JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 107, NUMBER 3 FEBR

FEBRUARY 6, 1985

Solid-State Structure and Reactivity in Solution. 6.¹ Flash Photolysis and Structural Investigations of (1-(Diethylamino)-2-(diphenylphosphino)ethane)tetracarbonylmolybdenum(0)

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Abstract: Pulsed laser time-resolved ligand-substitution photochemistry for $(NP)M_0(CO)_4$ (NP = 1-(diethylamino)-2-(diphenylphosphino)ethane) proceeds via initial fission of the Mo-N bond, affording five-coordinate monohapto $(NP)M_0(CO)_4$ intermediates in which the vacant (solvated) coordination sites are trans and cis to the coordinated phosphorus. The rates of reaction of these intermediates, via chelate ring closure and competitive bimolecular interaction with Lewis bases (=L, phosphines, and phosphites) for the cis intermediate, and via bimolecular interaction of L with the trans intermediate, together with activation parameters for these processes have been determined. The rate of interaction at the cis site is significantly faster than at the trans site. The crystal and molecular structure and absolute configuration of $(NP)M_0(CO)_4$ have also been determined by X-ray crystallographic methods. $(NP)Cr(CO)_4$ is isomorphous and isostructural to its Mo analogue.

Thermal ligand-substitution reactions of octahedral metal carbonyls and derivatives proceed predominantly through a dissociative pathway involving rate-determining fission of either a M-CO or M-L bond (eq 1a), although other pathways are also observed.⁴ These slow initial steps have been much studied, not

 $[L_{x-1}M(CO)_{6-x}] \qquad [L_xM(CO)_{5-x}] \qquad (1)$

$$L_{x-1}L'M(CO)_{6-x} \qquad L_{x}L'M(CO)_{5-x}$$

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only for dissociation of monodentate ligands but also where fission involves reversible chelate ring opening.⁵ However, steps sub-

sequent to these slow processes which involve bimolecular addition of L to a five-coordinate metal carbonyl species (eq 1b) have been less studied by direct methods such as flash photolysis, 1,6,7 although

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Table I. Summary of Data Collection and Processing Parameters

space group	$P2_{1}2_{1}2_{1}$
cell constants	a = 11.682 (6) Å
	b = 12.197 (6) Å
	c = 16.057 (7) Å
cell volume	2287.9 Å ³
molecular formula	C₂₂H₂₄NO₄PMo
molecular weight	493.2
density (calcd; $Z = 4$)	1.43 g cm ⁻³
radiation	Mo $K\alpha$ (λ = 0.71073 Å)
absorption coeff	5.90 cm ⁻¹
data collection range	$4^{\circ} \leq 2\theta \leq 50^{\circ}$
scan width	$\Delta \theta = 1.10 + 0.35 \tan \theta$, deg
maximum scan time	240
scan speed range	0.41-3.35° min ⁻¹
total data collected	3880
data with $I > 3(I)$	2549
total variables	167
$R = \sum F_{\rm o} - F_{\rm c} / \sum F_{\rm o} $	0.036
$R_{\rm w} = \left[\sum w^2 (F_{\rm o} - F_{\rm c})^2 / \sum w^2 F_{\rm o} ^2 \right]^{1/2}$	0.032
weights	$w = \sigma(F_{\rm o})^{-2}$
goodness of fit	1.23

the ability of five-coordinate intermediates to discriminate among incoming nucleophiles has been investigated for both unidentate⁸ and chelating⁵ substituents coordinated to the metal.

The influence of the properties of the chelating ligand upon the "competition ratios", k_{-1}/k_2 (eq 2), the ratios of the rate



constants for ring closure and bimolecular interaction of L at a vacant, "ring-opened" coordination site, has been the subject of several investigations in which those ratios were studied as a function of the structures of the (chelate) $M(CO)_4$ complexes, as determined through X-ray crystallography.^{5q,9} It has been concluded that conformational preferences of the chelating ring together with steric interactions between the ring system and the $M(CO)_4$ moiety exert an important influence on the competition ratios. Since, in general, five-coordinate metal carbonyl intermediates have been found to exhibit little ability to discriminate among incoming unidentate nucleophiles,⁸ observed changes in the "competition ratios" as a function of the nature of the chelating ring have been attributed to variations of the rate of chelate ring closure, governed by k_{-1} .

Darensbourg and Murphy¹⁰ have reported results for photolysis of cis-(PPh₃)₂Mo(CO)₄ which indicate that fission of a Mo-P bond is the predominant process upon irradiation at the 366-nm Hg line. In this complex, a band maximum at 370 nm has been assigned to population of a σ^* level, leading to the labilization of σ -bonding ligands.¹⁰ Thus a bidentate ligand in which one of the coordinating atoms was P, the other N, might be expected to undergo metal-nitrogen bond fission upon flash photolysis, permitting the evaluation of reaction steps subsequent to this initial process. Such data would be of great interest, since they could permit the direct evaluation of the rate constants for those processes; rate constants for unimolecular ring reclosure would be

Table III. Intramolecular Bond Distances (Å)

