tensity) 476 (M, 7), 448 (M – CO, 70), 422 (M – 2CO, 15), 392 (M – 3CO, 20), 364 (M – 4CO, 22), 348 ($PhPW(CO)_2$, 27), 336 (M – 5CO, 100), 320 (PhPW(CO), 15), 306 ($WPPhCH_2$, 76).

(1-Phenyl-2,4-diethoxyphospholane)pentacarbonyltungsten (21a). Complex 1 (2.5 g, 3.8 mmol), ethyl vinyl ether (2.2 mL, 23 mmol), and CuCl (0.38 g, 3.8 mmol) were heated in toluene at 55 °C for 3 h. After evaporation, the residue was chromatographed with hexane–toluene (80:20): $R_f \sim 0.6$; yield, 1.5 g (69%) of a mixture **21a**,**b**. Pure **21a** was obtained by chromatography with hexane–toluene (90:10) ($R_f \sim 0.5$) and crystallization in ethanol: colorless solid; mp 58 °C; ^{31}P NMR (C_6D_6) δ 19.5 ($^1J(^{183}W-^{31}P)$ = 236.8 Hz), IR (Decalin) $\nu(CO)$ 2070 (w), 1945 (vs), 1938 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 1.06 (t, $^3J(H-H)$ = 7.1 Hz, 3 H, CH_2CH_3), 1.15 (t, $^3J(H-H)$ = 6.8 Hz, 3 H, CH_2CH_3), 1.7–2.0 (m, 2 H, $CHCH_2CH$), 2.1–2.8 (m, 2 H, PCH_2), 2.9–3.5 (m, 5 H, OCH_2CH_3, CH_2CHCH_2), 3.83 (t, $^3J(H-H)$ = 6.3 Hz, $^2J(H-P) \approx 0$ Hz, 1 H, $PCHCH_2$); ^{13}C NMR (C_6D_6) δ 15.75 (s, CH_3), 16.00 (s, CH_3), 36.90 (d, $^1J(C-P)$ = 24.4 Hz, PCH_2), 39.20 (d, $^2J(CP)$ = 4.9 Hz, $PCHCH_2$), 65.25 (s, OCH_2CH_3), 67.43 (d, $^3J(C-P)$ = 9.8 Hz, OCH_2CH_3), 79.00 (s, CHOEt), 82.58 (d, $^1J(C-P)$ = 39.1 Hz, PCHOEt), 197.69 (d, $^2J(C-P)$ = 7.3 Hz, cis CO); mass spectrum (^{184}W), m/e (relative intensity) 576 (M, 63), 548 (M – CO, 20), 520 (M – 2CO, 89), 492 (M – 3CO, 20), 436 (M – 5CO, 30), 407 (M – 5CO – Et, 100). Anal. Calcd for $C_{19}H_{21}O_7PW$: C, 39.61; H, 3.67; P, 5.38; W, 31.91. Found: C, 39.35; H, 3.44; P, 5.29; W, 31.95. The phospholane **21a** is accompanied by a minor byproduct, **21b**, the formula of which has not been established. **21b** is very probably an isomeric compound of unknown structure: ^{31}P NMR (hexane) δ 1.71 ($^1J(^{183}W-^{31}P)$ = 239.2 Hz).

Registry No. **1**, 83603-06-9; **2**, 88000-28-6; **3** (isomer 1), 88000-29-7; **3** (isomer 2), 88080-13-1; **4** (isomer 1), 88000-30-0; **4** (isomer 2), 88080-14-2; **5** (isomer 1), 88000-31-1; **5** (isomer 2), 88081-26-9; **6** (isomer 1), 88000-32-2; **6** (isomer 2), 88080-15-3; **7**, 88000-33-3; **8a**, 88080-16-4; **8b**, 88080-17-5; **9**, 88000-34-4; **10**, 88000-35-5; **11** (isomer 1), 88000-36-6; **11** (isomer 2), 88080-18-6; **12a**, 88000-37-7; **12b**, 88080-19-7; **13** (isomer 1), 88000-38-8; **13** (isomer 2), 88080-20-0; **14**, 82281-49-0; **15** (isomer 1), 88000-39-9; **15** (isomer 2), 88080-21-1; **16** (isomer 1), 88000-40-2; **16** (isomer 2), 88080-22-2; **17** (isomer 1), 88080-23-3; **17** (isomer 2), 88000-41-3; **19**, 88000-42-4; **20**, 88015-24-1; **21a**, 88000-43-5; (*O*-methyl phenylphosphinite)pentacarbonyltungsten, 82265-66-5; [5,6,7-trimethyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadiene]pentacarbonyltungsten, 82265-65-4; [5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonylchromium, 82265-63-2; phenylacetylene, 536-74-3; cyclooctene, 931-88-4; 1-hexene, 592-41-6; cyclohexene, 110-83-8; styrene, 100-42-5; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; 2,3-dimethyl-1,3-butadiene, 513-81-5; *trans,trans*-1,4-diphenyl-1,3-butadiene, 538-81-8; cyclopentadiene, 542-92-7; benzalacetophenone, 94-41-7; benzalacetone, 122-57-6; methyl methacrylate, 80-62-6; ethyl vinyl ether, 109-92-2; CuCl, 7758-89-6.

A Mechanistic Study of the Reaction of the Dithiocarbene Complex $(CO)_5W[C(SMe)_2]$ with Amines

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The reactions of mono- and diamines (A) with $(CO)_5W[C(SMe)_2]$, 1, in THF solvent according to the equation $(CO)_5W[C(SMe)_2] + H_2NR \rightarrow (CO)_5WC{\equiv}NR + 2MeSH$ follow the two-term rate law rate = $k_1[1][A] + k_2[1][A]^2$. Monoamines (H_2NR) generally react by the k_2 pathway, which is proposed to involve initial amine nitrogen addition to the carbene carbon to give $(CO)_5W[C(SMe)_2(NH_2R)]$, followed by expulsion of the MeS^- group in a rate-determining step that is catalyzed by a second molecule of amine. The rate constant k_2 at 40.0 °C decreases with the amine in the order H_2N-*n*-Bu (41.9 $M^{-2}\ s^{-1}$) ≈ H_2N-*n*-Pr (40.2) > H_2NCH_2Ph (5.83) > $H_2NC_6H_{11}$ (0.800). The difference in rates for H_2N-*n*-Bu and $H_2NC_6H_{11}$ suggests that the bulkiness of the cyclohexyl group decreases the rate. In pyridine solvent, the reactions are still second order in the monoamine but are much faster than in THF. In MeOH solvent, the reaction with H_2NCH_2Ph is only first order in the amine concentration; in this case, MeOH instead of another molecule of H_2NCH_2Ph presumably catalyzes the breakdown of the intermediate in the rate-determining step. In cyclohexane solvent, the reaction becomes 4.1 order in the H_2NCH_2Ph concentration, which is interpreted to suggest that the amine is required to stabilize polar intermediates by solvation in this nonpolar solvent. In contrast with the second-order amine dependence of the monoamine reactions in THF solvent, the diamine $H_2N(CH_2)_nNH_2$ (n = 2 or 3) reactions in this solvent are much faster and are only first order in the diamine concentration. This result suggests that one end of the diamine attacks the carbene carbon while the other end promotes breakdown of the intermediate. The other diamines $H_2N(CH_2)_4NH_2$, $H_2N(CH_2)_2NMe_2$, and $H_2N(CH_2)_3NMe_2$ react not only by the pathway involving first-order dependence on the diamine concentration but also by one that is second order. The second-order pathway is probably similar to that for the monoamines but involves additional catalysis of the intermediate breakdown by the dangling amino groups at the other ends of the diamines. In general, the reactions appear to proceed by initial nucleophilic attack of the amine at the carbene carbon. A second mole of amine facilitates breakdown of the intermediate by removing a proton from the attacking amine and, where possible, protonating the departing MeS^-. Primary amines are much more effective than tertiary amines at promoting this breakdown. Details of the mechanisms are discussed.

