

Octahedral Metal Carbonyls. 69.¹ Kinetics Studies of the Formation of (NBD)Mo(CO)₄ (NBD = Norbornadiene) after Flash Photolysis of Mo(CO)₆/NBD

Solutions

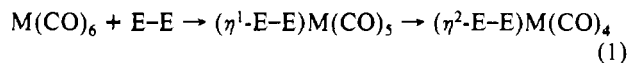
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Flash photolysis of Mo(CO)₆ in solutions containing norbornadiene (NBD = bicyclo[2.2.1]hepta-2,5-diene; solvent = chlorobenzene (CB), toluene, benzene, *n*-heptane) affords, initially, [(solvent)Mo(CO)₆] species in predominant concentration. These then react with NBD via solvent displacement to afford [(η²-NBD)Mo(CO)₅] (1) as a mixture of two species, the endo (1-end) and exo (1-ex) isomers. 1-end then reacts via rapid concerted ring-closure and expulsion of CO to afford the (η⁴-NBD)Mo(CO)₄ product (2). At ambient temperature, 1-end has a half-life in *n*-heptane of ca. 3 ms. Spectral evidence suggests that steric effects leading to ground-state destabilization in 1 facilitate chelate ring closure. On a much longer time scale (minutes), 1-ex reacts, probably via Mo-olefin bond fission and formation of 1-end to afford 2. The rapid ring closure observed in 1-end makes it unlikely that upon CW photolysis this species can afford significant quantities of endo-[(η²-NBD)Mo(CO)₄] (3). 3 has been proposed to be an intermediate in the hydrogenation of NBD to afford norbornene upon CW photolysis of M(CO)₆/NBD/H₂ solutions (M = Cr, Mo, W).

Introduction

Chelate ring closure in (η¹-bidentate)M(CO)₅ complexes (M = Cr, Mo, W), intermediates along the reaction pathway to formation of (chelate)M(CO)₄ reaction products (eq 1), has been



studied for a number of bidentate ligands coordinating through N, P, As, and S donor atoms (=E), where the (η¹-E-E)M(CO)₅ complex is isolable.² In other cases, where the reaction via chelate ring closure of (η¹-E-E)M(CO)₅ complexes is fairly rapid, these processes have been studied in situ by employing diode-array UV-visible^{3,4} or rapid-scan FTIR⁵ spectrophotometry. For the rigid chelating ligands *o*-phenanthroline (phen) and several substituted analogues, ring closure is extremely rapid and thus takes place after the rate-determining step, M-CO bond fission induced by CW photolysis.^{4,5} More recently, Oishi⁶ and Kalyanasundaram⁷ have employed flash photolysis for M(CO)₆/phen systems to determine these rates of chelate ring closure, which, for Mo and W, are on the millisecond time scale; for M = Cr, the rate of chelate ring closure, some 3 orders of magnitude slower, could not be determined with accuracy.

Complexes of the type (NBD)M(CO)₄ (NBD = norbornadiene, bicyclo[2.2.1]hepta-2,5-diene; M = Cr, Mo, W) are readily synthesized from NBD and either the hexacarbonyl (M = Cr, Mo)⁸ or a substituted complex such as (CH₃CN)₃W(CO)₃.⁹ In no instance, however, has an intermediate complex, (η²-NBD)M(CO)₅, been observed. This species has, however, been implicated in the photolytic hydrogenation of NBD in the presence of M(CO)₆ (M = Cr, Mo, W), where it is envisioned as a thermal steady-state intermediate along the reaction pathway to formation of *cis*-[(endo-η²-NBD)M(CO)₄].^{10,11} The latter has been proposed

to be the key precursor to the production of norbornene as the hydrogenation product.¹⁰

As the work of Oishi⁶ and Kalyanasundaram⁷ and several studies in this laboratory^{12,13} illustrate, fast ring closure reactions can be investigated kinetically where the species containing the monodentate and potentially chelating ligand is produced in predominant concentration via flash photolysis. This technique has been employed here in the investigation of chelate ring closure in [(η²-NBD)Mo(CO)₅] (1) produced after flash photolysis of Mo(CO)₆ in NBD-containing solutions.

