*Inorg. Chem.* **1983**, *22*, 849-851

# Metal-Metal Multiple Bonds. 13. Structural Diversity in the Reactions of $Cp_2Mo_2(CO)_4(Mo{\equiv}Mo)$ with Diazoalkanes and Aryl Azides[1]

*Sir:*

The Mo≡Mo triple bond in $Cp_2Mo_2(CO)_4$ (**1**) has exhibited a diverse reactivity with both electrophiles and nucleophiles,[2,3] but nowhere has this diversity been more evident than in the reactions of **1** with diazoalkanes. The reactions of **1** with diaryldiazomethanes, $Ar_2CN_2$, gives complexes **2** (Scheme I), which readily lose $N_2$ via an intramolecular process to produce the $\mu$-alkylidene complexes **3**.[4,5] These alkylidenes react with a further 1 equiv of $Ar_2CN_2$ to give the *terminal* carbene complexes **4**.

In addition, diazocyclopentadiene, $C_5H_4N_2$, reacts to give the $\mu$-$\eta^1$,$\eta^5$-cyclopentadienyl derivative **5**.[6] The $\mu_3$-nitride **6** was obtained in 5% yield from the reaction of **1** with ethyl diazoacetate, $N_2CH(CO_2Et)$, in refluxing toluene.[7] Even at −30 °C, this reagent gives a plethora of products with **1**.[8] We have also observed that **1** reacts with $CH_2N_2$ to give polymethylene, some $C_2H_4$, and recovered **1**.[3,8]

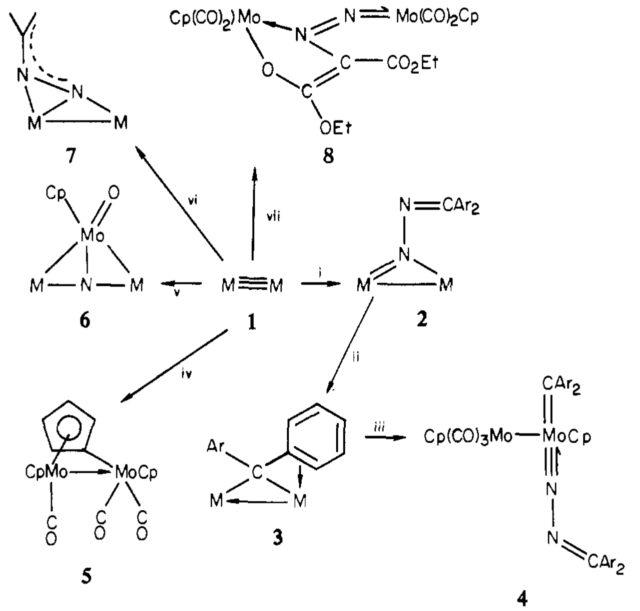
Since dimetallic alkyidene complexes prepared from **1** and diazoalkanes could function as alkylidene[10] transfer agents to olefins, CO, etc.,[4,9] it was of interest to establish the reactivity patterns of **1** with a variety of diazoalkanes. In this paper, we report the reactions of **1** with two diazoalkanes, $Me_2CN_2$ and $N_2C(CO_2Et)_2$, which reveal yet two more distinct coordination modes for the diazoalkane ligands. In addition, the reaction of **1** with aryl azides is presented and shows certain parallels to the sequence of conversions **1** → **2** → **3** → **4**.