Mo-P	2.510 (2)	N-C6	1.533 (7)	
Mo-N	2.436 (6)	N-C7	1.463 (7)	
Mo-C1	1.916 (8)	N-C9	1.544 (8)	
Mo-C2	2.004 (8)	C7-C8	1.523 (8)	
Mo-C3	2.002 (7)	C9-C10	1.538 (9)	
Mo-C4	1.996 (7)	C1-O1	1.182 (8)	
P-C5	1.858 (8)	C2-O2	1.161 (8)	
P-C11	1.835 (3)	C3-O3	1.147 (7)	
P-C17	1.828 (3)	C4-O4	1.163 (7)	
C5-C6	1.500 (8)			

Table IV. Intramolecular Bond An	igles	(deg
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able IV. Intramolecular Bond Angles (deg)					
P-Mo-N	79.0 (1)	Mo-C3-O3	177.6 (8)		
P-Mo-C1	96.9 (2)	Mo-C4-O4	176.6 (8)		
P-Mo-C2	90.9 (2)	Mo-P-C5	103.5 (2)		
P-Mo-C3	175.5 (3)	Mo-P-C11	118.5 (2)		
P-Mo-C4	95.1 (2)	Mo-P-C17	122.8 (2)		
N-Mo-C1	175.5 (3)	C5-P-C11	106.1 (3)		
N-Mo-C2	97.0 (3)	C5-P-C17	101.9 (3)		
N-Mo-C3	96.6 (3)	C11-P-C17	101.9 (2)		
N-Mo-C4	91.8 (3)	Mo-N-C6	107.4 (4)		
C1-Mo-C2	84.6 (3)	Mo-N-C7	113.6 (5)		
C1-Mo-C3	87.5 (3)	Mo-N-C9	108.2 (4)		
C1-Mo-C4	86.9 (3)	C6-N-C7	108.4 (5)		
C2-Mo-C3	88.9 (3)	C6-N-C9	105.1 (6)		
C2-Mo-C4	170.2 (3)	C7-N-C9	113.7 (5)		
C3-Mo-C4	85.8 (3)	P-C5-C6	109.8 (5)		
Mo-C1-O1	176.5 (8)	N-C6-C5	114.2 (6)		
Mo-C2-O2	172.8 (8)	N-C7-C8	113.8 (6)		
		N-C9-C10	114.6 (6)		

of particular interest. $(NP)Mo(CO)_4$ (NP = 1-(diethylamino)-2-(diphenylphosphine)ethane), synthesized in this laboratory some time ago¹¹ and in which the chelating NP ligand is coordinated through both N and P atoms, thus offered interesting possibilities for both flash photolysis and structural studies; herein are described the results of those investigations.

Experimental Section

The ligand, NP, and the complexes $(NP)M(CO)_4$ (M = Cr or Mo) were synthesized and purified as previously reported.¹¹

X-ray Structural Determination for (NP)Mo(CO)₄. The crystals were small yellow polyhedra with well-developed faces. A crystal of the dimensions $0.4 \times 0.2 \times 0.2$ mm was mounted on an Enraf-Nonius CAD-4 computer-controlled diffractometer. A summary of the crystallographically important parameters for data collection is given in Table I. Accurate cell constant determination and data collection were similar to those described elsewhere and thus are not repeated here.9a

Data decoding was accomplished by using a locally written program. Lorentz and polarization factors were applied in converting the intensities to structure factor amplitudes, $|F_0|$. No absorption corrections were made due to the low value of the absorption coefficient ($\mu = 5.90 \text{ cm}^{-1}$). Standard deviations in the structure factor amplitudes, $\sigma(|F_0|)$, were estimated as $\sigma(|F_0|) = \sigma(I)/2Lp|F_0|$. All data processing and calculations were carried out by employing the SHELX-76 system of programs.¹² A three-dimensional Patterson map was computed, and the position of the Mo atom was determined. All the remaining non-hydrogen atoms were found from successive difference Fourier maps. Since there was no reason to expect any distortion of the phenyl rings, these were refined as rigid bodies with idealized hydrogens. The hydrogens of the ethyl groups and those of CH2 were theoretically calculated and the C-H distances kept at 1.00 Å. Anisotropic refinement of all the non-hydrogen atoms except for the carbons of the phenyl and methyl groups and isotropic refinement of the rest of the atoms led to the final agreement factor listed in Table I. The estimated standard deviations were computed from the inverse matrix of the final full matrix least-squares cycle. No unusually high correlations were noted among any variables in the final cycle. Final atomic coordinates and thermal parameters are presented in Table IIA (supplementary material). Interatomic distances and angles are given in Tables III and IV. The equations of least-squares planes through selected groups of atoms are presented in Table V (supplementary ma-

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Figure 1. ORTEP stereo pair view of (NP)Mo(CO)₄, showing the numbering scheme employed in the crystallographic study. The thermal ellipsoids are 50% probability envelopes for the heavy atoms and are of convenient size for the hydrogen atoms.



Figure 2. Packing diagram for (NP)Mo(CO)₄.

terial). The stereo drawings (Figures 1 and 2) were obtained through use of Johnson's ORTEP.13

Data collection and refinement of the Cr analogue were similar. Structure factors were calculated using the atomic coordinates of the isomorphous Mo compound. Due to the very small size of the crystal, the number of observed reflections (405) was low, and only an isotropic refinement could be performed. Consequently, only the considerably more accurate results obtained for the isomorphous and isostructural Mo complex are presented and discussed. Atomic coordinates and isotropic temperature factors for the Cr complex are given in Table IIB (supplementary material).

