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OCTAHEDRAL METAL CARBONYLS

XLIII *. THE KINETICS AND MECHANISM OF THE REACTION OF ALLYL BROMIDE WITH (*o*-PHENANTHROLINE)TETRACARBONYLMOLYBDENUM(0)

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Summary

The reaction of allyl bromide with (*o*-phenanthroline)tetracarbonylmolybdenum(0), (phen)Mo(CO)$_4$, in 1,2-dichloroethane to afford (phen)Mo(CO)$_2$(η^3-C$_3$H$_5$)(Br) obeys the rate law, $-d[(phen)Mo(CO)_4]/dt = k_1[(phen)Mo(CO)_4]$. The reaction is envisioned to proceed via slow fission of a Mo—CO bond, probably solvent-assisted, and subsequent reaction with allyl bromide. With THF as solvent, a small second-order term is also observed in the rate law. Possible subsequent reaction steps involving coordination of the olefinic end of allyl bromide and ring-closure to afford product are also discussed.

Introduction

The Group VIB metal carbonyls and their derivatives (M = Cr, Mo, W) exhibit great versatility in their reactivity, and reactions of (phen)Mo(CO)$_4$ have been widely studied kinetically in this regard. Graham and Angelici [2] have reported that ligand-exchange reactions (eq. 1) of Lewis bases (L, phosphines and phosphites) and this substrate obey the two-term rate law 2, a rate law observed

$$(phen)Mo(CO)_4 + L \rightarrow fac\text{-}(phen)(L)Mo(CO)_3 + CO \quad (1)$$

$$-d[(phen)Mo(CO)_4]/dt = k_1[(phen)Mo(CO)_4] + k_2[(phen)Mo(CO)_4][L] \quad (2)$$

for many ligand-exchange reactions for other substrates [3]. The weight of evidence supports concurrent dissociative and interchange (*D* and *I*) [4] pathways for the exchange (eq. 3).

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* For part XLII see ref. 1.

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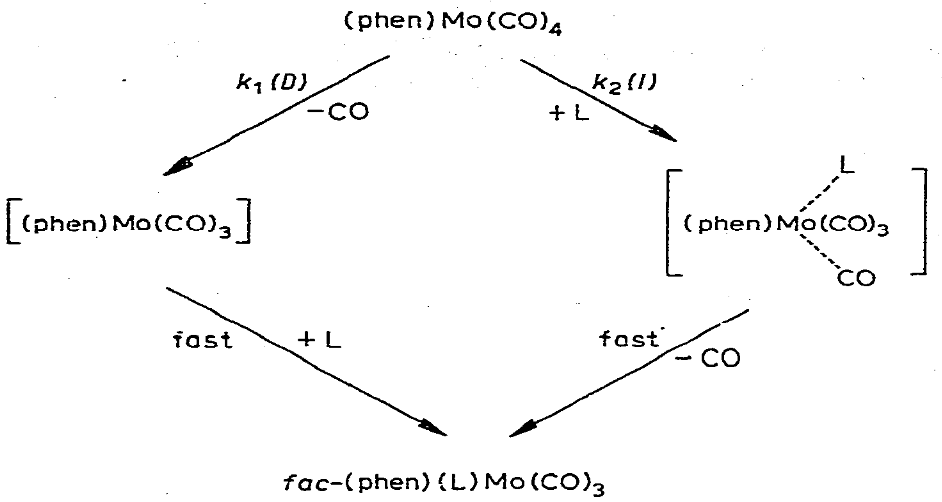


(3)

Synthetic studies by Kummer and Graham [5] and kinetics investigations by two groups [6—8] have shown that (phen)Mo(CO)$_4$ and related substrates are also susceptible to attack by electrophilic reagents such as organotin halides (R_nSnX$_{4-n}$) [5,8] and mercuric halides (HgX$_2$) [6,7] (= TX) (eq. 4) by mechanisms

$$\text{(phen)Mo(CO)}_4 + \text{TX} \rightarrow \text{(phen)Mo}^{\text{II}}\text{(CO)}_3\text{(T)(X)} + \text{CO} \qquad (4)$$

which usually involve the successive addition of two molecules of the electrophilic reagent to the substrate, followed by other rapid steps.

A type of reaction which might be considered to possess similarities both to eq. 1 and 4 is that of allyl halides with (phen)Mo(CO)$_4$ [9] (eq. 5), in which

$$\text{(phen)Mo(CO)}_4 + \text{C}_3\text{H}_5\text{Br} \rightarrow \text{(phen)Mo(CO)}_2(\eta^3\text{-C}_3\text{H}_5)\text{(Br)} + 2\,\text{CO} \qquad (5)$$

two carbonyls are replaced by an η^3-C$_3$H$_5$ (formal three-electron donor) and X (formal one electron donor).