Diazopropane, $Me_2CN_2$, reacts with **1** to give a 1:1 adduct, **7** (Scheme I, eq 1), which, unlike **2**, does *not* cleanly lose $N_2$

$$\mathbf{1} + Me_2CN_2 \xrightarrow[CH_2Cl_2]{0\ °C} \underset{\mathbf{7}}{Cp_2Mo_2(CO)_4(N_2CMe_2)} \qquad (1)$$

upon thermolysis or photolysis.[11] In solution, complex **7** exhibits unusual NMR behavior, which is attributed to the presence of two isomers that interconvert within minutes but too slowly to be fluxional on the NMR time scale. The relative amounts of these isomers, **7a** and **7b**, depend on the temperature and solvent polarity. In toluene-$d_8$ at 0 °C, isomer **7a** accounts for ca. 70% of the mixture and shows equivalent Cp groups in the $^1H$ and $^{13}C$ NMR spectra.[12] In acetone-$d_6$ at −40 °C, isomer **7b** is the major species (ca. 85%).[12]

Scheme I[a]



[a] Key: M = $Mo(CO)_2Cp$; i = $Ar_2CN_2$; ii = 60 °C; iii = $Ar_2CN_2$; iv = $C_5H_4N_2$; v = $N_2CH(CO_2Et)$; vi = $Me_2CN_2$; vii = $N_2C(CO_2Et)_2$.

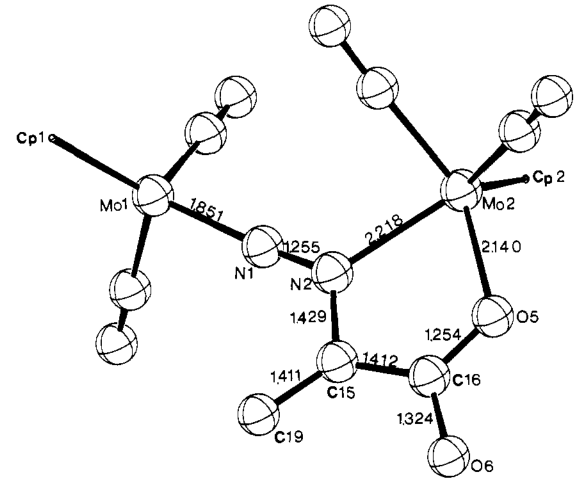
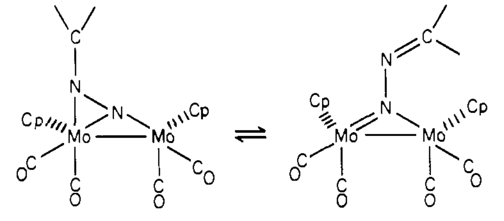


**Figure 1.** Inner coordination sphere of **8**.

Considerable difficulty was encountered in growing X-ray-quality single crystals of **7**. A data set was collected on a crystal that appeared to be marginally acceptable, but the resulting solution revealed a severe disorder about a crystallographically imposed mirror plane. However, the coordination mode of the $Me_2CN_2$ group was clearly discernible and is assigned to isomer **7b** (eq 2) since this structure requires



**7a** **7b** (2)

nonequivalent Cp groups.[13] Structure **7a** (eq 2) is assigned to the second isomer since the cis Cp groups are equivalent and the Me groups inequivalent, and this structural type has

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(9) Complex **3** reacts with $C_2H_4$ (50 °C, 2 atm) to give the homoligated olefin $Ph_2CHCHCH_2$: Curtis, M. D.; Messerle, L., unpublished results.

(10) Review: Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 160.

(11) Satisfactory elemental analyses have been obtained for all new compounds.

(12) $^1H$ NMR (360 MHz, 0 °C, toluene-$d_8$): **7a** $\delta$ 5.20 (Cp), 1.69 and 0.85 (Me); **7b** $\delta$ 5.18 and 4.76 (Cp), 2.33 and 1.43 (Me). $^1H$ NMR (360 MHz, −40 °C, acetone-$d_6$): **7a** $\delta$ 5.71 (Cp); 1.99 and 1.29 (Me); **7b** $\delta$ 5.68 and 5.63 (Cp), 2.37 and 1.80 (Me). $^{13}C$ NMR (90.55 MHz, −50 °C, $CD_2Cl_2$): **7a** $\delta$ 246.6 and 244.0 (CO), 137.3 ($Me_2CN_2$), 97.1 (Cp), 23.5 and 22.0 (Me); **7b** $\delta$ 250.0 and 247.8 (CO), 140.4 ($Me_2CN_2$), 95.9 and 95.2 (Cp), 24.2 and 16.1 (Me).

