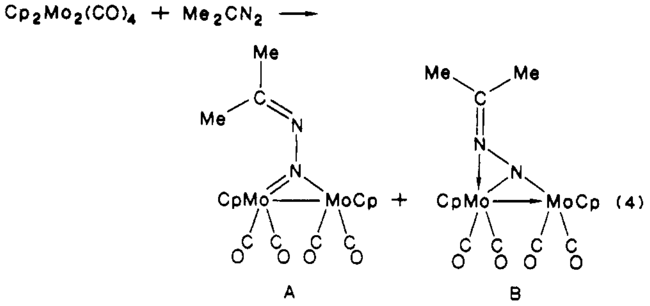
kcal/mol at 241 K) to a single peak at δ 5.01 as do the two carbonyl resonances (δ 245 (br)) at 295 K. The phenyl carbon resonances coalesce to six peaks at δ 136.5, 136.3, 131.9, 129.4, 128.9, and 128.1. Thus, the high-temperature fluxional process gives rise to an average magnetic environment of C_{2v} symmetry and may be represented by the motions described in Scheme I wherein the $Ar_2C{=}N$ group flips over the Mo—Mo bond with concomitant rotations of the $Cp(CO)_2Mo$ groups as shown. At −80 °C, the CO groups continue to undergo *pairwise* exchange so that only two CO resonances are observed.

The unique diazoalkane carbon resonance in these diaryldiazoalkane adducts appears to be buried under the phenyl carbon resonances (δ ~128–136). Other adducts also display the diazoalkane carbon resonance in the range δ 133–140 (see below). The corresponding resonances occur at δ 61.6 (Ar = phenyl) in the parent $Ar_2C{=}N_2$ compounds. Chisholm et al.[16] have prepared Ph_2CN_2 adducts of the M≡M triply bonded compounds $M_2(OR)_6$ (M = Mo, W) and find the diazoalkane carbon resonance in the region δ 160–170.

Ph_2CN_2 reacts with $Cp^*{}_2Mo_2(CO)_4$ ($Cp^* = C_5Me_5$) to give $Cp^*{}_2Mo_2(CO)_4(\mu\text{-}\eta^1\text{-}N_2CPh_2)$, which, unlike the Cp analogue, is nonfluxional at room temperature. Thus, there are two Cp* resonances at δ 1.79 and 1.51 in the ^1H NMR spectrum, and the ^{13}C NMR spectrum displays four resonances for the CO groups (δ 248.5, 249.0, 251.5, 257.1). Although the structures of these Cp* adducts have not been established crystallographically, we believe the Ph_2CN_2 ligand has the μ-η^1-structure found for the Cp analogues. Presumably the steric bulk of the pentamethylcyclopentadienyl ligands inhibit the fluxional motion found for the Cp derivatives.

The parent diazoalkane CH_2N_2 reacts rapidly with the unsubstituted cyclopentadienyldicarbonylmolybdenum dimer **1** as evidenced by gas evolution (containing C_2H_4 as determined by mass spectrometry) and formation of an insoluble organic polymer (presumably polymethylene) in the reaction flask; although color changes are observed during the course of the reaction, no evidence of stable adduct formation at −78 °C to room temperature was found, and **1** is recovered. Ethylene production is more pronounced the longer the reactants sit at 20 °C. The decomposition rate of the CH_2N_2 in the presence of the dimolybdenum starting material is qualitatively accelerated over that of the reactant CH_2N_2 solution. The mechanism of polymethylene formation and the role of the molybdenum reactant are unknown, and it should be noted that in control experiments CH_2N_2 solutions without added **1** also decompose to give C_2H_4 and an insoluble organic polymer. Polymethylene formation by metal-catalyzed decomposition of CH_2N_2 has been observed in numerous cases.[17] Our results stand in marked contrast to the analogous reaction with the η-C_5Me_5 analogue of **1** in which $(C_5Me_5)_2Mo_2(CO)_4(\mu\text{-}CH_2)(\mu\text{-}N_2CH_2)$ were isolated.[7d]

However, 2-diazopropane reacts readily with **1** to also give a thermally stable green adduct (eq 4). Both ^1H and ^{13}C NMR spectra are consistent with the presence of two different isomers whose relative ratio is a function of solvent and temperature; the resonance differences between the two isomers suggest that the Me_2CN_2 coordination modes differ substantially in each. In toluene-d_8 at 0 °C (^1H NMR) one isomer (A) with equivalent Cp resonances and inequivalent Me resonances accounts for ca. 55% of the sample and the other isomer (B) exhibits inequivalent Cp and Me resonances. In acetone-d_6 the relative isomer ratio is inverted, with the mixture containing about 85% of the isomer with magnetically inequivalent Cp and Me groups. Both isomers are also evident in the ^{13}C NMR spectra: in CD_2Cl_2 at −50 °C the major isomer (B) had inequivalent Cp and Me resonances, two resonances for the CO groups, and a resonance for the unique diazoalkane carbon at δ 140.4. The minor isomer exhibits a single resonance for the Cp groups, two resonances for the Me groups, two resonances for the carbonyls, and a diazoalkane carbon signal at δ 137.3. The molecular structure determination by X-ray diffraction of the Cp species was unsuccessful because of crystallographic disorder, while no suitable crystals were obtained for the η-C_5H_4Me analogue. However, the $Mo_2N_2CMe_2$ portion of the molecule was resolved and displayed structure B which was also found for the Cp* derivative $Cp^*{}_2Mo_2(CO)_4(N_2CMe_2)$.[13e] The latter compound exhibits a ^{13}C NMR resonance for the unique 2-diazopropane carbon at δ 133.8[13e] which is in the same range as observed for the isomers of the Cp complexes **3A** and **3B**. The fact that **3A** displays only one type of Cp group, two types of CO's, and two types of Me groups at −80 °C suggests that **3A** has mirror symmetry with the diazopropane portion lying in the mirror plane. Furthermore, the fluxional motion depicted for the trans isomer in Scheme I cannot be occurring in **3A** since this motion produces a higher average symmetry (C_{2v}). Therefore, the cis structure shown below is suggested for **3A** (m denotes the mirror plane). (Note: the NMR data do not rule out a librational motion of the CMe_2 portion of the molecule back and forth in the mirror plane over the Mo–Mo bond.)



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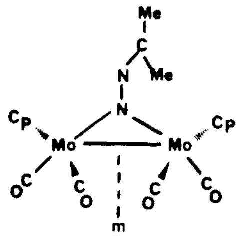
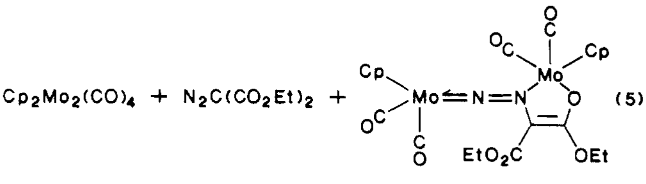


3A

Diethyl diazomalonate, $N_2{=}C(CO_2Et)_2$, reacts with the M≡M bond in **1** to give a black, crystalline adduct, **4A**, in 45% isolated yield (eq 5). The structure, determined



4A

by X-ray diffraction (see below), shows that a carbonyl

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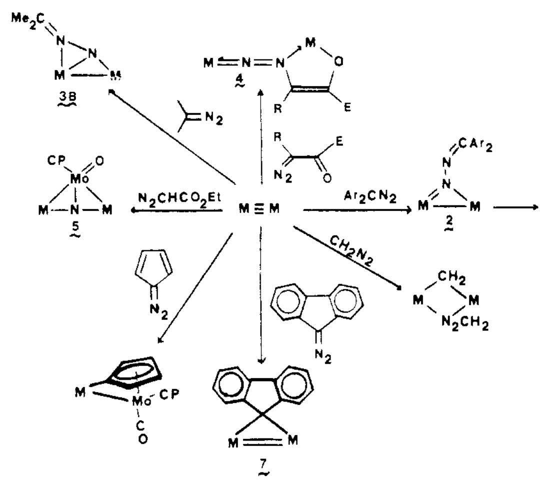
[16] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Ratermann, A. L. *Inorg. Chem.* **1984**, *23*, 2303.

[17] One example: Werner, H.; Richards, J. *J. Am. Chem. Soc.* **1968**, 90, 4976 and references therein.

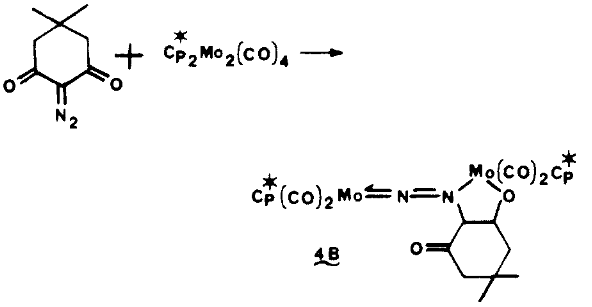
Scheme II[a]



[a] M = Mo(CO)₂Cp.

oxygen has coordinated to one Mo atom and the Mo–Mo bond is completely broken. The ^1H and ^{13}C NMR spectra are in complete accord with the solid-state structure and show inequivalent Et and Cp groups. The methylene protons in one of the Et groups are diasteriotopic and appear as an ABX_3 pattern.

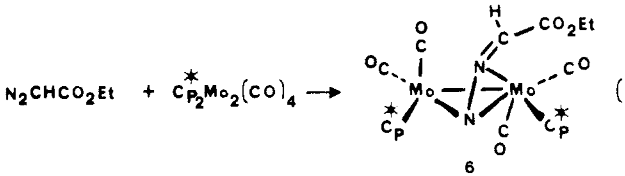
A related α-ketodiazoalkane, 2-diazodimedone, reacts with $Cp^*_2Mo_2(CO)_4$ to produce a black crystalline adduct (**4B**) which, from spectroscopic data, appears to have the same general structure as **4A** (eq 6). Thus, ν_{CO} bands are



(6)

observed at 1963, 1927, 1885, and 1935 cm^{-1}, and two additional bands at 1628 and 1512 cm^{-1} may be assigned to N=N and C=O stretches, respectively. Other α-ketodiazoalkanes react with $Cp^*_2Mo_2(CO)_4$ to give adducts with structures analogous to **4A** and **4B**.[13m]

The reaction of diazoacetate esters with **1** are quite different from those of the α-ketodiazoalkanes or diethyl diazomalonate described above. Ethyl diazoacetate reacts with **1** (R = C_5H_5 or C_5H_4Me) at temperatures from −78 to 110 °C to give a complex mixture of products. The triangulo cluster **5** (Scheme II) was isolated in 5% yield from the reaction of N_2CHCO_2Et with **1** in refluxing toluene.[13n] On the other hand, diazoacetate esters react smoothly with $Cp^*_2Mo_2(CO)_4$ to give adducts **6** (eq 7).

