Metal–Metal Multiple Bonds. 22. Addition Reactions of Organic Azides and Diethyl Azodicarboxylate with $Cp_2Mo_2(CO)_4$. Molecular Structures of $Cp_2Mo_2(CO)_2(NAr)(\mu\text{-}NNN(Ar)CO)$ (Ar = *p*-*t*-BuC_6H_4) and $[Cp'Mo(CO)_2]_2(\mu\text{-}EtO_2CN_2CO_2Et)$[1]

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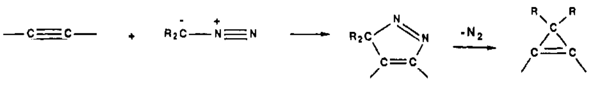
Organic azides react with $Cp_2Mo_2(CO)_4$ (1) to form an adduct, $Cp_2Mo_2(CO)_2(NAr)(\mu\text{-}NNN(AR)CO)$ (5), which contains a terminal nitrene ligand and a bridging ligand formed by coupling of a CO with the azide. This bridge forms a five-membered metallacycle, $\overline{\mathrm{Mo}(\mu\text{-N})\mathrm{NN(Ph)}}\mathrm{CO}$. There is NMR evidence that these adducts are formed from an intermediate μ-nitrene adduct. The dieneophile $EtO_2CN_2CO_2Et$ reacts with 1 with complete disruption of the metal–metal bond to give the adduct $[Cp'Mo(CO)_2]_2(\mu\text{-}\overline{EtO_2CN_2CO_2}Et)$ (7) in which the bridging ligand forms two, fused five-membered metallacycles, $\overline{\mathrm{MoOC(OEt)N}}\mathrm{N}$–. Crystallographic data for **5**·$^1/_2$PhMe (Ar = *p*-*t*-BuC_6H_4): $a = 12.724$ (3) Å, $b = 13.180$ (5) Å, $c = 21.646$ (9) Å; $\beta = 101.29$ (3)°; $V = 3530$ (2) Å^3; $Z = 4$; $\rho_{calcd} = 1.54$ g/mL; space group $P2_1/c$; $R_1 = 0.053$, $R_2 = 0.068$. Crystallographic data for **7**: $a = 7.989$ (2) Å, $b = 9.355$ (3) Å, $c = 9.491$ (4) Å; $\alpha = 112.86$ (3)°, $\beta = 73.60$ (3)°, $\gamma = 92.98$ (3)°; $V = 626.8$ (4) Å^3; $Z = 1$; $\rho_{calcd} = 1.69$ g/mL; space group $P\bar{1}$; $R_1 = 0.031$, $R_2 = 0.028$.

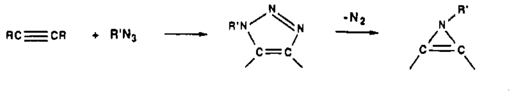
Introduction

It is instructive to compare the reactivity of metal–metal multiply bonded complexes and carbon–carbon multiply bonded compounds with 1,3-dipolar reagents.[2] The chemistry of the latter has been extensively explored, and the factors determining the reaction paths have been well established. We and others have reported previously on the reactivity pattern of the Mo≡Mo triple bond in $Cp_2Mo_2(CO)_4$ (1) and its derivatives with diazoalkanes, prototypal 1,3-dipoles.[1b–d] In contrast to the normal reaction path observed for C≡C bonds (eq 1), the reaction products of 1 with $R_2C{=}N_2$ show a remarkable diversity in their structures which is strongly dependent on the substitution of the Cp groups of 1 and on the diazoalkane.[1b,c]



(1)

A logical extension of the reactions of 1 with 1,3-dipoles is an investigation of the behavior of 1 with organic azides, RN_3, which also react with alkynes in a 1,3-dipolar fashion to give triazoles. Under thermolysis or photolysis, the triazoles may lose N_2 to give azirines (eq 2). The question is: will metal–metal triple bonds react to give μ-nitrene complexes, 3 (a dimetallaazirine), in a similar fashion and can a 1,3-dipolar cycloadduct, 2, be isolated (eq 3)? It was anticipated that complexes, e.g., 3, might be useful synthons for cluster complexes, e.g., $M_2M'(\mu_3\text{-}NR)$.



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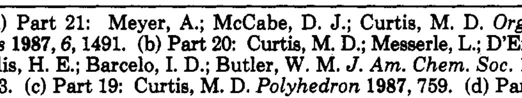
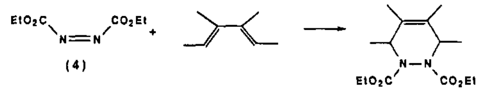


(3)

This paper reports the results of our investigation of the reactivity of 1 toward a variety of azides. A preliminary account of this work has appeared.[3] We also report here the reaction of 1 with the dienophile,[4] diethyl azodicarboxylate, EtOC(O)N=NC(O)OEt (4). Compound 4 reacts with conjugated dienes according to eq 4. The Mo≡Mo triple bond in 1 is expected to have some similarities to dienes since the π-bonding electrons in the M≡M bond may collapse into nonbonding d orbitals, thus allowing the Mo≡Mo unit to accept two to four electrons while maintaining the Mo–Mo bond (eq 5). Donation of six electrons to the dimetal unit completely disrupts the Mo–Mo bond.



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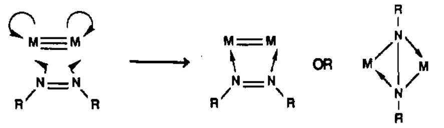

(5)

Results

Reaction of 1 with Organic Azides. Toluene solutions of $Cp_2Mo_2(CO)_4$ (1) react with aryl azides, *p*-$RC_6H_4N_3$ (R = H, Me, t-Bu), at 0 °C over a period of several hours, during which time the color of the mixture changes from brick red to dark green. Gas evolution is also observed during the course of the reaction. After 1 equiv of aryl azide has reacted, the ^1H NMR of the solution (R = *t*-Bu) shows the presence of a complex with two inequivalent Cp groups (δ 5.58, 5.01) and another complex with a single Cp resonance at δ 5.05. Signals due to $Cp_2Mo_2(CO)_6$ (δ 4.68) and unreacted 1 (δ 4.65) are also observed. Addition of a second equivalent of *t*-$BuC_6H_4N_3$ results in the disappearance of the δ 5.05 and 4.65 resonances, leaving only the signals of the final azide adduct and of $Cp_2Mo_2(CO)_6$.