When the refinement converged, the test for the enantiomorph was carried out. Sixteen reflections showed marked differences between $F_c(hkl)$ and $F_c(\bar{h}\bar{k}\bar{l})$ and were thus suitable for the Bijvoet test.¹⁴ These reflections were measured, and the results given in Table VI show that the coordinates initially chosen correspond to those of the correct enanatiomer. These are given in Table II. Figures 1 and 2 depict the molecule in its correct absolute configuration.

Since the crystals were obtained by spontaneous resolution, it is impossible at this stage, especially in view of the small size of the crystals, to correlate the absolute configuration to the CD spectrum.

Pulsed Laser Flash Photolytic Studies. Solvents (chlorobenzene (CB) and 1,2-dichloroethane (DCE)) were purified by fractional distillation over phosphorus pentoxide. Triisopropyl phosphite and tri-n-butylphosphine were fractionally distilled at reduced pressure (0.2 torr) over sodium. Triphenylphosphine was crystallized from ethanol and was dried in vacuo.

Pulsed laser flash photolytic studies were carried out at the Center for Fast Kinetics Research (CFKR), University of Texas at Austin, employing a Quantel Q-switched Nd:YAG laser (355-nm irradiating wavelength, 11-ns fwhi). Temperature at the jacketed observation cell was maintained through use of an external circulating bath (Lauda K-2/RD) and monitored by employing a digital thermometer (Cu-constantan thermocouple). Concentrations of substrate were approximately 5×10^{-4} M, and various concentrations of phosphite were employed. The pseudo-first-order rate constants, k_{obsd} , were evaluated by employing an iterative linearized least-squares analysis program (PDP 11/70 computer). Each value of k_{obsd} was determined from the average of results

Table VI. Determination of the Absolute Configuration

indices	$F_{c}(hkl)$	F.(ħk])	$F_{\rm c}(hkl)/F_{\rm c}(\bar{h}\bar{k}\bar{l})$	$F_{\text{obsd}}(hkl)/F_{\text{start}}(\bar{h}\bar{k}\bar{l})$
			1.02	- 00sd (1111)
1,3,2	11	/5	1.03	1.03
1,3,11	21	22	0.95	0.95
1,3,12	19	18	1.06	1.06
1,2,3	62	60	1.03	1.02
1,13,2	19	18	1.06	1.05
1,11,6	20	19	1.05	1.11
1,7,9	18	17	1.06	1.06
2,1,3	101	98	1.03	1.03
2,1,1	58	56	1.04	1.02
2,2,1	34	36	0.94	0.97
2,2,5	47	49	0.96	0.98
2,3,2	67	65	1.03	1.06
2,4,4	51	53	0.96	0.96
2,5,3	68	70	0.97	0.99
3,2,3	83	85	0.98	0.99
4,8,7	49	47	1.04	1.02

for five or more successive pulses for a given reaction solution. Pseudo-first-order rate constants are presented in Table VII.

Identification of the Photolysis Products. The products of photolysis for the Mo substrate in the presence of L = triisopropyl phosphite were found to be cis- and trans- $(\eta^1-NP)(L)Mo(CO)_4$ as follows: a solution of the substrate and L in DCE were irradiated at room temperature by employing a Hanovia 400-W medium-pressure Hg lamp and a filter (Oriel) which permitted passage only of 365-nm Hg light. Infrared spectra for the reaction solution were taken periodically in the carbonyl stretching region (Perkin-Elmer Model 621 grating infrared spectrophotometer). Since there was also expected to be significant thermal reaction taking place over the course of the irradiation, an identical experiment was carried out in the dark. Comparison of the spectra for the two runs indicated the presence of new carbonyl stretching bands at 2017, 1915, 1895, and 1880 cm⁻¹ upon photolysis, attributable to a cisdisubstituted reaction product containing two phosphorus atoms coordinated to Mo, through comparison of these bands to those observed for the "model" complex $(diphos)Mo(CO)_4$ (diphos = 1,2-bis(diphenylphosphino)ethane);¹¹ thus the N-Mo bond had ruptured during the ring-opening process. The relative increase in intensity of a carbonyl stretching band observed at ca. 1900 cm⁻¹ is attributable to the presence of a species containing two trans phosphorus atoms;¹¹ carbonyl stretching bands which might be attributable to a trisubstituted product, which might thus indicate Mo-CO bond fission during the irradiation, were not observed.

Results and Discussion

Structure of (NP)Mo(CO)₄. The compounds exist as discrete molecules in which the metal atom is bonded to the bidentate ligand, which contains P and N donor atoms.