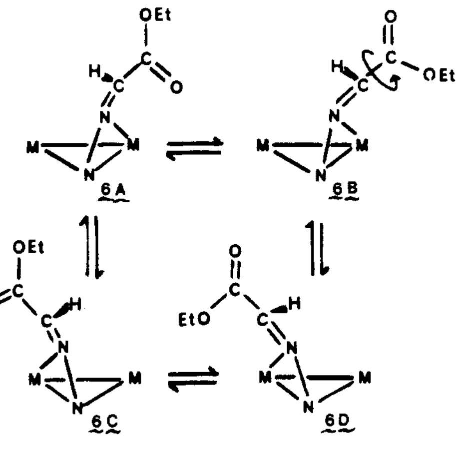


6

(7)

The coordination mode of the diazoacetate ligand was determined to be as shown in eq 7 by an X-ray structure determination (see below). Crystals of the methyl ester adduct were isomorphous to those of the ethyl ester adduct. These adducts are characterized by ν_{CO} bands at 1958 (s), 1900 (s), 1820 (s), and 1800 (s) cm^{-1}.

Scheme III

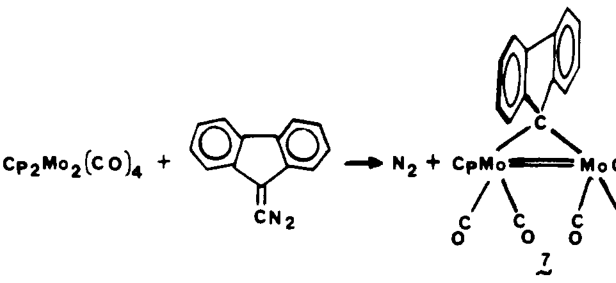


The NMR spectra of these adducts indicate they are fluxional. At room temperature, the ^1H NMR spectrum of the methyl ester adduct **6** (R = Me) shows one peak each for the C_5Me_5 protons at δ 1.85, the CO_2Me protons at δ 3.75, and the $N_2{=}CHCO_2$ proton at δ 7.75 (CD_2Cl_2 solution). At −60 °C (C_7D_8) the C_5Me_5 resonance is split into two peaks of equal intensity at δ 1.61 and 1.80. The CO_2Me and N_2CHCO_2 resonances appear at δ 3.20 and 7.35.

The temperature dependence of the ^1H NMR spectrum of the ethyl diazoacetate adduct is more complex. At −60 °C in C_7D_8, the C_5Me_5 groups resonate at δ 1.64 and 1.82 as expected. The OCH_2CH_3 group, however gives rise to *two* triplets (ca. 1:1) at δ 0.86 and 0.96 (J = 7 Hz). The methylene protons appear as two broad humps (ca. 1:1) at δ 3.71 and 3.96, and the unique N_2CHCO_2 proton shows as a sharp singlet at δ 7.48. Referenced to the Cp* peaks (30 protons), the total areas of the CH_3, CH_2, and CH peaks are δ 3.4, 2.1 and 0.3–0.4, respectively. As the temperature is increased, the two methyl triplets converge and coalesce at −20 °C. Likewise, the Cp* signals coalesce at ca. −10 °C, and the two methylene signals are coalesced at 0 °C. The unique diazo N_2CH proton signal broadens and moves upfield toward the signals due to the solvent, suggesting the presence of a second, hidden N_2CH peak (cf. the low integration of the N_2CH peak).

If the structure found in the solid state is maintained in solution, we expect two Cp* signals, one CH_3 (Et group) signal, one N_2CH signal, and an ABX_3 pattern for the diastereotopic methylene protons. The presence of two methyl signals but only one set of two Cp* peaks may be rationalized by assuming that at −60 °C, two orientations of the –COOEt group are frozen out (**6A** and **6B**, Scheme III). These two orientations give different signals for the CH_2 and CH_3 groups, but **6A** and **6B** must then have accidentally degenerate signals for the Cp* protons. As the temperature increases, rapid interconversion of **6A** and **6B** would lead to equivalent ethyl CH_3 groups but would leave the $-CH_2-$ protons diastereotopic and the Cp* groups inequivalent. As the temperature increases further, rapid interchange between **6A** and **6B** with their respective enantiomers (**6C** and **6D**) removes the diastereotopism of the methylene group *and* equivalences the two Cp* groups on the different metals.

The compound 9-diazofluorene also reacts readily with **1**, but no diazoalkane adduct is observed under the reaction conditions (0–25 °C). Dinitrogen is lost, and the μ-fluorenylidene complex **7** is formed (eq 8). This species does not show the expected reactivity for a dimetallacyclopropene functional group.[11d] Details of its structure, re-

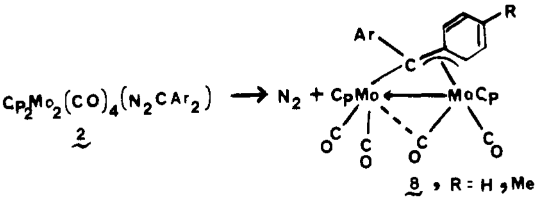


(8)

activity, and a molecular orbital analysis are to be presented elsewhere.[18]

The tungsten homologue of 1, $Cp_2W_2(CO)_4$ (**1B**), does not react cleanly with either Ph_2CN_2 or 2-diazodimedone. From the reaction of **1B** with Ph_2CN_2, the starting complex **1B** was isolated in 75% yield along with a 16% yield of singly bonded dimer, $Cp_2W_2(CO)_6$. No other organometallic product was isolated, but a GCMS analysis of the volatile material showed the presence of Ph_2CH_2 and Ph_2CHCO_2H. The latter presumably arises from hydrolysis of $Ph_2C{=}CO$ which in turn is formed by coupling of a diphenylcarbene fragment with CO. $Cp_2W_2(CO)_6$, recovered **1B**, and small amounts of product with high frequency stretches at 2237 and 2147 cm^{-1} were obtained from the reaction of **1B** with diazodimedone. The high-frequency stretching modes may be due to isocyanate groups formed from coordinated CO and the terminal N atom of the diazoalkane (cf. eq 12).[13f,g]

Reactions. The most interesting and important reaction of the new diazoalkane adducts is the ready thermal or photochemical elimination of dinitrogen from the diaryldiazomethane complexes. At temperatures of 60–70 °C in aromatic solvents a clean elimination occurs to afford the red μ-diarylmethylene product in greater than 80% isolated yields (eq 9); the dinitrogen extrusion can also be photochemically induced with broad-band UV radiation from a medium-pressure mercury lamp. Elemental analysis of the crystalline product (isolated as the aromatic solvate) confirmed the absence of dinitrogen, and the ^{13}C NMR spectrum had a signal at δ 174.9 (for Ar = Ph) which is the range reported[7a] for bridging alkylidene carbon resonances. A single-crystal X-ray diffraction study confirmed the formulation of 8 as a μ-diarylmethylene complex and revealed as asymmetric bridge in which one of the aryl groups is also coordinated to one of the molybdenum atoms in the solid-state structure.[11a] A molybdenum–molybdenum single bond was found in the ground-state structure, instead of the expected metal–metal double bond of a dimetallacyclopropene as observed in the μ-fluorenylidene compound.[11d] Full details on the structure, fluxional properties, and novel reactivity of the μ-diarylmethylene compounds toward small molecules will be given elsewhere.[18]



(9)

All present data are consistent with intramolecular loss of dinitrogen during thermolysis of the Ar_2CN_2 adducts. An isosbestic point at 554 nm is observed by spectrophotometry when the thermolysis of **2** (R = H) is done at 60 °C, so there is no appreciable concentration of an intermediate at this temperature. Solutions of the parent diaryldiazomethanes show no evidence for decomposition under the thermolysis conditions, so it seems reasonable to rule out any process whereby Ph_2CN_2 dissociates from the dinuclear center, decomposes thermally to diphenylmethylene, and is trapped by 1. Reversible diazoalkane coordination *without decomposition* has been noted in at least one dinuclear case,[19] but thermolysis of a solution containing $Cp_2Mo_2(CO)_4(N_2CPh_2)$ and $(C_5H_4Me)_2Mo_2(CO)_4$ gave only $Cp_2Mo_2(CO)_4(CPh_2)$ and unreacted $(C_5H_4Me)_2Mo_2(CO)_4$; no cross product, namely, $(C_5H_4Me_4)_2Mo_2(CO)_4(CPh_2)$, was observed by ^1H NMR spectroscopy in the reaction mixture. Finally, no cross products were observed in a double label thermolysis of a solution containing equal amounts of $Cp_2Mo_2(CO)_4(N_2CPh_2)$ and $Cp'_2Mo_2(CO)_4(CAr_2)$; the only products observed by ^1H NMR were the expected unimolecular reaction products $Cp_2Mo_2(CO)_4(CPh_2)$ and $Cp'_2Mo_2(CO)_2(CAr_2)$ ($Cp' = C_5H_4Me$, Ar = *p*-tolyl).

Discussion

Bonding Modes of the Diazoalkane. One of the goals of our research on compounds with metal–metal multiple bonds is to establish patterns of reactivity so that the M≡M unit, for example, may be used as a "functional group" for the elaboration of more complex inorganic structures in a controlled and rational manner.[20] However, the extreme range of structural diversity exhibited by the products of the reactions of $R_2M_2(CO)_4$ (M = Mo, W; R = Cp, C_5H_4Me, C_5Me_5) with various diazoalkanes clearly shows that the concept of "functional group" elaboration in organometallic chemistry must be applied with circumspection.

Thus, while the reactivity of C≡C triple bonds may be modified by neighboring functional groups, C≡C triple bonds *normally* react with diazoalkanes as shown in eq 1. In contrast, at least *seven* different reaction paths have been well characterized for the reactions of the Mo≡Mo bond in $R_2Mo_2(CO)_4$ (R = Cp, Cp*, etc.) compounds with diazoalkanes, and the factors which ultimately determine the bonding mode of the diazoalkane are by no means clear at this point. If functional groups, e.g., carboxyl, oxo, etc., are adjacent to the diazo group and are capable of coordinating to the metal, they generally do so. Examples of this behavior are afforded by $N_2C[CO_2Et]_2$, $C_5H_4N_2$, and N_2CHCO_2Et with $Cp_2Mo_2(CO)_4$ and/or $Cp^*_2Mo_2(CO)_4$) (Scheme II). However, N_2CHCO_2Et with $Cp^*_2Mo_2(CO)_4$ yields the same type of coordination as found for the Me_2CN_2 adduct with either $Cp_2Mo_2(CO)_4$ or $Cp^*_2Mo_2(CO)_4$. Therefore, neither the basicity of the internal nitrogen nor the steric bulk of the Cp* group seems to control the coordination mode. The steric bulk of the Cp* group does appear to be important in the decomposition modes of the diazoalkane adducts (see below).

