An Unusual Change in the Bonding Mode of a Bridging Alkylidene Ligand. Structure of $Cp(CO)_3Mo–Mo(CAr_2)(N_2CAr_2)Cp$ (Ar = *p*-Tolyl)

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The bridging alkylidene complex $Cp_2Mo_2(CO)_4(\mu\text{-}CAr_2)$ (Ar = *p*-tolyl) reacts with Ar_2CN_2 to give the terminal alkylidene complex $Cp(CO)_3Mo–Mo(CAr_2)(N_2CAr_2)Cp$ (2) in high yield. In this reaction, the bridging diarylalkylidene ligand changes its bonding mode from bridging to terminal, one carbonyl group is lost, and another is transferred across the Mo–Mo bond, and the diazoalkane ligand becomes bonded to one Mo via a $Mo\equiv N$ triple bond. A mechanism is proposed for this reaction, and the solid-state structure and unusual behavior in solution of 2 are reported. Relevant crystallographic data: $a = 12.247$ (6) Å, $b = 14.462$ (7) Å, $c = 11.486$ (5) Å; $\alpha = 113.22$ (3)°, $\beta = 95.60$ (4)°, $\gamma = 90.32$ (4)°; $V = 1858$ (1) Å^3; $Z = 2$, $\rho_{calcd} = 1.47$ g/mL; space group $P\bar{1}$; $R_1 = 0.053$, $R_2 = 0.054$ on 2396 reflections with $I > 3\sigma(I)$. Bonding parameters of interest: $Mo{=}C$(alkylidene), 1.98 (1) Å; $Mo\equiv N$, 1.74 (1) Å; Mo—Mo, 3.052 (2) Å; Mo—Mo—N, 91.4 (3)°; Mo—Mo—C(alkylidene), 100.5 (3)°, N—Mo—C(alkylidene), 97.6 (5)°.

Introduction

The reactions of metal alkylidene complexes with small molecules have received attention in recent years because of several factors, foremost of which is their implication in catalytic processes, e.g. olefin metathesis, polymerization of alkenes and alkynes, and the Fischer–Tropsch reduction of CO.[1] One of the most general routes to metal alkylidene complexes is the reaction of diazoalkanes with metal complexes.[1,2] However, other metal complexes, including those of Cu, Co, and Pd, catalyze the decomposition of diazoalkanes and the subsequent transfer of alkylidene fragments to olefins.[3-5]

The mechanisms of the alkylidene (carbene) transfer reactions are not well understood since carbene/diazoalkane complexes of the catalytically active metals have not been isolated and the nature of the diazoalkane–metal interaction is not known. Recent papers[1,2] from our laboratories have reported the formation of bridging alkylidene complexes from the reaction of $Cp_2Mo_2(CO)_4(Mo{\equiv}Mo)$ with diazoalkanes and subsequent transfer of the μ-alkylidene group to olefins and alkynes. The detailed course of these reactions were found to depend critically upon the nature of the diazoalkane and on the olefin or alkyne substrate.

We also observed[2] that the reaction of CH_2N_2 with $Cp_2Mo_2(CO)_4$ led to the formation of polymethylene which suggested that the diazomethane was reacting with a methylene complex formed from the dimolybdenum complex and CH_2N_2. Herrmann et al. have in fact isolated a diazomethane/methylene complex from the reaction of CH_2N_2 with $Cp^*{}_2Mo_2(CO)_4$ ($Cp^* = C_5Me_5$).[6]

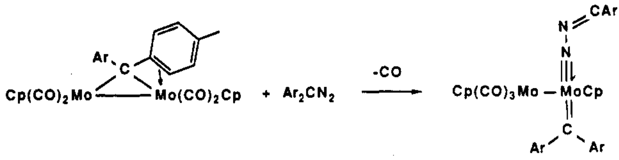
In view of these considerations, we decided to study the reaction of an isolable μ-alkylidene complex, $Cp_2Mo_2(CO)_4(\mu\text{-}CAr_2)$ (Ar = *p*-tolyl throughout this paper), with excess Ar_2CN_2. The results of this study are reported here.