The coordination about the central metal atom is a distorted octahedron, the equatorial plane being formed by the P and N atoms and by the two carbonyl ligands trans to them. The molybdenum atom is nearly in this plane, its deviation from the plane being slightly less than 0.01 Å. The distortions from the theoretical geometry are largely due to the formation of the five-membered

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Table VII. Pseudo-First-Order Rate Constants for Reactions of $(\eta^1-NP)Mo(CO)_4$

[L], M	$10^{-5}k_{\rm obsd}, {\rm s}^{-1}$	[L], M	$10^{-5}k_{\rm obsd}, {\rm s}^{-1}$
	Fast	Process	
CB		DCF	$\mathbf{P}(i_{r} \cap \mathbf{P}_{r})$
	$25 ^{\circ}C^{a}$	2	4.6 °C
0	0.884 (4)	0 -	0.477 (9)
0.118	0.99 (2)	0.0427	0.444 (6)
0.279	0.939 (9)	0.195	0.558 (16)
0.429	1.07 (2)	0.383	0.598 (36)
0.616	1.18 (2)	0.492	0.514 (19)
0.718	1.20 (1)	0.632	0.596 (24)
0.882	1.29 (1)	0.711	0.585 (23)
CB D(i)	DP-) 246 °C	0.870	0.613 (22)
0	158(3)	1.041	0.583 (29)
0118	1.50(3)	DCF	P(i=OPr)
0.279	1.71(1)	2:	5.9 °C
0.429	1.82 (6)	0	0.451 (5)
0.616	2.02 (2)		
0.718	2.09 (3)	DCE,	$P(i-OPr)_3$,
0.882	2.25 (2)	4	1.9 °C
1.048	2.32 (3)	0	1.08 (1)
DLOI	$\mathbf{D}(i \mathbf{O} \mathbf{P}_{r})$	DCE.	$P(i-OPr)_3$.
	$r(i-Orr)_3,$,	3.8 °C
0	3 11 (8)	0	1.95 (2)
0.218	3 44 (12)	AB B	
0.391	3.72(9)	СВ, РР	$h_3, 24.6 \ ^{\circ}C$
0.511	4.00 (22)	0	1.68 (3)
0.631	4.25 (18)	0.100	1.60 (2)
0.781	4.32 (9)	0.225	1.78(1) 1.80(4)
0.988	4.62 (10)	0.331	1.09 (4)
1.033	4.85 (30)	0.510	2.21(3) 2.31(7)
2.16	6.68 (45)	0.703	2.31(7) 2.31(12)
DOF		0.874	2.55(2)
DCE,	$P(1-OPr)_3$		1.00 (1)
	+.7 - 0	CB, P- <i>n</i> -	Bu ₃ , 24.6 °C
U	0.104 (4)	0.185	1.75 (6)
DCE,	$P(i-OPr)_3$,	0.353	2.10 (7)
-3	3.9 °C	0.536	2.18 (8)
0	0.107 (3)	0.080	2.40 (15)
DCE	$P(i_{r}OP_{r})$	0.041	2.08 (3)
12	2.3 °C		
0	0.246 (10)		
0.195	0.305 (22)		
0.427	0.337 (26)		
0.711	0.281 (18)		
1.041	0.314 (15)		
[L], M	$10^{-3}k_{obsd}$, s ⁻¹	[L]. M	$10^{-3}k_{obsd}$, s ⁻¹
	Slow]	Process	00307
	3104	100033	
СВ, Р	$P(i-OPr)_3$,	CB, P(i-C	Pr)3, 35.7 °C
12	.4 °C	0	0
0	0	0.144	2.27 (5)
0.119	0.270 (3)	0.286	3.74 (6)
0.459	1,1/(3)	0.376	3.77 (28)
0.750	1.88(5)	0.618	7.29 (4)
1.145	3.19 (11)	0.819	8.70 (25)
CB, P	$P(i-OPr)_3,$	0.905	10.0 (0)
26	.0 °C	CB, P-n-	Bu3, 24.6 °C
0	0	0	0
0.144	1.03 (3)	0.185	3.90 (39)
0.286	2.05 (10)	0.353	5.55 (31)
0.3/0	2.54 (7)	0.537	9.66 (21)
0.439 0.619	2.92 (4)	0.080	11.0 (4)
0.819	4.80 (6)	0.041	12.3 (7)
0.985	6.39 (8)		

^aSolvent, L, and temperature.

chelate ring and to the differences between the Mo-P, Mo-N, and Mo–C(CO) bond lengths (Mo–P = 2.510(2), Mo–N = 2.436(6), and Mo-C(CO) = 1.916 (8) to 2.004 (8) Å). A large deviation from ideal octahedral geometry is observed for the P-Mo-N angle, for which a contraction from 90 to 79.0 (1)° occurs.

This angle is almost identical with the value of 79.7 (3)° observed by Einstein and Field¹⁵ for the P-Mo-P fragment of a similar five-membered ring. Similar values such as 80.8 (1)° ^{9a} and 80.60 (4)^{o 9b} have been observed in related complexes having W and Cr as the central atoms. This contraction of the P-Mo-N angle is compensated in the equatorial plane by an increase in both of the adjacent angles; P-Mo-Cl = 96.9 (2)° and N-Mo-C3 = 96.6(3)°. This equal distribution of the strain caused by the contraction of the P-Mo-N bond is in contrast to the unsymmetrical deviations observed for some related complexes of Cr and W containing one bulky tert-butyl substituent at each of the two sulfurs coordinated to the metal.9 The C1-Mo-C3 angle remains largely undisturbed with a value of 87.5°. The distortion from ideal octahedral geometry is also reflected in the deviations from linearity of its principal axes (P-Mo-C3 = 175.5 (3)°, N-Mo-C1 = $177.5 (3)^{\circ}$, and, more significantly, C2-Mo-C4 = $170.2 (3)^{\circ}$).