Experimental Section

Materials. Molybdenum hexacarbonyl (Climax Molybdenum) was vacuum-sublimed before use. NBD (Aldrich) was freshly distilled under nitrogen, while chlorobenzene (CB) was fractionally distilled from P₄O₁₀ under nitrogen. Toluene and *n*-heptane (Mallinckrodt) and benzene (Baker Analyzed Reagent) were distilled over Na under nitrogen.

Flash Photolysis Studies. The flash photolysis instrumentation (Xe lamps) has been described in detail elsewhere.¹⁴ Solutions 1.2 × 10⁻³ M in Mo(CO)₆ and 0.02–1.5 M in norbornadiene were employed. Since NBD is present in large excess over Mo(CO)₆, pseudo-first-order reaction conditions applied. The monitoring wavelength typically was 425 nm.

Identification of the Reaction Product. A solution of Mo(CO)₆ (4 × 10⁻³ M) and NBD (1.05 M) in *n*-heptane was flashed a single time. An IR spectrum (Nicolet 20 SXB FTIR spectrometer; vs the unphotolyzed Mo(CO)₆/NBD/*n*-heptane solution as a reference) was obtained 15 min after the flash over the carbonyl stretching region (2100–1800 cm⁻¹). The spectrum exhibited bands at 2043.9 (w), 1958.1 (s), and 1911.7 (m) cm⁻¹ attributable to (NBD)Mo(CO)₄, the sole final reaction product (vide infra).¹⁰

Data Analyses. Kinetics data were analyzed by employing computer programs developed in-house; the limits of error, given in parentheses as the uncertainties of the last digit(s) of the cited rate constant or activation parameter, are 1 standard deviation. Supplementary Table I exhibits values of *k*_{obsd} and *k'*_{obsd} (vide infra) obtained for the two reaction steps observed at various temperatures and concentrations of NBD and in various solvents.

Results

Figure 1 exhibits a plot of absorbance (*A*) vs. time (*t*) after flash photolysis of a Mo(CO)₆/NBD/CB solution ([NBD] = 0.613 M) at 26.1 °C, monitoring at 425 nm, fitted as two first-order decays. The inset shows the corresponding plot of ln(*A*),

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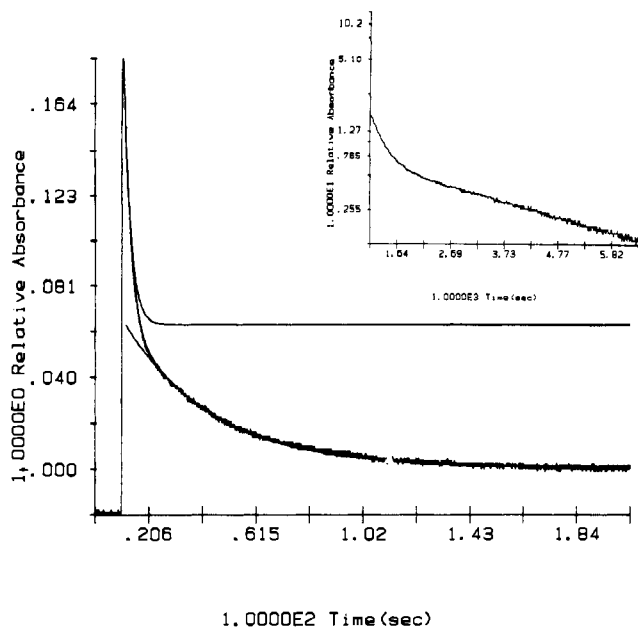


Figure 1. Plot of absorbance vs time monitoring 430 nm for reactions taking place after flash photolysis of $\text{Mo}(\text{CO})_6$ in 0.612 M NBD/CB solution at 26.1 °C. The inset shows these data plotted as $\ln(A_t - A_\infty)$ vs time.