Table I. Crystallographic Data for $Cp_2Mo_2(CO)_3(CAr_2)(N_2CAr_2)$ (2)

color	amber-red
chem formula	$C_{43}H_{38}Mo_2N_2O_3$
mol wt.	822.2
a, b, c (Å)	12.247 (6), 14.462 (7), 11.486 (5)
α, β, γ (deg)	113.22 (3), 95.60 (4), 90.32 (4)
Z, ρ (g/mL), V (Å^3)	2, 1.47 (calcd), 1858 (1)
cryst dimen (mm)	0.03 × 0.28 × 0.11
space group	$P\bar{1}$
radiatn	Mo Kα monochrom from graphite crystal
takeoff angle (deg)	4
μ(Mo Kα) (cm^{-1})(abs corr)	7.03 (yes)
scan speed (deg/min)	2–12 variable
scan range	Mo Kα_1 − 0.8° to Mo Kα_2 + 0.8°
background/scan time	0.8
std reflctns	$1\bar{7}0$, $20\bar{5}$, $40\bar{4}$
2θ limit (deg)	45
reflectns	4901 (2396 with $I > 3\sigma(I)$)
N_o/N_v	7.2
goodness of fit	1.33
R_1, R_2	0.053, 0.054

Results and Discussion

Synthesis. The μ-alkylidene complex[1,2] 1 reacts with Ar_2CN_2 rapidly at room temperature in CH_2Cl_2 solution according to eq 1. The structure of the product was confirmed by X-ray diffraction (see below). The new complex 2 is formed in essentially quantitative yield and forms amber-red crystals from a mixed methylcyclohexane/CH_2Cl_2 solvent. The compound is only slightly air-sensitive as a pure solid and is soluble in toluene, CH_2Cl_2, THF, etc. but is sparingly soluble in less polar solvents, e.g. hexanes or methylcyclohexane. In the course of the reaction, one CO is displaced, one is transferred across the Mo–Mo bond, and the bridging alkylidene ligand shifts to a terminal bonding mode.



(1)

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[1] Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Solis, H. E.; Barcelo, I. D.; Butler, S. W. *J. Am. Chem. Soc.* **1987**, *109*, 0000 and references therein.

[2] Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Butler, W. M.; Hay, M. S. *Organometallics* **1986**, *5*, 2283 and references therein.

[3] Carruthers, W. In *Comprehensive Organomet. Chem.* Pergamon: New York, 1982; Vol. 7, pp 696–700.

[4] Nakamura, A. *Pure Appl. Chem.* **1978**, *50*, 37.

[5] Bosnich, B.; Fryzuk, M. D. *Top. Inorg. Organomet. Stereochem.* **1981**, *12*, 119.

[6] Herrmann, W. A.; Bell, L. K.; Ziegler, M. L.; Pfisterer, H.; Pahl, C. *J. Organomet. Chem.* **1983**, *247*, 39.

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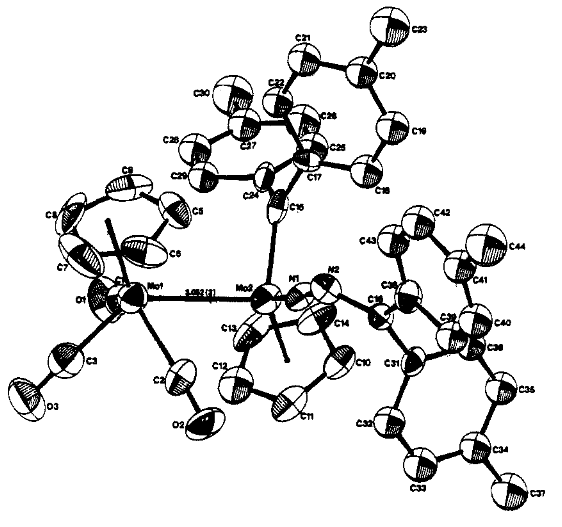

Figure 1. ORTEP drawing (50% ellipsoids) of $Cp_2Mo_2(CO)_3(C(p\text{-tol})_2)(N_2C(p\text{-tol})_2)$ (2).

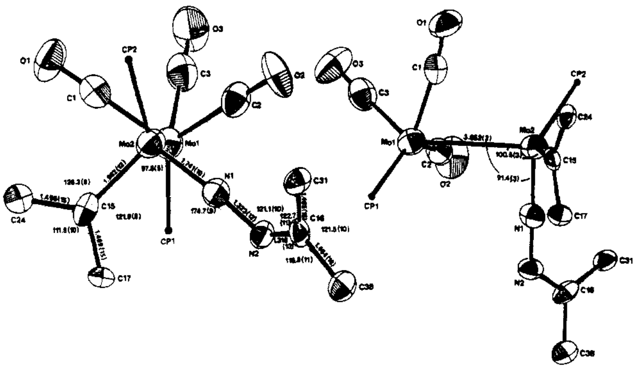

Figure 2. ORTEP drawings of 2 views of the inner coordination sphere of 2.