The metal–metal bond order in the dinuclear adducts ranges from 2 to 0 as the total number of electrons donated to the dimetal center goes from 2 to 6. As shown elsewhere,[9] the metal–metal bond order decreases by one unit for each pair of electrons donated to the M≡M bond so as to keep the total electron count for each metal at 18.

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[18] Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Solis, H. E.; Barcelo, I. D., manuscript in preparation.

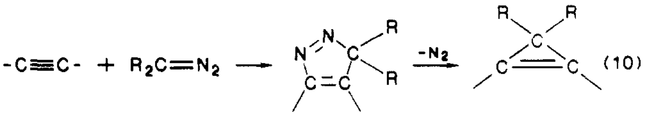
[19] Woodcock, C.; Eisenberg, R. *Organometallics* **1985**, *4*, 4.

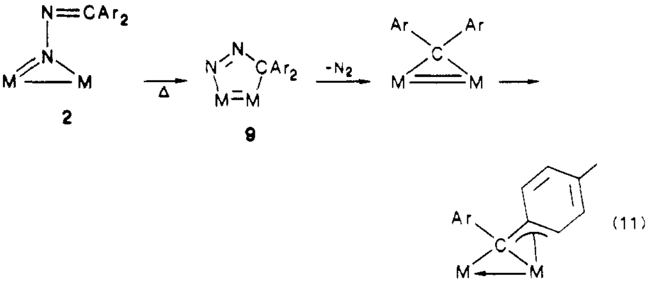
[20] For example: Williams, P. D.; Curtis, M. D.; Duffy, D. N.; Butler, W. M. *Organometallics* **1983**, *2*, 165.

[21] Sources of scattering factors, programs used in structure determination, refinement, etc. have been described previously: Curtis, M. D.; Han, K. R. *Inorg. Chem.* **1985**, *24*, 378.

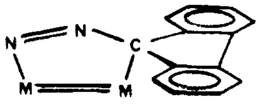
Furthermore, there appears to be a preference of the M≡M unit to become saturated, i.e., to pick up four electrons and form a single bond.[9]

Decomposition Pathways. As shown in eq 1 the interaction of an alkyne with a 1,3-dipolar reagent normally leads to a cyclic adduct which, in the case of diazoalkanes, may expel dinitrogen to give a cyclopropene (eq 10).[10] In contrast, none of the observed reactions of M≡M bonds with diazoalkanes has led to the formation of observable 1,3-dipolar cycloadducts (cf. Scheme II). However, the diaryl adducts 2 decompose by loss of N_2 via an *intramolecular* mechanism to give the μ-alkylidenes 8. Since the diazoalkane carbon atom in 2 is far removed from the dimetal center, and since this carbon becomes attached to the metals in the alkylidene product 8, it seems reasonable to propose that complex 2 rearranges upon gentle heating (60 °C) to the cycloadduct 9, which rapidly loses N_2 to form the alkylidene 8 (eq 11, M = Mo(CO)$_2$Cp or Cp′).





The effects observed when the steric constraints of the substituents on the diazomethane or the metal are changed are consistent with a proposed cycloadduct intermediate. Tying together the two aryl groups to make the planar fluorenyl group should decrease the steric barrier to the formation of intermediate 10 as compared to 9 in which the ortho hydrogens force the aryl groups into a nonplanar configuration which leads to increased repulsion between them and the Cp and/or CO groups on the metal. Consequently, the adduct formed from 1 and 9-diazofluorene rapidly rearranges to 10, expels N_2, and forms the observed μ-fluorenylidene 7. Furthermore, the aryl groups in 7 are restrained from coordinating to the metal as in 8, and a dimetallacyclopropene (d(Mo=Mo) = 2.798 (1) Å)[11a,18] results.



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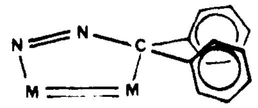
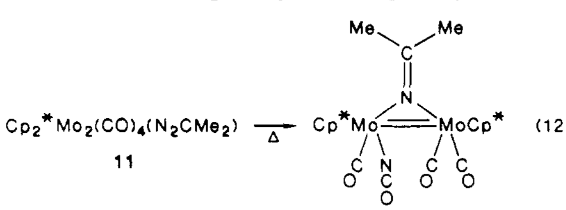


9

A similar argument can be used to explain the facile loss of N_2 (and subsequent coordination of the C_5H_4 fragment) in the reaction of diazocyclopentadiene[13a] and 1 (Scheme II). Conversely, the bulky C_5Me_5 ligand inhibits the formation of the 1,3-dipolar cycloadducts so that Cp*$_2$Mo$_2$(CO)$_4$(μ-N$_2$CPh$_2$), for example, does not cleanly lose N_2 when heated (at higher temperatures a complex mixture results).

Apparently, the μ-η^1 (terminal N) coordination mode, typified by the aryl derivatives, is a necessary prerequisite for the formation of the 1,3-dipolar cycloadduct intermediates and the ensuing, clean conversion to μ-alkylidene complexes. None of the other diazoalkane adducts known to date decompose to form μ-alkylidenes. Herrmann[13f,g] has observed a very interesting decomposition of the μ-η^2-complex 11 into the μ-imido isocyanate complex 12 (eq 12). Neither Cp$_2$Mo$_2$(CO)$_4$(μ-η^2-NN$_2$CMe$_2$) (3) nor Cp*$_2$Mo$_2$(CO)$_4$(μ-η^2-N$_2$CHCO$_2$Et) (6) decompose cleanly when heated in solution. The NMR spectra of the decomposition mixtures shown dozens of peaks in the Cp or Cp* region.



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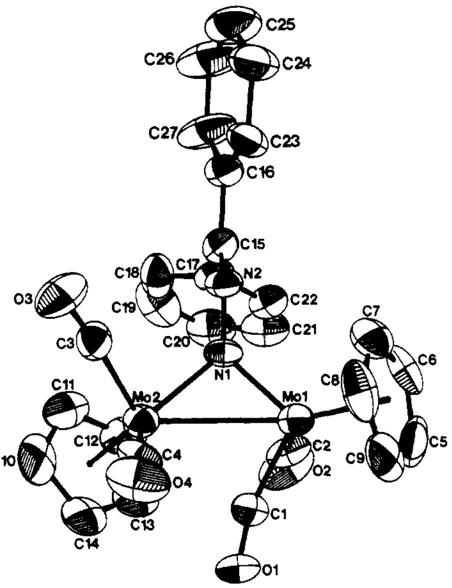


Figure 1. ORTEP drawing with numbering scheme of Cp$_2$Mo$_2$(CO)$_4$(N$_2$CPh$_2$) (2).

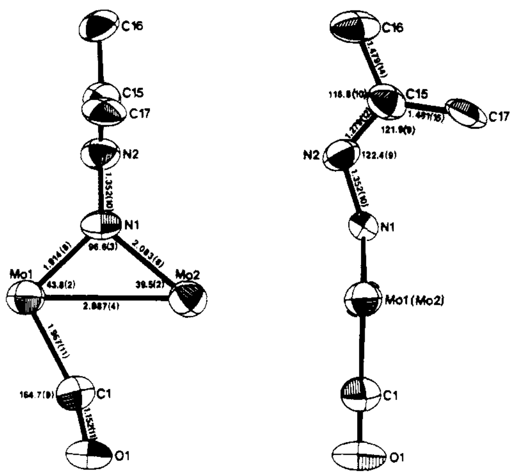


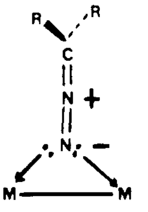
Figure 2. Details of the bridging ligands in Cp$_2$Mo$_2$(CO)$_4$(N$_2$CPh$_2$) (2). The view of the figure on the right is down the Mo1–Mo2 bond.

Structures. Cp$_2$Mo$_2$(CO)$_4$(N$_2$CPh$_2$). Figure 1 is an ORTEP plot of the molecule showing the atomic numbering scheme and Figure 2 a plot of the molecular core with all Cp, terminal CO, and phenyl atoms except C_{ipso} omitted for clarity.

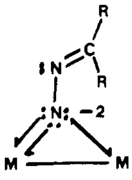
The most unusual aspect of the molecular structure is the μ, N-terminal diazoalkane coordination mode, further examples of which have been found subsequently.[13d,16]

In other reported structures of dinuclear complexes with diazoalkane ligands, the diazoalkane is either in a terminal bonding mode to only one metal atom[11b,13d,18] or in an unsymmetrical bridging position in which the terminal nitrogen N(1) bridges both metals while N(2) also bonds to one of the metals.[13f,g,22]

The Mo–Mo distance, 2.987 (4) Å, is characteristic[9] of bridged Mo–Mo single bonds so the addition of the diazoalkane unit to 1 has saturated the Mo≡Mo triple bond by adding four electrons to the dinuclear fragment. At first thought, the linear, canonical form **13A** would seem to be



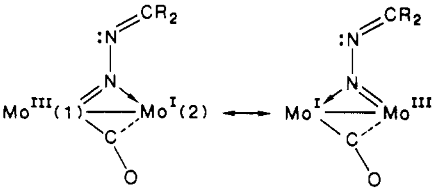
13A



13B

a probable bonding mode for the diazoalkane to act as a 4e donor through the terminal nitrogen. However, the observed structure is clearly inconsistent with the bonding depicted in **13A**. In particular, the bonds to the central nitrogen are decidedly nonlinear (∠CNN = 122.4 (9)°) and the pattern of bond lengths and angles in the diazoalkane fragment suggest this group is bonded to the dimetal fragment as a diazanido(2−) ligand, **13B**.

The C═N and N—N bond distances of 1.28 (1) and 1.35 (1) Å are suggestive of bond disorders of ca. 2.0 and 1.2[23,24] for the C═N and N—N bonds, respectively. The terminal nitrogen N2, is bonded unequally to the two molybdenums: Mo1-N2 = 1.914 (8) Å and Mo2-N2 = 2.083 (8) Å. These Mo-N bond distances are consistent with bond orders of ca. 2.0 and 1.3 for Mo1-N2 and Mo2-N2, respectively.[24] The bridge bonding in the dimetal complex is best described by the resonance structures **14A** and **14B** with **14A** predominant.



14A **14B**

The role of the semibridging carbonyl[9] is understandable if resonance from **14A** predominates and if the bridging diazoalkane is considered to be a $R_2CN_2^{2-}$ ligand. In **14A**, *formal* oxidation states of III and I may be assigned to Mo(1) and Mo(2), respectively. Thus, Mo(2) is *formally* electron-rich compared to Mo(1), and the acceptor semibridging carbonyl redistributes the excess (−) charge on Mo(2) by the mechanism originally proposed by Cotton et al.[25] The $R_2CN_2^{2-}$ ligand is acting as a six-electron donor, but one Mo has been formally oxidized from Mo(I) to Mo(III). Thus, four electrons net are donated to the dimetal fragment in this formalism.