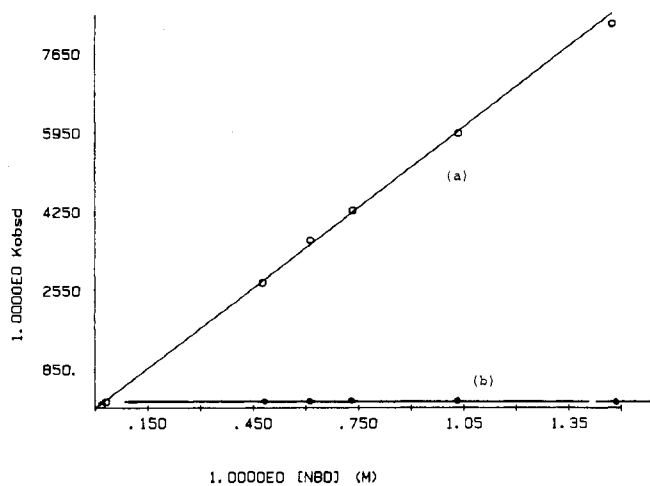


Figure 2. (a) Plot of k_{obsd} vs $[\text{NBD}]$ for the faster reaction taking place after flash photolysis of $\text{Mo}(\text{CO})_6$ in norbornadiene/chlorobenzene solutions. (b) Analogous plot for the slower reaction.

$-A_\infty$) vs. time, which consists of two linear segments. Considering the fact that conversion of $\text{Mo}(\text{CO})_6$ to $(\text{NBD})\text{Mo}(\text{CO})_4$ is probably stepwise, these kinetics plots suggest "biphasic" behavior, that is, two consecutive (pseudo) first-order processes in which the concentration of the intermediate generated via the first step is not negligible (eq 2).



For determination of reaction rates through measurement of some property linearly related to the concentrations of A, B, and C (eq 2), e.g., absorbance, the expression

$$A_t - A_\infty = \alpha \exp(-k_a t) + \beta \exp(-k_b t) \quad (3)$$

may be derived, where α and β are constants (vide infra).¹⁵ The plot of $\ln(A_t - A_\infty)$ vs time shown in the inset of Figure 1 obeys eq 3. For a number of experiments run by employing differing concentrations of NBD (pseudo-first-order reaction conditions, $[\text{NBD}] \gg [\text{Mo}(\text{CO})_6]$), plots of k_{obsd} vs time (faster decay), one

Table I. First- and Second-Order Rate Constants for Reactions Taking Place after Flash Photolysis of $\text{Mo}(\text{CO})_6$ /Norbornadiene Solutions

solvent	temp, °C	$10^{-3}(k_a' + k_a'')$, $\text{M}^{-1} \text{s}^{-1}$	$10^{-2}k_b$, s^{-1}
chlorobenzene ^a	14.7	3.00 (1)	1.61 (1)
	18.6	3.905 (6)	2.02 (2)
	23.5	5.19 (1)	2.75 (2)
	26.1	5.75 (15)	3.06 (12)
	28.1	6.30 (2)	3.57 (2)
	31.3	8.04 (4)	4.38 (5)
	35.0		5.51 (2)
<i>n</i> -heptane	26.1	17 000 (400)	2.69 (7)
toluene		1.01 (7)	0.95 (2)
benzene		2.44 (3)	0.810 (1)

^a $\Delta H_{a'+a''}^\ddagger = 9.3$ (4) kcal/mol; $\Delta S_{a'+a''}^\ddagger = -10.0$ (12) cal/(deg mol); $\Delta H_b^\ddagger = 10.0$ (2) kcal/mol; $\Delta S_b^\ddagger = -13.4$ (8) cal/(deg mol).

of which is shown in Figure 2 for data at 26.1 °C, obey the rate law

$$k_{\text{obsd}} = k_a[\text{NBD}] \quad (4)$$

while plots of k'_{obsd} vs time (slower decay; eq 2, Figure 2) obey the equation

$$k'_{\text{obsd}} = k_b \quad (5)$$

The disappearance of the segment of the plot obeying eq 5 at very low $[\text{NBD}]$ (<0.04 M), for which $k_a[\text{NBD}] < k_b$, implies consecutive reactions in which that governed by k_a precedes that governed by k_b .¹⁵ From an analysis of the time-resolved spectra for the two steps, λ_{max} for the first and second intermediates generated after flash photolysis were determined to be ca. 410 and 425 nm, respectively (vide infra). Rate constants for the two steps at various temperatures in CB, *n*-heptane, benzene, and toluene are given in Table I.