Structure. Figures 1 and 2 are ORTEP drawings with the numbering scheme and two views of the inner coordination sphere, respectively. Table I gives relevant crystallographic data, Table II the fractional atomic coordinates, and Table III lists selected bond distances and angles.

The Mo–Mo bond distance, 3.052 (2) Å, suggests the presence of a single bond between the two Mo atoms, so the combination of the Ar_2C and Ar_2CN_2 ligands must supply a total of six electrons to the dimetal fragment (cf. $Cp(CO)_3Mo{-}Mo(CO)_3Cp$). This is accomplished in the manner shown in eq 1: the terminal alkylidene donates two electrons forming a Mo=C double bond (Mo2–C15 = 1.98 (1) Å),[7] and the terminal nitrogen of the diazoalkane donates a total of four electrons forming a Mo≡N triple bond (Mo2–N1 = 1.74 (1) Å).[8]

Table II. Atomic Coordinates for 2

atom	*x*	*y*	*z*
Mo1	−0.0298 (1)	0.2115 (1)	0.0676 (1)
Mo2	−0.2308 (1)	0.3269 (1)	0.1712 (1)
C1	0.0267 (11)	0.3158 (11)	0.2300 (14)
O1	0.0691 (8)	0.3770 (8)	0.3256 (10)
C2	−0.1384 (11)	0.1328 (11)	0.1109 (12)
O2	−0.1967 (8)	0.0809 (7)	0.1309 (10)
C3	0.0681 (12)	0.1410 (11)	0.1416 (14)
O3	0.1255 (8)	0.0968 (8)	0.1873 (11)
N1	−0.3153 (8)	0.2497 (7)	0.0362 (10)
N2	−0.3771 (9)	0.1968 (7)	−0.0714 (9)
C5	−0.0975 (12)	0.2358 (13)	−0.1195 (13)
C6	−0.0736 (16)	0.1370 (14)	−0.1521 (14)
C7	0.0343 (21)	0.1256 (17)	−0.1286 (16)
C8	0.0831 (12)	0.2240 (20)	−0.0762 (17)
C9	0.0000 (16)	0.2903 (12)	−0.0687 (15)
C10	−0.3479 (11)	0.3624 (12)	0.3308 (12)
C11	−0.2826 (13)	0.2863 (11)	0.3406 (13)
C12	−0.1758 (12)	0.3260 (14)	0.3811 (13)
C13	−0.1754 (13)	0.4283 (13)	0.3970 (12)
C14	−0.2823 (13)	0.4476 (11)	0.3655 (12)
C15	−0.2146 (9)	0.4433 (9)	0.1232 (11)
C16	−0.4810 (10)	0.1727 (9)	−0.0713 (12)
C18	−0.3813 (11)	0.4201 (10)	−0.0370 (12)
C19	−0.4277 (11)	0.4198 (10)	−0.1515 (13)
C20	−0.3668 (10)	0.4420 (10)	−0.2320 (12)
C21	−0.2566 (11)	0.4676 (10)	−0.1949 (13)
C22	−0.2091 (10)	0.4695 (9)	−0.0799 (12)
C23	−0.4183 (12)	0.4390 (12)	−0.3588 (15)
C24	−0.1617 (9)	0.5413 (9)	0.2038 (11)
C25	−0.2204 (10)	0.6292 (10)	0.2403 (12)
C26	−0.1743 (11)	0.7240 (11)	0.3229 (13)
C27	−0.0678 (11)	0.7334 (10)	0.3707 (13)
C28	−0.0062 (10)	0.6506 (10)	0.3333 (12)
C29	−0.0503 (10)	0.5553 (9)	0.2527 (11)
C30	−0.0157 (13)	0.8352 (12)	0.4559 (15)
C31	−0.5317 (9)	0.1927 (9)	0.0462 (11)
C32	−0.5041 (10)	0.1414 (10)	0.1223 (12)
C33	−0.5536 (11)	0.1607 (10)	0.2339 (13)
C34	−0.6296 (10)	0.2330 (10)	0.2707 (12)
C35	−0.6612 (11)	0.2836 (10)	0.1944 (13)
C36	−0.6124 (10)	0.2641 (9)	0.0825 (12)
C37	−0.6821 (11)	0.2581 (11)	0.3922 (14)
C38	−0.5446 (10)	0.1264 (9)	−0.1967 (12)
C39	−0.6400 (11)	0.0672 (10)	−0.2116 (12)
C40	−0.6974 (11)	0.0200 (10)	−0.3302 (13)
C41	−0.6656 (11)	0.0319 (10)	−0.4293 (13)
C42	−0.5732 (11)	0.0929 (10)	−0.4198 (13)
C43	−0.5147 (10)	0.1389 (10)	−0.2998 (13)
C44	−0.7290 (13)	−0.0170 (12)	−0.5636 (16)

