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Hydrolysis and Intermolecular Silyl Exchange in *N*-(Trimethylsilyl)imidazole and *N*-(Trimethylsilyl)-2-methylimidazole

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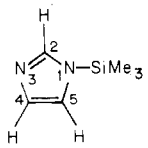
Carbon-13 and proton NMR studies demonstrate that trace amounts of water in *N*-(trimethylsilyl)imidazole and *N*-(trimethylsilyl)-2-methylimidazole are responsible for rapid intermolecular silyl exchange. Exchange can be slowed down by further purification or by addition of excess triethylamine. A mechanism is proposed which accounts for hydrolysis and intermolecular silyl exchange.

Introduction

The migration of silicon and other metals from one ring atom to another is well-known for imidazole,[1-3] pyrazole,[1,3,4] triazole,[3] cyclopentadiene,[5,6] and indene[7] derivatives and there appears to be general agreement that the dominant mechanism of metal exchange occurs via consecutive *intramolecular* 1,2



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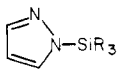

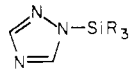

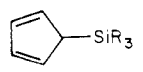

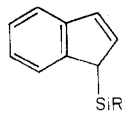

shifts. The intramolecularity can be proven directly, in some cases, by the retention of coupling from the ring carbon to metal, as in $C_5H_5Sn(CH_3)_3$,[5] while in other cases the intramolecularity is verified by line shape analysis or by the absence of dilution or solvent effects.

Several observations, however, seem to imply that rapid *intermolecular* exchange can also occur in these systems and that the intermolecular process may be faster, under certain conditions, than the intramolecular one. For example, O'Brien and Hrung found that for *N*-(trimethylsilyl)pyrazoles the activation energies calculated from line width measurements below coalescence in dilute solutions of diphenyl ether were inordinately low (3–6 kcal/mol) while activation energies for neat liquids above coalescence were 24–32 kcal/mol.[4] Torocheshnikov et al. were unable to slow down silyl migration in *N*-(trimethylsilyl)imidazole, **1**, even at −80 °C and they assumed that a complicated intermolecular exchange process was occurring.[3] Grishin, Sergeyev, and Ustynyuk found a singlet at room temperature for the ring carbons of $C_5H_5HgCH_3$ but no satellites arising from ^{199}Hg–^{13}C spin–spin coupling.[5]

Hydrolysis of silylimidazoles by trace water impurities might offer a reasonable explanation for *intermolecular* exchange since silicon–nitrogen compounds are known to be extremely reactive toward water. Previous studies of inter- and intramolecular exchange in compounds such as PF_5, SF_4, R_2NSF_3, SiF_5^-,[8] $CH_3SiF_4^-$,[9] $(CH_3)_3SiF$,[10] $C_6H_5PF_2$, and $C_6H_5PF_2HOR$[11] have clearly demonstrated that H_2O, HF, HOR, and base catalysts can bring about exchange processes which are rapid on the NMR time scale. These studies are all consistent with the coordination model[12] of reaction mechanisms which postulates that four-center reactions are accelerated if the coordination number of the central atom is increased; hence, we have the requirement, in many instances,

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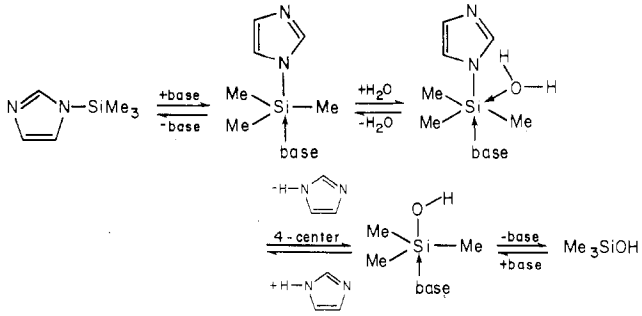
Scheme I. Proposed Mechanism of Base-Catalyzed Hydrolysis and Intermolecular Silyl Exchange in *N*-(Trimethylsilyl)imidazole



of a base catalyst which coordinates to the central atom. Application of the coordination model to hydrolysis of silylimidazoles predicts the mechanism of Scheme I.

The work described in this paper was designed to answer the following questions: (1) Under what conditions does silyl exchange occur by an intermolecular route? (2) Is hydrolysis responsible for intermolecular silyl exchange? (3) Does the mechanism of Scheme I adequately account for the experimental results?

Experimental Section

Proton-decoupled ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer (10-mm probe) using data acquisition times greater than 1.0 s. All ^{13}C NMR spectra were recorded at 34 ± 2 °C. Proton-coupled ^{13}C NMR spectra were obtained by gated decoupling in order to take advantage of the positive NOE.

