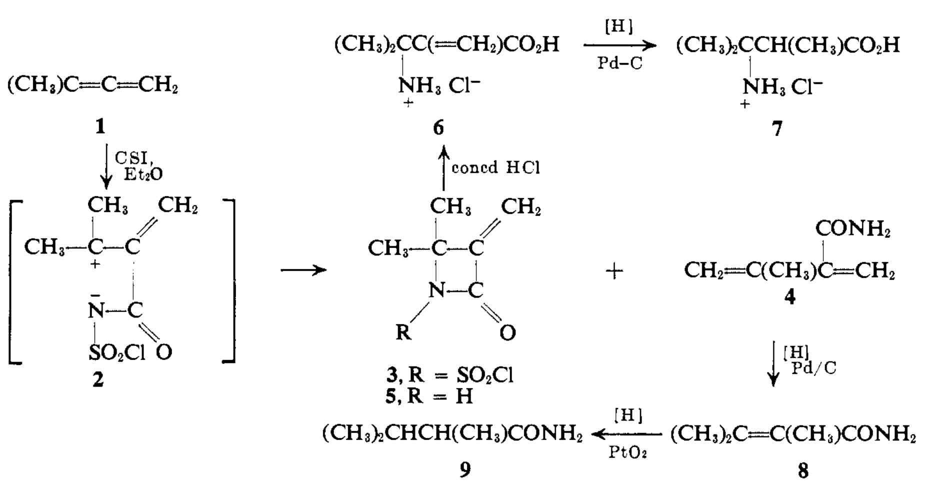
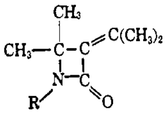
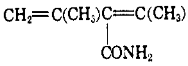
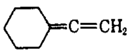
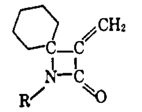
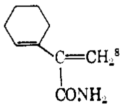
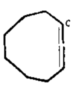
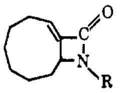
Scheme I



the known 2,3-dimethylcrotonamide (**8**),[10,11] and finally to the known 2,3-dimethylbutanamide (**9**)[13] (see Scheme I).

Table I. Products and Yields of CSI Addition to Allenes

Allene	β-Lactam	% yield	Diene	% yield
$(CH_3)_2C{=}C{=}C(CH_3)_2$		$R = SO_2Cl$[8] 73 $R = H$[8] 72[a]	 $CH_2{=}C(CH_3)\underset{\displaystyle CONH_2}{C}{=}C(CH_3)_2$[8]	22
		$R = SO_2Cl$[8] 38 $R = H$[8] 68[a]		32
		$R = SO_2Cl$ 89[b] $R = H$[8] 40[a]		

[a] Obtained by reduction of the N-chlorosulfonyl-β-lactam with benzenethiol and pyridine in acetone.[6] [b] Crude oil. [c] K. G. Untch, D. J Martin, and N. T. Castellucci, *J. Org. Chem.*, **30**, 3572 (1965).

The zwitterionic transition state **2** proposed is consistent with the two-step, 1,2-dipolar cycloaddition mechanism originally suggested by Graf.[6,14] The CSI adds predominantly to the central carbon of the allenic system[15] leading to the more stable, tertiary carbonium ion, which, after suitable rotation, receives additional stabilization as an allylic cation. The developing negative charge on the nitrogen atom in **2** is also stabilized by its two adjacent electronegative groups. Cyclization of **2** would lead to **3**, while proton transfer from C to N would produce **4**.

The results of CSI addition to three additional allenes are summarized in Table I.

Acknowledgment. We are grateful to Professor R. Norman Jones (National Research Council) for the determination and interpretation of the infrared and Raman spectra of **5**. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grants AF-AFOSR-62-18 and -488-64.

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[10] E. J. Corey, *J. Am. Chem. Soc.*, **75**, 1163 (1953).