The Mo-P distance of 2.510 (2) Å is significantly shorter than 2.71 Å, the sum of the covalent single bond radii (1.61 Å for Mo and 1.10 Å for P).¹⁶ This shortening is ascribed to significant π bonding between P and Mo. Values of 2.501 (2), 2.535 (3), 2.521 (2) and 2.495 (2) Å for the Mo-P bond have been found in similar complexes.¹⁷

This distance between Mo and the sp³-hybridized N is 2.436 (6) Å, which is, as expected, longer than the Mo-N sp² distances of 2.269 (9) and 2.274 (9) Å found in the related complex, bis-(2-pyridylamine)tetracarbonylmolybdenum(0).¹⁸ This value of 2.436 (6) Å is also significantly longer than that of 2.33 (2) Å reported for the Mo–N sp³ bond in cis-(diethylenetriamine)tri-carbonylmolybdenum(0).¹⁹ In view of the fact that both substituents at the N atom of diethylenetriamine are hydrogens, whereas for the present complex they are ethyl groups, it seems reasonable to assume that the lengthening of the Mo-N bond is at least partially due to steric effects. This lengthening is accompanied by a significant shortening of the Mo-C(CO) bond trans to the nitrogen atom (Mo–Cl = 1.916 (8) Å). The two axial Mo-C(CO) distances are virtually identical (Mo-C2 = 2.004 (8) Å and Mo-C4 = 1.996 (7) Å). The Mo-C(CO) distance of 2.002 (7) Å for the fourth carbonyl group, which is trans to the phosphorus atom, is virtually identical with the lengths of the two axial Mo-CO bonds. Concomitantly, the average C-O distance for the two axial carbonyls and the carbonyl trans to the P atom is significantly shorter (1.157 (7) Å) than is that of C1-O1, that trans to N (1.182 (8) Å).

Photolysis Studies. Infrared spectra taken upon photolysis of $(NP)Mo(CO)_4$ in the presence of triisopropyl phosphite in DCE at 365 nm indicate the absence of trisubstituted species; thus no Mo-CO bond breaking takes place. The data clearly indicate the formation of a cis disubstituted derivative containing two coordinated phosphorus atoms; such a species can be produced through ring-opening via fission of the Mo-N bond. There is also some evidence that the analogous product containing two phosphorus atoms trans to one another is produced, although the overlap of bands for the trans and cis products and the $(NP)Mo(CO)_4$ reactant are such that evidence in this regard is not conclusive.¹⁰ However, the infrared data do demonstrate conclusively that trans and cis disubstituted species derived through Mo-N bond fission are the only possible reaction products.

Figure 3 exhibits time-resolved spectra (absorbance vs. wavelength at various times after the flash) for the decay of an intermediate produced through pulsed laser flash photolysis at 355 nm of $(NP)Mo(CO)_4$ in CB which indicate that the optimal observation wavelength for decay of the intermediate is ca. 430 nm. Typical plots of absorbance vs. time at this wavelength at

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Figure 3. Time-resolved spectra for decay of $cis-(\eta^1-NP)Mo(CO)_4$ in CB at 24.6 °C in the absence of L. Times in microseconds, are (A) 0.800, (B) 2.00, (C) 3.40, (D) 5.40, (E) 14.9, and (F) 26.9.



Figure 4. Plot of absorbance vs. time for decay of $cis-(\eta^1-NP)Mo(CO)_4$ in CB at 24.6 °C in the absence of L, fitted as an exponential decay to a new base line.

24.6 °C at zero ligand concentration and at [L] = 1.048 M (L = triisopropyl phosphite, CB solvent) are exhibited in Figures 4–6.



Figure 5. Plot of absorbance vs. time for decay of $cis-(\eta^1-NP)Mo(CO)_4$ (fast process) and *trans*- $(\eta^1-NP)Mo(CO)_4$ (slow process) in CB at 24.6 °C. $[P(i-OPr)_3] = 1.048$ M. The plots are fitted as two parallel first-order processes to a new base line.



Figure 6. Plot of absorbance vs. time for decay of *trans*- $(\eta^1$ -NP)Mo-(CO)₄, fitted as an exponential decay to a new base line, for the system described in Figure 5.

A first-order plot to a new base line (Figure 4) is observed at zero ligand concentration. At [L] = 1.048 M (Figure 5), two first-order



Figure 7. Plots of k_{obsd} vs. $[P(i-OPr)_3]$ for reaction of $cis-(\eta^1-NP)$ Mo-(CO)₄ with $P(i-OPr)_3$ in CB at various temperatures.