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[1] (a) Part 21: Meyer, A.; McCabe, D. J.; Curtis, M. D. *Organometallics* **1987**, *6*, 1491. (b) Part 20: Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Solis, H. E.; Barcelo, I. D.; Butler, W. M. *J. Am. Chem. Soc.* **1987**, *109*, 3603. (c) Part 19: Curtis, M. D. *Polyhedron* **1987**, 759. (d) Part 18: Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Butler, W. M.; Hay, M. S. *Organometallics* **1986**, *5*, 2283.

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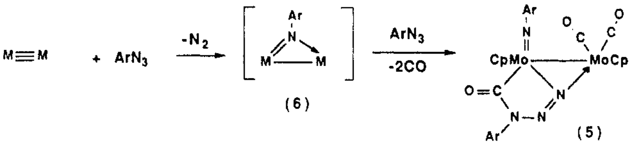
The *tert*-butyl signals of the final product are observed at δ 1.18 and 1.03. The corresponding signal for the intermediate appears at δ 1.19. The intensity of the latter signal parallels that of the δ 5.05 resonance (ratio ca. 1:1 (10:9 calculated)). The addition of 1 equiv, of *tert*-butyl azide to 2 equiv of 1 gave only signals due to the intermediate in addition to those of unreacted 1. Similar behavior with respect to the formation of intermediates was observed in the reactions of 1 with phenyl or *p*-tolyl azide.

Difficulties were encountered in separating the phenyl and *p*-tolyl azide adducts from the $Cp_2Mo_2(CO)_6$ byproduct. However, the more soluble *tert*-butyl derivative could be obtained in a pure state. Its IR spectrum (KBr) showed ν_{CO} peaks at 1910, 1830, and 1620 cm^{-1}. The low frequency of the last peak indicated the presence of an sp^2-type CO group. This conclusion was substantiated by the ^{13}C NMR of the product: two terminal CO resonances at δ 236.9 and 234.2 and an sp^2-CO resonance at δ 208.5 were observed. The analytical data suggested that two azide moieties had added to 1 and that one of them had lost N_2.

The structure of the adduct 5 (Ar = *p*-*t*-BuC_6H_4–), unequivocally established by a single-crystal X-ray structure determination (see below), is shown in eq 6 (M = $Mo(CO)_2Cp$).



(6)

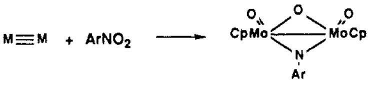
The intermediate μ-nitrene complex 6 is believed to be responsible for the extra peaks in the ^1H NMR spectra observed after the addition of 1 equiv of aryl azide, at which point the ratio of 6:5 is ca. 1:2. Intermediates 6 react with ArN_3 at approximately the same rate as does 1 and could not be obtained pure. The second product $Cp_2Mo_2(CO)_6$ is formed by the reaction of 1 with the CO liberated in the second step of reaction 6 (eq 7).

$$M{\equiv}M + 2CO \longrightarrow Cp_2Mo_2(CO)_6 \qquad (7)$$

The salient features of the structure of 5 are (1) a terminally bound nitrene ligand bonded to one Mo atom and (2) the incorporation of one carbonyl with one molecule of azide to form a ligand which then binds to the dimetal fragment as shown to form a five-membered metallatriazalone in which one nitrogen bridges the Mo–Mo bond.

Herrmann et al.[6] have shown that alkyl azides form the same type of products as the aryl azides.

Benzoyl azide and *p*-toluenesulfonyl azide gave only $Cp_2Mo_2(CO)_6$ and brown, intractable precipitates when allowed to react with 1. *p*-$(O_2N)C_6H_4N_3$ and 1 gave a complex mixture which appeared to contain Mo=O bonds (ν = 895 cm^{-1}). Alper et al.[7] have shown that nitroarenes react with 1 as shown in eq 8, so a complex mixture from the reaction with nitrophenyl azide is not a surprising result.



(8)

No reaction between 1 and NaN_3 or LiN_3 was observed at 25 °C, and the organometallic azide $CpFe(CO)_2N_3$ gave a complex mixture from which only the dimers $Cp_2Mo_2(CO)_6$ and $Cp_2Fe_2(CO)_4$ could be isolated in pure form.

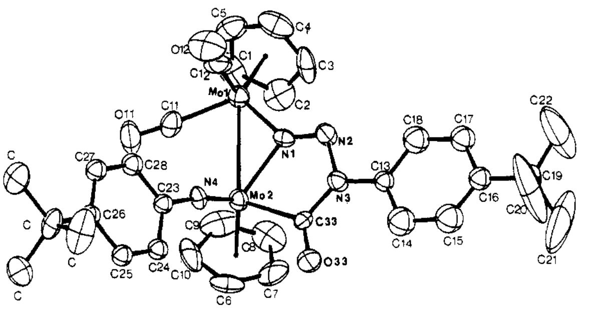
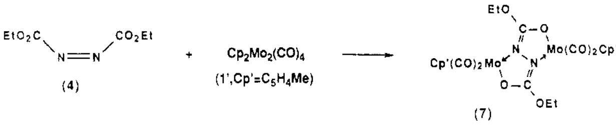


Figure 1. ORTEP plot (50% thermal ellipsoids) and numbering scheme of $Cp_2Mo_2(CO)_2(NAr)(\mu\text{-}N_3(Ar)CO)$ (5; Ar = *p*-*t*-BuC_6H_4).

Reaction of 1 with Azo Dienophiles. The dimer $Cp'Mo_2(CO)_4$ (1′, Cp′ = C_5H_4Me) reacted with an equimolar amount of ethyl azodicarboxylate, 4, in toluene solution at −23 °C according to eq 9.



(9)

The structure of the addduct 7 was determined by X-ray crystallography (see below). Complex 7 forms green solutions in aromatic or ether solvents and may be obtained as a black, crystalline complex in nearly quantitative yield.

The IR spectrum of 7 shows two strong absorptions at ca. 1940 and 1850 cm^{-1} due to the terminal carbonyl groups and further peaks at 1530, 1410, 1385, and 1343 cm^{-1}. The latter are ascribed to the C=N and C—O stretches of the coordinated azodicarboxylate. The lack of absorptions in the region 1600–1700 cm^{-1} is consistent with the absence of ketonic carbonyls in the complex.

The ^1H NMR spectrum of 7 has peaks at δ 1.00 (t) and 3.94 (q, J = 7.1 Hz) due to the equivalent ethyl groups and multiplets at δ 4.77, 4.82, 4.88, and 5.08 (ABCD pattern) due to the diastereotopic protons of the equivalent Cp′ groups. Peaks of interest in the ^{13}C NMR spectrum are found at δ 263.5 and 260.9 (terminal CO groups) and δ 168.2 (sp^2 CO). The latter is in the range expected for organic esters.[8]

The reactions between 4 and the triply bonded dimers $Cp_2W_2(CO)_4$ and $Cp_2Cr_2(CO)_4$ were also investigated. The tungsten complex reacted immediately at −23 °C to give an intractable brown precipitate. The chromium dimer reacted only upon heating to 50 °C for several hours to form an insoluble, oily, green solid which could not be adequately characterized. Intractable brown precipitates were also obtained from 1 and 4-phenyl-1,2,4-triazoline-3,5-dione at −23 °C.