Discussion

The First Reaction Step—Solvent Displacement from [(solvent)Mo(CO)₅] by NBD. Two reaction steps are observed on the millisecond time scale after flash photolysis of $\text{Mo}(\text{CO})_6$ /NBD solutions, and there is much evidence that the first of these involves displacement of a solvent molecule from $[(\text{solvent})\text{Mo}(\text{CO})_5]$ by NBD. Solvation after production of $[\text{Cr}(\text{CO})_5]$ following flash photolysis is rapid,¹⁶ and it is likely that the same is true for the Mo analogue. The $[(\text{solvent})\text{Mo}(\text{CO})_5]$ species thus produced in predominant concentration then can react with NBD via solvent displacement to afford **1**. By analogy, it is observed that flash photolysis of $(\eta^2\text{-NP})\text{Mo}(\text{CO})_4$ (NP = 1-(diethylamino)-2-(diphenylphosphino)ethane) in CB solution results in Mo–N bond fission and rapid solvation of the *cis*- $[(\eta^1\text{-NP})\text{Mo}(\text{CO})_4]$ thus produced to afford *cis*- $[(\eta^1\text{-NP})(\text{CB})\text{Mo}(\text{CO})_4]$;¹² this yields *cis*- $(\eta^1\text{-NP})(\text{P}(\text{O}-i\text{-Pr})_3)\text{Mo}(\text{CO})_4$ upon reaction with $\text{P}(\text{O}-i\text{-Pr})_3$. The second-order rate constant for this step, $7.3(2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 24.6 °C, is not too different from the rate observed here for the first step observed here, $5.75(15) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in CB at 26.1 °C.^{12,17}

It has long been known that (olefin)Mo(CO)₅ complexes are produced in solution upon photolysis of $\text{Mo}(\text{CO})_6$ in the presence of olefins. Thus, for example, photolysis of $\text{Mo}(\text{CO})_6$ in *n*-hexane/ethene solutions affords (ethene)Mo(CO)₅.¹⁸ However, for solvent displacement by NBD from $[(\text{solvent})\text{Mo}(\text{CO})_5]$, two pentacarbonyl species, in which Mo is coordinated exo or endo, can be envisioned. In Cr carbonyl complexes, exo-olefin coordination is observed for norbornadienes containing an alkoxy group

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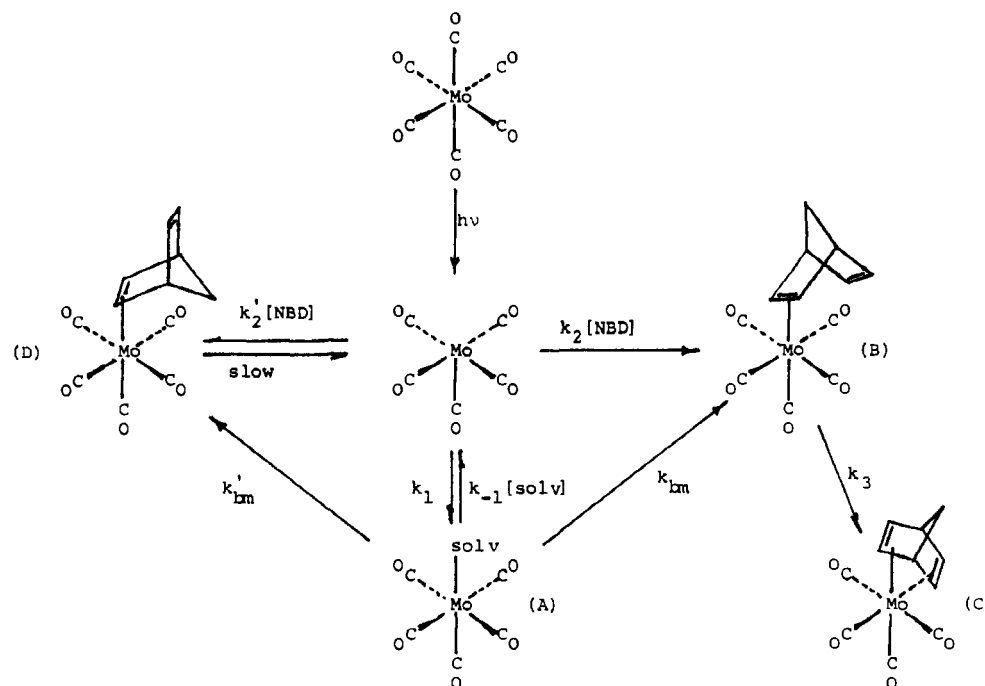
(17) Solvent dissociation is anticipated to be somewhat faster from *cis*- $[(\eta^1\text{-NP})(\text{CB})\text{Mo}(\text{CO})_4]$ than from $[(\text{CB})\text{Mo}(\text{CO})_5]$ as the result of steric acceleration induced in the departing CB molecule in the former by bulky NP cis to it: Asali, K. J.; Kimbrough, J.; Awad, H. H.; Dobson, G. R. Manuscript in preparation; cf. ref 25.