(13) This type of coordination is also observed in the adduct of $Me_2CN_2$ and $Cp^*{}_2M_2(CO)_4$: Hermann, WA., personal communication.

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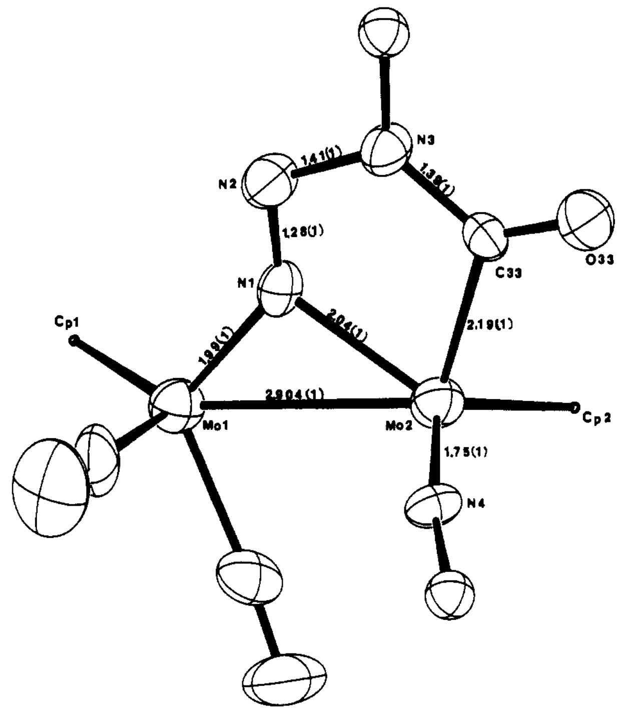
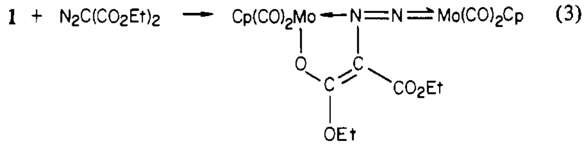


**Figure 2.** Inner coordination sphere of **9** (Ar = 4-*t*-$BuC_6H_4$).

been documented for complex **2**.[4] Structure **7b** is very similar to that of the $Me_2NCN$ adduct of **1**.[14]

The reaction of **1** with diethyl diazomalonate, $N_2C(CO_2Et)_2$, yields an entirely different coordination mode. Adduct **8** forms in 45% yield after purification.[15] The structure of **8** (eq 3,



$$1 + N_2C(CO_2Et)_2 \longrightarrow Cp(CO)_2Mo \leftarrow N{=}N \rightleftharpoons Mo(CO)_2Cp \quad (3)$$

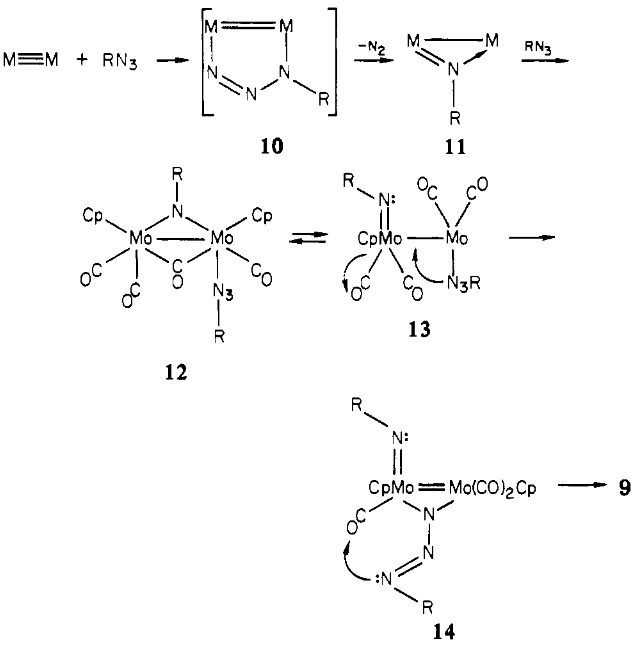
**8**

Figure 1) was elucidated by a single-crystal X-ray analysis.[16]