Introduction

Although numerous reactions of transition-metal carbene complexes have been reported,[2-4] few kinetic studies of carbene ligand reactions are available.[5-8] A common reaction of carbene ligands is that involving addition of

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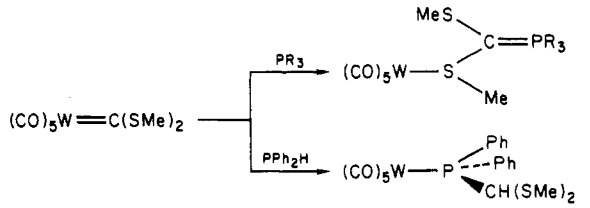
a nucleophile to the carbene carbon. Among the simplest reactions of this type are the additions of phosphines and phosphites to complexes such as $(CO)_5W[C(OR^1)R^2]$, where M = Cr or W and R^2 = Me or Ph:[9-14]

$$(CO)_5M[C(OR^1)R^2] + PR^3_3 \rightleftharpoons (CO)_5M[C(OR^1)(R^2)(PR^3_3)] \quad (1)$$

The reactions of $(CO)_5M[C(OEt)R]$, where M = Cr or W and R = Me or Ph, with P-*n*-Bu_3 or P(O-*n*-$Bu)_3$ in acetone solvent at 25 °C were studied kinetically by stopped-flow techniques[15] and observed to follow a rate law that is first order each in the carbene complex and in the P-*n*-Bu_3 or P(O-*n*-$Bu)_3$ nucleophile. These adducts (eq 1) react further and more slowly to form $(CO)_4M(PR^3_3)[C(OR^1)R^2]$ and $(CO)_5M(PR^3_3)$.[12,16-19]

The reactions of dithiocarbene complexes $(CO)_5W[C(SR)_2]$ with phosphines and phosphites[5,20] give phosphorane or phosphine complexes as shown in eq 2 and 3.



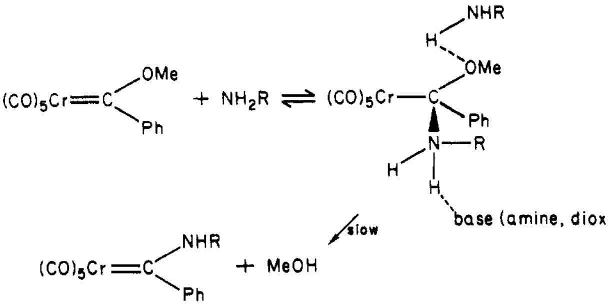
(2)

(3)

Kinetic studies[5] show these reactions to be first order each in the carbene complex and the phosphine in cyclohexane solvent at temperatures of 20–40 °C. These results were interpreted to indicate that the mechanism involved initial nucleophilic attack of the phosphorus atom at the carbene carbon to form an adduct of the type in eq 1. This adduct then rapidly rearranged to the observed products.

Although no kinetic studies have been performed, the tertiary bicyclic nitrogen donor bases quinuclidine and 1,4-diazabicyclo[2.2.2]octane (DABCO) also form isolable adducts with $(CO)_5M[C(OMe)Ph]$, where M = Cr or W.[21,22] The 2–3-h reaction time suggests that these rates of reaction are slower than observed for the phosphine reactions (eq 1).

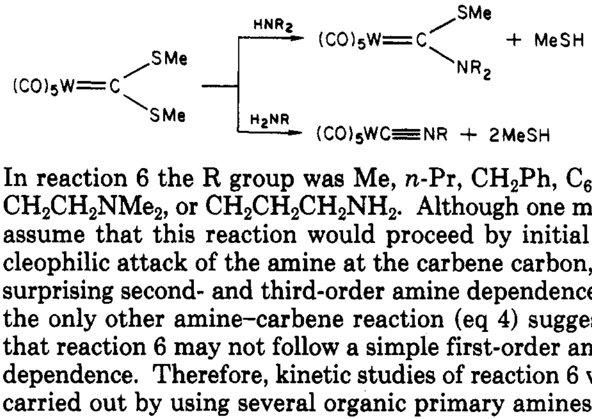
A kinetic study of the reaction of $(CO)_5Cr[C(OMe)Ph]$ with primary amines (NH_2R) to form $(CO)_5Cr[C(NHR)Ph]$ and MeOH has yielded the result that the reaction is first order in the carbene complex in all solvents studied but is second order in the amine concentration in dioxane solvent and third order in amine in *n*-decane.[23,24] The suggested mechanism involves hydrogen bonding of the amine with the OMe leaving group and nucleophilic attack at the carbene carbon by an activated amine (base---HNHR); the resulting intermediate undergoes rate-determining breakdown to the products. An abbreviated form of the mechanism is shown in eq 4. In dioxane



(4)

solvent, a dioxane molecule assumes the role of the base that hydrogen bonds to the attacking amine; in *n*-decane, an amine serves this function. These hydrogen bonding interactions were also suggested to account for the negative activation energies for the overall reactions. No other kinetic studies of reactions of amines with carbene complexes have been reported.

Recently, the reactions of the dithiocarbene complex $Cp(CO)_2Fe{=}C(SMe)_2^+$ with secondary amines (HNR_2) to give $Cp(CO)_2Fe{=}C(SMe)(NR_2)^+$ and with primary amines (H_2NR) to give the isocyanide complexes $Cp(CO)_2FeC{\equiv}NR^+$ and MeSH[25,26] were described. Similar reactions of the dithiocarbene $(CO)_5W{=}C(SMe)_2$ have also been published:[27]



(5)

(6)

In reaction 6 the R group was Me, *n*-Pr, CH_2Ph, C_6H_{11}, $CH_2CH_2NMe_2$, or $CH_2CH_2CH_2NH_2$. Although one might assume that this reaction would proceed by initial nucleophilic attack of the amine at the carbene carbon, the surprising second- and third-order amine dependence for the only other amine–carbene reaction (eq 4) suggested that reaction 6 may not follow a simple first-order amine dependence. Therefore, kinetic studies of reaction 6 were carried out by using several organic primary amines, including those with one and two amine groups.