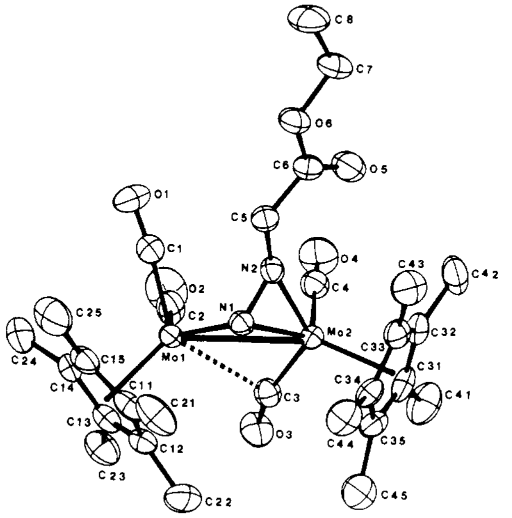


Figure 3. ORTEP plot of $Cp^*_2Mo_2(CO)_4(N_2CHCO_2Et)$ (6) showing the numbering scheme.

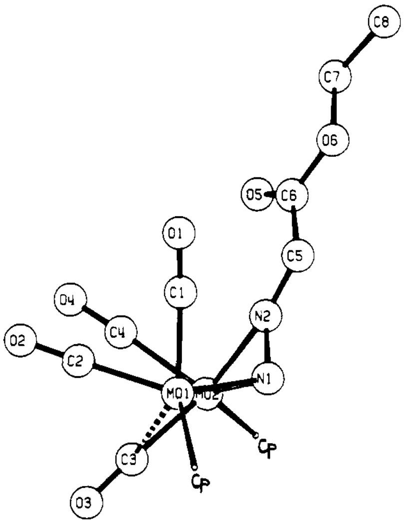
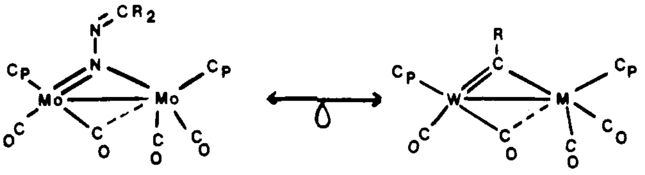


Figure 4. View of $Cp^*_2Mo_2(CO)_4(N_2CHCO_2Et)$ from slightly off the Mo1-Mo2 vector. Points marked "Cp" are the centroids of the C_5Me_5 rings.

It is interesting to note that the bonding mode shown in **14A** is isolobal and isoelectronic with the bridging alkylidyne[26] shown.



$Cp^*_2Mo_2(CO)_4(N_2CHCO_2Et)$ (6). The molecular structure with the numbering scheme is shown in Figure 3, and Figure 4 is a view of the inner coordination sphere. Rather surprisingly, the fragment consisting of Mo2 and

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[22] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 7295.

[23] Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

[24] A bond order–bond distance graph was constructed by using the values (Mo—N) = 2.20, (Mo═N) = 1.92, and (Mo≡N) = 1.74 Å. The Mo≡N value approximates observed values in *low*-valent complexes. The Mo═N and Mo—N values are derived from the sums of the radii: (Mo═) = 1.31 and (Mo—) = 1.52; (N═) = 0.61 and (N—) = 0.68. The (Mo—) value is half of the observed Mo–Mo distances, and the (Mo═) value was obtained by subtracting r(C═) from observed Mo═C distances. These radii give bond distances in fairly good agreement with observed distances in *low*-valent Mo complexes.

[25] Cotton, F. A.; Kruczynski, L.; Frenz, B. A. *J. Organomet. Chem.* **1978**, *160*, 93.

[26] Abad, J. A.; Bateman, L. W.; Jefferey, J. C.; Mead, K. A.; Razay, H.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2075.

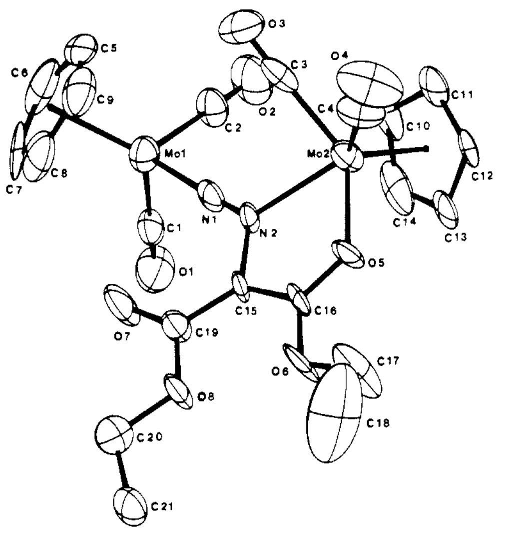
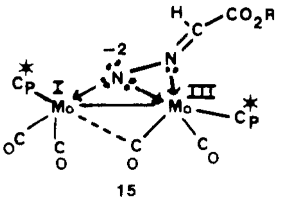


Figure 5. ORTEP plot of $Cp_2Mo_2(CO)_4[N_2C(CO_2Et)_2]$ (**4A**) with the numbering scheme.

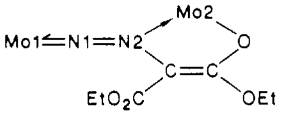
the entire skeleton of the ethyl diazoacetate is planar (maximum deviation of any one atom = ±0.05 Å). The N2–C5 bond length (1.288 (7) Å) is typical for a C=N double bond. Therefore, both C5 and N2 are sp^2-hybridized which sets Mo2, N1, N2, C5, and C6 into one plane. The C5–C6 bond length (1.47 (1) Å) suggests a bond order of about 1.3 due to conjugation between the N=CC=O bonds. Therefore, the C6–O5–O6 fragment would tend to be coplanar with N2–C5–C6 plane. Finally, the ethoxy group is in its "extended" conformation which has been shown to be the most stable conformation of several esters in the gas phase.[27] The Mo2→Mo1 vector makes an angle of 50.8° with the least-squares plane of the (Mo2 + diazo ester) atoms.

The Mo1–Mo2 bond length, 3.040 (1) Å, is again typical for a bridged Mo–Mo single bond, so that the diazo ester donates a net four electrons to the dinuclear metal fragment. All Mo–N bonds are about 2.1 Å long, a length indicative of Mo–N single bonds (bond order ≈ 1.2). The bonding in **6** can be adequately accounted for by again assuming the metal fragment to be oxidized and the diazo ester group again acting as a $R_2CN_2^{2-}$ ligand. The difference between the μ-η^2-bonding mode **15** and the μ-η^1 mode **14** lies simply in which N donates its lone pair to the Mo. In **14**, the terminal N donates its lone pair, while in **15**, the central N donates the lone pair. It is interesting to note that in spite of the greatly different appearance of the coordination modes of the diazo ligands in **14** and **15**, the structural parameters of the R_2CN_2 fragment as found in **2** and **6** are virtually identical. Note also that the semibridging CO in **6** again removes the excess negative charge from the less oxidized Mo.



15

$Cp_2Mo_2(CO)_4[N_4C(CO_2Et)_2]$ (4A). The molecular structure is drawn in Figure 5 which also shows the numbering scheme. The diethyl diazomalonate ligand is behaving as a chelate which has completely disrupted the Mo≡Mo triple bond without CO loss. Therefore, the ligand must supply three electrons to each $CpMo(CO)_2$ group in order to maintain the 18-electron count at each Mo. Mo1 is bonded to the terminal nitrogen N1 so N1 must donate three electrons to Mo1. Thus, a representation of this bond as Mo⇐N implies a formal Mo=N double bond. In fact, the Mo1–N1 distance, 1.86 (1) Å, is suggestive of a bond order of ca. 2.1.[24,28] The N1–N2, N2–C15, and C15–C16 distances are consistent with bond orders of 2, 1, and ca. 1.5 for these respective bonds. The C16–O5 bond distance, 1.26 (1) Å, may be in error as this bond length is rather shorter than similar bonds in α-ketodiazoalkane adducts of **1**. However, in **4A**, the chelating oxygen is derived from a carboxyl group rather than a ketone so some difference in bond length may be expected. The Mo2–N2 and Mo2–O5 appear to be single bonds. Thus the best representation of the bonding in this structure is as shown below, although other resonance extremes may be drawn.



As was the case with the adducts **2** and **6**, the diazo ligand is formally reduced by two electrons.

Conclusions

The M≡M triple bonds in $Cp_2M_2(CO)_4$ (M = Mo, W) are extremely reactive toward diazoalkanes and show an amazing diversity in the structures of the products. Only in the case of *diaryldiazomethanes* is there evidence that 1,3-dipolar cycloadducts may be formed. These reactive intermediates are unstable and expel N_2 to form bridging alkylidenes. Further studies of reactions of metal–metal multiple bonds with other types of 1,3-dipoles are in progress.

Experimental Section

Manipulation of air-sensitive compounds was achieved with standard Schlenk techniques or in a Vacuum Atmospheres glovebox filled with helium and equipped with −40 °C freezer and internal vacuum system for filtration and solvent removal. Toluene, diethyl ether, and THF were purified by distillation under nitrogen from sodium/benzophenone ketyl, hexane and methylcyclohexane from sodium/benzophenone ketyl with tetraglyme as a ketyl solubilization agent, and methylene chloride by rigorous degassing followed by distillation from P_4O_{10}. All solvents were distilled prior to use or stored in the glovebox. $Mo(CO)_6$ (Pressure Chemical), $(p\text{-}MeC_6H_4)_2CO$ (Eastman), and fluorenone (Aldrich) were used as received.

IR spectra were recorded on Perkin-Elmer 457 or Beckman IR 4240 spectrometers. Routine ^1H NMR spectra were recorded on a Varian T-60 instrument, while higher field ^1H and ^{13}C NMR spectra were obtained on a Bruker WM-360 or JEOL FX-90Q multinuclear NMR spectrometer utilizing internal deuterium locking on the deuterated solvent resonance. ^{13}C NMR spectra were recorded with either complete or gated proton decoupling. Mass spectra were obtained on a Finnigan 4023 GC/MS system under EI or CI conditions. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

The compounds $Cp_2Mo_2(CO)_4$,[29] $(C_5H_4Me)_2Mo_2(CO)_4$,[29] Ph_2CN_2,[30] Me_2CN_2,[31] CH_2N_2,[32] 9-diazofluorene,[33] diethyl diazo-

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malonate,[34] and 2-diazodimedone[35] were prepared by published procedures, while $(p\text{-MeC}_6H_4)_2CN_2$ was prepared by using the same procedure as for the Ph derivative. The low-melting solid diaryldiazomethanes were recrystallized from hexane and then stored at −40 °C prior to use. The volatile diazoalkanes CH_2N_2 and Me_2CN_2 were obtained as CH_2Cl_2 solutions and stored at −78 °C under nitrogen prior to use; their concentrations were determined by quenching with concentrated acetic acid solutions followed by gas volumetric analysis of the evolved N_2.