Table VIII. Rate Constants and Activation Parameters for Reactions of *cis*- and *trans*- $(\eta^1$ -NP)Mo(CO)₄

L	solvent	<i>т</i> , °С	$10^{-5}k_1, s^{-1}$	$10^{-5}k_2,$ M ⁻¹ s ⁻¹	$10^{-4}k'_{2},$ M ⁻¹ s ⁻¹
$P(i-OPr)_3^{a,b}$	CB	12.5	0.88 (2)	0.45 (5)	
$P(i-OPr)_3^c$	СВ	12.4			0.28 (1)
$P(i-OPr)_3^{a,b}$	СВ	24.6	1.55 (2)	0.73 (2)	
$P(i-OPr)_3^c$	СВ	26.0			0.61 (2)
$P(i-OPr)_3^{a,b}$	CB	37.4	3.10 (3)	1.65 (4)	
$P(i-OPr)_3^c$	CB	35.7			1.00 (5)
PPh ₃	CB	24.6	1.58 (5)	1.02 (9)	
P-n-Bu ₃	CB	24.6	1.62 (5)	1.19 (10)	1.49 (11)
$P(i-OPr)_3^d$	DCE	12.3	0.279 (3)	0.04 (4)	
$P(i-OPr)_3^d$	DCE	24.6	0.49 (2)	0.13 (4)	

 $\frac{{}^{a}\Delta H_{-1}^{*} = 8.2 \text{ (5) kcal mol}^{-1}; \Delta S_{-1}^{*} = -6.9 \text{ (15) cal deg}^{-1} \text{ mol}^{-1}.}{b\Delta H_{2}^{*} = 8.4 \text{ (10) kcal mol}^{-1}; \Delta S_{2}^{*} = -7.4 \text{ (35) cal deg}^{-1} \text{ mol}^{-1}. {}^{c}\Delta H_{2}^{*} = 9.0 \text{ (5) kcal mol}^{-1}; \Delta S_{2}^{*} = -10.8 \text{ (18) cal deg}^{-1} \text{ mol}^{-1}. {}^{d}\Delta H_{-1}^{*} = 7.7 \text{ (2) kcal mol}^{-1} \text{ and } \Delta S_{-1}^{*} = -10.5 \text{ (5) cal deg}^{-1} \text{ mol}^{-1} \text{ determined from data at seven temperatures. See Table VII.}$

plots are noted. Figure 6 indicates that the slow process of Figure 5 also obeys pseudo-first-order kinetics. These plots indicate that two species are produced via the flash.

Analyses of such plots (the rate constants are the pseudofirst-order constants k_{obsd}) as a function of varying concentrations of L demonstrate that the fast process obeys the rate law

$$-d[Int]/dt = k_{-1}[Int] + k_{2}[Int][L]$$
(3)

while the slower process obeys the rate law

$$-d[Int']/dt = k'_{2}[Int'][L]$$
(4)

Plots of k_{obsd} vs. [L] for the two processes, supportive of these rate laws, are exhibited in Figures 7 and 8; the rate constants k_{-1} , k_2 , and k'_2 derived from these plots are presented in Table VIII. The mechanisms proposed for the fast and slow processes will be discussed in turn.

For the fast process, the rate behavior is best interpreted in terms of competitive ring closure and attack by L at a ring-opened five-coordinate intermediate in which the vacant coordination site is cis to coordinated phosphorus (eq 5). Of the two possible species

produced upon photolysis (vide supra), only that with a vacant coordination site cis to coordinated phosphorus can react via a unimolecular pathway.

For the slower process, second-order kinetics are observed. The absence of a first-order term indicates that ring reclosure is not



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Figure 8. Plots of k_{obsd} vs. $[P(i-OPr)_3]$ for reaction of *trans*- $(\eta^1-NP)-Mo(CO)_4$ with $P(i-OPr)_3$ in CB at various temperatures.

a competitive process for this reaction pathway. Yet the reaction is quite fast, very much faster than would be expected for a process involving a bimolecular interaction at a coordinatively saturated Mo, ca. $10^{-4} \text{ M}^{-1} \text{ s}^{-1.4c}$ It is thus highly unlikely that this pathway involves further reaction of the species formed via the faster step. It thus is attributed to bimolecular addition of L at a vacant coordination site trans to coordinated phosphorus (eq 6). This



attribution was further tested through the synthesis of (1-(dimethylamino)-2-(diphenylphosphino)ethane)tetracarbonylmolybdenum(0) ((MeNP)Mo(CO)₄) and preliminary studies of its pulsed laser flash photolysis kinetics under conditions identical with those employed for (NP)Mo(CO)₄.²⁰ The five-coordinate intermediates generated through flash photolysis of these two substrates should be virtually identical in their reactivity via the observed bimolecular path governed by k'_2 , differing as they do only in the fifth atom of the R₂NCH₂CH₂ group bound to coordinated P. However, reactivities of these two complexes through the unimolecular pathway, ascribable to chelate ring closure, might be expected to differ significantly.

These expectations are realized in that the rate constant, k_{-1} , for the unimolecular path for (MeNP)Mo(CO)₄ at 24.7 °C, is 1.07 (2) × 10⁶ s⁻¹, 7 times greater than that for (NP)Mo(CO)₄ under identical reaction conditions (Table VIII). Values for k'_2 are 6.5 (6) × 10³ M⁻¹ s⁻¹ for (MeNP)Mo(CO)₄ at 26.0 °C vs. 6.1 (2) × 10³ M⁻¹ s⁻¹ for (NP)Mo(CO)₄ at 24.6 °C. Unfortunately, k_2 for (MeNP)Mo(CO)₄ could not be determined, given that it was expected to be ca. 7% as large as the competitive k_{-1} .