Structural Results and Discussions. $Cp_2Mo_2(\mu\text{-}(CO)(NAr)N_2)(NAr)(CO)_2$ (5, Ar = *p*-*t*-BuC_6H_4–). Figure 1 shows an ORTEP plot of the molecular structure of 5 with the numbering scheme, and a view down the Mo–Mo bond is shown in Figure 2. Table I lists crystallographic data, Table II lists the atomic coordinaters, and selected bond distances and angles are given in Table III.

The Mo–Mo distance (2.904 (1) Å) is indicative of a single bond between the two molybdenum atoms. This bond is symmetrically bridged by the γ-nitrogen (N1) of the coordinated azide fragment. The Mo–N1 distances (1.991 (8) and 2.042 (8) Å) are consistent with single Mo–N

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(7) Alper, H.; Petrignani, J.-F.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 1701.

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Table I. X-ray Crystallographic Data for Compounds 5 (Ar = *p*-*t*-BuC_6H_4) and 7

	5·$^1/_2$PhMe	7
color	black	black (transmits red)
formula	$C_{36.5}H_{40}Mo_2N_4O_3$	$C_{22}H_{24}Mo_2N_2O_8$
mol wt	792.27	636.06
a, *b*, *c*, Å	12.724 (3), 13.180 (5), 21.646 (9)	7.989 (2), 9.355 (3), 9.491 (4)
α, β, γ, deg	90.0, 101.29 (3), 90.0	112.86 (3), 73.50 (3), 92.98 (3)
Z, *V* (Å^3)	4, 3530 (2)	1, 626.8 (4)
ρ_{calcd}, g/mL	1.54	1.69
space group	$P2_1/c$	$P\bar{1}$
cryst dimen, mm	not measured (irregular)	0.22 × 0.22 × 0.26
radiatn	Mo Kα	Mo Kα
takeoff angle, deg	4	4°
μ (Mo Kα), cm^{-1}	7.4	10.2
scan speed, deg/min	2–15 (variable)	2–15 (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°
background/scan time	0.8	0.8
std reflctns	600, 271, 208	210, 0$\bar{2}$2, 003
2θ limit (deg)	45	50
reflctns	9141 (3144 with $I > 3\sigma(I)$)	2369 (2204 with $I > 3\sigma(I)$)
N_0/N_v	9.27	11.6
R_1, R_2^{a}	0.053, 0.068	0.031, 0.028

^{a} $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

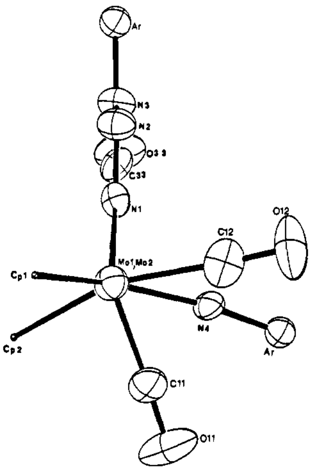

Figure 2. ORTEP plot of 5 as viewed down the Mo1→Mo2 bond vector.

bonds[9] and are similar to Mo-N(bridge) bond distances in related complexes.[6,10]

Table II. Fractional Atomic Coordinates for $Cp_2Mo_2(CO)_2(NAr)(\mu\text{-}CON_3Ar)\bullet{}^1/_2PhMe$ (5; Ar = 4-*t*-$BuC_6H_4^-$)

atom	*x*	*y*	*z*
Mo1	−0.0254 (1)	0.0132 (1)	0.1341 (0)
Mo2	0.1832 (1)	0.0573 (1)	0.2119 (0)
C1	−0.2033 (9)	−0.0365 (11)	0.1040 (8)
C2	−0.1680 (10)	−0.0703 (10)	0.1649 (7)
C3	−0.0874 (11)	−0.1458 (10)	0.1651 (8)
C4	−0.0774 (10)	−0.1538 (9)	0.1030 (8)
C5	−0.1482 (12)	−0.0852 (12)	0.0662 (6)
C6	0.2808 (11)	0.0498 (12)	0.3145 (5)
C7	0.2812 (12)	−0.0477 (13)	0.2945 (6)
C8	0.1779 (15)	−0.0827 (10)	0.2848 (6)
C9	0.1091 (11)	−0.0086 (14)	0.2988 (6)
C10	0.1767 (14)	0.0801 (10)	0.3199 (5)
C11	−0.0334 (8)	0.1285 (9)	0.1910 (6)
O11	−0.0465 (7)	0.1945 (7)	0.2234 (5)
C12	−0.0233 (9)	0.1194 (10)	0.0711 (6)
O12	−0.0180 (8)	0.1809 (7)	0.0326 (5)
N1	0.1260 (6)	−0.0130 (6)	0.1272 (4)
N2	0.1793 (7)	−0.0580 (7)	0.0905 (4)
N3	0.2898 (6)	−0.0507 (7)	0.1160 (4)
N4	0.2058 (6)	0.1839 (6)	0.1945 (4)
C33	0.3195 (8)	0.0021 (8)	0.1729 (5)
O33	0.4129 (6)	0.0156 (6)	0.1966 (4)
C13	0.3531 (8)	−0.1008 (8)	0.0798 (5)
C14	0.4642 (10)	−0.0959 (10)	0.0931 (6)
C15	0.5243 (10)	−0.1495 (10)	0.0537 (6)
C16	0.4791 (8)	−0.2071 (9)	0.0038 (5)
C17	0.3692 (9)	−0.2112 (9)	−0.0091 (6)
C18	0.3066 (10)	−0.1602 (10)	0.0283 (6)
C19	0.5455 (9)	−0.2681 (9)	−0.0350 (6)
C20	0.6241 (18)	−0.2016 (16)	−0.0596 (11)
C21	0.6161 (22)	−0.3389 (20)	0.0088 (11)
C22	0.4869 (14)	−0.3189 (18)	−0.0879 (12)
C23	0.2300 (8)	0.2853 (8)	0.1922 (5)
C24	0.3267 (8)	0.3226 (8)	0.2231 (5)
C25	0.3511 (8)	0.4253 (8)	0.2209 (5)
C26	0.2771 (8)	0.4941 (8)	0.1865 (5)
C27	0.1817 (8)	0.4563 (8)	0.1554 (5)
C28	0.1572 (8)	0.3522 (8)	0.1584 (5)
C29	0.3077 (9)	0.6069 (8)	0.1847 (6)
C30	0.2138 (11)	0.6723 (9)	0.1519 (6)
C31	0.3998 (11)	0.6149 (10)	0.1473 (8)
C32	0.3450 (11)	0.6470 (10)	0.2535 (7)
C34	0.0060 (15)	0.4095 (14)	−0.0055 (8)
C35	0.0934 (32)	0.4279 (32)	−0.0273 (18)
C36	0.1528 (22)	0.5232 (22)	−0.0286 (13)
C37	0.0907 (28)	0.5893 (29)	−0.0184 (16)
C38	0.0619 (29)	0.5170 (34)	−0.0109 (18)