Experimental Section

General Data. The carbene complex $(CO)_5W[C(SMe)_2]$, 1, was prepared according to the literature procedure.[20] Amines were dried over KOH and distilled from BaO under an N_2 atmosphere. Tetrahydrofuran (THF) was distilled under N_2 from sodium benzophenone ketyl. Cyclohexane was stirred over concentrated H_2SO_4, washed three times with H_2O, dried over $MgSO_4$, and distilled from CaH_2 under N_2. Methanol was dried over Mg and distilled. Diazabicyclo[2.2.2]octane (DABCO) was sublimed at 80 °C (~10 mmHg).

Kinetic Measurements. Rates of reaction 6 were determined by following the disappearance of the visible absorption band (429

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nm in THF, 436 nm in MeOH, and 439 nm in C_6H_{12}) of $(CO)_5W[C(SMe)_2]$. At the concentration of 1 used (4.65×10^{-5} M) in these studies, the $(CO)_5W(C{\equiv}NR)$ products did not absorb in this region. The identities of the $W(CO)_5(CNR)$ products were established by concentrating representative reaction mixtures and comparing their IR spectra in the ν(CO) region with those of known complexes made by using the same reaction on a preparative scale.[27] The products of all reactions were the isocyanide complexes $(CO)_5W(C{\equiv}NR)$, except for the reaction with $H_2N(CH_2)_2NH_2$ which gave the diaminocarbene complex $(CO)_5W[\overline{CNH(CH_2)_2N}H]$ whose preparation is given at the end of this section.

Reactions of all amines were carried out under an argon atmosphere. Solvents were purged by bubbling with Ar. Solutions of 1 (4.65×10^{-5} M) were thermostated for 15 min at the desired temperature in volumetric flasks capped with a rubber septum and containing a magnetic stirring bar, and the flasks were wrapped in aluminum foil to reduce exposure to light although there was no evidence that the reaction rates were affected by light. Either of two procedures were followed at this point. The first involved adding the required quantity of neat amine to the volumetric flask and mixing the solution thoroughly with the magnetic stirrer. By syringe a portion (1–2 mL) of this reaction solution was transferred to a septum-capped, 1-cm UV cuvette, which had been purged with Ar and was in the thermostated cell holder of the spectrophotometer. The spectrophotometer then began recording the absorbance at the specified wavelength at the desired time intervals. The second procedure involved transferring 1 or 2 mL of the $(CO)_5W[C(SMe)_2]$ solution to the septum-capped, Ar-purged 1-cm cuvette, which contained a tiny magnetic stirring bar. The cuvette was placed in the thermostated cell holder of the spectrophotometer for 15 min. Then, the neat amine or a solution of it in the appropriate solvent was added by syringe to the cuvette; the solution was stirred with the bar and quickly returned to the spectrophotometer, and absorbance readings were begun. Reactions with H_2N-*n*-Bu and $H_2NCH_2CH_2NMe_2$ were performed by using both procedures, and the rate constants obtained from both were in excellent agreement.

In these studies, a Beckman DU-8 UV–vis spectrometer with the kinetic analyzer compuset and thermoelectric temperature control of the cuvette holder was employed. The instrument was programmed to record automatically absorbance readings of the reaction mixtures at specific time intervals. During all the above manipulations, it is imperative that contact between the reaction solution and the rubber septa be prevented; such contact gave irreproducible rates.

Reactions involving H_2N-*n*-Pr were carried out under N_2 in a 100-mL volumetric flask containing 4.65×10^{-5} M $(CO)_5W[C(SMe)_2]$ and capped with a rubber septum. The flask was wrapped in Al foil and thermostated for 15 min in a constant temperature bath. An N_2-filled balloon was attached to the flask via a needle in the septum to aid withdrawal of samples. At the start of the reaction, the neat amine was added, and the solution was mixed. At appropriate times 3-mL samples of the reaction solution were transferred by syringe to a 1-cm cuvette, and the % *T* was recorded vs. a solvent blank on a Beckman DB-G grating UV–vis spectrophotometer.

Pseudo-first-order rate constants k_{obsd} were obtained from slopes of plots of ln $(A - A_\infty)$ vs. t, where A is the absorbance at time t and A_∞ is the absorbance at the completion of the reaction. For each type of reaction, A_∞ was experimentally determined to be zero within experimental error. The plots were linear for at least the first 75% of the reaction. Rate constants for different kinetic runs under the same conditions were reproducible to within approximately 5%.

Preparation of $(CO)_5W[\overline{CNH(CH_2)_2N}H]$. A solution of $(CO)_5W[C(SMe)_2]$ (100 mg, 0.23 mmol) and $H_2N(CH_2)_2NH_2$ (160 μL, 2.4 mmol) in 20 mL of THF under an N_2 atmosphere was stirred for 30 min during which time the solution turned from deep orange to pale yellow. The solvent was removed under vacuum, and the residue was dissolved in a minimum amount of $CHCl_3$. This solution was chromatographed on a silica gel column prepared in cyclohexane with a 3:1 $C_6H_{12}/CHCl_3$ eluent mixture. After vacuum removal of the solvent from the product fraction, the residue was dissolved in 1.5 mL of $CHCl_3$. Hexanes were added to this solution until precipitation began; cooling to −20 °C overnight gave pale yellow crystals that were filtered and dried under vacuum. Although the isolated yield was only 64 mg (70%), an IR spectrum of the reaction mixture indicated that $(CO)_5W[\overline{CNH(CH_2)_2N}H]$ was the only carbonyl-containing product: IR (hexane) ν(CO) 2060 (w), 1931 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.67 (s, $(CH_2)_2$), 6.07 (br, NH); the EI mass spectrum showed M^+ at *m/e* 396 (for ^{186}W) and peaks for $[M - n(CO)]^+$, n = 1–5. Anal. Calcd for $C_8H_6N_2O_5W$: C, 24.39; H, 1.54; N, 7.11. Found: C, 24.42; H, 1.74; N, 7.07.