Rates of reaction differ significantly in DCE and chlorobenzene (Table VIII), indicative of solvation of the five-coordinate cis and trans species. That two first-order processes are observed in plots of absorbance vs. time at high ligand concentrations rule out the possibility of a rapid equilibrium between the solvated species. The formation of the trans species from the cis isomer initially produced via Mo–N bond fission thus must occur prior to solvation. Examination of time-resolved spectra after photolysis on the nanosecond time scale reveals no other processes save those discussed above which occur on a time scale slower than the pulse width (11 ns). It also has been shown that solvation of $[Cr(CO)_5]$ produced upon picosecond pulsed laser flash photolysis at a 355-nm irradiating wavelength takes place within 25 ps for the solvents cyclohexane, benzene, methanol, and THF.^{6d,f}

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The data support an overall mechanism (eq 7) for the flash photolysis of (NP)Mo(CO)₄ which is strongly corroborated by other investigations. Matrix isolation photolysis studies of



five-coordinate species derived from octahedral metal carbonyls by Turner and co-workers have provided conclusive evidence that such species are square-pyramidal in which the vacant coordination site is occupied by a solvent molecule.²¹ Moreover, Poliakoff has investigated the matrix isolation photolysis of $trans-(1^{3}CO)(CS)W(CO)_{4}$, which afforded five-coordinate (thiocarbonyl)tetracarbonyltungsten(0) species containing either a vacant coordination site cis or trans to CS. He also observed that scrambling of the coordinated groups took place during photolysis, results he interpreted as indicative of creation of a square-pyramidal vibrationally or electronically excited species following carbonyl ejection, and decay of this state via ligand randomization to afford the (CS)W(CO)₄ species of square-pyramidal geometry in which the vacant coordination site is either trans or cis to CS.²² Photolysis studies of trans- and cis- $L_2Mo(CO)_4$ species (L = PPh₃) by Darensbourg and Murphy¹⁰ at 366 nm which, it is to be noted, produce very similar five-coordinate intermediates via ejection of triphenylphosphine as are proposed to be created through ring opening in this investigation, are in accord with the proposal of Poliakoff as to the nature of the photochemical process. Moreover, Hyde and Darensbourg,^{8a} in thermal ligand-exchange investigations of cis-(PPh₃)-(amine)Mo(CO)₄ complexes, which proceed via initial loss of the amine, have shown that there is no scrambling which takes place on the time scale of the ligand-exchange process. This is consistent with the observation of two first-order processes during the flash photolysis of $(NP)Mo(CO)_4$. The intermediates which would be generated through photolytic cleavage of a Mo-P bond in the former and a Mo-N bond in the latter complex differ only in one group bonded to coordinated P.

It is probable that the five-coordinate intermediates generated thermally and those produced photochemically are one and the same given the evidence presented above that photophysical processes resulting through photolysis are very fast; that is, that loss of CO and decay of a thermally or electronically excited intermediate to afford both trans and cis five-coordinate ringopened species and even their subsequent solvation occur within the time scale of the photolysis pulse. Moreover, it has been found that ratios of bimolecular rate constants for interaction of various L with (o-phenanthroline)Cr(CO)₃ generated both photochemically and thermally are the same, within experimental error.^{7b} Thus, the comparison of rate constants derived thermally and photochemically can provide strong additional corroborating evidence as to the mechanism. For example, "competition ratios" k_{-1}/k_2 for decay of the five-coordinate cis intermediates generated upon photolysis by ring reclosure and attack by L may be evaluated from rate data for $L = P(i-OPr)_3$, PPh₃, and P-n-Bu₃, exhibited in Table VIII. These ratios show little ability of the intermediate to discriminate among the incoming nucleophiles; thus, based on Hammond's postulate²³ and the significant differences in the ground-state energies of the reaction products which have been observed,²⁴ it is likely that the transition states leading to interaction of the intermediate with L involve little M-L bond making. This conclusion had been drawn for other group 6 metal carbonyl systems for which competition ratios have been determined via thermal methods.^{5k,8} It is of particular interest to compare competition ratios $k_2(P-n-Bu_3)/k_2(PPh_3)$ obtained in this study and by Hyde and Darensbourg through ligand-exchange investigations of $cis-(PPh_3)(amine)Mo(CO)_4$ with those L in *n*-hexane. The five-coordinate intermediates are almost identical, differing only in an R group bonded to the coordinated P (R = $Et_2NCH_2CH_2$ in this study and C_6H_5 in that of Hyde and Darensbourg).^{8a} The values are 1.3 (2) in chlorobenzene at 24.6 °C and 0.49 (2) in n-hexane at 36.5 °C, respectively; a value greater than one is expected both on steric (cone angles)²⁵ and electronic (basicities)²⁶ grounds. Further, in similar octahedral systems, it is known that Cr-L bonds are stronger for tri-n-butyl-phosphine than for triphenylphosphine.24b

Data in Table VIII indicate that the rates of interaction by L at a vacant coordinate site cis to P are some 2 orders of magnitude faster than at the trans site, despite the expected steric interference between the incoming L and the uncoordinated end of the NP ligand at the cis site. This trend is not unreasonable in view of expected greater intermediate-solvent interaction at the more polar site trans to the electron-releasing P atom. This observation may help to explain the preference for formation of cis disubstituted and fac trisubstituted octahedral metal carbonyl substitution products where the L do not impose significant steric demands on one another.