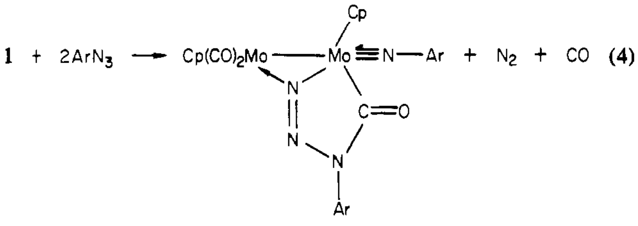
The diazomalonate acts as a 6e donor and completely disrupts the Mo≡Mo triple bond.[17] The Mo1–N1 distance is consistent with a Mo=N double bond (cf. the Mo2—N2 single bond), and the N1–N2 and C15–C16 distances are compatible with bond orders of 2. Drawing the structure as in eq 3 (N1 = 3e donor, N2 = 2e donor, O5 = 1e donor) gives each Mo an 18e count.

Organic azides are known to react with the Mo≡Mo bond in $Mo_2(OR)_6$ to give nitrene complexes.[18] We wished to determine whether bridging nitrenes, similar to bridging alkylidenes **3**, could be prepared and, if so, whether these species would transfer the nitrene to groups such as CO or alkenes.[4,9]

**Scheme II**



Aryl azides react with **1** to give a 1:1 adduct,[19] which reacts with $ArN_3$ nearly as fast as it forms to produce the diadduct **9** (eq 4; Ar = 4-$RC_6H_4$ (R = H, Me, *t*-Bu, $NO_2$)).[20,21] The



$$1 + 2ArN_3 \longrightarrow Cp(CO)_2Mo{-}Mo(Cp){\equiv}N{-}Ar + N_2 + CO \quad (4)$$

**9**

structure of the 1:2 adduct is shown in eq 4 and Figure 2.

The Mo–N1 distances are commensurate with their being Mo–N single bonds bridging a metal–metal bond, and the Mo–Mo distance (2.904 Å) is relatively short and reflects the tightness of the N-bridged metal–metal bond.

A possible mechanism for the formation of **9** is shown in Scheme II. The monoadduct is believed to be the bridging nitrene **11** formed by $N_2$ loss from the 1,3-dipolar adduct **10**. The conversion **2** → **3**, which also involves a loss of $N_2$, has been postulated to occur via a 1,3-dipolar adduct.[4] The nitrene complex **11** then reacts with an additional 1 equiv of azide to give a terminal nitrene, **13**, which then collapses to the final product via nucleophilic attack on the coordinated CO (**14**). This sequence of events is very similar to the bridge → terminal carbene conversion **3** → **4**.[5] Regardless of the exact sequence of steps, the terminal nitrene must at some point change its coordination mode from a 2e donor to a 4e donor, a behavior reminiscent of the 1e → 3e interconversion proposed for bent vs. linear nitrosyl groups.

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(15) Selected spectral parameters of **8**: $\nu_{CO}$(KBr) 1935, 1915, 1855, 1795, 1665 $cm^{-1}$; $^1H$ NMR (360 (MHz) $\delta$ 5.41, 5.07 (Cp), 4.22 ($CH_2$ AB mult, $J_{MeH_A}$ = 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 (t, $J$ = 7.10 Hz); $^{13}C\{H\}$ NMR (90.55 MHz) $\delta$ 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 ($CH_3$). (All NMR spectra were recorded in $C_6D_6$ at 30 °C.)