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Table II. Carbonyl Stretching Spectral Data for Model Complexes, Intermediates, and the Reaction Product

complex	$\nu(\text{CO}), \text{cm}^{-1}$				
$(\eta^2\text{-butadiene})\text{Mo}(\text{CO})_5^a$	2087	1961		1977	
$(\eta^2\text{-ethene})\text{Mo}(\text{CO})_5^a$	2087	1960		1976	
$\text{NBE} + \text{Mo}(\text{CO})_6^b$	2078.1	1959.4		1948.2	
$(\eta^4\text{-NBD})\text{Mo}(\text{CO})_4^c$		2044.0		1959.4	1914.2
$\text{NBD} + \text{Mo}(\text{CO})_6^d$	2077.1	2943.7	1958.6	1948.3	1911.4
$\text{NBD} + \text{Mo}(\text{CO})_6^e$		2043.9	1958.1		1911.7

^a Reference 18; *n*-hexane solution. ^b Observed 4 min after flash photolysis of $\text{Mo}(\text{CO})_6/\text{NBE}$ in *n*-heptane solution. ^c Reference 10. ^d Observed 4 min after flash photolysis of $\text{Mo}(\text{CO})_6/\text{NBD}$ in *n*-heptane solution. ^e Observed 15 min after flash photolysis of $\text{Mo}(\text{CO})_6/\text{NBD}$ in *n*-heptane solution.

Scheme 1

in the 7-position, which thus can form a chelating ring containing coordinated O and olefin;¹⁹ similar behavior has been observed upon NBD attack at $\text{Fe}(\text{CO})_5$.^{20,21} Evidence has also been presented which indicates that preferential exo coordination of Fe in iron carbonyls takes place in analogy to observations in organic systems.²² On the other hand, NBD, when functioning as a chelating ligand, is coordinated in an endo fashion.²³ On the basis of these observations, it is reasonable to expect that solvent displacement by NBD can take place both in an endo and in an exo fashion.

Chelate Ring Closure in *endo*- $[(\eta^2\text{-NBD})\text{Mo}(\text{CO})_5]$ (1-en). The second, slower unimolecular step is reasonably attributed to chelate ring closure in the 1-end intermediate (vide supra). Any *exo*- $[(\eta^2\text{-NBD})\text{Mo}(\text{CO})_5]$ (1-ex) present is not expected to undergo chelate ring closure and should disappear yet more slowly.

The Fate of *exo*- $[(\eta^2\text{-NBD})\text{Mo}(\text{CO})_5]$ (2). Given that 15 min after a flash only $(\eta^4\text{-NBD})\text{Mo}(\text{CO})_4$ is present in solution (see Experimental Section), any 1-ex produced must disappear more slowly than ca. 20 ms and more rapidly than 15 min. Regions of this time domain were probed by infrared spectroscopy. Figure 3 illustrates carbonyl stretching difference spectra of (A) a $\text{Mo}(\text{CO})_6/\text{norbornene}/n\text{-heptane}$ solution before and 4 min after a single flash, (B) a $\text{Mo}(\text{CO})_6/\text{NBD}/n\text{-heptane}$ solution before and 4 min after a single flash, and (C) this same solution before and 15 min after a single flash. Positions of the observed carbonyl