Comparisons of carbonyl stretching frequencies for substrates and products for all three reaction types reveal that little electron density is transferred from the metal to the remaining carbonyls upon substitution of allyl bromide for two carbonyls [9], in contrast to ligand-exchange reactions, which usually involve replacement of CO by L which are net charge relative to CO [3], and to the "oxidative addition—elimination" reactions, in which electron density at the metal is decreased [5]. Thus both the systematics of substitution (eq. 1, 4, 5) and electronic factors suggest reactions of allyl halides and Group VIB metal carbonyl derivatives to be distinctly different from other, much studied reaction types. It was therefore deemed importance to investigate the mechanism of substitution of allyl bromide with (phen)Mo(CO)$_4$ [9]. The results of that investigation are the subject of this report.

Experimental

General. Infrared spectra were obtained, and reaction rates were monitored employing a Perkin—Elmer Model 621 grating spectrophotometer, Spectra were calibrated employing a band of water vapor at 1869.4 cm^{-1} [10].

Preparation and purification of reagents. Allyl bromide (Fisher Certified) was fractionally distilled under nitrogen. $(Phen)Mo(CO)_4$ was prepared through use of the method of Stiddard [11]. 1,2-Dichloroethane (Baker) was dried over P_2O_5 and distilled under nitrogen. Tetrahydrofuran (THF, Fisher Certified) was refluxed for three hours over Na, and was then fractionally distilled under nitrogen.

Determination of reaction rates. Kinetics runs were carried out by monitoring the disappearance of an intense carbonyl stretching band of the substrate at ca. 1900 cm^{-1}. Initial substrate concentrations of approximately 5×10^{-3} *M* (0.2 mm cell pathlength) were employed, and pseudo first-order reaction conditions obtained through use of at least a ten-fold excess of allyl bromide. Plots of $\ln(A_t - A_\infty)$ vs. time (A_t and A_∞ being the absorbance at time t and at > ten half-lives, respectively) were linear to over 90 per cent completion of the reactions, although only data taken over the first three half-lives were analyzed. Other experimental procedures have been described elsewhere [12]. Rate data were analyzed employing a linear least-squares computer program and the North Texas State University IBM 360 Model 50 computer. Rate data (values of k_{obsd}, the pseudo first-order rate constants) are presented in Table 1. First and second order rate constants, together with activation parameters are exhibited in Table

TABLE 1

RATE CONSTANTS FOR REACTION OF $(phen)Mo(CO)_4$ WITH ALLYL BROMIDE IN 1,2-DICHLOROETHANE AND TETRAHYDROFURAN AT VARIOUS TEMPERATURES

Solvent	T (°C)	$[C_3H_5Br]$ (*M*)	$10^4 k_{obsd}$ (sec^{-1})
1,2-Dichloroethane			
	47.9	0.0487	1.20(1)
		0.0897	1.24(2)
		0.2188	1.27(2)
		0.4109	1.26(1)
		0.5699	1.25(1)
		0.7932	1.21(1)
		0.8001	1.23(2)
		1.0107	1.24(1)
		1.3412	1.25(1)
Tetrahydrofuran			
	49.0	0.0809	0.58(1)
		0.0826	0.58(4)
	53.9	0.0759	1.09(1)
		0.0772	1.09(1)
		0.0782	1.10(1)
	58.1	0.0513	1.85(2)
		0.0607	1.96(10)
		0.0753	1.82(2)
		0.2484	1.86(1)
		0.5124	2.01(4)
		0.8881	2.01(3)
		1.1550	2.08(1)
	60.2	0.0768	2.26(2)
		0.2535	2.47(2)
		0.4692	2.66(3)
		0.8039	2.71(4)

TABLE 2

FIRST- AND SECOND-ORDER RATE CONSTANTS, AND ACTIVATION PARAMETERS FOR REACTIO OF (phen)Mo(CO)$_4$ WITH ALLYL BROMIDE IN 1,2-DICHLOROETHANE AND TETRAHYDROFURAN

Solvent	T (°C)	$10^4 k_1$ (sec^{-1})	$10^5 k_2$ (M^{-1} sec^{-1})
1,2-Dichloroethane			
	47.9	1.24(2)	...
Tetrahydrofuran [a]			
	49.0	0.58(1)	not determined
	53.9	1.09(1)	not determined
	58.1	1.86(3)	1.9(5)
	60.2	2.28(9)	6.1(18)

[a] $\Delta H_1^{\neq}$ 25.7(14) kcal/mol; $\Delta S_1^{\neq} = -0.2(38)$ cal/deg mol. Activation parameters reported in ref. 3 for reaction of (phen)Mo(CO)$_4$ with L in 1,3-dichloroethane: $\Delta H_1^{\neq}$ 25.1(12) kcal/mol; $\Delta S_1^{\neq}$ 2.4(24) cal/deg mol.

