Table I. Product Ratios from the Reaction of Substituted Silanes, $(CH_3)_2RSiCH_2Cl$, with Fluoride Ion and Constants Used in Analysis

R	$(CH_3)_2(F)Si$-CH_2R^a (**4**)/$CH_3(R)$-$(CH_3CH_2)SiF$ (**5**)	ΔH°_{acid}	σ^* constant	σ_I constant
ethyl	1.5	421^b	-0.10^c	-0.055^g
methyl	1.0	416.6^b	0.00^c	-0.046^g
isopropyl	0.67	419^b	-0.19^c	-0.064^g
cyclopropyl	7.0	412^b	0.11^g	
butyl	0.87	420^c	-0.13^c	-0.060^g
vinyl	20	406^b	0.56^f	0.05^c
phenyl	16	399^b	0.60^c	0.10^c

[a] Statistically corrected. These ratios are obtained early in the reaction before secondary reactions occur. [b] Reference 3. [c] Hine, J. "Structural Effects on Equilibrium in Organic Chemistry"; Wiley-Interscience: New York, 1975. [d] Brown, T. L. *J. Am. Chem. Soc.* **1958**, *80*, 6489–6491. [e] Estimated from ref 3. [f] Barlin, G. B.; Perrin, D. D. *Q. Rev., Chem. Soc.* **1966**, *20*, 77–101. Values greater than that of phenyl have also been reported (Hine, J.; Bailey, W. C., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 2075–2078). [g] Shorter, S. "Correlation Analysis of Organic Reactivity"; Research Studies Press: New York, 1982.

Table II. Correlation of log **4**/**5** with ΔH°_{acid}, σ^* Constants, and σ_I Constants

	slope (correlation coefficient) correlated with		
reactn	σ^* constant	σ_I constant	ΔH°_{acid}
solution phase (eq 3)	1.81 (0.943)	9.06 (0.952)	−0.0674 (0.904)
gas phase (eq 1)	1.45 (0.858)	9.29 (0.826)	−0.0784 (0.999)

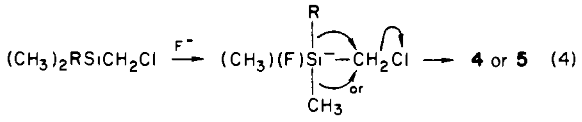
study: (1) Voronkov and co-workers have demonstrated low yields of alkyl migration in (chloromethyl)silanes reacting with KF at high temperature in polar solvents,[6] and (2) Hopper and co-workers have reported methyl migration in hot-tube reactions over solid KOMe.[7] Both examples demonstrate alkyl migration, but in neither case do the authors attempt to examine the migration in any detail.

Therefore, to explore the nature of this reaction in detail, we prepared or obtained ethyl, isopropyl, cyclopropyl, phenyl, *n*-butyl, and vinyl compounds of the type $(CH_3)_2RSiCH_2Cl$. These were each reacted with fluoride ion as in eq 3. When the log of the

$$(CH_3)_2RSiCH_2Cl \xrightarrow[\text{toluene}]{\overset{\text{18-crown-6}}{F^-}} \underset{\mathbf{4}}{(CH_3)_2SiFCH_2R} + \underset{\mathbf{5}}{CH_3RSiFCH_2CH_3} \quad (3)$$

ratio of products (**4**/**5**) is plotted vs. (1) the gas-phase acidities,[3] (2) σ^* constants, or (3) σ_I constants, roughly linear correlations were obtained, a comparable fit being found for σ^* and σ_I (the correlation coefficients are 0.943 and 0.952, respectively), a poorer fit for ΔH°_{acid} (correlation coefficient 0.904). The gas-phase data correlate only with ΔH°_{acid} (correlation coefficient 0.999). Tables I and II summarize these data. There is a definite correspondence between the gas- and solution-phase data when plotted against ΔH°_{acid}, indicating that eq 1 and 3 are sensitive to substituent properties in a similar way. A more focused look at these data, however, reveals some interesting differences. In solution the data are better accommodated by solution parameters while in the gas phase, gas-phase parameters work best. If the solution reaction behaved exactly like the gas-phase one and if these data more perfectly correlated with σ^* and σ_I constants, then ethyl and vinyl would migrate less readily than methyl and phenyl. That they do not may be the result of solvent interactions that we presently do not understand. What is clear is the similarity between the gas- and solution-phase experiments, resulting because substituents tend to stabilize the negative charge localized on the migrating group. The rough correlation with σ^* suggests that the amount of negative charge localization is modest (Taft ρ^*).