(16) Crystal data for **8**: $a$ = 11.144 (2), $b$ = 7.497 (1), $c$ = 28.939 (7) Å; $\beta$ = 95.13 (2)°; $V$ = 2408 (1) $Å^3$; $Z$ = 4; space group $P2_1/c$ (No. 14); $R$ = 0.048 on 1755 reflections with $I \geq 3\sigma(I)$ (full-matrix anisotropic refinement).

(17) This type of coordination was reported recently for the adducts $M_2(RC(O)C(N_2)R')$, suggesting the generality of this reaction type for **1** and $\beta$-carbonyl diazoalkanes: Hermann, W. A.; Kriechbaum, G. W.; Ziegler, M.; Pfisterer, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 707.

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(19) The 1:1 adduct may be observed spectroscopyically, but its lability and high reactivity toward $ArN_3$ have so far precluded its isolation in the pure state.

(20) Selected spectral data for **9** (Ar = 4-*t*-$BuC_6H_4$): $\nu_{CO}$(KBr) 1910, 1830, 1620 $cm^{-1}$; $^1H$ NMR (360 MHz) $\delta$ 1.07, 1.22 (*t*-Bu), 5.05, 5.63 (Cp), 6.95 (d), 8.14 (d) ($J$ = 8.70 Hz, ring A), 7.36 (d), 7.39 (d) $J$ = 8.74 Hz, ring B); $^{13}C\{H\}$ NMR (90.5 MHz) $\delta$ 236.9, 234.2 (CO), 208.5 ($sp^2$ CO), 103.5, 93.6 (Cp), 34.8, 34.5 ($CMe_3$), 31.4, 31.1 ($CMe_3$).

(21) Crystal data for **9**: $a$ = 12.724 (3), $b$ = 13.180 (5), $c$ = 21.464 (9) Å; $\beta$ = 101.29 (3)°; $V$ = 3530 (2) $Å^3$; $Z$ = 4; space group $P2_1/c$ (No. 14); $R$ = 0.053 on 3144 reflections with $I > 3\sigma(I)$ (full-matrix anisotropic refinement).

The reactions of **1** with diazoalkanes (and organic azides) show an amazing structural diversity. The nature of the products depends on subtle electronic and steric factors and on the availability of other electron-donor groups adjacent to the terminal nitrogens.[22]

**Acknowledgment.** This work was supported by the National Science Foundation (Grant No. CHE-8206153).

**Supplementary Material Available:** Atomic coordinates (Table I) and crystal data collection statistics (Table II) for $Cp_2Mo_2(CO)_4(\mu\text{-}N_2C(CO_2Et)_2)$ (**8**) and atomic coordinates (Table III) and crystal data collection statistics (Table IV) for $Cp_2Mo_2(CO)_2(NAr)(\mu\text{-}CoN_3Ar)$ (**9**, Ar = 4-*t*-$BuC_6H_4$) (4 pages). Ordering information is given on any current masthead page.

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[22] Since submission of this manuscript, several pertinent papers have emerged: (a) $Cp^*{}_2Mo_2(CO)_4$ + $RC(O)C(N_2)R$: Bell, L. K.; Herrmann, W. A.; Kriechbaum, G. W.; Ziegler, M. L.; Pfisterer, H. *Organometallics* **1982**, *1*, 1673. (b) $Cp^*{}_2Mo_2(CO)_4$ + $Me_2CN_2$: Bell, L. K.; Herrmann, W. A.; Kriechbaum, G. W.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *240*, 381. (c) $Cp^*{}_2Mo_2(CO)_4$ + $CH_2N_2$: Herrmann, W. A.; Bell, L. K. *Ibid.* **1982**, *239*, C4.