Results

Rates of reaction 6 were determined by using pseudo-first-order conditions in which the amines were present in large excess. Monoamine concentrations were usually at least 40 times as large as those of $(CO)_5W[C(SMe)_2]$, 1, while diamines were generally present in at least 10-fold excess. Even reactions of $H_2N(CH_2)_2NH_2$ and $H_2N(CH_2)_3NH_2$ in which the amines were present in 7-fold excess gave ln $(A - A_\infty)$ vs. t plots that were linear for more than 2 half-lives. Pseudo-first-order rate constants k_{obsd} for the reactions are given in Table I. Each listed k_{obsd} value is an average of values from three or four runs. All of the reactions, except those in cyclohexane solvent, in Table I can be fit to the two-term rate law

$$-d[1]/dt = k_1[1][A] + k_2[1][A]^2 \qquad (7)$$

in which [A] represents the amine concentration. Values of k_1 and k_2 were obtained from the intercept and slope, respectively, of plots of $k_{obsd}/[A]$ vs. [A]; such plots were based on the expression $k_{obsd} = k_1[A] + k_2[A]^2$. In cases where the k_2 term contribution was negligible, k_1 was obtained from the slope of plots of k_{obsd} vs. [A]. Values of k_1 and k_2 for the various reactions are collected in Table II.

For the monoamine (H_2NR) reactions in THF solvent, the k_1 term was negligible, and the reactions followed the rate law

$$-d[1]/dt = k_2[1][A]^2 \qquad (8)$$

The addition of DABCO in concentrations approximately equal to that (41.3×10^{-3} M) of cyclohexylamine gave no significant change in the rate of the $H_2NC_6H_{11}$ reaction, but 0.20 and 0.60 M DABCO increased the rate by factors of 2.1 and 3.5, respectively (Table I). Similarly, low concentrations of 4-picoline produced little effect on the rate, whereas 0.93 M picoline increased the k_{obsd} by a factor of approximately 2.3. Also, the addition of 2.19×10^{-2} and 2.19×10^{-1} M aniline to the reaction of 1 with 32.8×10^{-2} M $H_2NC_6H_{11}$ in THF at 40 °C changed the rate insignificantly. Therefore, these bases at concentrations comparable to the reacting amine appear not to act as catalysts, but at higher concentrations they do become involved.

To probe for a possible radical mechanism, the *t*-Bu_2NO radical was added in moderately high concentration (6.9×10^{-2} M) to a reaction of $H_2NC_6H_{11}$ (6.61×10^{-2} M) in THF at 40 °C; within experimental error, the rate was unchanged. This result suggests that radicals are not involved. In another experiment, the reaction with $H_2NC_6H_{11}$ (6.61×10^{-2} M) at 40 °C in THF was studied in the presence of MeSH (5.6×10^{-3} M). Although the MeSH concentration was substantially higher than that (4.65×10^{-5} M) of the carbene complex, the MeSH did not affect the rate, which indicates that the MeSH product does not retard or accelerate the reaction.

While the reactions of 1 with all monoamines at 40.0 °C in THF are second order in the amine concentration, the reactions of H_2N-*n*-Pr and H_2NCH_2Ph in cyclohexane solvent are higher order (4.3 and 4.1, respectively) in the

Table I. Pseudo-First-Order Rate Constants k_{obsd} for the Reactions of $(CO)_5W[C(SMe)_2]$ (4.65×10^{-5} M) with Amines according to Eq 6

temp,[a] °C	10^3[amine], M	10^4k_{obsd}, s^{-1}	temp,[a] °C	10^3[amine], M	10^4k_{obsd}, s^{-1}
H_2N-*n*-Pr					
40.0	38.0	0.0116[b]	40.0	1.21	4.60[e]
40.0	58.6	0.0735[b]	40.0	1.82	10.3[e]
40.0	89.7	4.83[b]	40.0	2.31	15.1[e]
40.0	9.22	4.02[c]	40.0	0.485	7.52[f]
40.0	12.1	7.26[c]	40.0	0.606	9.68[f]
40.0	13.8	7.71[c]	40.0	0.728	15.4[f]
40.0	16.1	13.8[c]	40.0	0.849	17.3[f]
40.0	2.31	2.12[d]			
40.0	4.61	7.30[d]			
40.0	6.92	22.3[d]			
H_2N-*n*-Bu					
40.0	5.07	11.5[d]	40.0	10.1	43.3[d]
40.0	7.60	25.4[d]	40.0	12.7	67.0[d]
$H_2NC_6H_{11}$					
15.0	49.5	20.7[d]	35.0	49.5	19.6[d]
15.0	66.1	31.6[d]	35.0	66.1	33.6[d]
15.0	82.6	42.5[d]	35.0	82.6	50.1[d]
15.0	99.1	55.5[d]			
20.0	49.5	20.5[d]	35.0	99.1	70.4[d]
20.0	66.1	34.5[d]	40.0	24.8	4.80[d]
20.0	82.6	46.7[d]	40.0	33.0	8.93[d]
20.0	99.1	60.1[d]	40.0	37.5	25.0[d,g]
25.0	49.5	21.1[d]	40.0	41.3	13.1[d]
25.0	66.1	35.0[d]	40.0	41.3	27.1[d,h]
25.0	82.6	50.9[d]	40.0	41.3	46.0[d,i]
25.0	99.1	65.3[d]	40.0	49.5	17.7[d]
30.0	49.5	19.9[d]	40.0	66.1	33.0[d]
30.0	66.1	34.3[d]	40.0	82.6	46.7[d]
30.0	82.6	49.3[d]	40.0	99.1	70.4[d]
30.0	99.1	68.8[d]			
H_2NCH_2Ph					
40.0	9.20	5.12[d]	40.0	91.6	1.85[b]
40.0	13.7	12.0[d]	40.0	137	5.74[b]
40.0	18.3	19.3[d]	40.0	183	27.3[b]
40.0	27.5	42.4[d]	40.0	229	76.8[b]
40.0	18.3	15.0[j]			
40.0	36.6	31.8[j]			
40.0	45.8	41.1[j]			
40.0	54.9	48.3[j]			
$H_2N(CH_2)_2NH_2$					
40.0	0.299	16.4[d]	40.0	0.599	35.5[d]
40.0	0.449	26.3[d]	40.0	0.748	44.6[d]
$H_2N(CH_2)_3NH_2$					
20.0	0.599	25.7[d]	45.0	0.599	48.2[d]
30.0	0.599	34.4[d]			
40.0	0.359	24.7[d]			
40.0	0.479	34.8[d]			
40.0	0.599	43.6[d]			
40.0	0.719	51.2[d]			
$H_2N(CH_2)_4NH_2$					
40.0	0.476	15.7[d]	40.0	0.952	39.0[d]
40.0	0.714	26.0[d]	40.0	1.19	52.2[d]
$H_2N(CH_2)_2NMe_2$					
40.0	1.70	18.1[d]	40.0	3.40	38.9[d]
40.0	2.55	29.1[d]	40.0	4.25	53.5[d]
$H_2N(CH_2)_3NMe_2$					
40.0	1.27	11.9[d]	40.0	2.54	29.9[d]
40.0	1.91	20.1[d]	40.0	3.18	40.7[d]

[a] ±0.1 °C. [b] In cyclohexane solvent. [c] In 50:50 cyclohexane/THF solvent. [d] In THF solvent. [e] In 50:50 cyclohexane/pyridine solvent. [f] In pyridine solvent. [g] 0.93 M 4-picoline added. [h] 0.20 M DABCO added. [i] 0.60 M DABCO added. [j] In MeOH solvent.