A consistent mechanistic model for reaction of fluoride ion and these chloromethyl-substituted silanes (eq 4) involves the formation



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of a pentacoordinate adduct (**6**), where CH_3 and R migrate competitively to displace chloride ion. The driving force for pentacoordination is the high fluoride affinity of silanes demonstrated both in solution and the gas phase;[8] the migratory efficiency is controlled largely by anion stability.

In conclusion, we report a new reaction of chloromethyl-substituted silanes, one whose mechanism we have briefly explored. Our data suggest that fluoride ion induces alkyl and/or aryl migration through a pentacoordinate intermediate where the ease of migration correlates with the ability of the migrating group to stabilize the negative charge which is developed in the transition state.

Acknowledgment. We gratefully acknowledge support from Research Corporation, the National Science Foundation, and the University of Colorado at Denver Graduate School. We also thank Professor C. H. DePuy for several stimulating discussions and the University of Colorado Health Sciences Center Clinical Mass Spectrometry Resource for extensive use of their GC-MS facility.

Registry No. 18-Crown-6, 17455-13-9; $(CH_3)_2RSiCH_2Cl$ (R = ethyl), 3121-77-5; $(CH_3)_2RSiCH_2Cl$ (R = methyl), 2344-80-1; $(CH_3)_2RSiCH_2Cl$ (R = isopropyl), 22429-26-1; $(CH_3)_2RSiCH_2Cl$ (R = cyclopropyl), 54690-67-4; $(CH_3)_2RSiCH_2Cl$ (R = butyl), 3121-75-3; $(CH_3)_2RSiCH_2Cl$ (R = vinyl), 16709-86-7; $(CH_3)_2RSiCH_2Cl$ (R = phenyl), 1833-51-8; KF, 7789-23-3; CsF, 13400-13-0.

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Transition-State Structure and the Temperature Dependence of the Kinetic Isotope Effect

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The temperature dependence of the kinetic hydrogen isotope effect (KIE) as a mechanistic criterion has attracted great attention during recent years.[1] In particular, a temperature-independent KIE coupled with an anomalous A_H/A_D ratio has been taken as a probe of a nonlinear transition state for the hydrogen transfer. This simple rule has already come into common use[2-4] despite some published results which indicate that there might be limitations to its usefulness.[5]

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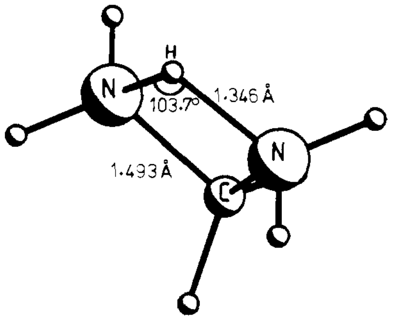

Figure 1. Transition-state structure as calculated by MNDO for the intramolecular proton transfer in monprotonated methylenediamine.

In view of this, we would like to comment on some of the underlying theory and in a simple, straightforward manner point out its implications.

Within the transition-state theory the kinetic isotope effect for an elementary step is given[6] by (1). The complexity of the VP, EXC, and ZPE factors will introduce a temperature dependence of k_H/k_D, which, in general, is not easily predicted. However, if the assumption is made that the ZPE factor is decisive (i.e., VP × EXC = 1) (1) can be recast into (2). According to the Arrhenius theory, applied to a single reaction step, the corresponding expression is

$$k_H/k_D = \nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger} \times \mathrm{VP} \times \mathrm{EXC} \times \mathrm{ZPE} \qquad (1)$$

$$\ln (k_H/k_D) = \ln (\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}) + \frac{h}{2kT}\left[\sum_i^{3N-6} (\nu_{iH} - \nu_{iD}) - \sum_i^{3N^{\ddagger}-7} (\nu_{iH}^{\ddagger} - \nu_{iD}^{\ddagger})\right] \qquad (2)$$

$$\ln (k_H/k_D) = \ln (A_H/A_D) - [E_H - E_D]/(RT) \qquad (3)$$

A_H/A_D being the Arrhenius preexponential factors for isotope H and D, respectively, and E_H and E_D being the corresponding Arrhenius activation energies.