stretching modes are listed in Table II. The "negative peak", c, observed in each spectrum at ca. 1986 (*s*) cm^{-1} is attributable to the depletion of $\text{Mo}(\text{CO})_6$ upon flash photolysis. The bands labeled a in spectrum A in Figure 3 exhibit the pattern characteristic of a $\text{M}(\text{CO})_5$ moiety (C_{4v} symmetry)²⁴ and thus are attributable to the presence of $(\eta^2\text{-norbornene})\text{Mo}(\text{CO})_5$ (norbornene = NBE). They may be compared to those reported for $(\eta^2\text{-ethene})\text{Mo}(\text{CO})_5$ (*n*-hexane solution), observed at 2085 (*w*), 1976 (*s*), and 1960 (*ms*) cm^{-1} .¹⁸ In Figure 3B (a $\text{Mo}(\text{CO})_6/\text{NBD}/n\text{-heptane}$ solution, 4 min after the flash), absorptions attributable to $[(\eta^2\text{-NBD})\text{Mo}(\text{CO})_5]$, very similar to those for $(\eta^2\text{-NBE})\text{Mo}(\text{CO})_5$, are observed, together with those for $(\eta^4\text{-NBD})\text{Mo}(\text{CO})_4$ (labeled b). After 15 min, this spectrum exhibits only absorptions due to the latter complex, and comparison of the intensity changes which have taken place indicates that bands attributable to the tetracarbonyl have increased in intensity at the expense of those for 1. Since it is most reasonable to attribute the ligand-independent pathway observed on the millisecond time scale to chelate ring closure in 1-en, the pentacarbonyl complex observed in Figure 3B is assigned as 1-ex. The most likely pathway for its conversion to the 2 finally produced is via reversible dissociation of NBD to produce its endo counterpart.

Overall Reaction Mechanism and Rate Law for Formation of $(\eta^4\text{-NBD})\text{Mo}(\text{CO})_4$. The overall mechanism for formation of 2 upon flash photolysis of $\text{Mo}(\text{CO})_6/\text{NBD}$ solutions thus is that illustrated in Scheme I, where solvent displacement is assumed to be a dissociative, rather than an interchange process. Studies of related Cr and W systems have supported dissociative desolvation of CB.^{25,26} For this mechanism the biphasic process

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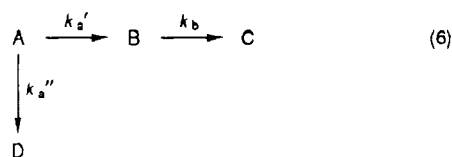
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illustrated in Figure 1 may be represented by eq 6 rather than



eq 2, where A is $[(CB)Mo(CO)_5]$, B is 1-cn, C is 2, and D is 1-ex and $k_a' + k_a'' = k_a$ in eq 2. The mechanism illustrated in Scheme I is similar to that proposed by Oishi⁶ and Kalyanasundaram⁷ for the formation of $(phen)M(CO)_4$ after flash photolysis of $Mo(CO)_6/phen$ solutions.^{6,27} It also obeys eq 3 (cf. ref 15).²⁸

For the mechanism affording *exo*- and *endo*-(η^2 -NBD)Mo(CO)₅ illustrated in Scheme I and governed by rate constants k_1 , k_2 , k_2' and k_{-1} , the steady-state rate law is

$$k_{obsd} = k_1(k_2 + k_2')[NBD]/(k_{-1}[CB] + (k_2 + k_2')[NBD]) \quad (7)$$

Since $[CB] \gg [NBD]$, $[CB]$ is constant and it is reasonable that $k_{-1}[CB] \gg (k_2 + k_2')[NBD]$; thus

$$k_{obsd} = k_1(k_2 + k_2')[NBD]/k_{-1}[CB] \quad (8)$$

consistent with the observed rate law (eq 4).

The activation parameters (based on eq 8) for this step are $\Delta H^\ddagger = 9.3$ (4) kcal/mol and $\Delta S^\ddagger = -5.4$ (13) cal/(deg mol), and the latter may indeed suggest an interchange pathway for desolvation. Recent studies of displacement of *n*-heptane by amines from $[(n\text{-heptane})Cr(CO)_5]$ suggest that an interchange process (governed by k_{bm} and k_{bm}' , Scheme I), in which there is significant residual hydrocarbon-Cr bonding, which also is consistent with eq 4, also is accessible.^{29,30} However, such negative entropies of activation have been observed even in systems where other evidence strongly supports a dissociative mechanism for solvent displacement by an incoming nucleophile.²⁶ If the dissociative mechanism is correct, the enthalpy of activation may closely approximate the Mo-CB bond strength, since reactions of CB and NBD with $[Mo(CO)_5]$ are expected to be very rapid, with enthalpies of activation approaching zero.¹⁶ This enthalpy of activation, (9.3 (4) kcal/mol) may be compared to that for dissociation of CB from $[(CB)Cr(CO)_5]$, 9.8 (1) kcal/mol.²⁶ This order for activation energies for bond dissociation (Cr > Mo) is that usually observed for group VIB metal carbonyls.³¹