(μ-Diphenyldiazomethane)bis(cyclopentadienyldicarbonylmolybdenum), $Cp_2Mo_2(CO)_4(N_2CPh_2)$. $Cp_2Mo_2(CO)_4$ (1.73 g, 4.0 mmol) and Ph_2CN_2 (0.77 g, 4.0 mmol) were stirred in CH_2Cl_2 at room temperature for 5 min; the brick-red color of 1 and the purple color of the Ph_2CN_2 immediately gave upon reaction the deep green color of the adduct. Hexane (70 mL) was slowly added and the solution placed in a −40 °C freezer. After several hours, 2.08 g (83%) of product was filtered off and dried in vacuo.

Anal. Calcd for $Mo_2C_{27}H_{20}O_4N_2$: C, 51.60; H, 3.21; N, 4.46. Found: C, 50.41; H, 3.19; N, 4.16. ^{1}H NMR (δ, $C_6D_5CD_3$, −70 °C, 89.56 MHz): 4.69 (s, 5, Cp), 4.94 (s, 5, Cp′), 6.37–6.45 (br d, 4, H_o), 6.86–7.78 (m, 6, H_m and H_p). ^{13}C NMR (δ, $CDCl_3$, −38 °C, 22.5 MHz, ^{1}H): 95.5 and 97.3 (s, Cp and Cp′), 127.8, 128.5, 129.1, 131.5, 135.8, and 136.2 (s, Ph and Ph′), 247 and 241 (br s, CO and CO′). IR (cm^{-1}, KBr) 1970 m, 1925 s, 1845 s, 1815 m (ν_{CO}), 1535 w ($\nu_{C=N}$). The resonance due to the diazoalkane carbon CN_2 is buried in the phenyl carbon resonances.

The related derivatives $Cp'_2Mo_2(CO)_2(N_2CPh_2)$, $Cp'_2Mo_2(CO)_4(N_2CAr_2)$, and $Cp_2Mo_2(CO)_4(N_2CAr_2)$ (Cp′ = C_5H_4Me, Ar = p-tolyl) were prepared by identical procedures from the appropriate reagents in yields of isolated products ranging from 82% to 97%. The spectral properties (IR and ^{1}H and ^{13}C NMR) of these homologues differ from those of the parent compound $Cp_2Mo_2(CO)_4(N_2CPh_2)$, only in the manner expected for substitution of H by Me.

(μ-2-Diazopropane)bis(cyclopentadienyldicarbonylmolybdenum), $Cp_2Mo_2(CO)_4(N_2CMe_2)$. To a solution of $Cp_2Mo_2(CO)_4$ (4.7 g, 10.8 mmol) in CH_2Cl_2 (250 mL) at 0 °C was added slowly with stirring a cold solution of Me_2CN_2 (35 mL, 0.64 M, 100% excess) in CH_2Cl_2. The mixture was stirred for several minutes at 0 °C and then warmed to room temperature. All volatile material was removed under vacuum on a rotary evaporator, leaving 5.28 g (97%) of brown powder pure by ^{1}H NMR. The compound can be recrystallized from CH_2Cl_2/methylcyclohexane mixtures.

Anal. Calcd for $Mo_2C_{17}H_{16}N_2O_4$: Mo, 38.05; C, 40.49; H, 3.20; N, 5.56. Found: Mo, 35.03; C, 38.85; H, 3.33; N, 5.24. ^{1}H NMR (δ, $C_6D_5CD_3$, 360 MHz, −50 °C): major isomer (~60%), 5.157 (s, 10, Cp), 2.373 and 1.367 (s, 6, Me and Me′); minor isomer, 5.133 and 4.641 (s, 10, Cp and Cp′), 1.677 and 0.738 (s, 6, Me and Me′). ^{1}H NMR acetone-d_6, (δ, −40 °C): major isomer (~85%), 5.681 and 5.628 (s, 10, Cp and Cp′), 2.367 and 1.798 (s, 6, Me and Me′); minor isomer, 5.711 (s, 10, Cp), 1.995 and 1.292 (s, 6, Me and Me′). ^{13}C NMR (δ, CD_2Cl_2, −50 °C, 90.56 MHz): major isomer (~70%), 250.0 and 247.8 (s, CO and CO′), 140.4 (s, CH_2), 95.5 and 95.2 (s, Cp and Cp′), 23.5 and 22.0 (s, Me and Me′); minor isomer, 246.6 and 244.0 (s, CO and CO′), 137.3 (CN_2), 97.1 (s, Cp), 24.2 and 16.1 (s, Me and Me′).

Reaction of $Cp_2Mo_2(CO)_4$ with CH_2N_2. $Cp_2Mo_2(CO)_4$ (0.1 g, 0.2 mmol) in CH_2Cl_2 (20 mL) was frozen. CH_2N_2 solution (7.8 mL of 0.126 M CH_2Cl_2 solution, ~4 equiv) was added and frozen. Vacuum was applied to remove all gases, and the solutions were thawed to −78 °C, at which temperature no apparent reaction was noted. The solution was warmed to 0 °C, whereupon the solution color went red and then amber red; the appearance is different from a control solution of 1 of the same concentration and temperature. The solution was stirred 10 min and then warmed to 20 °C. After 30 min at room temperature, no change was noted. The reaction mixture was then heated to 35 °C for 1 h, and the solution gradually turned the red color of 1. The volatiles were trap-to-trap distilled to an ethanol/slush bath cooled receiver and the remaining gases transferred to a gas bulb. A mass spectrum of the gases showed the presence of C_2H_4, and the involatiles were shown by ^{1}H NMR spectroscopy to be 1.

(μ-Diphenyldiazomethane)bis(pentamethylcyclopentadienyldicarbonylmolybdenum), $Cp^*_2Mo_2(CO)_4(\mu\text{-}N_2CPh_2)$. In a 100-mL Schlenk flask, 1.74 mmol (1.0 g) of $(C_5Me_5)_2Mo_2(CO)_4$ was dissolved in 10 mL of toluene and cooled to 0 °C. To this was added 1.75 mmol (0.3380 g) of $(C_6H_5)_2CN_2$ in 2 mL of toluene over a 5-min period via syringe. The mixture was stirred at 0 °C for 1 h, during which time the reaction mixture turned from a brick red to a yellow-green color. The mixture was concentrated under vacuum to a volume of ca. 5 mL, and 5 mL of hexane was added. After the mixture was cooled to −23 °C overnight, a green solid was filtered, washed with hexane, and dried under vacuum. Anal. Calcd for $(C_5Me_5)_2Mo_2(CO)_4(N_2C(C_6H_5)_2)$: C, 57.81; H, 3.21; N, 3.65. Found: C, 57.71; H, 5.32; N, 3.61. IR (KBr, cm^{-1}): ν_{CO} 1940, 1885, 1825, 1795, 1625 (w). IR (C_7H_8, cm^{-1}): ν_{CO} 1949, 1895, 1838, 1975. ^{1}H NMR (360 MHz, C_6D_6, 30 °C): δ 1.79, 1.51 (C_5Me_5), 7.02–7.40 (Ph). ^{13}C{^{1}H} NMR (90.5 MHz, C_6D_6, 30 °C): δ 10.14, 10.51 ($C_5\mathit{Me}_5$), 105.68, 106.03 (C_5Me_5), 128.42, 128.58, 129.41, 131.38, 134.93, 137.54, 137.68 (C_6H_5), 248.47, 248.99, 251.46, 257.09 (CO). Melting point: 170–171 °C with decomposition. The diazoalkane carbon resonance is buried in the phenyl carbon resonances.

Thermolysis of $(C_5Me_5)_2Mo_2(CO)_4(N_2CPh_2)$. In a 100-mL Schlenk flask, 0.26 mmol (0.20 g) of $(C_5Me_5)_2Mo_2(CO)_4(N_2CPh_2)$ was dissolved in 10 mL of toluene and the mixture warmed to 65 °C overnight. A ^{1}H NMR of the reaction mixture indicated that only unchanged reactant was present. The mixture was then heated to reflux for 15 min, during which time the reaction changed from yellow-green to a red-brown color. A ^{1}H NMR of the mixture indicated the presence of a complex mixture of compounds. The mixture was warmed to reflux an additional 0.5 h, and a ^{1}H NMR of the mixture was obtained. Again, several products were present, and the reaction was not pursued further.

(μ-9-Fluorenylidene)bis(methylcyclopentadienyldicarbonylmolybdenum). In a 100-mL Schlenk flask, 2.16 mmol (1.0 g) of $(C_5H_4CH_3)_2Mo_2(CO)_4$ was dissolved in 10 mL of toluene. To this was added a solution of 2.16 mmol (0.42 g) of 9-diazofluorene in 5 mL of toluene via syringe over a 5-min period. The mixture was stirred at room temperature for 45 min and then concentrated to dryness under vacuum. The residue was extracted several times with diethyl ether at −80 °C, until the extracts were clear. The remaining solid was chromatographed by using 60–100 mesh Florisil and a 50/50 toluene/hexane mixture as the eluent. The first fraction off the column (dark red-brown) was collected and taken to dryness in vacuo. The microcrystalline black solid was recrystallized from a THF/hexane mixture, resulting in 40–50% yields of product. Anal. Calcd for $(C_5H_4CH_3)_2Mo_2(CO)_4(\mu\text{-}C_{13}H_8)$: C, 55.61; H, 3.54. Found: C, 55.68; H, 3.43. IR (KBr, cm^{-1}): ν_{CO} 1975, 1930, 1845. IR (C_7H_8, cm^{-1}): ν_{CO} 1980, 1925, 1850. ^{1}H NMR (360 MHz, C_6D_6, 25 °C): δ 1.18 (CH_3), 4.11 (A_2B_2, $\Delta\delta_{AB}$ = 112 Hz, J_{AB} = 2.4 Hz, Cp), 7.2–8.0 (ABCD, Ar). ^{13}C{^{1}H} NMR (90.56 MHz, C_7D_8, 25 °C): δ 236.1 (CO), 164.5 (μ-C), 132.1, 128.3, 127.1, 125.6, 123.1, 118.9 (Ar), 107.6, 95.1, 93.2 (Cp), 12.4 (CH_3). Melting point: 198–200 °C.