From eq 2 and 3 the following relations are obtained:

$$E_H - E_D = -\frac{Nh}{2}\left[\sum_i^{3N-6} (\nu_{iH} - \nu_{iD}) - \sum_i^{3N^{\ddagger}-7} (\nu_{iH}^{\ddagger} - \nu_{iD}^{\ddagger})\right] \qquad (4)$$

$$\ln (A_H/A_D) = \ln (\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}) \qquad (5)$$

If it is assumed that the ZPE factor is decisive, then it follows that (1) every factor that tends to minimize the difference between the zero-point energies of the transition state and the reactant also tends to decrease the temperature dependence of the KIE (eq 4) and (2) the ratio A_H/A_D obtained from an Arrhenius plot is given by $\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}$ (eq 5). This is of course an oversimplication, and the underlying assumption, VP × EXC = 1, is not exactly valid in the general case.

The approximate treatment does show, however, that a bent transition state should be associated with a weaker KIE (and thus a smaller temperature coefficient) than a linear one due to a greater isotopic sensitivity of the vibrations of a bent TS.[7] Provided that the transition-state theory is applicable "normal" A_H/A_D values are also expected. Extensive theoretical considerations also show that A_H/A_D ratios greater than ~1.4 can hardly be accommodated by the theory.[8]

To illustrate the above-mentioned principles, we have performed some model calculations of the temperature dependence of the kinetic isotope effect of a bent TS.

The calculations refer to the intramolecular proton transfer in the monoprotonated methylenediamine. This model has also been used by Menger in his investigation of transition-state pliability in N-to-N proton transfer.[9]

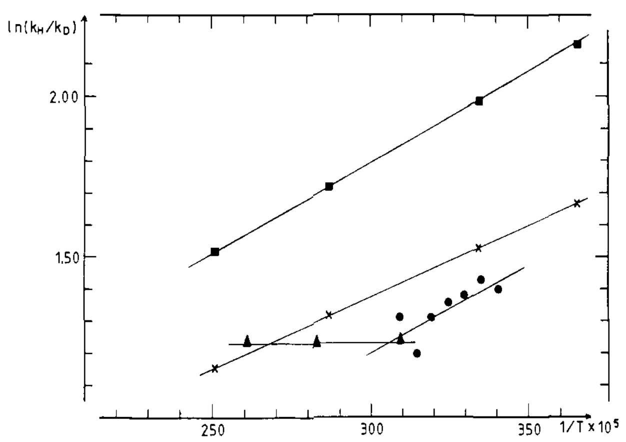

Figure 2. Temperature dependence on k_H/k_D. (■) Linear transition state (see text), $\Delta E = E_D - E_H = 1.11$ kcal/mol, $A_H/A_D = 1.12$; (X) bent transition state (see text), $\Delta E = 0.88$ kcal/mol, $A_H/A_D = 1.04$; (▲) ref 2, $\Delta E = 0$ kcal/mol, $A_H/A_D = 3.43$; (●) ref 4, $\Delta E = 1.05 \pm 0.38$ kcal/mol, $A_H/A_D = 0.74 \pm 0.46$.

The calculations were made at the MNDO[10] level using complete geometric optimization with the only restriction that the TS should have a symmetry plane bisecting the NCN angle and perpendicular to the NCN plane. The TS structure obtained is shown in Figure 1. The k_H/k_D values were calculated from the force fields of the transition state and the reactant using the complete kinetic isotope effect expression.