Table III. Selected Bond Distances (Å) and Angles (deg) for 2

	Bond Distances		
Mo2–N1	1.741 (10)	C2–O2	1.134 (14)
Mo2–C15	1.982 (12)	C3–O3	1.173 (15)
Mo1–C3	1.922 (17)	N1–N2	1.323 (12)
Mo1–C1	1.937 (15)	N2–C11	1.318 (13)
Mo1–C2	1.968 (14)	C15–C24	1.456 (15)
Mo1–Mo2	3.052 (2)	C15–C17	1.489 (15)
Mo2–C2	2.879 (14)	C16–C38	1.464 (16)
C1–O1	1.173 (14)	C16–C31	1.465 (16)
	Bond Angles		
Co-Mo1–C1	77.0 (6)	O3–C3–Mo1	178.3 (14)
C3–Mo1–C2	80.6 (6)	N2–N1–Mo2	174.7 (9)
C3–Mo1–Mo2	128.9 (4)	C16–N2–N1	121.1 (10)
Cl–Mo1–C2	104.3 (5)	N1–Mo2–C15	97.6 (5)
C1–Mo1–Mo2	75.5 (4)	C24–C15–C17	111.5 (10)
C2–Mo1–Mo2	66.0 (4)	C38–C16–C31	121.5 (10)
N1–Mo2–Mo1	91.4 (3)	N2–C16–C38	115.8 (11)
C2–Mo2–Mo1	38.6 (3)	N2–C16–C31	122.7 (11)
O1–C1–Mo1	174.7 (12)	C16–Mo2–Mo1	100.5 (3)
O2–C2–Mo1	174.6 (12)		

The sp hybridization at N1 is also indicated by the Mo2–N1–N2 bond angle of 174.7 (9)°. The angles around C16 sum to 359.7°, consistent with a planar, sp^2-hybridized carbon in the terminal alkylidene. The N1–N2–C16 angle, 121.1 (1)°, is consistent with sp^2 hybridization for N2. The N1–N2 and N2–C16 bond lengths are both 1.32 (1) Å and are in the ranges found for N(sp)—N(sp^2) and N(sp^2)=C(sp^2) bond lengths in mononuclear tungsten diazoalkane complexes.[9] The sum of the angles about C16 is 358.4° and indicates a planar sp^2 hybridization for C16. Thus, the metrical parameters of the ligands coordinated to Mo2

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[7] There is an excellent bond order–bond length correlation for Mo–C bonds: Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550.

[8] Organoimidomolybdenum complexes with formal Mo≡N triple bonds typically have bond lengths near 1.73 Å: Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

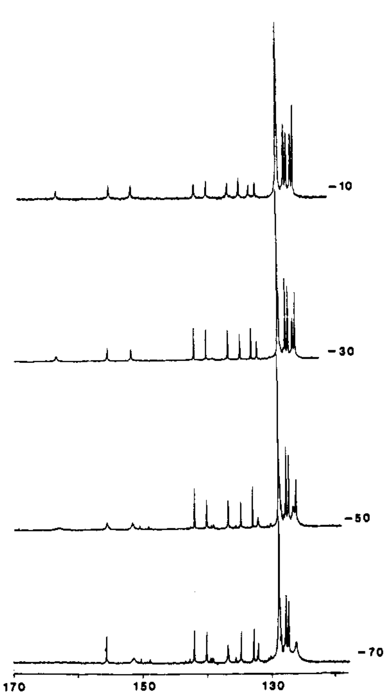
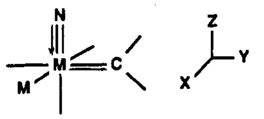


Figure 3. Variable-temperature ^{13}C NMR spectra (aryl carbon region) of **2**.

are all consistent with the formulation as drawn in eq 1.