The α-nitrogen of the coordinated azide group is bonded to a carbonyl group, in turn bonded to the molybdenum, to give a five-membered chelate ring. Similar structures have been reported for a triosmium cluster[11] and a manganese A-frame complex.[12] As shown in Figure 2, the two metal atoms and the atoms of the five-membered ring all lie in one plane. The N1—N2 bond length 1.28 (1) Å suggests significant multiple-bond character (N=N double-bond length = 1.25 Å[13]), and the N2—N3 separation, 1.41 (1) Å, is somewhat shorter than the N—N distance in N_2H_4.[14] A contraction in the N-N single-bond distance between sp^2-hybridized N atoms is expected. The C33—O33 distance, 1.21 (1) Å, is as expected for a C=O double bond. The planarity of the ring and the individual bond distances suggest the "lone pair" on N3 is delocalized over the metallacycle.

In addition to the aryl azide molecule that forms the metallacycle, another azide molecule has reacted with loss of N_2 to give a nitrene ligand coordinated to Mo2. The 18-electron rule requires this terminal nitrene to donate four electrons to Mo2: $\mathrm{ArN}\equiv\mathrm{Mo}$. The Mo2–N4 distance, 1.746 (8) Å, is consistent with a bond order of 3.[9] The sp hybridization of N4 is also supported by the Mo2–N4–C23 angle, 169.9 (5)°. The deviation from 180° is presumably caused by steric interactions between the aryl ring and the core of the dimolybdenum complex. For comparison, in the molecule $(Et_2NCS_2)_2Mo(NPh)_2$, one nitrene ligand is a 4e donor (Mo–N–Ph = 169°) and one is a 2e donor (Mo–N–Ph = 139°).[15]

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Table III. Bond Distances (Å) and Angles (deg) for $5 \bullet {}^1/_2$PhMe

Bond Distances			
Mo1–Mo2	2.904 (1)	N3–C33	1.392 (13)
Mol–N1	1.991 (8)	N4–C23	1.374 (12)
Mo2–N1	2.042 (8)	C33–O33	1.211 (11)
Mo2–N4	1.746 (8)	N3–C13	1.390 (12)
Mo1–C1	2.323 (11)	C13–C14	1.388 (16)
Mo1–C2	2.325 (9)	C13–C18	1.388 (15)
Mo1–C3	2.379 (11)	C14–C15	1.432 (17)
Mol–Cr	2.357 (11)	C15–C16	1.346 (16)
Mo1–C5	2.315 (12)	C16–C17	1.373 (15)
Mo2–C6	2.310 (11)	C17–C18	1.407 (16)
Mo2–C7	2.398 (11)	C16–C19	1.525 (15)
Mo2–C8	2.429 (11)	C19–C20	1.502 (21)
Mo2–C9	2.410 (11)	C19–C21	1.494 (24)
Mo2–C10	2.355 (11)	C19–C22	1.400 (21)
Mo1–C11	1.963 (12)	C23–C24	1.370 (13)
Mo1–C12	1.951 (13)	C23–C28	1.377 (14)
Mo2–C33	2.193 (10)	C24–C25	1.392 (14)
C1–C2	1.372 (18)	C25–C26	1.406 (14)
C1–C5	1.335 (19)	C26–C27	1.360 (14)
C2–C3	1.428 (18)	C27–C28	1.411 (14)
C3–C4	1.368 (18)	C26–C29	1.540 (15)
C4–C5	1.405 (19)	C29–C30	1.529 (16)
C6–C7	1.356 (19)	C29–C31	1.548 (16)
C6–C10	1.409 (18)	C29–C32	1.551 (18)
C7–C8	1.369 (19)	C34–C35	1.311 (38)
C8–C9	1.384 (19)	C34–C38	1.600 (42)
C9–C10	1.469 (20)	C34–C38	1.311 (49)
C11–O11	1.147 (13)	C35–C36	1.469 (46)
C12–O12	1.169 (14)	C36–C37	1.224 (40)
N1–N2	1.282 (11)	C36–C38	1.288 (41)
N2–N3	1.408 (11)	C37–C38	1.046 (45)

Bond Angles			
Mo1–N1–Mo2	92.08 (34)	C1–C5–C4	108.85
Mo2–N4–C23	169.87 (50)	C7–C6–C10	110.87
N1–N2–N3	109.78 (78)	C6–C7–C8	107.74
N2–N3–C33	103.15 (38)	C7–C8–C9	110.97
N3–C33–Mo2	113.69 (68)	C8–C9–C10	105.77
C33–Mo2–N1	71.34 (35)	C9–C10–C6	104.62
N3–C33–O3	121.24 (95)	C13–C14–C15	119.69
Mo1–C11–O11	174.69 (99)	C14–C15–C16	123.63
Mo1–C12–O12	176.86 (85)	C15–C16–C17	116.22
Mo2–Mo1–C11	68.95 (31)	C16–C17–C18	122.30
Mo2–Mo1–C12	96.86 (30)	C17–C18–C13	121.54
N1–Mo1–Mo2	44.66 (22)	C18–C13–C14	116.59
N1–Mo2–Mo1	43.26 (22)	C23–C24–C25	121.12 (96)
N2–N1–Mo1	139.68 (66)	C24–C25–C26	120.94 (94)
N2–N1–Mo2	128.15 (63)	C25–C26–C27	117.57 (98)
C5–C1–C2	108.10	C26–C27–C28	121.17 (99)
C1–C2–C3	109.22	C27–C28–C23	120.92 (97)
C2–C3–C4	104.79	C28–C23–C24	118.27 (97)
C3–C4–C5	109.02		