(μ-Diphenylmethylene)bis(cyclopentadienyldicarbonylmolybdenum), $Cp_2Mo_2(CO)_4(CPh_2)$. $Cp_2Mo_2(CO)_4(N_2CPh_2)$ (1.00 g, 1.6 mmol) in benzene (10 mL) was heated 2.5 h at 50 °C in a small vial. The solution volume was reduced in vacuo, and methylcyclohexane (30 mL) was added slowly. A first crop of 0.45 g was later filtered off and dried; filtrate concentration followed by methylcyclohexane addition gave a 0.27-g second crop. Yield: 66% (as $Cp_2Mo_2(CO)_4(CPh_2)(PhH)$, the benzene solvate).

Anal. Calcd for $Mo_2C_{27}H_{20}O_4$: C, 54.01; H, 3.36; N, 0.00. Found: C, 55.23; H, 3.63; N, <0.1. ^{1}H NMR (δ, C_6D_6, 25 °C, 360 MHz): 4.270 (s, 10, Cp), 6.545 (v br s, 4, H_o), 6.688 (t, 2, J_{HH} = 8 Hz, H_p), 6.898 (t, 4, J_{HH} = 4 Hz, H_m). ^{13}C NMR (δ, CD_2Cl_2, −60 °C, 90.56 MHz, {^{1}H}): 88.8, 110.8–157.4 (Ph and Ph′), 94.9 and 98.2 (Cp and Cp′), 174.9 (C), 241.7, 244.1, 251.1, and 251.7 (CO).

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Table I. Summary of Crystal and Data Collection Statistics

	$Cp_2Mo_2(CO)_4(N_2CPh_2)$ **(2)**	$Cp_2Mo_2(CO)_4[N_2C(CO_2Et)_2]$ **(4A)**	$Cp^*{}_2Mo_2(CO)_4(N_2CHCO_2Et)$ **(6)**
color	green	black	black
chem. formula	$C_{27}H_{20}Mo_2N_2O_4$	$C_{21}H_{20}Mo_2N_2O_8$	$C_{28}H_{36}Mo_2N_2O_6$
M_r	628.37	620.05	688.50
a, b, c, Å	11.847 (4), 10.407 (3), 20.572 (6)	11.144 (2), 7.497 (1), 28.939 (7)	10.515 (3), 18.868 (6), 15.334 (4)
β, deg; V, Å^3; z	97.81 (2); 2513 (1); 4	95.13 (2); 2408.2 (9); 4	104.43 (2); 2946 (1); 4
ρ_{calcd}, g/mL	1.64 (= ρ_{obsd})	1.71	1.55
cryst dimens, mm	0.41 × 0.18 × 0.04	0.19 × 0.24 × 0.20	irregular, $\bar{d} \approx 0.15$
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
radiatn	Mo Kα, monochromatized from a graphite crystal	Mo Kα, monochromatized from a graphite crystal	Mo Kα, monochromatized from a graphite crystal
takeoff angle, deg	4	4	4
μ(Mo Kα), cm^{-1}	10.1	10.6	8.7
scan speed, deg/min	2.0–15 (variable)	2.0–15 (variable)	2.0–15 (variable)
scan range	Mo Kα_1 − 0.8° to Mo Kα_2 + 0.8°	Mo Kα_1 − 0.8° to Mo Kα_2 + 0.8°	Mo Kα_1 − 0.8° to Mo Kα_2 + 0.8°
background/scan time	0.8	0.8	0.8
std reflctns	021, 101, 3$\bar{2}$0	402, 120, 006	330, 166, 41$\bar{4}$
2θ limit	45°	45°	45°
reflctns	3918 (2306 with $I > 3\sigma(I)$)	3874 (1755 with $I > 3\sigma(I)$)	4549 (3164 with $I > 3\sigma(I)$)
N_o/N_v	7.3	5.9	9.2
goodness of fit	1.73	2.18	2.17
R_1, R_2	0.048, 0.059	0.048, 0.061	0.034, 0.034

The μ-di-*p*-tolylmethylene derivative was prepared in an analogous fashion from 4.00 g (6.1 mmol) of $Cp_2Mo_2(CO)_4(\mu\text{-}N_2CAr_2)$. The product was isolated in 77% yield as the benzene solvate from PhH/methylcyclohexane mixtures. ^{13}C NMR (δ, CD_2Cl_2, −60 °C, 90.56 MHz, $\{^1H\}$): 251.9, 251.2, 244.3, 242.9 (s, carbonyls), 177.0 (s, μ-CPh_2), 154.5, 137.5, 132.8, 129.6, 129.5, 129.4, 128.9, 128.5, 127.9, 107.9, and 92.2 (s, aromatic), 98.2 and 94.5 (s, Cp and Cp′), 21.0 and 20.5 (s, Me and Me′); the alkylidene resonance and the aromatic resonances at 154.5, 137.5, 132.8, and 107.9 remain singlets in the gated $\{^1H\}$ spectrum.

Thermal Decomposition of $Cp_2Mo_2(CO)_4(N_2CPh_2)$: Molecularity Studies. (a) $Cp_2Mo_2(CO)_4(N_2CPh_2)$ (0.06 g) and $(C_5H_4Me)_2Mo_2(CO)_4$ (0.04 g) were dissolved in C_6D_6 and the sample heated to 60 °C for 1 h. A ^1H NMR spectrum at 60 MHz showed resonances only for $Cp_2Mo_2(CO)_4(CPh_2)$ and unreacted $(C_5H_4Me)_2Mo_2(CO)_4$; no $(C_5H_4Me)_2Mo_2(CO)_4(CPh_2)$ was detected, under conditions where the Me signals of both C_5H_4Me species can be distinguished.

(b) $Cp_2Mo_2(CO)_4(N_2CPh_2)$ (0.03 g) and $(C_5H_4Me)_2Mo_2(CO)_4[N_2C(C_6H_4\text{-}p\text{-}Me)_2]$ (0.03 g) were dissolved in C_6D_6, and the sample was heated to 60 °C for 1 h. A ^1H NMR spectrum at 60 MHz of the reaction mixture showed the presence of only the direct products $Cp_2Mo_2(CO)_4(CPh_2)$ and $(C_5H_4Me)_2Mo_2(CO)_4[C(C_6H_4\text{-}p\text{-}Me)_2]$. Control experiments showed that all possible direct and cross product combinations could be distinguished by NMR.

(μ-Diethyl diazomalonate)bis(cyclopentadienyldicarbonylmolybdenum). In a 100-mL Schlenk flask, 2.30 mmol (1.00 g) of $Cp_2Mo_2(CO)_4$ was dissolved in 15 mL of toluene and cooled to −23 °C. To this was added a solution of 4.60 mmol (0.858 g) of diethyl diazomalonate in 2 mL of toluene via syringe over a 5-min period. The mixture was stirred at −23 °C for 2 h, and 10 mL of hexane was added. A red solid was filtered, an IR spectrum of which indicated it to be $Cp_2Mo_2(CO)_6$. The filtrate was removed under vacuum, hexane was added, and the mixture was cooled to −23 °C. A black, microcrystalline solid was filtered, washed with hexane, and dried. Anal. Calcd for $C_{21}H_{20}N_2O_8Mo_2$: C, 40.70; H, 3.23; N, 4.51. Found: C, 41.24; H, 3.32; N, 3.86. IR (KBr, cm^{-1}, ν_{CO}): 1935, 1915, 1855, 1795, 1665. ^1H NMR (360 MHz, C_6D_6, 30 °C): δ 5.41, 5.07 (Cp), 4.22 (CH_2, AB multiplet, $J_{MeH_A} = 7.05$ Hz, $J_{MeH_B} = 6.99$ Hz, $J_{H_AH_B} = 3.87$ Hz), 3.91 (q, $J = 7.05$ Hz), 1.13 (t, $J = 7.09$ Hz), 0.97 ($J = 7.10$ Hz). $^{13}C\{^1H\}$ NMR (90.56 MHz, C_6D_6, 30 °C): δ 261.0, 255.8, 244.5, 240.44 (CO), 168.6, 161.9 (sp^2 CO), 98.0, 97.5 (Cp), 61.7, 58.8 (CH_2), 15.0, 14.9 (CH_3). Melting point: 45–50 °C with decomposition.

(μ-2-Diazodimedone)bis(pentamethylcyclopentadienyldicarbonylmolybdenum). In a 100-mL Schlenk flask, 0.87 mmol (0.50 g) of $(C_5Me_5)_2Mo_2(CO)_4$ was dissolved in 15 mL of toluene and the mixture cooled to 0 °C. To this was added a solution of 0.87 mmol (0.145 g) of 2-diazodimedone in 3 mL of toluene via syringe. The toluene was removed under vacuum, hexane was added, and the mixture was cooled to −23 °C overnight. A black, microcrystalline solid was filtered, washed with hexane, and dried. Anal. Calcd for $C_{32}H_{40}N_2O_6Mo_2$: C, 51.89; H, 5.41; N, 3.79. Found: C, 51.79; H, 5.38; N, 3.71. IR (KBr, cm^{-1}): ν_{CO} 1965, 1927, 1885, 1835, 1628, 1512 cm^{-1}. ^1H NMR (360 MHz, C_6D_6, 30 °C): δ 0.79, 0.74 (CH_3), 1.66, 1.88 (C_5Me_5), 1.75 (CH_2), 2.16 (CH_2, m). $^{13}C\{^1H\}$

Table II. Fractional Atomic Coordinates of $Cp_2Mo_2(CO)_4(N_2CPh_2)$[a]

atom	x	y	z
Mo1	0.2170 (1)	0.0640 (1)	−0.0517 (0)
Mo2	0.2804 (1)	0.2990 (1)	0.0285 (0)
C1	0.1540 (9)	0.0844 (10)	0.0314 (5)
O1	0.1060 (7)	0.0704 (8)	0.0760 (4)
C2	0.0674 (10)	0.1451 (12)	−0.0922 (6)
O2	−0.0146 (7)	0.1873 (9)	−0.1156 (5)
C3	0.4430 (10)	0.3470 (11)	0.0389 (5)
O3	0.5357 (7)	0.3796 (9)	0.0490 (4)
C4	0.3479 (9)	0.1938 (11)	0.1025 (5)
O4	0.3878 (7)	0.1335 (10)	0.1468 (4)
C5	0.1700 (12)	−0.1456 (13)	−0.0864 (11)
C6	0.2409 (14)	−0.0938 (13)	−0.1295 (6)
C7	0.3484 (11)	−0.0711 (12)	−0.0943 (7)
C8	0.3463 (14)	−0.1078 (13)	−0.0303 (8)
C9	0.2362 (20)	−0.1517 (12)	−0.0238 (8)
C10	0.2332 (12)	0.4840 (14)	0.0791 (9)
C11	0.2262 (13)	0.5104 (12)	0.0102 (10)
C12	0.1357 (10)	0.4394 (12)	−0.0252 (7)
C13	0.0856 (10)	0.3676 (13)	0.0210 (8)
C14	0.1435 (12)	0.3933 (13)	0.0852 (7)
N1	0.3114 (6)	0.2114 (8)	−0.0584 (3)
N2	0.4013 (6)	0.2282 (8)	−0.0915 (4)
C15	0.3953 (9)	0.2966 (11)	−0.1435 (5)
C16	0.4992 (10)	0.3041 (13)	−0.1759 (5)
C17	0.2889 (10)	0.3623 (12)	−0.1714 (5)
C18	0.2726 (13)	0.4956 (13)	−0.1650 (6)
C19	0.1663 (16)	0.5514 (14)	−0.1930 (6)
C20	0.0797 (13)	0.4742 (18)	−0.2260 (6)
C21	0.0969 (11)	0.3431 (16)	−0.2319 (6)
C22	0.2010 (9)	0.2886 (11)	−0.2053 (5)
C23	0.5884 (10)	0.2167 (13)	−0.1577 (6)
C24	0.6876 (11)	0.2220 (17)	−0.1908 (7)
C25	0.6942 (16)	0.3161 (23)	−0.2389 (8)
C26	0.6063 (15)	0.4046 (23)	−0.2558 (7)
C27	0.5049 (11)	0.3981 (16)	−0.2253 (6)

[a] Number in parentheses is the standard deviation of the last significant figure in this and all subsequent tables.