Table II. k_1 and k_2 Rate Constants for the Reactions of $(CO)_5W[C(SMe)_2]$ with Amines according to Eq 6 at 40.0 °C in THF Solvent

amine	pK_a[a]	k_1, M^{-1} s^{-1}	k_2, M^{-2} s^{-1}
$H_2NC_6H_{11}$	10.7		0.800
H_2NCH_2Ph	9.6		5.83
H_2NCH_2Ph	9.6	0.0866[b]	
H_2N-*n*-Pr	10.7		4.76[c]
H_2N-*n*-Pr	10.7		40.2
H_2N-*n*-Pr	10.7		303[d]
H_2N-*n*-Pr	10.7		2790[e]
H_2NBu	10.7		41.9
$H_2N(CH_2)_2NH_2$	9.9	5.91	
$H_2N(CH_2)_3NH_2$	10.3	7.20	
$H_2N(CH_2)_4NH_2$	10.2	2.6	1540
$H_2N(CH_2)_2NMe_2$	9.5	0.85	100
$H_2N(CH_2)_3NMe_2$	10.2	0.72	180

[a] In H_2O at 25 °C; from ref 38. [b] In MeOH solvent. [c] In 50:50 cyclohexane/THF solvent. [d] In 50:50 cyclohexane/pyridine solvent. [e] In pyridine solvent.

amine concentration (Table I) as shown by slopes of plots log k_{obsd} vs. log [A]. Clearly, more amine molecules are involved in the transition state in cyclohexane than in THF solvent. When 50:50 solvent mixtures of cyclohexane with THF or pyridine are used, the reactions again become second order in the amine concentration. Also, they are second order in amine when pure pyridine is the solvent. The k_2 rate constant for the reaction in pyridine is substantially larger than that in THF (Table I). In MeOH solvent, the reaction of H_2NCH_2Ph with 1 is only first order in the amine concentration; the MeOH must play a different role than either THF or pyridine.

Unlike the monoamines (H_2NR), which showed a second-order dependence on the amine concentration, the diamines $H_2N(CH_2)_nNH_2$ (n = 2 or 3) in THF solvent followed a rate law that was just first order in the amine concentration (Table I):

$$-d[1]/dt = k_1[1][A] \tag{9}$$

The longer chain $H_2N(CH_2)_4NH_2$ followed rate law 7 in which both the k_1 and k_2 terms contribute. The diamines with primary and tertiary amine groups, $H_2N(CH_2)_nNMe_2$ (n = 2 or 3), also followed eq 7.

Reactions of $H_2N(CH_2)_3NH_2$ and $H_2NC_6H_{11}$ were carried out at several different temperatures in THF solvent. The reactions of $H_2N(CH_2)_3NH_2$ are first order in the amine, and a plot of ln (k_1/T) vs. $1/T$ gives activation parameters for the reaction (Table III). The reaction of $H_2NC_6H_{11}$ is second order in amine at temperatures of 40.0 °C, but a first-order amine term becomes more and more important at lower temperatures. Activation energies for both the k_1 and k_2 paths are given in Table III. The error limits given in Table III for the activation parameters are one standard deviation.

Several attempts were made to identify reaction intermediates by scanning the IR spectrum of reaction solutions in the ν(CO) region. However, in no case were we able to identify absorptions due to compounds other than the reactant $(CO)_5W[C(SMe)_2]$ or product.

Secondary amines (HNR_2) are known[27] to react with 1 to form the aminothiocarbene complexes $(CO)_5W[C(SMe)(NR_2)]$. Rates of reaction with $HNEt_2$ and HN-*n*-Bu_2 were not reproducible from week to week, while piperidine reactions could be reproduced for longer periods but then suddenly changed for no obvious reason. When rate constants were reproducible, the reactions of piperidine with 1 at 40.0 °C in THF were slower than those with $H_2NC_6H_{11}$ under the same conditions; they also followed a rate law that was second order in the piperidine concentration. Rates of reactions with the primary amines were occasionally unexpected, but repurification of the amine or solvent always gave the expected rate constants. Such repurification with secondary amines did not give reproducible rate constants.

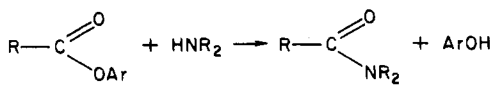
Table III. k_1 and k_2 Rate Constants for the Reactions of $(CO)_5W[C(SMe)_2]$ with $H_2NC_6H_{11}$ and $H_2N(CH_2)_3NH_2$ in THF at Various Temperatures

$H_2N(CH_2)_3NH_2$[a]		$H_2NC_6H_{11}$[b]		
temp, °C	k_1, M^{-1} s^{-1}	temp, °C	10^2k_1, M^{-1} s^{-1}	$10k_2$, M^{-2} s^{-1}
20.0	4.29	15.0	2.75	2.89
30.0	5.74	20.0	2.40	3.80
40.0	7.20	25.0	1.96	4.94
45.0	8.05	30.0	1.14	5.86
		35.0	0.78	6.40
		40.0	0	8.00

[a] $\Delta H^{\ddagger}$ = 4.03 ± 0.15 kcal/mol and $\Delta S^{\ddagger}$ = −41.8 ± 0.5 eu. [b] $\Delta H_1^{\ddagger}$ = −12.1 ± 1.7 kcal/mol and $\Delta S_1^{\ddagger}$ = −107 ± 6 eu. $\Delta H_2^{\ddagger}$ = 6.42 ± 0.5 kcal/mol and $\Delta S^{\ddagger}$ = −38.5 ± 1.7 eu.