As shown in Figure 2, the plane of the Ar_2C fragment lines up with the Mo2–N1 bond so that C15, C17, C24, Mo2, and N1 essentially lie in one plane which is nearly perpendicular to the Mo–Mo bond (Mo1–Mo2–N1 = 91.4 (3)° and Mo1–Mo2–C15 = 100.5 (3)°). Furthermore, the Mo2–N1 and Mo2–C15 bonds are nearly orthogonal; N1–Mo2–C15 = 97.6 (5)°. This orientation of the carbene ligand can be understood in the context of Templeton's calculations on complexes with strongly π-donating ligands, e.g. $L_4Mo{=}O \leftrightarrow L_4Mo{\equiv}O$,[10] and the coordinate system shown below.



The imido nitrogen is placed on the *z* axis, the Mo–Mo bond lies along the x axis, and the alkylidene ligand lies on the *y* axis as shown. The Cp ligand occupies the remaining coordination sites. The strong π-donating character of the imido nitrogen raises the energies of the *xz* and *yz* orbitals, leaving only the *xy* populated (the $x^2 - y^2$ and z^2 orbitals are pushed to high energy by σ-bonding). The most favorable alignment of the alkylidene carbon p orbital is then parallel to the *x* axis where it can π-bond with the occupied *xy* orbital. This alignment of the p and *xy* orbitals causes the Ar_2C fragment to lie in the *yz* plane, which is the alignment observed in the solid state.

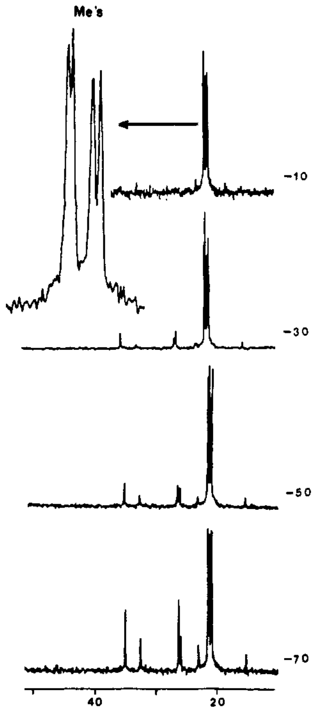


Figure 4. Variable-temperature ^{13}C NMR spectra (methyl region) of **2**.

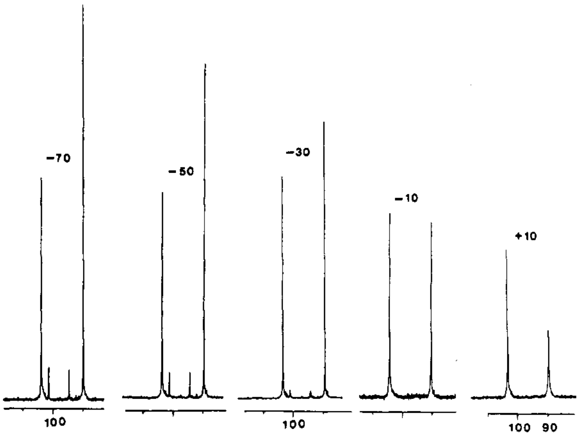


Figure 5. Variable-temperature ^{13}C NMR spectra (Cp region) of **2**.

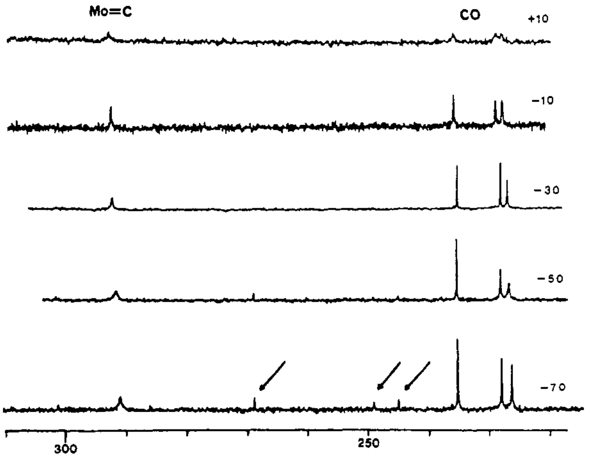


Figure 6. Variable-temperature ^{13}C NMR spectra (carbonyl plus alkylidene region) of **2**.