The reaction was also briefly investigated in the solvents *n*-heptane, benzene and toluene. In *n*-heptane, employing pulsed laser flash photolysis,³² the rate constant for solvent-displacement by NBD was found to be 1.70 (4) $\times 10^7$ M⁻¹ s⁻¹ at 26.1 °C.³³ Relative rates of solvent displacement from $[(\text{solvent})Mo(CO)_6]$ by NBD at 26.1 °C thus vary *n*-heptane (18 000) \gg CB (6.1) > benzene (2.6) > toluene (1.0). The rates in the three aromatic solvents (RX) are of particular interest in that they increase with the increasing electron-withdrawing nature of X, perhaps sug-

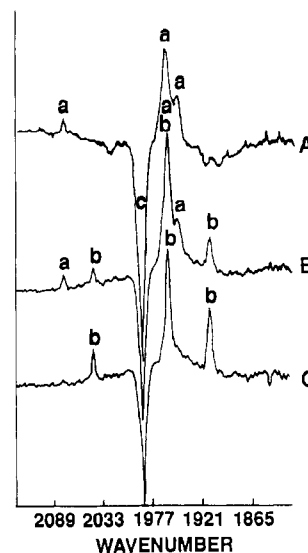


Figure 3. Infrared difference spectra: (A) $Mo(CO)_6/NBE/n$ -heptane solution before and 4 min after a single flash; (B) $Mo(CO)_6/NBD/n$ -heptane solution before and 4 min after a single flash; (C) $Mo(CO)_6/NBD/n$ -heptane solution 15 min after a single flash.

gestive of bonding via an "agostic" hydrogen³⁴ or through an isolated double bond,³⁵ even in CB, although many examples of R-Cl-M bonding have been documented.³⁶ The ratio of rates observed in CB and toluene (6.1) may be contrasted to that observed for *cis*- $[(\text{solvent})(\eta^1\text{-DTN})W(CO)_4]$ complexes, 0.29 (via chelate ring reclosure; DTN = 2,2,8,8-tetramethyl-3,7-dithianone),³⁷ and for *cis*- $[(\text{solvent})(L)W(CO)_4]$, 0.006 (via dissociation of solvent and subsequent reaction with L (=P(O-*i*-Pr)₃)).²⁵ These differences may arise not only from differing metal atoms, substituents thereon, and "trapping" reagents but also from differing modes of bonding of CB to the metals.

Activation parameters for the second, slower step, $\Delta H_3^\ddagger = 10.1$ (2) kcal/mol and $\Delta S_3^\ddagger = -13.4$ (8) cal/(deg mol), are consistent with the proposed unimolecular ring-closure mechanism. A comparison of this enthalpy of activation for CO extrusion with, for example, those observed for CO loss from $Mo(CO)_6$, 30–32 kcal/mol,³⁸ also is strongly indicative of an associative displacement

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 (27) The plane of symmetry present in phen dictates that only one stereoisomer is formed through reaction of phen with $Mo(CO)_6$.
 (28) For the mechanism shown in eq 6, the values of α and β are as follows:

$$\alpha = (\epsilon_A - \epsilon_C)[A]_0 + (\epsilon_B - \epsilon_C) \frac{k_a'[A]_0}{k_b - (k_a' + k_a'')} + (\epsilon_C - \epsilon_D) \frac{k_a''[A]_0}{k_a' + k_a''}$$

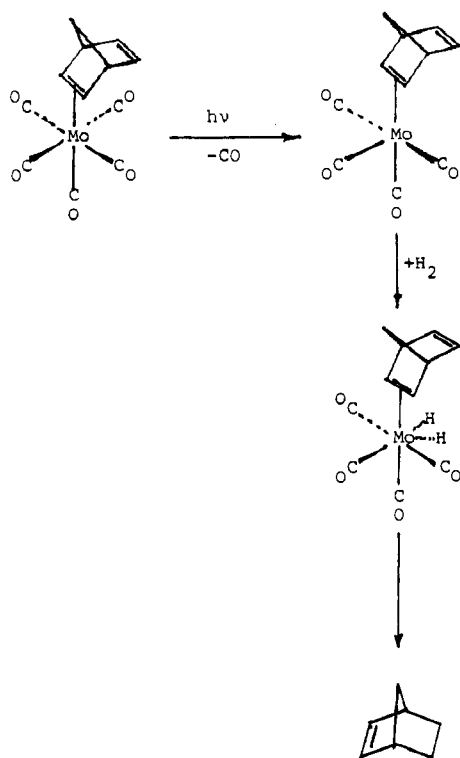
$$\beta = (\epsilon_C - \epsilon_B) \frac{k_a'[A]_0}{k_b - (k_a' + k_a'')}$$

(ϵ 's are molar absorptivities).