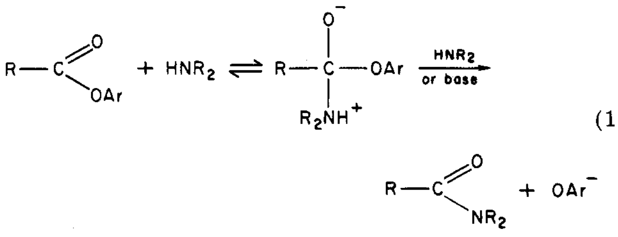
Discussion

Reactions with Monoamines. The aminolysis of substituted phenyl acetate esters, such a *p*-nitrophenyl acetate (eq 10), follows a rate law, rate = k_1[ester][amine]



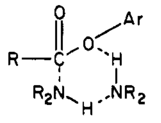
(10)

+ k_2[ester][amino]^2, in Et_2O[28] and dioxane.[29] Only the k_1 term is important in MeCN solvent,[28] whereas only the k_2 term is important in chlorobenzene.[30] The reaction is found to be catalyzed by various kinds of bases,[31-35] including amines such as DABCO, which is at least as effective a catalyst as *n*-butylamine.[31-33,35] A general mechanism for these aminolyses involves the steps shown in eq 11. The second and rate-determining step of this



(11)

mechanism is the collapse of the tetrahedral carbon intermediate that may or may not, depending upon the ester, amine, and solvent, be catalyzed by a HNR_2 or base molecule that accepts the amine proton and facilitates OAr^- expulsion. Another mechanism suggested[28,33] for HNR_2-catalyzed collapse of the intermediate involves a cyclic transition state such as



although this seems less likely.[32,35]

Werner et al.[24] have noted the similarity between organic ester aminolysis and aminolysis of the carbene complex

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[29] Shawali, A. S. A. S.; Biechler, S. S. *J. Am. Chem. Soc.* **1967**, *89*, 3020.

[30] Menger, F. M. *J. Am. Chem. Soc.* **1966**, *88*, 3081.

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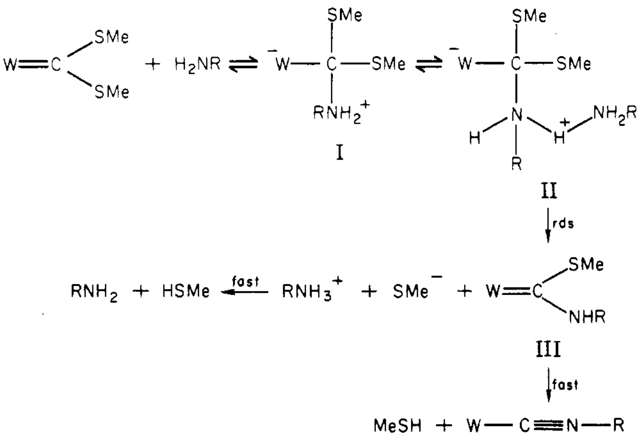
[32] Su, C.-W.; Watson, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 1854.

[33] Satchell, D. P. N.; Secemski, I. I. *J. Chem. Soc. B* **1970**, 1013.

[34] Menger, F. M.; Vitale, A. C. *J. Am. Chem. Soc.* **1973**, *95*, 4931.

[35] Menger, F. M.; Smith, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 3824.

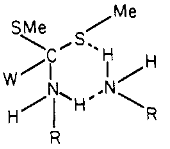
Scheme I



$(CO)_5Cr[C(OMe)Ph]$. Indeed, their suggested mechanism (eq 4) is very similar to that in eq 11. The most obvious difference is the suggestion for the carbene reaction that an amine (H_2NR) molecule facilitates OMe^- expulsion by hydrogen bonding to the oxygen in the tetrahedral intermediate.

In the present study, reaction 6 follows a rate law (eq 8) involving a second-order dependence on the monoamine (H_2N-*n*-Bu, H_2NCH_2Ph, or $H_2NC_6H_{11}$) concentration in THF solvent at 40 °C. By analogy with the mechanism (eq 11) for the aminolysis of esters, a possible mechanism for the carbene reaction is as shown in Scheme I. This mechanism involves initial rapid, reversible attack[36a] at the carbene carbon atom to give intermediate I with a tetrahedral carbon atom. The equilibrium constant for this step must be small since there is no spectroscopic evidence for intermediates during the reaction. The second step involves H bond formation of the second amine molecule to the amine proton of intermediate I. Then proton transfer to the second amine and expulsion of MeS^- leads to the intermediate aminothiocarbene III which is similar to the product of the reaction of 1 with secondary amines (eq 5). Intermediate III must then be rapidly converted to the isocyanide product.

As in the mechanism for the aminolysis of organic esters, there is no evidence to exclude the possibility that intermediate II has a cyclic structure, IV, in which the proton is transferred directly to the leaving mercapto group. The observation that the reaction of $H_2NC_6H_{11}$ with 1 is catalyzed by DABCO only at very high concentrations (0.20 and 0.60 M, Table I) indicates that DABCO is not as effective as $H_2NC_6H_{11}$ as a base in the role of the second amine molecule, assuming the intermediate has structure II. For organic esters, DABCO is at least as effective a catalyst as *n*-$BuNH_2$.[31-33,35] The low catalytic properties of DABCO and 4-picoline in reaction 6 suggest that either the intermediate in the absence of DABCO has cyclic structure IV or the larger size of DABCO makes it less effective than $H_2NC_6H_{11}$ (and presumably also H_2N-*n*-Bu) as a catalytic base in structure II.



IV

The reactions of $(CO)_5Cr[C(OMe)Ph]$ with H_2NR were suggested[24] to involve a hydrogen bond interaction between the OMe oxygen and a hydrogen bonding molecule such as H_2NR or MeOH (in MeOH solvent). This interaction was supported by ^1H NMR studies of the nonreacting amine $HN(i\text{-}Pr)_2$ in the absence and presence of $(CO)_5Cr[C(OMe)Ph]$. Similar studies of MeOH in the absence and presence of the carbene complex were also conducted. In both studies, the carbene complex caused the amine and alcohol protons to shift significantly; these results were interpreted to indicate a H bond interaction with the OMe oxygen in the carbene. Further evidence for hydrogen bonding to the carbene methoxy group was the observation that the aminolysis of the carbene complex with $H_2NC_6H_{11}$ was much faster in MeOH solvent than in dioxane. More specifically, the third-order rate constant (k' in rate = $k'[H_2NR]^2$)[24] is more than 250 times larger in MeOH than in THF.

In the present study of the $(CO)_5W[C(SMe)_2]$ reaction, there is no evidence to support a similar type of H bonding to a SMe group. Unlike the observation for $(CO)_5Cr[C(OMe)Ph]$, a ^1H NMR study of $HN(i\text{-}Pr)_2$ (7.1×10^{-2} M) in the absence and presence of 1 (9.3×10^{-2} M) in C_6D_6 solvent showed that the amine proton was unaffected by the presence of the carbene complex. An IR study of 1 (1.2×10^{-3} M) in the absence and presence of piperidine ($\overline{HN(CH_2)_4CH_2}$) ($5.1 \times 10^{-2}$ M) in C_6H_{12} solvent showed no change in the ν(CO) bands of 1 upon addition of the amine. Both of these studies indicate no H bonding between the amine and the carbon complex.