Proton NMR spectra were recorded on Varian A-56/60A and HA-100D spectrometers equipped with variable-temperature probes. Temperatures were calibrated with the aid of methanol temperature vs. chemical shift chart[13] and are accurate to ±1 °C.

N-(Trimethylsilyl)imidazole, **1**, was obtained commercially (Aldrich, Eastman, and Pierce) and prepared from trimethylchlorosilane and imidazole.[14] The compound was redistilled and transferred to NMR tubes by standard vacuum techniques. Methylene chloride was distilled from P_2O_5 and triethylamine from molecular sieves.

Preparation of *N*-(Trimethylsilyl)-2-methylimidazole, 2. Me_3SiCl (17 g) was added dropwise to a stirred solution of 2-methylimidazole (10 g) and Et_3N (12 g) in CH_2Cl_2 (100 ml) under a nitrogen atmosphere. After 24 h of stirring, Et_3NHCl was filtered off and solvent was removed under vacuum. Vacuum distillation gave **2** in 85% yield, identified by ^1H and ^{13}C NMR.

Results and Discussion

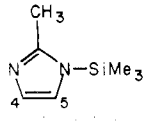
Evidence for Intermolecular Silyl Migration in Silylimidazoles. Previous ^{13}C, ^1H, and ^{15}N NMR studies[1-3] of *N*-(trimethylsilyl)imidazole, **1**, have demonstrated the equivalence of nuclei $C_{4,5}$, $H_{4,5}$, and $N_{1,3}$ in **1**, but the mechanism responsible for this equivalence, particularly the choice between intra- or intermolecular silyl migration, has not been established. In this work, several experiments were carried out which confirm that silyl migration in **1** occurs by an intermolecular pathway. In one experiment, imidazole was

Table I. ^{13}C and ^{1}H Chemical Shifts of **1** and **2** in the Slow- and Fast-Exchange Limits[a]

Sample	^{13}C shifts, ppm				Sample	^{1}H shifts, ppm				
	C_2	C_4	C_5	CH_3		H_2	H_4	H_5	CH_3	$(CH_3)_3Si$
1, slow exchange (20% v/v in Et_3N)	140.0	131.5	119.5		**1**, slow exchange (50% v/v in Et_3N at +7 °C)	7.58	7.16	6.98		0.452
1, fast exchange (neat)	140.1	125.5 ($C_{4,5}$)			**1**, fast exchange (10% v/v in CH_2Cl_2)	7.56	7.06 ($H_{4,5}$)			0.445
2, slow exchange (neat)	149.0	129.4	121.3	16.6						
2, slow exchange (50% v/v in Et_3N)	148.7	129.5	120.8	16.3						
2, fast exchange (50% v/v mixture of 1 and 2)	148.0	124.6 ($C_{4,5}$)		16.0	2, fast exchange (10% v/v in CH_2Cl_2)		6.87 ($H_{4,5}$)		2.43	0.450

[a] All ^{13}C and ^{1}H chemical shifts in this table are to low field of internal TMS. ^{13}C and ^{1}H NMR spectra were recorded at 20 and 60 MHz, respectively.

added to rapidly exchanging **1**, but the ^{13}C and ^{1}H NMR spectra did not show separate imidazole peaks; instead, the C_2, H_2 and $C_{4,5}$, $H_{4,5}$ peaks shifted, with increasing imidazole concentration, toward the chemical shift of pure imidazole. Evidently, imidazole is exchanging rapidly with **1** and this result is entirely consistent with the mechanism of Scheme I since hydrolysis and silicon–nitrogen bond cleavage liberate imidazole. Of course, once imidazole is in solution very rapid tautomerism[15] leads to equivalence of positions 4 and 5. Similar results were found when 2-methylimidazole was added to rapidly exchanging *N*-(trimethylsilyl)-2-methylimidazole, **2**.



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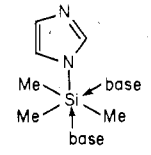
The ^{13}C chemical shifts of the Me_3Si group of **1** and **2** differ by ~0.7 ppm; nevertheless, an equimolar mixture of rapidly exchanging **1** and **2** showed only a single, averaged Me_3Si peak. If it is assumed that hydrolysis and silyl migration in **2** is identical with that in **1**, then this result is consistent with Scheme I since both compounds are in rapid equilibrium with the common species Me_3SiOH. The aromatic region showed, as expected, equivalence of C_4 and C_5 in **1** and equivalence of C_4 and C_5 in **2**.