Activation parameters for the pathways governed by k_{-1} , k_2 , and k'_2 in chlorobenzene and for k_{-1} in DCE are presented in Table VIII. They are, in general, within experimental error of one another. Negative entropies of activation are observed for all pathways, consistent with associative processes for which more bond making than bond breaking in attaining the transition state is anticipated.

The near zero values of $\Delta H_{-1}^{*} - \Delta H_{2}^{*}$ and those of the corresponding entropies of activation are very similar to those obtained thermally by Angelici and Knebel^{5g} for (NP)Mo(CO)₄ in 1,4dichlorobutane with L = CO; their agreement again suggests that the intermediate generated thermally and photochemically is one and the same.

The observation that activation parameters for ring closure vs. competitive attack by L are very similar is somewhat surprising, since it might be expected that unimolecular chelate ring closure would be less disfavored entropically than bimolecular interaction of the intermediate with L,²⁷ and this effect would be balanced

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by a less favorable enthalpy of activation for ring closure, given the distortions observed in $(NP)Mo(CO)_4$. It is evident that both kinetics and structural studies such as these for other chelating systems will be required before relationships between reactivity and substrate structure can be elucidated. In the (chelate)M(CO)₄ complexes thus far investigated structurally, only one of the two major distortions observed, diminuition of the N-Mo-P angle from its expected value of 90°, is also noted in (NP)Mo(CO)₄. It will be important to investigate systems for which the other major distortion, an unsymmetrical angular distribution of ligands in the equatorial plane containing the non-carbonyl substituents,⁹ is also present.

Acknowledgment. The financial support of this research by the Robert A. Welch Foundation (Grant B-434) and the North Texas State University Faculty Research Fund is gratefully acknowledged. Support by the University of Houston Computing Center, which contributed a generous supply of services, is also most appreciated. The pulsed laser flash photolysis studies and analyses of the data produced were performed at the Center of Fast Kinetics Research (CFKR) at the University of Texas at Austin. The CFKR is supported jointly by the Biotechnology Branch of the Division of Research Resources of the National Institutes of Health (RR00886) and by the University of Texas at Austin. The experimental help and technical expertise of the staff at CFKR, in particular that of Dr. Stephen J. Atherton, are greatly appreciated. We also thank D. Eric Halverson for experimental assistance in the early phases of this work.

Supplementary Material Available: Atomic coordinates and thermal parameters for $(NP)Mo(CO)_4$ (Table IIA) and for $(NP)Cr(CO)_4$ (Table IIB) and least-squares planes through groups of atoms and their deviations from the planes (Table V) (3 pages). Ordering information is given on any current masthead page.

Small-Ring Cyclic Cumulenes: Theoretical Studies of the Structure and Barrier to Inversion in Cyclic Allenes

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Abstract: Results of ab initio SCF, MCSCF, and Möller–Plesset calculations on 1,2-cyclopentadiene and 1,2-cyclohexadiene are described. 1,2-Cyclohexadiene is calculated to prefer a chiral allenic structure, with a barrier to inversion of ca. 15 kcal/mol. 1,2-Cyclopentadiene is predicted to have an inversion barrier of 2–5 kcal/mol, with a chiral equilibrium geometry. MCSCF calculations on planar allene (C_{2v}) show that the open-shell singlet ($^{1}A_{2}$) should be below the triplet ($^{3}A_{2}$), owing to differences in correlation energy. Semiempirical (MNDO) calculations on four- to nine-membered ring allenes and on bicyclo[3.2.1]-octa-2,3,6-triene are reported.

Introduction

One primary goal of experimentalists and theoreticians has been to explore structural limitations of hydrocarbons. Allenes are an important class of unsaturated hydrocarbons which contain two cumulated double bonds in an orthogonal geometry. Ring constraints bend and twist the normally linear, perpendicular allene and will engender substantial strain and resultant kinetic reactivity.² One fundamental question is the influence of ring size on the barrier to π -bond rotation. In cyclic allenes, this is most accurately described as an inversion barrier, since rotation interconverts enantiomers. Equally fundamental questions are at what point π -bonding will yield to ring strain, affording a planar allene, and what is the electronic nature of planar allene? Such



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questions have proven difficult to answer unambiguously through experiment;² thus, theory should be an important adjunct in their resolution.

It is well known experimentally that allene kinetic stability decreases rapidly with smaller ring size, presumably because reaction is accompanied by substantial strain relief. 1,2-Cyclononadiene (9) is a distillable liquid,² while 1,2-cyclooctadiene (8) rapidly dimerizes at ambient temperature.³ Its ¹H NMR spectrum proved measurable at -60 °C.⁴ 1,2-Cycloheptadiene (7) and a number of derivatives have been chemically trapped,

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