Table IV. Bond Distances (Å) and Bond Angles (deg) for $Cp_2Mo_2(CO)_4(N_2CPh_2)$

	Bond Distances		
Mo(1)–Mo(2)	2.987 (5)		
Mo(1)–N(1)	1.914 (8)	Mo(2)–N(1)	2.083 (8)
–C(1)	1.97 (1)	–C(3)	1.97 (1)
–C(2)	2.04 (1)	–C(4)	1.96 (1)
–C(5)	2.34 (1)	–C(10)	2.29 (1)
–C(6)	2.34 (1)	–C(11)	2.31 (1)
–C(7)	2.35 (1)	–C(12)	2.40 (1)
–C(8)	2.36 (1)	–C(13)	2.40 (1)
–C(9)	2.32 (1)	–C(14)	2.34 (1)
N(1)–N(2)	1.35 (1)	C(1)–O(1)	1.15 (1)
N(2)–C(15)	1.28 (1)	C(2)–O(2)	1.11 (1)
C(15)–C(16)	1.48 (1)	C(3)–O(3)	1.14 (1)
–C(17)	1.48 (1)	C(4)–O(4)	1.15 (1)
	Bond Angles		
Mo(1)–N(1)–Mo(2)	96.6 (3)	Mo(1)–C(1)–O(1)	164.7 (9)
N(1)–Mo(1)–Mo(2)	43.8 (2)	Mo(1)–C(2)–O(2)	178.2 (14)
N(1)–Mo(2)–Mo(1)	39.5 (2)	Mo(2)–C(3)–O(3)	174.9 (10)
Mo(1)–N(1)–N(2)	130.4 (6)	Mo(2)–C(4)–O(4)	179.0 (18)
Mo(2)–N(1)–N(2)	128.2 (6)	N(2)–C(15)–C(17)	121.9 (9)
N(1)–N(2)–C(15)	122.4 (9)	C(16)–C(15)–C(17)	121.2 (10)
N(2)–C(15)–C(16)	116.8 (10)		

Table VI. Atomic Fractional Coordinates for $Cp_2Mo_2(CO)_4[C(CO_2Et)_2]$ (4A)

atom	*x*	*y*	*z*
Mo1	0.26061 (10)	0.12754 (14)	–0.21319 (3)
Mo2	0.09333 (10)	0.30073 (14)	–0.08060 (3)
C1	0.2555 (12)	0.3225 (17)	–0.2585 (4)
O1	0.2512 (9)	0.4356 (13)	–0.2851 (3)
C2	0.0918 (16)	0.1230 (18)	–0.2350 (4)
O2	–0.0076 (11)	0.1193 (15)	–0.2482 (4)
C3	0.1223 (12)	0.0479 (22)	–0.0936 (4)
O3	0.1357 (11)	–0.1015 (15)	–0.1011 (4)
C4	0.1082 (13)	0.1805 (18)	–0.0180 (5)
O4	0.1118 (10)	0.1127 (15)	0.0157 (3)
C5	0.2826 (15)	–0.1810 (17)	–0.2108 (10)
C6	0.3242 (20)	–0.1203 (25)	–0.2532 (6)
C7	0.4243 (17)	–0.0173 (23)	–0.2438 (6)
C8	0.4507 (15)	–0.0089 (20)	–0.1951 (6)
C9	0.3611 (18)	–0.1119 (22)	–0.1740 (5)
C10	–0.0675 (12)	0.2877 (25)	–0.1364 (4)
C11	–0.1107 (12)	0.2621 (18)	–0.0902 (4)
C12	–0.0878 (12)	0.4242 (17)	–0.0646 (5)
C13	–0.0374 (12)	0.5474 (18)	–0.0948 (6)
C14	–0.0257 (14)	0.4668 (25)	–0.1371 (5)
N1	0.2483 (9)	0.2679 (12)	–0.1607 (3)
N2	0.2488 (9)	0.3388 (11)	–0.1220 (3)
C15	0.3352 (12)	0.4682 (15)	–0.1061 (4)
C16	0.3010 (14)	0.5430 (17)	–0.0644 (5)
O5	0.2099 (9)	0.4926 (10)	–0.0448 (3)
O6	0.3706 (9)	0.6706 (13)	–0.0440 (3)
C17	0.3418 (19)	0.7279 (31)	0.0029 (8)
C18	0.4365 (24)	0.7772 (42)	0.0257 (7)
C19	0.4450 (13)	0.4874 (17)	–0.1257 (4)
O7	0.4806 (9)	0.3929 (14)	–0.1553 (3)
O8	0.4871 (8)	0.3791 (11)	0.1080 (3)
C20	0.3721 (15)	0.3532 (16)	0.1262 (4)
C21	0.3140 (12)	0.1930 (19)	0.1013 (5)

NMR (90.56 MHz, C_6D_6, 30 °C): δ 10.36, 10.88 (C_5Me_5), 27.95, 28.46 (CH_3), 31.70 (ipso-C), 48.84, 53.34 (CH_2), 108.76, 198.93 (C_5Me_5), 182.93, 187.65 (sp^2 CO), 238.76, 259.34, 265.03 (CO). Melting point: 166–168 °C with decomposition.

Table VIII. Selected Bond Distances (Å) and Angles (deg) for $Cp_2Mo_2(CO)_4[C(CO_2Et)_2]$ (4A)

	Bond Distances		
Mo1–N1	1.864 (10)	Mo2–C12	2.304 (12)
Mo1–C2	1.930 (17)	Mo2–C10	2.305 (12)
Mo1–C1	1.961 (14)	Mo2–C14	2.365 (13)
Mo1–C5	2.326 (13)	Mo2–C13	2.367 (13)
Mo1–C6	2.333 (14)	C1–O1	1.144 (13)
Mo1–C9	2.353 (13)	C2–O2	1.139 (14)
Mo1–C7	2.362 (14)	C3–O3	1.153 (15)
Mo1–C8	2.369 (14)	C4–O4	1.098 (14)
Mo2–C3	1.965 (17)	N1–N2	1.238 (11)
Mo2–C4	2.017 (14)	N2–C15	1.415 (14)
Mo2–O5	2.142 (8)	C15–C19	1.401 (16)
Mo2–N2	2.211 (9)	C15–C16	1.413 (16)
Mo2–C11	2.284 (14)	C16–O5	1.265 (14)
	Bond Angles		
N1–Mo1–C2	97.9 (5)	O5–Mo2–N2	72.8 (3)
N1–Mo1–C1	97.2 (4)	N1–N2–C15	122.4 (9)
C2–Mo1–C1	79.9 (5)	C19–C15–C16	128.1 (12)
C3–Mo2–C4	74.9 (5)	C19–C15–N2	122.2 (10)
C3–Mo2–O5	129.6 (5)	C16–C15–N2	108.8 (11)
C3–Mo2–N2	82.6 (4)	O5–C16–O6	118.2 (11)
C4–Mo2–O5	82.4 (4)	O5–C16–C15	123.6 (12)
C4–Mo2–N2	122.6 (5)	O6–C16–C15	118.2 (13)

Table X. Atomic Fractional Coordinates for $Cp^*_2Mo_2(CO)_4(N_2CHCO_2Et)$ (6)

atom	*x*	*y*	*z*	*U*, $Å^2$
Mo1	0.29642 (5)	0.30726 (2)	0.48554 (3)	0.0291
Mo2	0.13586 (5)	0.21055 (2)	0.57544 (3)	0.0271
C1	0.4162 (06)	0.2441 (03)	0.4478 (04)	0.0433
O1	0.4917 (05)	0.2110 (03)	0.4201 (04)	0.0767
C2	0.1975 (07)	0.2750 (03)	0.3659 (04)	0.0472
O2	0.1466 (06)	0.2579 (03)	0.2944 (03)	0.0782
C3	0.0448 (06)	0.2868 (03)	0.4957 (04)	0.0375
O3	–0.0352 (04)	0.3248 (02)	0.4551 (03)	0.0489
C4	0.0748 (06)	0.1544 (03)	0.4632 (04)	0.0399
O4	0.0327 (05)	0.1226 (02)	0.3992 (03)	0.0647
N1	0.3276 (04)	0.2528 (02)	0.6089 (03)	0.0315
N2	0.3357 (05)	0.1827 (02)	0.5991 (03)	0.0321
C5	0.4393 (06)	0.1436 (03)	0.6128 (04)	0.0379
C6	0.4240 (06)	0.0662 (03)	0.6052 (04)	0.0394
O5	0.3232 (05)	0.0342 (02)	0.5837 (03)	0.0622
O6	0.5435 (04)	0.0365 (02)	0.6272 (03)	0.0466
C7	0.5449 (06)	–0.0405 (03)	0.6263 (04)	0.0506
C8	0.6929 (07)	–0.0610 (04)	0.6532 (05)	0.0643
C11	0.3857 (06)	0.4061 (03)	0.5802 (04)	0.0436
C12	0.2574 (06)	0.4244 (03)	0.5361 (04)	0.0374
C13	0.2462 (06)	0.4243 (03)	0.4412 (04)	0.0372
C14	0.3719 (06)	0.4058 (03)	0.4273 (04)	0.0480
C15	0.4573 (06)	0.3942 (03)	0.5142 (05)	0.0468
C21	0.4400 (07)	0.4015 (04)	0.6805 (05)	0.0618
C22	0.1522 (07)	0.4483 (03)	0.5795 (05)	0.0637
C23	0.1287 (07)	0.4490 (03)	0.3699 (05)	0.0558
C24	0.4104 (08)	0.4076 (04)	0.3407 (05)	0.0779
C25	0.6023 (07)	0.3804 (04)	0.5320 (06)	0.0814
C31	–0.0533 (06)	0.1877 (03)	0.6197 (04)	0.0457
C32	0.0312 (06)	0.1298 (03)	0.6466 (04)	0.0422
C33	0.1425 (06)	0.1541 (03)	0.7142 (04)	0.0412
C34	0.1260 (06)	0.2274 (03)	0.7281 (04)	0.0386
C35	0.0045 (06)	0.2481 (03)	0.6695 (04)	0.0403
C41	–0.1917 (06)	0.1850 (04)	0.5594 (05)	0.0663
C42	0.0036 (07)	0.0533 (03)	0.6179 (05)	0.0608
C43	0.2513 (07)	0.1092 (04)	0.7686 (04)	0.0592
C44	0.2183 (07)	0.2726 (04)	0.7951 (04)	0.0562
C45	–0.0631 (07)	0.3186 (04)	0.6706 (05)	0.0641