Variable-Temperature NMR Spectroscopy. The ^1H and ^{13}C-NMR spectra of **2** at -10 °C are completely consistent with the solid-state structure, and the molecule *appears* to be rigid on the NMR time scale at this temperature. Thus, at -10 °C, eight ipso carbons are expected and observed in the range δ ~132–155, and the unique diazoalkane carbon (C=N) appears at δ 163.8 (Figure 3). Four *p*-tolyl methyl resonances are located near δ 21 (Figure 4). Two Cp peaks of equal height are found at δ 90.0 and 104.0 (Figure 5). Three carbonyl peaks appear

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(9) (a) Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740. (b) Ben-Shoshan, R.; Chatt, J.; Leigh, G. J.; Hussain, W. *J. Chem. Soc., Dalton Trans.* **1980**, 771 and references therein.

(10) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713

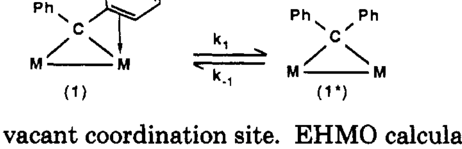
at δ 227.9, 228.9, and 235.8, and the alkylidene carbon (C_α) resonates at δ 292.6 (Figure 6). The latter resonance is shifted far downfield from its position in the bridging alkylidene complex 1 (δ 176) and is characteristic of a terminal alkylidene resonance.[11]

At −30 °C, the signals at δ 163 (*C*=N) and 292 (C_α) begin to broaden as new peaks appear in the Cp and methyl regions (Figures 3–6). At −50 °C, the *C*=N and C_α peaks are very broad, the C(ipso) peaks at δ 156 and 152 are beginning to broaden, the intensities of the new Cp and methyl peaks continue to increase, and two new C(ipso) peaks near δ 150 appear. At −70 °C, many of the aryl peaks have coalesced, but several new ones appear (Figure 3). Three new carbonyl peaks at very low filed, δ 269, 249, and 245 are discernible (Figure 6), and a total of *10* methyl resonances are observed (Figure 4).

The Cp resonances show selective broadening as a function of temperature. At +10 °C, the high-field signal at δ 90.0 is about twice as broad as the lower field signal at δ 104; the converse is true at −70 °C (Figure 5). All these spectral changes are completely reversible.

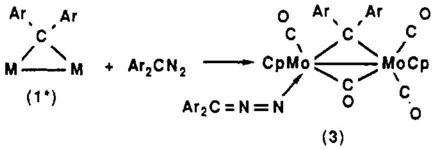
This spectral behavior was deemed to be too complex for detailed analysis. However, a few conclusions can be made. It is clear that there is a temperature-dependent equilibrium involving at least *three* isomers since 10 methyl resonances are observed at low temperature. The major isomer (isomer 1) at all temperatures studied is the one which gives the −10 °C spectrum and is presumably the one which is structurally characterized (the solution spectrum at −10 °C is consistent with the solid-state structure). At lower temperatures, equilibrium populations of other isomers increase relative to isomer 1. The next abundant isomer (isomer 2) at low temperature has nonequivalent Cp groups (δ 102, 94) and only two sets of methyl resonances (δ 36, 27). The minor isomer (isomer 3) has four methyl resonances at δ 33, 26, 23, and 16. Isomer 2 appears to have a bridging carbonyl (δ 269). *Each* isomer exhibits complex fluxional behavior involving C_α, *C*=N, and the aryl groups (which *begin* to be frozen out at −70 °C), but the interconversions among isomers is slow on the NMR time scale below +10 °C (at higher temperature, a new set of fluxional processes starts to broaden the peaks—this was not investigated due to sample decomposition. Since equilibrium among the isomers is established during the NMR experiments, the half-lives for these interconversions can be no longer than a few minutes, even at −70 °C.

Mechanism of Formation of 2. Previous kinetic work[1] has established that the reaction of the μ-alkylidene complex 1 with CO proceeds through a pre-equilibrium step which presumably involves the detachment of the coordinated aryl group (eq 2) to generate an intermediate (1*) with a vacant coordination site. EHMO calculations[1] indicated the presence of a low-lying acceptor orbital localized on only one of the Mo atoms in 1*.



(2)

The reaction of 1 with Ar_2CN_2 to give 2 can be interpreted as proceeding through the same intermediate. Initial detachment of the phenyl ring (eq 2) is now followed by the nucleophilic attack of the diazoalkane (eq 3). Symmetric bridge opening converts 3 to 4, and an "internal" displacement of CO by the lone pair on nitrogen leads to the final product 2 (eq 4).