Also, we have compared the reactions of H_2NCH_2Ph and 1 in THF and MeOH solvents. Unlike the reaction of $(CO)_5Cr[C(OMe)Ph]$, the k_{obsd} values are very similar (Table I) in the two solvents at 40.0 °C. This suggests that MeOH H bonding to a leaving mercapto group does not occur, in the manner postulated for $(CO)_5Cr[C(OMe)Ph]$.[24] This is not surprising in view of the better H bonding ability of oxygen as compared with sulfur.[36b] Although the rates of reaction in the two solvents are similar in the amine concentration range used, the rate law is second order in the amine concentration in THF but only first order in MeOH. This change in rate expression probably reflects two changes in the mechanism of reaction: (1) H bonding of MeOH to the amine ($MeO\text{–}H\cdots NH_2R$)[37] reduces the activity of H_2NR as a nucleophile and base (in intermediate II or IV); (2) the large excess of MeOH may now take over the role of the base (the second amine molecule) in intermediate II (or more likely IV) which reduces to one the amine concentration dependence in the rate law. As contrasted with the first-order amine dependence in MeOH solvent, the amine (H_2N-*n*-Pr) dependence is second order in pyridine solvent. Thus, whereas MeOH is able to assume one order of amine dependence, pyridine cannot. This result suggests that MeOH participates in a cyclic intermediate such as IV by H bonding to the attacking amine, but pyridine cannot for lack of a H bonding proton. This result is also supporting evidence for structure IV as the intermediate for the monoamine reactions which are second order in the amine concentration. The substantially higher rate of reaction in pyridine as compared with that in THF (both second order in amine) may be due to polar solvent stabilization of the polar intermediates I, IV, or the transition state leading to III (Scheme I) or to pyridine H bonding to the

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(36) (a) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974. Kostić, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1982**, *104*, 3879. (b) Bell, R. P. "The Proton in Chemistry", 2nd ed.; Chapman and Hall: London, 1973.

(37) Ratkovics, F.; Laszlo, M. *Acta Chim. Acad. Scien. Hung.* **1977**, *93*, 267.

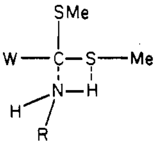
other proton of the attacking amine in IV.

While the reaction of 1 with H_2NCH_2Ph is first order in amine concentration in MeOH solvent and second order in THF, it is 4.1 order in cyclohexane solvent at 40 °C (Table I); the analogous reaction with H_2N-*n*-Pr is 4.3 order in amine. Werner et al.[24] observed that the reaction of $(CO)_5Cr[C(OMe)Ph]$ with primary amines was second order in the amine in dioxane solvent but third order in *n*-decane solvent. They postulated the involvement of three amine molecules as shown in eq 4. In the present study, the 4.1- and 4.3-order amine dependences are more difficult to understand. In such a nonpolar solvent as cyclohexane, the amine will increase the polarity of the solvent and may thereby stabilize polar intermediates such as I and IV or the transition state by solvation. This explanation is supported by the observation that for a given amine concentration used in this study the rates of reaction decrease in the order pyridine > THF > cyclohexane. It thus appears that the polar THF and pyridine solvents accelerate the reaction and solvation by the H_2N-*n*-Bu or H_2N-*n*-Pr is not important in THF as it is in cyclohexane.

The k_2 rate constant for the reaction of 1 with H_2NR in THF is affected by the bulkiness of the amine R group. The values are nearly the same for the similar H_2N-*n*-Bu and H_2N-*n*-Pr. Although H_2N-*n*-Bu and $H_2NC_6H_{11}$ have nearly identical pK_a values[38] (Table II), the k_2 rate constant for H_2N-*n*-Bu is 52.5 times larger. Bulky R groups would presumably reduce the rate of these reactions by reducing accessibility of both amine molecules to their positions in intermediate IV. The basicity of the amine seems less important than its bulkiness since k_2 for H_2N-*n*-Bu is only 7.2 times faster than for H_2NCH_2Ph, whose pK_a is 1.1 units[38] lower than that of H_2N-*n*-Bu. Some of this difference in rate may even be due to the greater bulkiness of the benzyl group as compared with the butyl.

A temperature-dependent study of the reaction of 1 with $H_2NC_6H_{11}$ in THF (Table III) shows that below 40 °C, the rate law (eq 7) includes terms that are first (k_1) and second (k_2) order in amine concentration. As the temperature is reduced, the k_2 pathway becomes slower, while the k_1 rate increases. The activation parameters for the k_2 pathway are $\Delta H^\ddagger = 6.42 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -38.5 \pm 1.7$ eu. The activation energy is low but not negative as found for reaction 4. The negative entropy of activation is consistent with Scheme I probably involving intermediate IV in which the carbene complex and two amine molecules are brought together in the activated complex. These activation parameters are very similar to those ($\Delta H^\ddagger = 7.0$ kcal/mol and $\Delta S^\ddagger = -39.0$ eu) for the reaction of $W(CO)_5(CS)$ with N_2N-*n*-Bu to give $W(CO)_5(CN$-*n*-Bu$)$ by a pathway that is second order in the amine.[39]

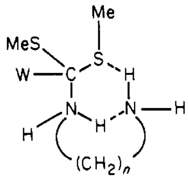
The activation parameters for the pathway (k_1) that is only first order in amine concentration are $\Delta H^\ddagger = -12.1 \pm 1.7$ kcal/mol and $\Delta S^\ddagger = -107 \pm 6$ eu. The mechanism for this reaction may involve an intermediate such as I (Scheme I) from which the MeS^- is expelled.[28,29] However, the intermediate may also be of type V[28] in which an amine proton assists the dissociation of MeS^-. The negative $\Delta H^\ddagger$ for this reaction is unusual but not unknown for carbene reactions.[40] Reaction 4 in dioxane, which is second order in amine, has the parameters:[24] $\Delta H^\ddagger = -8.8$ kcal/mol and $\Delta S^\ddagger = -86.2$ eu. The negative $\Delta H^\ddagger$ was attributed to a negative ΔH for the equilibrium association (H bonding) of two amine molecules. Since only one amine molecule is involved in the present reaction, another explanation is required. Such an explanation might involve assuming that ΔH is negative for the equilibrium formation of I (or V) from the carbene complex and amine. That this is reasonable is supported by ΔH values[14] for equilibrium adduct formation between $(CO)_5W{=}C(OMe)(aryl)$ and P-*n*-Bu_3; these values range from −12 to −14 kcal/mol. Thus, if rate-determining breakdown of I (or V) has a low enthalpy of activation, the overall $\Delta H^\ddagger$ for reaction 6 would be negative.



V

The extremely negative $\Delta S^\ddagger$ for the k_1 path of reaction 6 is surprising. The ΔS associated with the equilibrium formation of intermediate I (or V) might be similar to those for adduct formation between $(CO)_5W{=}C(OMe)(aryl)$ and P-*n*-Bu_3 in toluene solvent, which range from −39 to −43.5 eu. It is difficult to rationalize the even more negative $\Delta S^\ddagger$ for reaction 6, unless a highly polar transition state strongly orients solvent molecules.