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Scheme II



of CO upon chelate ring closure. The decrease in the enthalpy of activation from the hexacarbonyl to this ring-closure process is much greater than was observed for reactions of nonrigid chelating ligands.²⁻⁵ The greatly enhanced rate of ring closure observed in **1**-end is, however, comparable to that observed by Oishi⁶ and by Kalyanasundaram⁷ in (η^2 -phen)M(CO)₅ complexes, where phen also can form a rigid chelate ring. Oishi has postulated very significant interactions between the metal atoms and the nonbonded nitrogen in (η^2 -phen)M(CO)₅ complexes on the basis of pronounced differences in its visible spectrum vs that observed in the "nonrigid" (η^2 -bpy)M(CO)₅ analogues (bpy = 2,2'-bipyridyl).⁶

Evidence for a similar interaction between the metal pentacarbonyl moiety and the rigid NBE ring is noted in the present study based upon a comparison of the carbonyl stretching spectrum of (η^2 -NBE)Mo(CO)₅ and those for related complexes containing

coordinated alkenes such as (η^2 -butadiene)Mo(CO)₅, which contains a nonrigid bidentate ligand, and (η^2 -ethene)Mo(CO)₅ (Table II).¹⁸ The latter two spectra are very similar to one another, but dramatic decreases in $\nu(\text{CO})$ are observed in the (η^2 -NBE)-Mo(CO)₅ spectrum. These decreases are interpretable, by analogy to Oishi's observations for the related phen systems,⁶ in terms of significant "nonbonding" interaction of NBE with the Mo(CO)₅ moiety,³⁹ which can lead to olefin-Mo bond lengthening. A decrease, some 30 cm⁻¹, is noted in the position of the A₁ stretching mode for the carbonyl trans to the coordinated olefin, the stretching mode most sensitive to changes in olefin-to-metal π -bonding. Mo-olefin bond lengthening should afford decreased π -bonding. The two effects, the strong nonbonding interaction and lengthened Mo-olefin bond, should lead to an increase in the ground-state energy in (η^2 -NBE)Mo(CO)₅ vs that in (η^2 -butadiene)Mo(CO)₅ and (η^2 -ethene)Mo(CO)₅. Only one "set" of carbonyl stretching bands is observed in (η^2 -NBE)Mo(CO)₅ despite the likelihood, in analogy to **1** (vide supra), that both exo and endo isomers are produced after photolysis. Thus, the similarity of the carbonyl stretching spectra for this isomeric mixture and that of **1**-ex renders it highly probable that similar destabilizing effects also are present in **1**-end.

As would be expected where no coordinatively unsaturated species is involved, solvent effects on the CO-extrusion step are much less pronounced than for the solvent-displacement step.

Photoinduced Hydrogenation of NBD. The transitory existence of **1**-end ($t_{1/2}$ of ca. 3 ms in alkane solvent at room temperature) renders it improbable that CO loss through its CW photolysis in situ can afford coordinatively unsaturated *endo*-[(η^2 -NBD)Mo(CO)₄] and subsequently lead to the formation of NBE (Scheme II). This pathway has been proposed to account for the differing product ratios (NBE vs nortricycline) observed for photoinduced hydrogenation of NBD in the presence of **2** compared to photoinduced hydrogenation in the M(CO)₆/NBD/H₂ solutions.¹⁰ Irradiation of Cr(CO)₆/NBD/D₂ solutions affords *endo,endo*-NBE-5,6-*d*₂,⁴⁰ and thus this hydrogenation product arises via an intermediate in which the metal atom is *endo* to the coordinated NBD ligand. It also would appear unlikely that CW photolysis of **1**-ex could afford a suitable *endo* hydrogenation precursor.

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Supplementary Material Available: Pseudo-first-order rate constants for thermal reactions after flash photolysis of Mo(CO)₆ and norbornadiene in various solvents and temperatures (Supplementary Table I) (1 page). Ordering information is given on any current masthead page.

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