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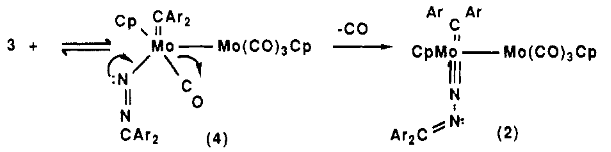

(4)

Conclusions

The reaction of the μ-alkylidene complex 1 with Ar_2CN_2 is the first example of reaction in which a μ-alkylidene ligand changes its coordination mode to a terminal alkylidene ligand, possibly in response to the strong π-donor character of the coordinated diazoalkane. The π-acceptor properties of alkylidene ligands promotes synergic bonding of the diazoalkanes, and mixed alkylidene/diazoalkane complexes may be important in metal salt catalyzed transfer of alkylidene groups.

Experimental Section

All experimental work involving air-sensitive material was carried out under pure N_2 in an inert-atmosphere box equipped with a purification train or in standard Schlenk ware. Toluene, benzene, ether, and THF were dried over sodium benzophenone and distilled under N_2 immediately prior to use. Methylene chloride was dried over P_4O_{10}. IR spectra was recorded on a PE 457 or 1330 instrument; NMR spectra were recorded on a Bruker WM-360 spectrometer (360 MHz for ^{1}H, 90.5 MHz for ^{13}C, and 55.25 MHz for ^{2}D). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. The synthesis of the μ-alkylidene complex 1 was reported elsewhere.[1]

Preparation of $Cp_2Mo_2(CO)_3[C(C_6H_4\text{-}p\text{-}Me)_2][N_2C(C_6H_4\text{-}p\text{-}Me)_2]$ (2). $Cp_2Mo_2(CO)_4(\mu\text{-}C(C_6H_4\text{-}p\text{-}Me)_2]\cdot C_6H_6$ (0.95 g, 1.3 mmol) was dissolved in CH_2Cl_2 (~15 mL). $(p\text{-}MeC_6H_4)_2CN_2$ (0.30 g, 1.3 mmol) was added and the mixture stirred; the solution immediately became amber-red. Methylcyclohexane (~40 mL) was carefully added and the layered solution cooled to −30 °C. A first crop (0.72 g) of product, an amber yellow powder, was isolated by filtration. Addition of methylcyclohexane gave, upon cooling, 0.10 g of additional product; total 0.82 g (74%).

X-ray Structure Determination. Crystals were grown from an ether solution at ambient temperature. X-ray data were collected on a Syntex $P2_1$ diffractometer using standard Syntex software. Cell parameters were determined from 15 accurately centered high-angle reflections scattered in reciprocal space. Three standard reflections were measured every 50 reflections. The programs used to solve and refine the structures have been described previously.[12] All computations were performed on an Amdahl 5860 computer. The weight factors were $w = 4F_o^2/(\sigma^2(F_o^2) + (PF_o^2)^2)$ ($P = 0.04$). Relevant crystal and data collection statistics are in Table I.

Metal atom positions were determined from a Patterson map, and subsequent difference maps located all non-hydrogen atoms. After isotropic convergence, 26 atoms (Mol, 2, Cp's, C_{ipso}'s, CO's, C16 (alkylidene carbon), and C6 (diazo carbon)) were refined anisotropically, and the remaining ring and methyl carbons were refined isotropically. After convergence, H-atom positions were calculated (C–H = 1.00 Å, $B_H = B_C + 1$) and their contributions subtracted from F_o. The structure converged in the following two cycles. Final atomic positions are in Table II, temperature factors

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(12) Sources of scattering factors, programs used in the structure solution and refinement, etc. have been described previously: Curtis, M. D.; Han, K. R. *Inorg. Chem.* **1985**, *24*, 378.

in Table IVS, a complete listing of bond distances and angles in Table VS, and F_o vs. F_c in Table VIS.

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Registry No. **2**, 80398-83-0; $Cp_2Mo_2(CO)_4[\mu-C(C_6H_4-p-Me)_2]$, 76114-00-6; $(p-MeC_6H_4)_2CN_2$, 1143-91-5.

Supplementary Material Available: Tables IVS, temperature factors, Table VS, a complete listing of bond distances and angles (4 pages); Table VIS, F_o vs. F_c (11 pages). Ordering information is on any current masthead page.