[11] This 1,4 reduction seems unlikely; more probably, 1,2 reduction of the terminal methylene group in **4** occurs initially to give 2-methylene-3-methylbutanamide (**10**) followed by isomerization to **8**. Significantly, the isomeric 1,2-reduction product (**11**)[10,12] did not isomerize under the reaction conditions.

$CH_3CH(CH_3)C({=}CH_2)CONH_2$ **10** $CH_3C({=}CH_2)CH(CH_3)CONH_2$ **11**

[12] Obtained by us as one of the CSI addition products to trimethylethylene.[6]

[13] C. D. Nenitzescu and I. Chicos, *Ber.*, **68**, 1584 (1935); also prepared by us *via* reduction (Pd-C) of **11**.

[14] A concerted mechanism has been shown to be disallowed in such cases by recently developed selection rules for such cycloaddition reactions [R. Hoffman and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965)].

[15] As has also been reported to occur in the oxymercuration of substituted allenes [E. F. Kiefer and W. L. Waters, Organic Division, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstracts, Paper K44].

Kinetic Studies of Group VI Metal Carbonyl Complexes. III. Substitution Reactions of Molybdenum Hexacarbonyl

Sir:

Recent kinetic studies[1] indicate that the substitution reactions of $Mo(CO)_6$ with phosphines and amines

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[1] H. Werner, *J. Organometal Chem.*, **5**, 100 (1966).

proceed by way of an SN1 mechanism. These investigations were carried out at relatively low phosphine concentrations (less than 0.025 *M*). At higher concentrations (greater than 0.050 *M*) of the phosphine, L, we have found that the rate of the reaction

$$Mo(CO)_6 + L \longrightarrow Mo(CO)_5L + CO,$$

depends on the concentration of L (Figure 1) and obeys the following rate law.

$$\text{rate} = k_1[Mo(CO)_6] + k_2[Mo(CO)_6][L]$$

These reactions were carried out in a syringe immersed in a constant-temperature oil bath. Solutions of $Mo(CO)_6$ and L in decalin solvent were sampled periodically through the long syringe needle which had been bent up above the surface of the oil bath. There was no gas phase above the reaction solution in the syringe, thus avoiding any problems due to the sublimation of $Mo(CO)_6$ at these temperatures.

The two terms in the rate expression suggest that the reaction proceeds by two mechanisms. The first-order term, k_1, indicates an SN1 mechanism in which the rate-determining step is the dissociation of a CO group from $Mo(CO)_6$. This is the term that was observed by Werner.[1] Our value of k_1 (6.22×10^{-5} sec^{-1}) at 97.8° is in good agreement with that reported by him (6.01×10^{-5} sec^{-1}), obtained in refluxing *n*-decane–cyclohexane solvent. The enthalpy and entropy of activation for the first-order process are 31.7 kcal/mole and 6.7 eu, respectively. The positive ΔS^* is consistent with a dissociative mechanism. Within experimental error, the enthalpy of activation is the same as that (E_a = 30.8 kcal/mole) reported for the exchange of ^{14}CO with $Mo(CO)_6$ in the gas phase by an SN1 mechanism.[2]

The second-order term suggests an SN2 pathway in which the phosphine, L, attacks the complex to form a seven-coordinated activated complex or intermediate. It is not possible, however, to rule out an attack at the carbonyl carbon, with a subsequent rearrangement. This latter mechanism has been suggested for the reactions of $Mn(CO)_6^+$ and $Re(CO)_6^+$ with alkoxide ions.[3] At 112.0°, the second-order rate constants increase with the nature of L in the following order: $P(OC_6H_5)_3$, 1.43×10^{-4} M^{-1} sec^{-1} < $P(C_6H_5)_3$, 1.77×10^{-4} < $P(OCH_2)_3CC_2H_5$, 3.56×10^{-4} < $P(OC_2H_5)_3$, 6.69×10^{-4} < $P(n\text{-}C_4H_9)_3$, 20.5×10^{-4}. The activation parameters for the second-order portion of the reaction of $Mo(CO)_6$ with $P(n\text{-}C_4H_9)_3$ are $\Delta H^* = 21.7$ kcal/mole and $\Delta S^* = -14.9$ eu. The negative ΔS^* is also consistent with an SN2 mechanism.[4]