Reducing the Rate of Intermolecular Silyl Migration. The mechanism of Scheme I suggests a number of ways of reducing the rate of intermolecular silyl migration, the most obvious one being the removal of all traces of water. This proved to be impossible for **1**, as checked by proton NMR down to −50 °C and ^{13}C NMR at +34 °C, despite redistillations and drying of solvents, reagents, and glassware, but our purification technique was successful in stopping exchange in neat samples of **2** at +34 °C and under these conditions C_4 and C_5 are nonequivalent in the ^{13}C NMR spectrum.

The fact that exchange can be slowed down in **2** strongly suggests that careful purification should suffice to reduce hydrolysis in **1**. However, Scheme I points to an easier method of slowing down hydrolysis and intermolecular silyl exchange: prevent four-center reactions by displacing water from the sixth coordinate site around silicon, perhaps by adding an excess of Lewis base and shifting the equilibrium toward adduct **3**.



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The latter approach was found to be successul since addition of triethylamine to rapidly exchanging **1** gave NMR spectra which showed nonequivalent H_4 and H_5 as well as nonequivalent C_4 and C_5, consistent with a "rigid" structure of **1**. Similarly, Et_3N stopped exchange in unpurified **2** at +34 °C.

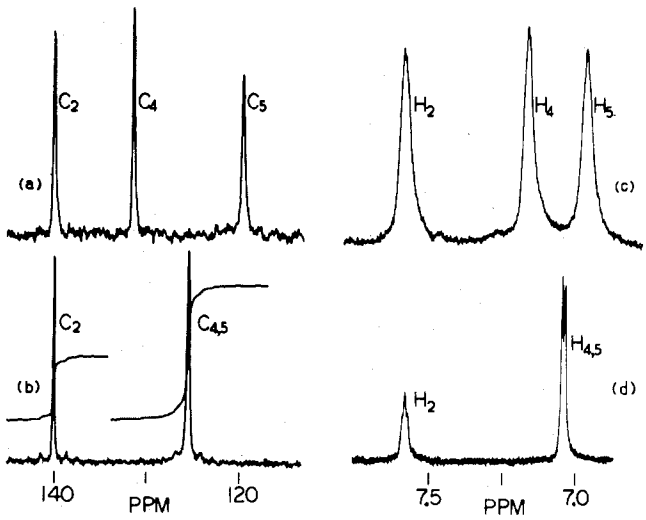


Figure 1. ^{13}C and ^{1}H NMR spectra of *N*-(trimethylsilyl)-imidazole, **1**, in the slow-exchange and fast-exchange limits: (a) ^{13}C NMR of **1**, slow exchange (20% v/v in Et_3N) at +34 °C; (b) ^{13}C NMR of **1**, fast exchange (neat) at +34 °C; (c) ^{1}H NMR of **1**, slow exchange (10% **1** plus 10% Et_3N v/v in $CDCl_3$) at −21 °C; (d) ^{1}H NMR of **1**, fast exchange (10% v/v in CH_2Cl_2) at +38 °C.

Pyridine also slowed down exchange in **1**, to some extent, and broadened the $C_{4,5}$ peak at +34 °C, but pyridine was less effective than triethylamine, which is consistent with their relative basicity toward silicon compounds.[16]

If Et_3N is added to a mixture of rapidly exchanging **1** and **2**, exchange is stopped and the ^{13}C NMR spectrum shows the presence of a mixture of "rigid" **1** and **2**.

A comparison of the ^{13}C and ^{1}H NMR spectra of rapidly exchanging and rigid **1** is shown in Figure 1. ^{13}C and ^{1}H chemical shifts of **1** and **2** in the fast- and slow-exchange limit are presented in Table I and ^{13}C–^{1}H nuclear spin–spin coupling constants of **1** and **2** are given in Table II.

As can be seen from Figure 1 and Table I, the chemical shift of C_4 and C_5 in the case of rapidly exchanging samples is the average of C_4 and C_5 of the rigid compounds. Similarly, the chemical shift of H_4 and H_5 in rapidly exchanging **1** is the average of H_4 and H_5 of rigid **1**. Rapidly exchanging samples of **1** and **2** give rise to averaged coupling constants, as seen in Table II. For example, **1** in the slow-exchange limit has $^{3}J(C_2–H_4)$ = 11.6 Hz and $^{3}J(C_2–H_5)$ = 8.0 Hz while rapidly exchanging **1** has an average coupling constant of 9.9 ± 0.2 Hz.