The results are shown in Figure 2 together with the results from an MNDO calculation on the intermolecular proton transfer between methylenediamine and monoprotonated methylenediamine where a linear TS is obtained.

The results are obvious, the KIE of the bent TS being weaker than for the linear TS. According to the present calculations, the effect is not dramatic, however. Moreover, the ratios of the Arrhenius preexponential factors obtained by linear extrapolation are quite normal in the two cases.

Some experimental results from two recent investigations are also included in Figure 2.

In one of the investigations the temperature dependence of the KIE in hydride transfer from 1-benzyl-1,4-dihydronicotinamide to the 10-methyl-9-phenylacridinium ion was studied.[4] From the temperature dependence of the KIE, the authors concluded that the hydride transfer proceeded via a linear transition state. Such a conclusion based solely upon the temperature dependence of the KIE is not justifiable according to the present results.

In the other investigation, of syn elimination in the reaction of bicyclo[2.2.1]heptan-2-*exo*-yl toluene-*p*-sulfonate,[2] a temperature-independent KIE was observed giving rise to $A_H/A_D = 3.4$. The authors concluded that the elimination proceeded via a bent transition state. Such a large A_H/A_D ratio is not compatible with an elementary step as shown above.

It ought to be mentioned that temperature-independent KIEs and anomalous A_H/A_D ratios have been observed earlier in elimination reactions. These findings have been interpreted in terms of substantial internal return in the proton-abstraction step,[11,12] i.e., the observed rate constant does not correspond to a rate constant for a single step.

The results from the present investigation and earlier ones[5,8] clearly indicate that the temperature dependence of the KIE should not be used as a mechanistic tool in differentiating between linear and bent transition states. We also suggest that in the case

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of observed temperature-independent isotope effects giving rise to large anomalous A_H/A_D values the possibility of alternative mechanisms should be carefully considered.

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Deprotonation and Anionic Rearrangements of Organometallic Compounds. 1. Reactions of Cyclopentadienylrhenium Acyl and Alkyl Complexes with Strong Bases

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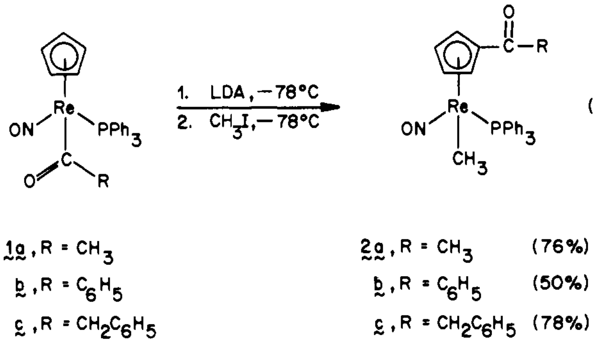
Carbanions generated by reactions of organometallic complexes with strong, nonnucleophilic bases are seeing increased applications in organic and organometallic synthesis.[1,2] However, few if any parallels[3] have been noted to the rich migration chemistry observed upon deprotonation of ligands attached to main-group elements[4] (e.g., Wittig,[4a] Stevens,[4b] and Brook[4d] rearrangements). We disclose herein (1) a novel sequence of reactions which occurs upon treatment of rhenium acyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COR)$ with strong bases, (2) mechanistic details thereof, and (3) related chemistry of alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)$. These observations presage a new class of organometallic reactions[5] of potentially broad generality and utility.[3,6]

Treatment of acetyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_3)$[7] (**1a**) with Li^+ $(i\text{-}Pr)_2N^-$ (LDA) (1.6–2.1 equiv) in THF at −78 °C (5 min), followed by CH_3I (2 equiv) gave, after workup, methyl complex $(\eta^5\text{-}C_5H_4COCH_3)Re(NO)(PPh_3)(CH_3)$ (**2a**) in 76% yield (eq i). The structure of **2a** was evident from its spectral features,[8] which included ^1H and ^{13}C NMR patterns characteristic of monosubstituted cyclopentadienyl complexes. No products derived from the methylation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2Li)$ were detected. Bases *n*-BuLi and *n*-BuLi·TMEDA gave chemistry identical with LDA.