Table IV. Fractional Atomic Coordinates for $[Cp'Mo(CO)_2]_2(\mu\text{-}EtO_2CN_2CO_2Et)$ (7)

atom	*x*	*y*	*z*
Mo	−0.0617 (0)	0.6513 (00)	0.3010 (0)
C2	−0.4381 (7)	0.5052 (07)	0.1828 (6)
C3	−0.3614 (5)	0.5805 (06)	0.3198 (5)
C4	−0.3501 (5)	0.7419 (06)	0.4019 (5)
C5	−0.2781 (6)	0.7629 (06)	0.5284 (5)
C6	−0.2371 (6)	0.6137 (07)	0.5187 (5)
C7	−0.2916 (6)	0.5030 (06)	0.3910 (5)
N8	−0.0383 (4)	0.5764 (03)	0.0491 (3)
C9	−0.1014 (5)	0.6352 (04)	−0.0307 (4)
O10	−0.0955 (3)	0.5672 (03)	−0.1768 (3)
O11	−0.1816 (4)	0.7775 (03)	0.0544 (3)
C12	−0.2354 (8)	0.8574 (05)	−0.0287 (6)
C13	−0.2995 (11)	1.0174 (07)	0.0872 (8)
C14	0.0139 (6)	0.8448 (05)	0.2807 (5)
O15	0.0596 (6)	0.9608 (04)	0.2728 (5)
C16	0.1199 (6)	0.7213 (05)	0.4098 (5)
O17	0.2252 (5)	0.7713 (05)	0.4762 (5)

Table V. Bond Distances (Å) and Angles (deg) for 7

Bond Distances			
C3–Mo	2.427 (3)	C7–C3	1.389 (6)
C4–Mo	2.296 (4)	C5–C4	1.417 (6)
C5–Mo	2.251 (4)	C6–C5	1.412 (7)
C6–Mo	2.288 (4)	C7–C6	1.416 (6)
C7–Mo	2.408 (4)	C9–N8	1.303 (4)
N8–Mo	2.168	O10–C9	1.269 (4)
N8–N8′	1.423 (7)	O11–C9	1.340 (4)
C14–Mo	1.942 (4)	O13–C12	1.481 (6)
C16–Mo	1.955 (4)	O15–C14	1.151 (5)
C4–C3	1.417 (6)	O17–C16	1.163 (5)
O10–Mo	2.168 (6)		

Bond Angles			
C4–Mo–C3	34.8 (1)	C16–Mo–N8	128.6 (1)
C5–Mo–C3	58.7 (1)	C16–Mo–C14	72.7 (2)
C5–Mo–C4	36.3 (1)	C4–C3–Mo	67.6 (2)
C6–Mo–C3	57.9 (1)	C7–C3–Mo	72.6 (2)
C6–Mo–C4	59.6 (2)	C7–C3–C4	107.6 (3)
C6–Mo–C5	36.2 (2)	C3–C4–Mo	77.6 (2)
C7–Mo–C3	33.4 (1)	C5–C4–Mo	70.1 (2)
C7–Mo–C4	57.5 (2)	C5–C4–C3	108.3 (4)
C7–Mo–C5	58.6 (2)	C4–C5–Mo	73.6 (2)
C7–Mo–C6	35.0 (1)	C6–C5–Mo	73.3 (2)
N8–Mo–C3	83.8 (1)	C6–C5–C4	107.4 (4)
N8–Mo–C4	98.7 (1)	C5–C6–Mo	70.5 (2)
N8–Mo–C5	135.0 (1)	C7–C6–Mo	77.1 (2)
N8–Mo–C6	138.5 (1)	C7–C6–C5	107.6 (4)
N8–Mo–C7	103.7 (1)	C3–C7–Mo	74.1 (2)
C14–Mo–C3	121.3 (2)	C6–C7–Mo	67.9 (2)
C14–Mo–C4	92.2 (2)	C6–C7–C3	109.0 (4)
C14–Mo–C5	95.5 (2)	C9–N8–Mo	132.6 (2)
C14–Mo–C6	128.9 (2)	N8′–N8–C9	110.9 (3)
C14–Mo–C7	149.5 (2)	N8′–NA–Mo	115.8 (2)
C14–Mo–N8	82.9 (1)	O10–C9–N8	125.3 (3)
C16–Mo–C3	147.4 (1)	O11–C9–N8	115.0 (3)
C16–Mo–C4	126.1 (1)	O11–C9–O10	119.7 (3)
C16–Mo–C5	92.6 (1)	O15–C14–Mo	178.1 (3)
C16–Mo–C6	90.0 (2)	O17–C16–Mo	176.2 (4)
C16–Mo–C7	120.2 (2)		

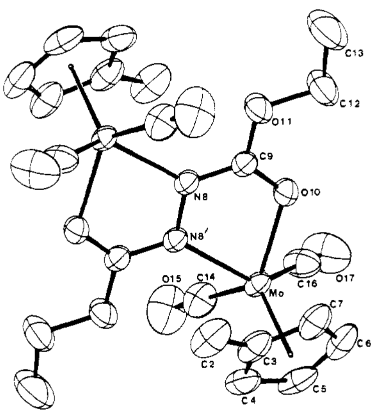

Figure 3. ORTEP plot (50% thermal ellipsoids) and numbering scheme of $[Cp'Mo(CO)_2]_2(\mu\text{-}EtO_2CN_2CO_2Et)$ (7).

The carbonyl group C11–O11 adopts a weakly semibridging position and is probably responsible for the low CO stretching frequency observed at 1830 cm^{-1}.

$[Cp'(CO)_2Mo]_2(\mu\text{-}EtO_2CNNCO_2Et)$ (7, Cp′ = C_5H_4Me). The molecular structure of 7 has a crystallographically imposed inversion center in the solid state. The Mo–Mo separation (5.1 Å) is well outside a bonding distance; hence, the coordinated azodicarboxylate ligand donates a total of six electrons to the dimetal fragment.[1c] As shown in Figure 3, this is accomplished by incorporation

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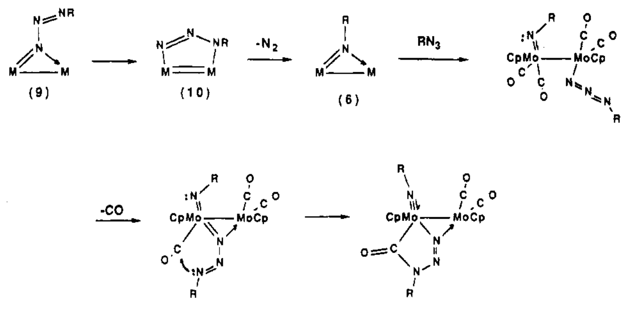
(15) Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Abstracts of Papers*, 176th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, 1978; INOR 38.