Transformations of a Methylene Ligand in a Metal Cluster Containing Sulfur. A Model for Sulfur Poisoning in a Molecular Complex

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The reactions of $Os_3(CO)_{10}(\mu-CO)(\mu-CH_2)$ (**1**) with ethylene or cyclohexene sulfides at 80 °C lead to formation of the two new thioformaldehyde complexes $Os_3(CO)_{11}(\mu-SCH_2)$ (**2**, 23–24%) and $Os_3(CO)_{10}(\mu_3-SCH_2)$ (**3**, 15–18%) in addition to the known compound $Os_3(CO)_9(\mu_3-S)_2$ (**4**, 7%). Compounds **2** and **3** can be interconverted quantitatively by decarbonylation (80 °C) and carbonylation (85 °C (55 atm of CO)). Compounds **2** and **3** were both characterized by single-crystal X-ray diffraction analyses. Compound **2** consists of an open triangular cluster of three metal atoms with a σ,π-bonded thioformaldehyde ligand bridging the unbonded pair of metal atoms, C–S = 1.77 (2) Å. Compound **3** contains a closed triangular cluster of metal atoms with a triply bridging thioformaldehyde ligand, C–S = 1.82 (3) Å. At 125 °C **3** is decarbonylated and undergoes a C–H activation to form the new compound $Os_3(CO)_9(\mu_3-SCH)(\mu-H)$ (**5**) which contains a triply bridging thioformyl ligand: ^1H NMR δ 10.34. **5** reacts with tertiary phosphines by addition of the phosphorus atom to the thioformyl ligand. The compounds $Os_3(CO)_9[\mu_3-SC(H)PR_3](\mu-H)$ (**7a**, $PR_3 = PMe_2Ph$; **7b**, $PR_3 = PMePh_2$; **7c**, $PR_3 = PPh_3$) have been prepared. **7b** was characterized by a single-crystal diffraction analysis. **7b** contains a triply bridging $SC(H)PMePh_2$ ligand on a closed triosmium cluster, P–C = 1.82 (2) and S–C = 1.85 (2) Å. When heated, compounds **7** eliminate the PR_3 molecule and regenerate **5**. In the presence of Me_3NO and PPh_3, **5** is decarbonylated and the PPh_3 ligand is added to a metal atom. The product $Os_3(CO)_8(PPh_3)(\mu_3-SCH)(\mu-H)$ (**8**) was characterized by a single-crystal X-ray diffraction analysis. The molecule consists of a closed triangular cluster of three osmium atoms with a triply briding thioformyl ligand. The C–S distance (average 1.74 (2) Å) is shorter than those of the thioformaldehyde ligands and indicates a higher degree of C–S unsaturation. Compound **3** reacts with hydrogen to yield $Os_3(CO)_{10}(\mu-SMe)(\mu-H)$ (**9**). At 150 °C (1 atm of H_2), **9** eliminates methane and adds H_2 to yield $Os_3(CO)_9(\mu_3-S)(\mu-H)_2$ (**10**). The transformations of the CH_2 ligand in these sulfur-containing complexes are compared with those of the non-sulfur-containing complex $Os_3(CO)_{10}(\mu-CH_2)(\mu-H)_2$.

Introduction

The adverse effects produced by sulfur upon reactions performed by metal catalysts is one of the most important problems faced by the petrochemical industry.[1] In most cases, the mechanisms of sulfur poisoning on heterogeneous catalysts are not clearly understood. The geometric blocking of active sites and surface reconstruction (faceting) are the most widely discussed mechanisms.[1,2] Although the notion of direct chemical interactions between sulfur and adsorbed molecules has been mentioned, very little evidence to demonstrate this has been obtained.[2c] There is now considerable evidence to indicate that the methylene (CH_2) ligand is a key intermediate in the Fischer–Tropsch reaction.[3] This reaction is well-known to be severely inhibited by sulfur contamination of the catalysts.[2]

In our recent studies of the reactions of sulfur-containing osmium carbonyl cluster compounds with alkynes we have observed several examples in which the formation of bonds between the alkyne molecules and the sulfido ligands occurred.[4,5]

To obtain evidence concerning the importance of methylene–sulfur interactions and their effect on transformations of the methylene ligand at multinuclear metal sites, we have now investigated the reactions of ethylene and cyclohexene sulfides with $Os_3(CO)_{10}(\mu-CO)(\mu-CH_2)$ (**1**).

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. THF was freshly distilled from sodium diphenylketyl before use. $Os_3(CO)_{10}(\mu-CO)(\mu-CH_2)$ (**1**) was prepared by the procedure of Geoffroy.[7] Ethylene sulfide, cyclohexene sulfide, PMe_2Ph, PPh_2Me, and PPh_3 were purchased from Aldrich Chemical Co. The ethylene sulfide was freshly distilled before

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