The generality of this transformation was probed with additional substrates. Similar treatment of benzoyl complex **1b**[7] and phenylacetyl complex **1c**[7] (eq i) with LDA and CH_3I gave methyl complexes **2b**[8] and **2c**[8] in 50% and 78% yields, respectively. Substitution of Br_2 for CH_3I in the latter reaction gave bromide complex $(\eta^5\text{-}C_5H_4COCH_2C_6H_5)Re(NO)(PPh_3)(Br)$ (58%).[8]



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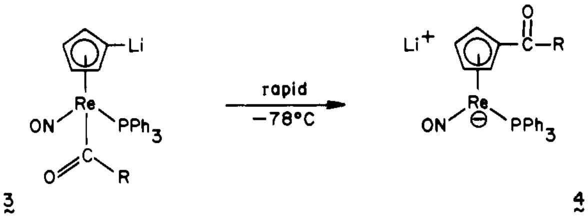

Plausible steps in the transformations **1** → **2** would include initial cyclopentadienyl ring deprotonation to give $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(COR)$ (**3**), followed by acyl ligand migration to give rhenium anion $Li^+[(\eta^5\text{-}C_5H_4COR)Re(NO)(PPh_3)]^-$ (**4**). We sought evidence for and mechanistic data on these processes. First, reaction of $(\eta^5\text{-}C_5D_5)Re(NO)(PPh_3)(COCH_3)$ (**1a**-d_5; ca. 90:10 d_5/d_4)[8] with LDA and CH_3I as described above gave **2a**-d_4 (<2% d_3), as assayed by careful mass spectrometric analysis. This indicates that LDA initially abstracts a cyclopentadienyl proton of **1**; also, since the product **2a**-d_4 is of greater isotopic purity than the starting material, deprotonation must occur with a substantial k_H/k_D. Second, the reaction of **1a** with LDA was monitored by ^{31}P NMR at −78 °C. A new resonance (43.8 ppm, br m) appeared immediately, and did not diminish upon warming to −5 °C. Addition of CH_3I gave **2a**; hence, the resonance was assigned to **4a**. Also, **2a** was isolated in good yield following addition of LDA to a −78 °C *mixture* of **1a** and CH_3I. These observations indicate that the rearrangement **3** → **4** is rapid at −78 °C. Finally, coreaction of a mixture of **1b** and $(\eta^5\text{-}C_5D_5)Re(NO)(PPh_3)(COC_6D_5)$ (**1b**-d_{10})[8] with LDA and CH_3I as above gave *exclusively* **2b**-d_0 and **2b**-d_9. Hence, **3** → **4** is intramolecular.

Before attempting stereochemical experiments, the deprotonation of analogous rhenium alkyl complexes was studied. Treatment of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$[9] with 1.5 equiv of *n*-BuLi·TMEDA in THF at −78 °C gave rapid (<5 min) and quantitative conversion to $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(CH_2C_6H_5)$ (**5**), as assayed by ^{31}P NMR (25.8 ppm) and subsequent methylation (CH_3I, −78 °C) to $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(CH_2C_6H_5)$ (**6**, 74%, eq ii).[8] Treatment of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**7**)[10] with 2.1 equiv of *n*-BuLi·TMEDA in THF at −78 °C gave a slower (10 min) but still quantitative conversion to $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(CH_3)$ (**8**), as assayed by ^{31}P NMR (28.2 ppm) and subsequent acylation (acetic anhydride, −24 °C, 38%) to **2a** and (benzoic anhydride, −78 °C, 60%) **2b**. In separate ^{31}P NMR experiments, neither **5** nor **8** showed any appreciable rearrangement or decomposition over the course of 30 min at 25 °C.

With two distinct routes to **2a** established, the stereochemistry of the rearrangement **3a** → **4a** could be probed. First, it was determined that addition of the chiral shift reagent tris[(trifluoromethyl)hydroxymethylene-*d*-camphorato]europium to CD_2Cl_2 solutions of **2a** differentiated the CH_3 ^1H NMR reso-

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