2. Limits of error cited (in parentheses, uncertainty of last digit(s)) are one standard deviation.

Identification of reaction product. The reaction product, (phen)Mo(CO)$_2$(η-C$_3$H$_5$)(Br), was independently synthesized employing the method of Hull and Stiddard [8]. Periodic scans of the carbonyl stretching region for reaction solutions for trial kinetics runs revealed the presence only of bands attributable to the substrate [11] and the reaction product [8].

Results and discussion

Rate data for the reaction of (phen)Mo(CO)$_4$ with allyl bromide in 1,2-dichloroethane and THF (Tables 1 and 2) support the rate law 6, analogous to

$$-d[(\text{phen})\text{Mo(CO)}_4]/dt = k_1[(\text{phen})\text{Mo(CO)}_4] + k_2[(\text{phen})\text{Mo(CO)}_4][\text{C}_3\text{H}_5\text{Br}] \quad (6)$$

that observed for this substrate in its reaction with Lewis bases (eq. 2) [2]. For reaction in 1,2-dichloroethane at 47.9°C, the path governed by k_2 was not observed over a 25-fold range of allyl bromide concentrations. The average value of the first order rate constant, k_1 at 47.0°C, 1.24(2) × 10^{-4} sec^{-1} is, however, in excellent agreement with that observed by Graham and Angelici under those conditions for the reaction of (phen)Mo(CO)$_4$ with phosphines and phosphites according to eq. 1, 1.14 × 10^{-4} sec^{-1} [2]. The data in 1,2-dichloroethane thus are consistent with mechanism 7 for the initial (rate-determining) step.

$$(\text{phen})\text{Mo(CO)}_4 \xrightarrow{k_1, -\text{CO}} [(\text{phen})\text{Mo(CO)}_3] \quad (7)$$

Recent isotopic labeling studies for (phen)Mo(CO)$_4$ indicate it to be highly probable that initial loss of CO occurs *cis* to the two phen nitrogens [13].

However, the only slightly positive (2.4(24) cal/deg mol) entropy of activation for the unimolecular path determined by Graham and Angelici from data at three temperatures is suggestive of significant association between solvent and substrate in the transition state, and thus both for this work and that of

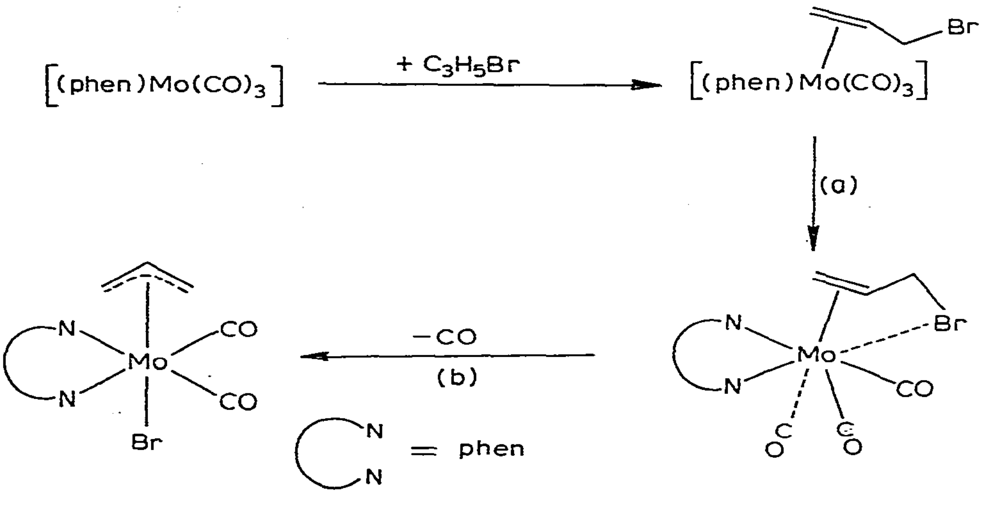
Graham and Angelici, some solvation in the transition state formed during Mo—CO bond-breaking is probable.