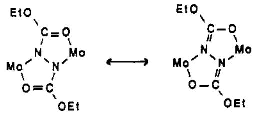
Scheme I



of the carboxyl oxygen atoms, in addition to the N atoms, into the coordination sphere of the Mo atoms. Table I lists crystallographic data, and Tables IV and V show the atomic coordinates and selected bond distances and angles, respectively.

In the free azodicarboxylate ligand, the two N atoms are joined by a double bond; but in complex 7, the N–N distance, 1.423 (7) Å, is in the range expected for a N(sp^2)–N(sp^2) single bond. the C—N distance, 1.303 (4) Å, is longer than C(sp^2)=N double bonds in organic molecules (1.23–1.26 Å[13]) but is similar to C=N bond distances found in related organometallic complexes (1.29–1.31 Å).[16]

The endocyclic C9—O10 bond length, 1.269 (4) Å, is long for a C=O double bond (ca. 1.22 Å), while the exocyclic C9–O11 distance, 1.340 (4) Å, is in the range found for organic esters.[17] These parameters suggest that the electronic structure of the coordinated azodicarboxylate is best expressed as lying between those of the canonical extremes shown below:



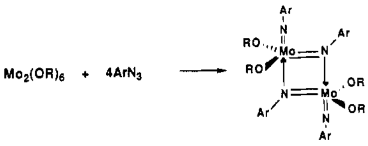
The Mo–N and Mo–O coincidentally have the same length, 2.168 (8) Å, which is longer than corresponding bonds in similar compounds.[16b,d] We ascribe this lengthening to the unfavorable bite angle of the azodicarboxylate ligand when it is complexed on both sides of the N–N bond, as opposed to the cases where only one metal is coordinated to one side of the azodicarboxylate. In the free ligand, the N···O separation may be estimated to be about 2.6 Å, whereas this distance is about 3.6 Å in complex 7.

The Cp′ rings in complex 7 show an interesting tilt as a consequence of the fact that there are two good π-donors (N and O) trans to two good π-acceptors (CO). The average of the Mo–C_4, –C_5, and –C_6 bond lengths is 2.28 [2] Å. The remaining two Mo–C(Cp) distances are considerably longer, Mo–C3 = 2.43 and Mo–C7 = 2.41 Å. The C3 and C7 carbon atoms are more or less trans to the CO ligands, and the large disparity in the bonding between the Mo and the CO and N or O groups causes the observed tilt of the Cp ring. This effect was also observed in the η^2-carbonato complex ion $CpMo(CO)_2(\eta^2\text{-}O_2CO)^-$, and a molecular orbital interpretation of the effect has been offered.[18,19]

Discussion

Reaction of 1 with RN_3. A possible mechanism for the formation of 5 is shown in Scheme I. By analogy with the reaction of 1 with diazoalkanes, the first step is postulated to be the formation of a bridging (N-terminal) azide complex 8 (cf. $M_2(\mu\text{-}N_2CR_2)$[1c,d]). This complex may then rearrange to the 1,3-dipolar cycloadduct 9, which loses N_2 to give the μ-nitrene complex 6 (eq 6 and Scheme I). Complex 6 is believed to be the intermediate observed when only 1 equiv of RN_3 is allowed to react with 1. Complex 6 then adds a second equivalent of azide with bridge opening, followed by loss of CO and nucleophilic attack of the α-nitrogen of the coordinated azide on a carbonyl ligand to give the final structure. A similar attack of coordinated diazomethane on a carbonyl was postulated previously.[12]

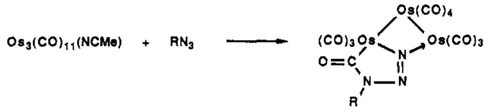
In connection with the proposed mechanism, it is interesting to note that several other complexes with metal–metal multiple bonds have been shown to form nitrene or nitrene-derived complexes when allowed to react with organic azides. Thus, $Mo_2(OR)_6$ (R = *tert*-butyl) reacts according to eq 10[20] and the triosmuim cluster $Os_3(CO)_{10}(\mu\text{-}H)_2$(*Os*=*Os*) according to eq 11.[21] In the latter case, the nitrene inserts into an Os–H bond to give a μ-amido ligand.



(10)

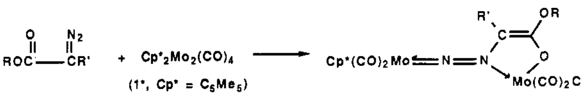
(11)

In contrast, the saturated cluster $Os_3(CO)_{11}(NCMe)$ reacts with RN_3 *without* loss of N_2 according to eq 12.[11] The loss of N_2 represented in eq 10 and 11 may proceed via 1,3-dipolar cycloadducts afforded by the metal–metal unsaturation whereas with the saturated cluster (eq 12), a low-energy pathway to a 1,3-dipolar cycloadduct is not available.



(12)

Reaction of 1 with $EtO_2CN{=}NCO_2Et$. The reaction of diethyl azodicarboxylate with 1′ has some striking similarities to the reaction of $Cp_2{}^*Mo_2(CO)_4$ (1*, $Cp^* = C_5Me_5$) with α-diazo esters, $RO_2CCR'N_2$.[1d,22] In most of the latter reactions, the carboxyl oxygen becomes coordinated to one Mo atom with complete breakage of the Mo–Mo bond (eq 13).



(13)

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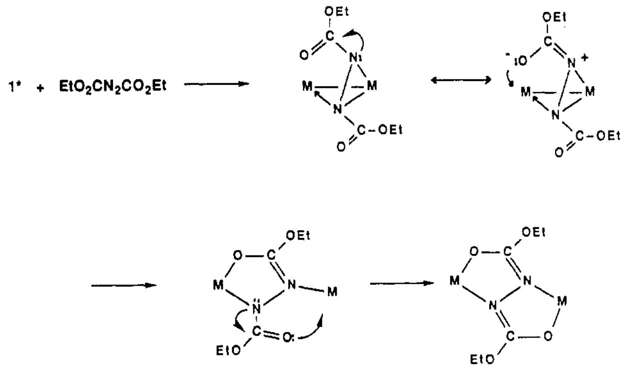
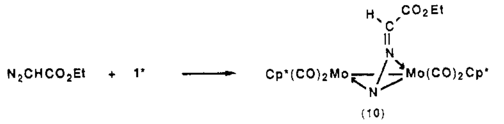
Scheme II



In the case of ethyl diazoacetate, however, the addduct **10** was isolated.[1d] The reactions represented by eq 13 and 14 and theoretical considerations of the reactivity patterns



(10) (14)

of the Mo≡Mo triple bonds in **1**,[1c] suggest that the formation of **7** may occur through an intermediate with a structure similar to that of **10** (Scheme II).