The unusual feature of these reactions is that they indicate that octahedral complexes of transition metals can, in fact, undergo substitution reactions by way of an SN2 mechanism. Since the vast majority of octahedral complexes are known to undergo ligand substitution *via* an SN1 mechanism,[5] there has been some question as to the correctness of an assignment of an SN2 mechanism to some fairly complicated systems.[6] Reasons why octahedral complexes of transition metals would not be expected to participate in an SN2 mechanism have been discussed in terms of steric crowding and electronic configurations.[5] The present $Mo(CO)_6$ system, however, offers the most straightforward evidence for ligand attack on an octahedral complex. The possibility that $Mo(CO)_6$ *is* able to undergo nucleophilic attack at a rate which is comparable to the rate of dissociation of a CO group suggests that the rates of substitution reactions of other complexes containing relatively large second- and third-row transition metal atoms might also exhibit ligand dependences. Examples are the closely related $Mo(CO)_4$(dipy) and $W(CO)_4$(dipy).[7]

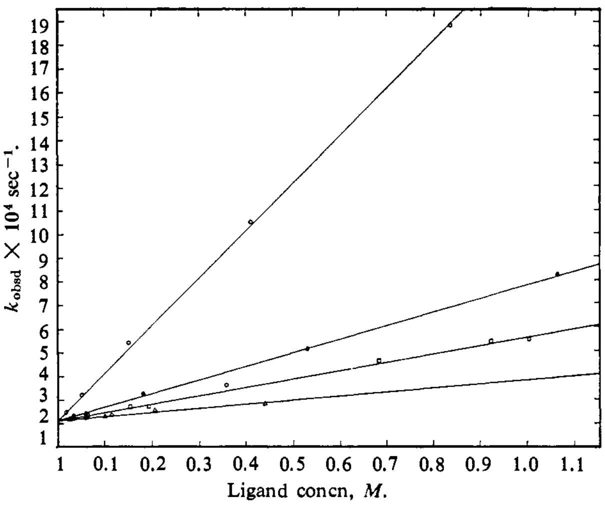

Figure 1. Plots of k_{obsd} *vs.* ligand concentrations for the reaction of $Mo(CO)_6$ in decalin at 112.0° with $P(n\text{-}C_4H_9)_3$, ○; $P(OC_2H_5)_3$, ●; $P(OCH_2)_3CC_2H_5$, □; and $P(C_6H_5)_3$, △ ($[Mo(CO)_6] = 6 \times 10^{-4}$ *M*).

Since the ΔH^* of the second-order path is significantly less than that of the first-order path, it appears that the primary reason why the SN1 mechanism is so common for octahedral complexes is not the lower activation energy but instead the rather large positive entropy of activation associated with this mechanism as compared to the negative entropy of activation involved in the SN2 process.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(2) G. Cetini and O. Gambino, *Atti Accad. Sci. Torino*, **97**, 757 (1963).

(3) T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

(4) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, **88**, 1657 (1966).

(5) R. G. Pearson, D. N. Edgington, and F. Basolo, *ibid.*, **84**, 3233 (1962).

(6) D. W. Margerum and L. P. Morgenthaler, *ibid.*, **84**, 706 (1962).

(7) J. R. Graham and R. J. Angelici, *ibid.*, **87**, 5590 (1965).

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Structure of $B_{20}H_{16}(NCCH_3)_2 \cdot CH_3CN$

Sir:

Reaction of the new boron hydride,[1,2] $B_{20}H_{16}$, with ligands occurs[1,2] without loss of hydrogen and usually

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(1) (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 12; (b) L. B. Friedman, R. D. Dobrott, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 3505 (1963); (c) R. D. Dobrott, L. B. Friedman, and W. N. Lipscomb, *J. Chem. Phys.*, **40**, 866 (1964).

(2) (a) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3506 (1963); (b) N. E. Miller, H. C. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1690 (1964).