Department of Chemistry
The University of Michigan
Ann Arbor, Michigan 48109

**John J. D'Errico**
**Louis Messerle**
**M. David Curtis***

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# Hydrogen Bonding from Coordinated Imidazole in Ferric Porphyrin Complexes. Effect on the Fe(III)/Fe(II) Reduction Potential

*Sir:*

Most heme proteins contain one or more histidine residues bound to the iron through the imidazole imine nitrogen. The acidity of the imidazole NH proton is increased by coordination, e.g., by about 4 $pK_a$ units in methemoglobin and metmyoglobin.[1,2] Several studies involving simple imidazole complexes of ferrous and ferric porphyrins show that hydrogen bonding or deprotonation of the imidazole $N_\delta$–H moiety can have substantial effects on stability constants,[3,4] visible and Raman spectra,[4-7] and addition[8] and substitution[9] kinetics. X-ray structures of several heme proteins suggest that the proximal imidazole NH is hydrogen bonded to electron-rich groups in the protein.[10-13] MO calculations[14] and resonance Raman[15,16] and ESR[17,18] results have also been interpreted in terms of proximal imidazole hydrogen bonding in hemoglobin, cytochrome *c*, and horseradish peroxidase.

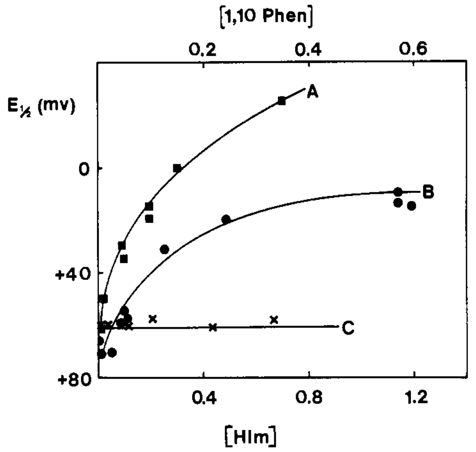

**Figure 1.** Half-wave potentials of the Fe(III)/Fe(II) couple in acetone at room temperature for (A) $[[Fe(TPP)(HIm)_2]Cl] = 1.00 \times 10^{-3}$ M, [HIm] = 0.020 M, [phen] as shown; (B) $[[Fe(TPP)(HIm)_2]Cl] = 1.00 \times 10^{-3}$ M, [HIm] as shown; (C) $[[Fe(TPP)(N\text{-}MeIm)_2]Cl] = 1.00 \times 10^{-3}$ M, [*N*-MeIm] = 0.101 M, [phen] as shown.

Several groups have discussed the possible significance of hydrogen bonding from the proximal imidazole in heme proteins. It has been suggested that such hydrogen bonding allows alterations in the electron density at the metal and thereby affects the kinetics and thermodynamics of trans ligand binding, the Fe(III)/Fe(II) reduction potential, and the ease of protein conformational change.[4,14,19,20] These ideas have been suggested to account in part for the cooperative binding of ligands and for the control of the $O_2/CO$ affinity ratio in hemoglobin.[6,8,14,16,17,21,22]

Hydrogen bonding from the proximal imidazole increases the electron density on the metal and therefore would be expected to stabilize the ferric state (relative to ferrous). Changes in the hydrogen-bond strength with the metal oxidation state may be coupled to tertiary structural changes in the protein.[4,14] This provides a mechanism whereby the protein can modulate the redox potential. A correlation of redox potential with the extent of hydrogen bonding to sulfur has been suggested for iron–sulfur proteins.[23,24]

In this report we show that hydrogen bonding from coordinated imidazole in $[Fe(TPP)(HIm)_2]Cl$ (**1**; TPP = anion of *meso*-tetraphenylporphyrin; HIm = imidazole) has a substantial effect on the Fe(III)/Fe(II) reduction potential. Walker[3] has shown that excess imidazole forms hydrogen bonds to the coordinated HIm in **1**. It is also known[25,26] that 1,10-phenanthroline (phen) forms similar hydrogen bonds to **1**. phen is a particularly useful base for hydrogen-bonding studies with complexes such as **1** because it is not able to replace the imidazole ligands.[25]

The electrochemistry of complexes **1** and $[Fe(TPP)(N\text{-}MeIm)_2]Cl$ (**2**) was studied by cyclic voltammetry at room temperature in acetone solvent. The metalloporphyrin com-

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