Conclusions

The reaction of organic azides, examples of 1,3-dipolar reagents, with the Mo≡Mo triple bond in $Cp_2Mo_2(CO)_4$ do not give isolable 1,3-dipolar cycloadducts, in contrast with the reactions of 1,3-dipoles with C≡C triple bonds. This difference in reactivity has been ascribed to the ease with which the π-electrons in the metal–metal triple bond can collapse into nonbonding d orbitals that are not available to carbon.[1c] However, the formation of coordinated nitrenes may proceed through 1,3-dipolar cycloadduct intermediates.

Experimental Section

All of the experiments were performed under an inert atmosphere employing a dual nitrogen/vacuum manifold and standard Schlenk equipment. Toluene, benzene, ether, and THF were distilled from sodium benzophenone. Methylene chloride was distilled from P_4O_{10}. Aryl azides were prepared by diazotization of the corresponding amine, followed by addition of NaN_3.[23]

Infrared spectra were recorded on a Perkin-Elmer 457 or 1330 spectrometer. Nuclear magnetic resonance spectra were recorded on a Bruker WM-360. Mass spectra were obtained on a Finnigan automated gas chromatography/EI-CI mass spectrometer system. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or by the Spang Microanalytical Laboratory, Eagle Harbor, MI. All melting points were taken by using capillaries sealed under vacuum.

Synthesis of $Cp_2Mo_2(CO)_2(NAr)(\mu\text{-}N_3(CO)Ar)$ (5, Ar = *p*-*t*-BuC_6H_4–). In a 100-mL Schlenk flask, 2.3 mmol (1.0 g) of $Cp_2Mo_2(CO)_4$ was dissolved in 10 mL of toluene and cooled to 0 °C. To this solution was added a solution of 4.6 mmol (0.81 g) of *p*-*tert*-butylphenyl azide in 1 mL of toluene via syringe. Gas evolution was observed, and the solution turned from brick red to dark green. The reaction mixture was allowed to warm to room temperature. After addition of 20 mL of hexane, the mixture was cooled to 0 °C. $Cp_2Mo_2(CO)_6$ precipitated and was removed by filtration. The filtrate was concentrated in vacuo, then 10 mL of hexane was added, and the mixture was cooled to −23 °C. A black microcrystalline solid was collected by filtration, washed with hexane, and dried under vacuum. IR (KBr, cm^{-1}): ν_{CO} 1910, 1830; ν_{CO} 1620. ^1H NMR (360 MHz, C_6D_6, 30 °C): δ 1.03, 1.18 (*t*-Bu), 5.01, 5.58 (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). $^{13}C\{^1H\}$ NMR (90.5 MHz, C_6D_6, 30 °C): δ 236.9, 234.2 (CO), 208.5 (sp^2-CO), 103.5, 93.6 (Cp), 34.8, 34.5 (CMe_3), 31.4, 31.3 (CMe_3). Anal. Calcd for $C_{33}H_{36}Mo_2N_4O_3 \cdot 0.5C_7H_8$: C, 56.59; H, 5.20; N, 7.23. Found: C, 56.72; H, 5.31; N, 7.14. There were peaks due to toluene in both the ^1H and ^{13}C NMR, the integration of which indicated 0.5 mol of C_7H_8/mol of **5**. Melting point (sealed capillary): 125–126 °C.

Reaction of $Cp_2Mo_2(CO)_4$ with $RC_6H_4N_3$ (R = H, Me). Phenyl azide and *p*-tolyl azide reacted with $Cp_2Mo_2(CO)_4$ (2:1 molar ratios) in toluene solution to afford, after workups similar to that described above, black crystalline solids. ^1H NMR spectra indicated these solids contained 8–10% $Cp_2Mo_2(CO)_6$ which, because of its similar solubility, could not be separated from the azide adducts by recrystallization or by chromatography over Florosil. However, the spectroscopic data leave little doubt that the phenyl and *p*-tolyl azide adducts have the same structure as the *p*-*tert*-butylphenyl azide adduct. For the phenyl azide adduct: ^1H NMR δ 5.10, 5.50 (Cp, 1:1), 7.0, 7.2 (m, Ph). The NMR also showed peaks for toluene of crystallization. IR: ν_{CO} 1905, 1843, 1635 cm^{-1}. Anal. Calcd for $Cp_2Mo_2(CO)_2(NPh)(N_3(CO)Ph) \cdot {}^1/_2PhMe$ + 8.5% (NMR) $Cp_2Mo_2(CO)_6$: C, 50.83; H 3.5; N, 7.91. Found: C, 51.25; H, 4.10; N, 7.63. Essentially identical spectral data were obtained for **5** (Ar = *p*-tolyl).

Synthesis of $[Cp'Mo(CO)_2](\mu\text{-}EtO_2CN{=}NCO_2Et)$ (7). In a 100-mL Schlenk flask, 1.08 mmol (0.5 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 1.08 mmol (0.17 mL) of diethyl azodicarboxylate in 10 mL of toluene via a dropping funnel over a 10-min period. The reaction mixture was maintained at −23 °C for 12 h, during which time the color changed from brick red to green. The solution was concentrated under vacuum, hexane was added, and the mixture was cooled to −23 °C overnight. A black microcrystalline solid was filtered cold, washed with hexane, and dried under vacuum. The isolated yield based on $Cp'_2Mo_2(CO)_4$ was 85%. Compound **7** melts >280 °C. Anal. Calcd for $C_{22}H_{24}Mo_2N_2O_8$: C, 41.53: H, 3.81; N, 4.40. Found: C, 40.77; H, 3.76; N, 4.42. IR spectrum (KBr, cm^{-1}): ν_{CO} 1940, 1850; $\nu_{C=O}$ 1530; $\nu_{C=N}$ 1488; $\nu_{C\text{-}OR}$ 1440, 1385, 1343. IR spectrum (C_7H_8, cm^{-1}): ν_{CO} 1947, 1841; $\nu_{C=O}$ 1542; $\nu_{C=N}$ 1479; $\nu_{C\text{-}OR}$ 1436, 1381, 1344. ^1H NMR (360 MHz, 30 °C, C_6D_6): δ 4.77–5.08 ($C_5H_4CH_3$, ABCD); 3.94 (CH_2, q, J_{HH} = 7.13 Hz); 1.49 ($C_5H_4CH_3$, s); 1.00 (CH_3, t, J_{HH} = 7.13 Hz). $^{13}C\{^1H\}$ NMR (90.55 MHz, 30 °C, C_6D_6): δ 263.5, 260.9 (CO); 168.2 (sp^2-CO); 124.8 (ipso C_5H_4Me); 100.8, 96.8, 89.5, 89.1 (Cp′); 14.8 (C_5H_4Me); 13.0 (CH_2CH_3).