(μ-Ethyl diazoacetate)bis(pentamethylcyclopentadienyldicarbonylmolybdenum) (6). $Cp^*_2Mo(CO)_4$ (0.50 g, 0.87 mmol) was suspended with stirring in a mixture of 10 mL of hexane and 3 mL of CH_2Cl_2 at –10 °C. Addition of 3 equiv of N_2CHCO_2Et in 3 mL of hexane was carried out over a 20-min period. The reaction mixture was stirred at –10 °C for an additional 1.5 h during which time the color of the solution changed from red to black. The volume was reduced to 2–3 mL under vacuum while the solution temperature was kept ≤0 °C. The concentrated solution was then cooled to –50 °C and the mother liquor carefully removed from the crystals with a syringe. The solid product was washed with two 2-mL portions of cold ether and dried in vacuo: yield 83%; mp 128–130 °C with decomposition. The product may be recrystallized from CH_2Cl_2/hexane. IR: ν_{CO} 1980, 1900, 1820, 1800, 1715 cm^{-1}. Anal. Calcd for $C_{28}H_{36}Mo_2N_2O_6$: C, 48.87; H, 5.23; N, 4.07. Found: C, 48.89, H, 5.36; N, 4.13. The methyl ester may be prepared in an analogous manner from N_2CHCO_2Me. IR: ν_{CO} 1958, 1900, 1826, 1797, 1723 cm^{-1}. ^1H NMR of the ethyl and methyl diazoacetate adducts are

Table XII. Selected Bond Distances (Å) and Bond Angles (deg) for $Cp^*_2Mo_2(CO)_4(N_2CHCO_2Et)$ (6)

Bond Distances

Mo1–Mo2	3.040 (01)	C5–C6	1.472 (08)
Mo1–C1	1.926 (07)	C6–O5	1.193 (07)
Mo1–C2	1.966 (07)	C6–O6	1.340 (07)
Mo1–C3	2.717 (06)	O6–C7	1.454 (07)
Mo1–N1	2.105 (04)	C7–C8	1.555 (09)
Mo1–N2	2.894 (04)	C11–C12	1.393 (08)
Mo1–C11	2.406 (06)	C11–C15	1.423 (09)
Mo1–C12	2.411 (05)	C11–C21	1.504 (09)
Mo1–C13	2.332 (05)	C12–C13	1.431 (08)
Mo1–C14	2.289 (06)	C12–C22	1.494 (08)
Mo1–C15	2.319 (06)	C13–C14	1.434 (08)
Mo2–C3	1.974 (06)	C13–C23	1.507 (08)
Mo2–C4	1.986 (06)	C14–C15	1.427 (09)
Mo2–N1	2.109 (04)	C14–C24	1.483 (09)
Mo2–N2	2.108 (05)	C15–C25	1.501 (09)
Mo2–C31	2.297 (06)	C31–C32	1.404 (08)
Mo2–C32	2.307 (06)	C31–C35	1.419 (08)
Mo2–C33	2.366 (06)	C31–C41	1.519 (08)
Mo2–C34	2.390 (05)	C32–C33	1.432 (08)
Mo2–C35	2.342 (06)	C32–C42	1.516 (09)
C1–O1	1.168 (07)	C33–C34	1.418 (08)
C2–O2	1.142 (07)	C33–C43	1.497 (08)
C3–O3	1.161 (06)	C34–C35	1.421 (08)
C4–O4	1.142 (07)	C34–C44	1.492 (08)
N1–N2	1.336 (06)	C35–C45	1.510 (09)
N2–C5	1.288 (07)		

Bond Angles

Mo2–Mo1–C1	104.1 (2)	C4–Mo2–N2	96.3 (2)
Mo2–Mo1–C2	90.7 (2)	N1–Mo2–N2	36.9 (2)
C1–Mo1–C2	76.2 (3)	Mo1–C1–O1	173.4 (5)
Mo2–Mo1–C3	39.6 (1)	Mo1–C2–O2	175.5 (6)
C1–Mo1–C3	130.4 (2)	Mo1–C3–Mo2	79.1 (2)
C2–Mo1–C3	73.3 (2)	Mo1–C3–O3	117.8 (4)
Mo2–Mo1–N1	43.9 (1)	Mo2–C3–O3	163.1 (5)
C1–Mo1–N1	90.0 (2)	Mo2–C4–O4	176.1 (6)
C2–Mo1–N1	127.9 (2)	Mo1–N1–Mo2	92.3 (2)
C3–Mo1–N1	79.3 (2)	Mo1–N1–N2	112.6 (3)
Mo2–Mo1–N2	41.5 (1)	Mo2–N1–N2	71.5 (3)
C1–Mo1–N2	70.8 (2)	Mo1–N2–Mo2	73.0 (1)
C2–Mo1–N2	105.8 (2)	Mo1–N2–N1	42.2 (2)
C3–Mo1–N2	81.1 (2)	Mo2–N2–N1	71.6 (3)
N1–Mo1–N2	25.2 (1)	Mo1–N2–C5	123.4 (4)
Mo1–Mo2–C3	61.3 (2)	Mo2–N2–C5	159.5 (4)
Mo1–Mo2–C4	91.3 (2)	N1–N2–C5	128.6 (5)
C3–Mo2–C4	81.4 (2)	N2–C5–C6	119.0 (5)
Mo1–Mo2–N1	43.8 (1)	C5–C6–O5	126.6 (6)
C3–Mo2–N1	99.3 (2)	C5–C6–O6	108.5 (5)
C4–Mo2–N1	119.7 (2)	O5–C6–O6	124.9 (6)
Mo1–Mo2–N2	65.5 (1)	C6–O6–C7	115.2 (5)
C3–Mo2–N2	126.7 (2)	O6–C7–C8	104.9 (5)

described in the Results.

Crystal Structure Determinations. $Cp_2Mo_2(CO)_4(N_2CPh_2)$. Crystals of the diphenyldiazoalkane adduct of 1 were obtained by slowly cooling to −20 °C a saturated CH_2Cl_2/hexane solution which had been layered with additional heptane. A Syntex $P2_1$ diffractometer was used to collect the data at ambient temperature. Lattice parameters were obtained from 16 reflections scattered in reciprocal space by using the autocentering routine. The Mo atom positions were found in a sharpened Patterson map, and the light atoms were subsequently found from difference Fourier maps. The refinement proceeded normally. Table I lists relevant statistics,[21] the atomic coordinates are in Table II, Table III (supplementary material) contains the temperature factors, selected bond distances and angles are in Table IV (Table IVS, supplementary material) and Table V (supplementary material) contains a listing of F_o vs F_c.

$Cp_2Mo_2(CO)_4[N_4C(CO)_2Et)_2]$ (4A). Difficulty was experienced in growing high quality crystals of **4A**, but marginally acceptable crystals were obtained from a CH_2Cl_2/hexane mixture at −20 °C. Data were obtained on a Syntex $P2_1$ diffractometer under ambient conditions. Lattice parameters were determined by a least-squares refinement of 16 reflections scattered in reciprocal space. The data were collected in two shells: 1.4°–30° and 30°–45°. About halfway through the second shell, the intensities of the check reflections became erratic, and this behavior was later traced to a faulty shutter operation. Consequently, only about half of the 30°–45° data available were used in the solution and refinement of the structure. Remaining crystal and data collection statistics are collected in Table I.[21]

The structure was solved by Patterson and Fourier techniques, and all the non-H atoms were refined with isotropic temperature factors to convergence (R_1 = 13%). After two cycles of refinement with anisotropic temperature factors (R_1 = 5.7%), the temperature factors for C12, C13, C17, and C20 were not positive definite. These were reset and their B values refined isotropically. When allowed to go anisotropic, all atoms except C20 were well-behaved. Therefore, for the last two refinement cycles, all atoms were refined with anisotropic factors except for C20 which were refined with an isotropic B value. This model converged with the R values shown in Table I. The poor behavior of the temperature factors and the scatter in the values of bond lengths of light atoms are probably related to the marginal crystal quality and the fact that an incomplete data set was used in the refinement.

The final atomic positions are collected in Table VI, temperature factors in Table VII (supplementary material), and selected bond distances and angles in Table VIII (complete listing in Table VIIIS, supplementary material); Table IX (supplementary material) contains a listing of F_o vs. F_c.

$Cp^*_2Mo_2(CO)_4(N_2CHCO_2Et)$ (6). Crystals of 6 were grown from CH_2Cl_2/hexane solution at −20 °C and mounted in a capillary on a Syntex $P2_1$ diffractometer. Lattice parameters were determined from least-squares settings of 15 reflections distributed in reciprocal space. Intensity data were collected at ambient temperature. Standard reflections were monitored every 50 reflections. The structure was solved with the direct methods included in the SHELX package.[36] Refinement proceeded smoothly. Positions for all hydrogen atoms were calculated but not refined. All H atoms were assigned isotropic temperature factors; U = 0.05 Å^2.

Relevant statistics are listed in Table I. Table X contains the final atomic coordinates; temperature factors are in Table XI (supplementary material). Bond distances and angles are in Table XII (complete listing in Table XIIS—supplementary material), and Table XIII (supplementary material) contains a listing of F_o vs. F_c.

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Supplementary Material Available: Tables III, VII, and XI, thermal parameters for **2**, **4A**, and **6**, and Tables IVS, VIIS, and XIIS, complete tables of bond distances and angles for **2**, **4A**, and **6** (11 pages); Tables V, IX, and XIII, F_o vs. F_c for **2**, **4A**, and **6** (30 pages). Ordering information is given on any current masthead page.

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(36) SHELX package of crystallographic programs by G. Sheldrick. Other programs included ORTEP by C. K. Johnson. All computations were performed on an Amdahl 5860 computer.