Reactions with Diamines. Reactions of the diamines $H_2N(CH_2)_nNH_2$ (n = 2 or 3) with 1 in THF are substantially faster than those of the monoamines in the amine concentration range studied. The rate law, which contrasts with the second-order amine dependence of the monoamines, exhibits only a first-order dependence on the diamine concentration. Thus, the other end of the attacking amine appears to be functioning as the catalytic molecule of amine as, for example, in the possible intermediate VI.



VI

If the k_1 value for the diamines is divided by k_2 (41.9 M^{-2} s^{-1}) for intermolecular catalysis in the H_2N-*n*-Bu reaction, one obtains an "effective molarity" for the catalyzing end of the diamine; the "effective molarity", therefore, is the concentration of H_2N-*n*-Bu that would be required to give the same rate as the diamine.[41] The "effective molarities" for $H_2N(CH_2)_2NH_2$ and $H_2N(CH_2)_3NH_2$ are 0.14 and 0.17 M, respectively. These are less than the 1 M "effective molarities" of diamine aminolysis reactions of *p*-nitrophenyl acetate in chlorobenzene[31] and acetylimidazole and methyl formate in water.[41]

Activation parameters, $\Delta H^\ddagger = 4.03 \pm 0.15$ kcal/mol and $\Delta S^\ddagger = -41.8 \pm 0.5$ eu, were calculated for the reaction of 1 with $H_2N(CH_2)_3NH_2$ from rate data at different temperatures (Table III). The low activation energy for this reaction may, as in the case of the $H_2NC_6H_{11}$ reaction discussed earlier, be due to negative ΔH values for the first two steps of Scheme I (carbene adduct formation and intramolecular H bonding in intermediate VI) which are slightly outweighed by a positive activation energy for the rate-determining breakdown of VI to the products. The

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(38) Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solution"; Butterworths: London, 1965; and 1972 supplement.

(39) Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 2403.

(40) Negative activation energies for reactions of free carbenes with olefins have been reported: Turro, N. J.; Lehr, G. F.; Butcher, J. A.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* **1982**, *104*, 1754.

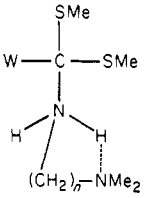
(41) Page, M. I.; Jencks, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 8818, 8828.

negative ΔS^{*}, which is similar to that (−38.5 eu) for the k_2 path of the $H_2NC_6H_{11}$ reaction, probably also results primarily from the two pre-rate-determining equilibria which result in the coming together of two molecules in intermediate VI. Thus, the values of both ΔH^{*} and ΔS^{*} are quite reasonable for the type of mechanism given in Scheme I.

The reaction of $H_2N(CH_2)_4NH_2$ has two terms in its rate law; one is first order in amine and the other is second. The rate constant k_1 (Table II) is less than half that of k_1 values for $H_2N(CH_2)_nNH_2$ (n = 2 or 3), perhaps reflecting a somewhat less favorable 7-membered ring in intermediate VI. However, it is surprising that the k_1 values of the three diamines do not differ more. Rates for the intramolecular catalysis of acetylimidazole aminolysis by diamines also depend little on the nature of the diamine;[40] although this point has been discussed,[41] it is not clear why these differences are so small. The somewhat higher basicities of $H_2N(CH_2)_nNH_2$ (n = 3 and 4) may partially account for their relatively high reactivities.

The k_2 value (1540 $M^{-2}\ s^{-1}$) for $H_2N(CH_2)_4NH_2$ is high as compared with 41.9 $M^{-2}\ s^{-1}$ for H_2N-n-Bu. Even taking into account a statistical factor of 4 for the diamine, the $H_2N(CH_2)_4NH_2$ rate is still 9.2 times faster than the reaction of H_2N-n-Bu. This suggests that in addition to activation as in structure VI, the dangling NH_2 groups may increase the rate of breakdown of the tetrahedral intermediate by hydrogen bonding to both NH_2 protons on the attacking nitrogen; this rate enhancement may be similar to the accelerating effect of pyridine solvent on the reaction of H_2N-n-Pr, as noted above.

The reactions of $H_2N(CH_2)_nNMe_2$ (n = 2 or 3) follow a rate law that includes terms which are first and second order in the amine concentration. Although scatter in the plot for $H_2N(CH_2)_2NMe_2$ gave k_1 and k_2 values of lower precision, it is obvious that k_1 values for $H_2N(CH_2)_nNMe_2$ (n = 2 and 3) are lower than for the corresponding $H_2N(CH_2)_nNH_2$ (n = 2 and 3) by factors of 7.0 (n = 2) and 10 (n = 3). Part of the difference may be accounted for by a statistical factor of 2 which favors the $H_2N(CH_2)_nNH_2$ reactions. This leaves the $H_2N(CH_2)_nNMe_2$ (n = 2 or 3) reactions slower than those of $H_2N(CH_2)_nNH_2$ by factors of 3.5 and 5.0, respectively. Since the NMe_2 group cannot catalyze the reaction by an intermediate of structure VI, these results suggest that structure VII is the most likely intermediate in the k_1 reactions of the diamines.



VII

It is interesting that the tertiary NMe_2 group in the diamines is such an effective catalyst as contrasted with DABCO in the monoamine reactions. This probably is the result of a higher "effective molarity" of the NMe_2 group in the diamine as compared with that of DABCO in the intermolecular reaction.

The k_2 values for $H_2N(CH_2)_nNMe_2$ (n = 2 or 3) are larger than that for H_2N-n-Bu, by factors of 2.4 (n = 2) and 4.3 (n = 3). While these results suggest that the dangling NMe_2 groups accelerate the reactions as compared with H_2N-n-Bu, the acceleration is somewhat less than that (9.2) noted above for $H_2N(CH_2)_4NH_2$. The NMe_2 group would be expected to be less effective than NH_2 because it would be less likely to H bond to the other NH_2 proton due to the greater bulkiness of the NMe_2 group.

Registry No. 1, 76262-42-5; $(CO)_5W[\overline{CNH(CH_2)_2NH}]$, 88157-00-0; H_2NPr-n, 107-10-8; H_2NBu-n, 109-73-9; $H_2NC_6H_{11}$, 108-91-8; H_2NCH_2Ph, 100-46-9; $H_2N(CH_2)_2NHa$, 107-15-3; $H_2N(CH_2)_3NH_2$, 109-76-2; $H_2N(CH_2)_4NH_2$, 110-60-1; $H_2N(CH_2)_2NMe_2$, 108-00-9; $H_2N(CH_2)_3NMe_2$, 109-55-7.