Crystal Structure Determinations. (a) Compound 5 (Ar = *p*-*t*-BuC_6H_5)·$^1/_2$PhMe. Crystals suitable for X-ray analysis were obtained as a toluene solvate by allowing a toluene/hexane mixture to stand at 0 °C for several days. A crystal was mounted on a Syntex $P2_1$ diffractometer, and the lattice parameters were determined by a least-squares refinement of 15-reflection settings obtained from the automatic centering routine.

Intensity data were obtained at −45 °C by using Mo Kα radiation monochromatized from a graphite crystal. Three standard reflections were measured every 50 reflections. The structure was solved by Patterson and Fourier techniques.[24] An absorption correction was not necessary.

In the refinement of the data, the function $\sum w(|F_o| - |F_c|)^2$ was minimized where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The weight factors w were taken as $w = 4F_o^2|[\sigma^2(F_o)^2 + (PF_o^2)^2]$, where P, the factor preventing overweighting of strong reflections, was set equal to 0.04. All atoms except the carbon atoms of the phenyl rings and the toluene solvate molecule were refined with anisotropic temperature factors.

The crystal contained $^1/_2$ mol of toluene of solvation per molecule of **5**, a result in agreement with the NMR spectra. The toluene molecule was disordered about an inversion center and

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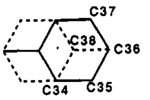
[23] Noelting, E.; Michel, O. *Ber. Deutsch. Chem. Ges.* **1893**, *26*, 86.

[24] Calculations were made on Amdahl 470 or 5890 Computers using the programs: SYNCOR (data reduction by W. Schmonsees), FORDAP (Fourier synthesis by A. Zalkin), ORFLS (least-squares refinement by Busing, Martin, and Levy), ORTEP (thermal ellipsoid plot routine by C. K. Johnson), and PLANES (least-squares planes by D. M. Blow). Scattering factors were obtained from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

was modelled as shown in the diagram below with occupancy factors of $^1/_2$ for C35, C37, and C38. Temperature factors and a list of F_o vs. F_c are in Tables VI and VII (supplementary material), respectively. The largest shift/error on the last cycle for any parameter was less than 1.5. The largest residual in the final difference map was 0.7 e/Å^3.



(b) Compound 7. Single crystals were grown from a toluene solution of 7 at −23 °C. Lattice parameters were determined and intensity data collected as described above. The structure was solved and refined with the SHELX package of crystallographic programs.[25] The final difference map was featureless. Scattering factors were taken from ref 24. Tables VIII and IX (supplementary material) contain the temperature factors and lists of F_o vs. F_c, respectively.

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Registry No. 1, 56200-27-2; 1′, 69140-73-4; 4, 1972-28-7; 5, 84624-70-4; 5·1/2PhMe, 109585-15-1; 5 (Ar = Ph), 84624-68-0; 5 (Ar = *p*-tolyl), 84624-69-1; 7, 109585-16-2; $Cp_2W_2(CO)_4$, 62853-03-6; $Cp_2Cr_2(CO)_4$, 54667-87-7; $Cp_2Mo_2(CO)_6$, 12091-64-4; $CpFe(CO)_2N_3$, 42765-82-2; NaN_3, 26628-22-8; LiN_3, 19597-69-4; *p*-$(O_2N)C_6H_4N_3$, 1516-60-5; $PhCoN_3$, 582-61-6; *p*-$(CH_3)C_6H_4SO_2N_3$, 941-55-9; *p*-(*t*-Bu)$C_6H_4N_3$, 18522-89-9; *p*-$(CH_3)C_6H_4N_3$, 2101-86-2; PhN_3, 622-37-7; 4-phenyl-1,2,4-triazoline-3,5-dione, 4233-33-4.

Supplementary Material Available: Tables of temperature factors for 5·$^1/_2$PhMe and 7 (2 pages); listings of F_o vs. F_c for 5·$^1/_2$PhMe and 7 (21 pages). Ordering information is given on any current masthead page.

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Reaction of Diiron μ-Alkylidyne Complexes with Diazo Compounds

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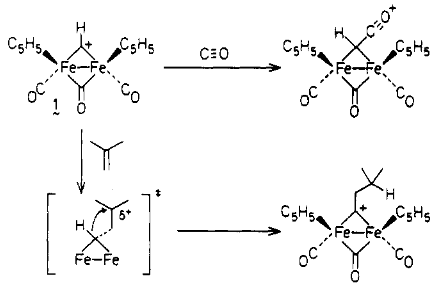
The reaction of μ-methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (1) with ethyl diazoacetate gave the ester-substituted μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCO_2Et)^+PF_6^-$ (2) in 86% yield. 1 also reacted with diazomethane, diazoethane, methyl 2-diazopropionate, and (trimethylsilyl)diazomethane to give similar μ-alkenyl products. μ-Alkenyl complex 2 reacted with the nucleophiles $NEt_4^+[HFe(CO)_4]^-$ and lithium diethyl malonate to give the carbene complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CO_2Et)$ (17) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH(CO_2Et)CH(CO_2Et)_2)$ (16). Reductive dimerization of 2 gave the tetrairon carbene complex $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCHCO_2Et)\}_2$ (25). The structure of 25 was determined by X-ray crystallography, monoclinic space group $P2_1/c$, with unit cell constants a = 12.318 (2) Å, b = 16.443 (2) Å, c = 17.679 (2) Å, β = 105.20 (1)°, and Z = 4.

Introduction

The diiron μ-methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (1) forms 1:1 adducts with nucleophiles such as NMe_3 and CO.[1] 1 also adds the C–H bond of the methylidyne group across the double bond of alkenes in a carbon–carbon bond forming reaction that involves an initial nucleophilic interaction of the alkene and the methylidyne carbon.[2,3]



In a search for new carbon–carbon bond forming reactions of diiron-bridging complexes, we have explored the reactivity of μ-alkylidyne complexes with diazo compounds. We envisioned a process in which nucleophilic attack of a diazo compound on a μ-alkylidyne complex would generate an intermediate that could lose dinitrogen and form a μ-alkenyl complex.

Here we report that this process works efficiently for the μ-methylidyne complex 1 but fails for alkyl- and aryl-substituted μ-alkylidyne complexes. In addition, a novel reductive dimerization of a diiron μ-alkenyl complex to a tetrairon carbene complex was discovered.

Results and Discussion

Reaction of μ-Methylidyne Complex 1 with Diazo Compounds. The diiron methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (1) reacts rapidly with a variety of diazo compounds to produce new μ-alkenyl diiron complexes. When ethyl diazoacetate was added to

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[1] Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 7360–7361.

[2] Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950–4951.

[3] Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043–4053.

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