For reaction of (phen)Mo$(CO)_4$ with allyl bromide in the coordinating solvent THF, observed reaction rates were significantly lower (Tables 1, 2) than in 1,2-dichloroethane, and a slight dependence of rate on allyl bromide concentration, suggestive of a concurrent reaction path governed by k_2 (eq. 6), involving rate-determining association between allyl bromide and the substrate was also observed. The rate constant for this path governed by k_2 (eq. 6) was, however, only ca. ten per cent as large as that for the path governed by k_1, and thus an accurate determination of its magnitude was not possible. Activation parameters derived from rate data at four temperatures were the same, within experimental uncertainties as those observed by Graham and Angelici for reaction in 1,2-dichloroethane (Table 2) [2].

The faster rates observed for reaction in the more polar 1,2-dichloroethane than in the coordinating solvent THF suggest charge-separation in the transition state leading to solvation, and are consistent with data of Graham and Angelici for ligand-exchange reactions (according to eq. 1) of (2,2'-dipyridyl)Mo$(CO)_4$ in various solvents [14], which also showed an increase in rate via the ligand-independent path with increased solvent polarity (as inferred from solvent dielectric constants). In contrast, the reaction of Ni$(CO)_4$ with triphenylphosphine via rate-determining dissociation of CO has been found to proceed faster in THF than in 1,2-dichloroethane [15].

These results demonstrate that the mechanism of reaction of (phen)Mo$(CO)_4$ with allyl bromide is closely related to those of other ligand-exchange processes involving this and other substrates, and is unlike oxidative addition—elimination processes.

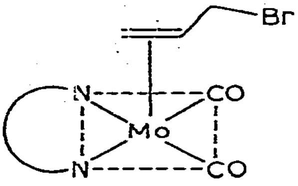
While the rate data shed no direct light on reaction steps subsequent to Mo—CO bond-breaking, speculation based on the known chemistry of the metal carbonyls is instructive. Given the well-documented stabilities of mono- and polyolefinic complexes of the Group VIB metal carbonyls [16], it is reasonable to presume that coordination of allyl bromide through the olefinic function takes place, and is followed by "ring-closure", with expulsion of an additional carbonyl, to afford the observed reaction product (reaction pathway 8).



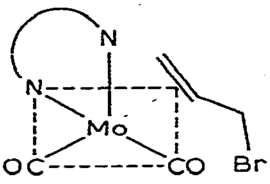
(8)

Based upon available crystallographic and spectroscopic evidence [17—20], it is probable that the ultimate reaction product is the one in which the η^3-allyl and Br groups are mutually *trans*, and the carbonyls are *cis* (reaction 8b). Thus the structure is probably analogous to that for (phen)Mo$(CO)_2(L)_2$ complexes [21].

The kinetics and mechanism for the formation of (phen)Mo$(CO)_2(L)_2$ (for L = P$(OEt)_3$) from *fac*-(phen)(L)Mo$(CO)_3$ has been studied, and evidence indicates the process to proceed via a unimolecular path involving rate-determining fission of a Mo—CO bond [22]. Thus it seems probable that the ring-closure (eq. 8) is a concerted process, both on the basis of the kinetics evidence [22] and since the carbonyl expelled upon ring-closure is that expected to be least tightly-held in intermediate (8a). Simple π-bonding arguments suggest that a carbonyl *trans* to a strongly π-accepting substituent should be most labile [23] and the lability of the carbonyl *trans* to the olefin also is consistent with the "site preference" model of Atwood and Brown [24], which presumes that non-π-accepting ligands (such as the phen nitrogens) preferentially adopt positions in the equatorial plane of the sixteen-electron, probably square-pyramidal [3], intermediate formed through metal—CO bond fission. Thus, formation of Ia preferentially to Ib would suggest stabilization of the transition state leading to production of the observed reaction product. Attack at Mo by the Br atom, which bears a partial negative charge, is not unreasonable given the known [25] susceptibility of the Group VIB metal carbonyls to attack by halide ions [26].



(Ia)



(Ib)

Reasonable analogies to mechanisms of known reactions can thus be drawn to afford an overall mechanism for reaction of (phen)Mo$(CO)_4$ with allyl bromide which is also consistent with currently-discussed bonding theories.

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* Based upon π-bonding effects and the Atwood-Brown "site preference" view, it would appear much less probable that initial interaction of Br at the vacant coordination site in mechanism 8, followed by ring-closure involving the olefinic functionality would afford a product in which the η-allyl and Br groups are mutually *trans*.

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