Table II. ^{13}C–^{1}H Coupling Constants for Compounds **1** and **2** in the Slow- and Fast-Exchange Limits[a]

	J values, Hz		
	1, slow exchange (20% v/v in Et_3N)	**1**, fast exchange (neat)	**2**, slow exchange (neat)
$^1J(C_2-H_2)$	204.4	203.9 ± 0.2	
$^1J(C_4-H_4)$	186.8	186.2 ± 0.2	183.8
$^1J(C_5-H_5)$	185.3		184.7
$^2J(C_4-H_5)$	11.2	13.9 ± 0.2	9.0
$^2J(C_5-H_4)$	17.0 ± 2.0		16.7
$^3J(C_2-H_4)$	11.6	9.9 ± 0.2	
$^3J(C_2-H_5)$	8.0		
$^3J(C_4-H_2)$	11.2	7.7 ± 0.2	
$^3J(C_5-H_2)$	5.0 ± 2.0		

[a] The error in all coupling constants is ±1 Hz, unless otherwise indicated.

Approximate activation parameters for intermolecular silyl exchange in **1** were obtained by recording the variable-temperature ^1H NMR spectrum of a sample containing **1** (4.0×10^{-4} mol) and Et_3N (3.3×10^{-4} mol) in CH_2Cl_2 (0.3 ml) and comparing the coalescence of the H_4 and H_5 peaks with theoretically calculated spectra (kindly supplied by Mr. Kirk Marat). A plot of ln $(1/\tau)$ vs. $1/T$ gave $E_a = 7.7$ kcal/mol. From the coalescence temperature of +35 ± 5 °C we estimate $\Delta G^{\ddagger}_{308} = 14.2$ kcal/mol and therefore $\Delta S^{\ddagger} = -29.3$ eu. The large and negative entropy of activation is in agreement with the constrained intermediates postulated in Scheme I.

Water, Trimethylsilanol, and Base in Intermolecular Silyl Exchange. If all equilibria of Scheme I are rapid, NMR cannot directly verify the presence of H_2O, imidazole, or Me_3SiOH, since these species exchange rapidly with silylimidazole. That water is involved in silyl migration was demonstrated by adding H_2O (2.8×10^{-4} mol) to a sample of Et_3N (2×10^{-4} mol) and rigid **1** (2×10^{-4} mol) in CH_2Cl_2 (0.3 ml), which resulted in the immediate appearance of the spectrum of rapidly exchanging **1**.

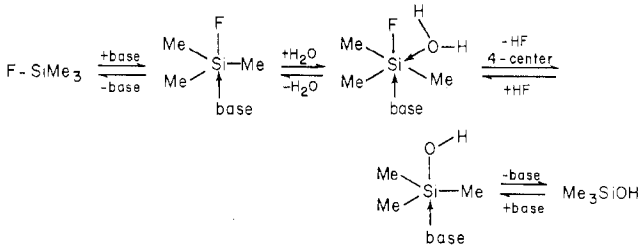
Commercial or once-distilled samples of **1** or **2** generally contained a sharp peak at 0.065 (^1H) and 1.95 (^{13}C) ppm downfield from TMS which was identified as $Me_3SiOSiMe_3$ by comparison with an authentic sample. Mass spectral investigation of **1** and **2** showed a peak at m/e 147 assigned to $Me_3SiOSiMe_2^+$.[17] Since $Me_3SiOSiMe_3$ is known to be a condensation product, its presence in samples of **1** and **2** is strong evidence for the formation of Me_3SiOH as postulated in Scheme I. A crude estimate of the minimum amount of water in samples can be made by assuming that $Me_3SiOSiMe_3$ and H_2O are present in equimolar quantities (eq 1). In that

$$2Me_3SiOH \rightarrow Me_3SiOSiMe_3 + H_2O \quad (1)$$

case, from integration of the $Me_3SiOSiMe_3$ peak, H_2O is present in 0.36–6.2 mol % in typical commercial or once-distilled samples of **1** and **2**. A second distillation reduces the amount of $Me_3SiOSiMe_3$ to below the NMR detection limit.

The requirement of a base catalyst in Scheme I is imposed by the coordination model and, while we assume that imidazole or silylimidazole can function as a base by coordination of N_3 to silicon, this aspect of the mechanism was not verified. However, kinetic and mechanistic studies of hydrolysis and exchange in the analogous Me_3SiF system[10] have confirmed the requirement of a base catalyst. In the latter study, for moderate concentrations of base (Et_2NH), the rate of hydrolysis and fluorine exchange was first order in Et_2NH,

Scheme II. Proposed Mechanism of Hydrolysis and Fluorine Exchange in Trimethylfluorosilane



Me_3SiF, and H_2O, and the coordination model[12] predicts the mechanism of Scheme II. The similarity between Schemes I and II suggests that the type of behavior postulated for silylimidazoles is entirely consistent with the behavior postulated for silicon–fluorine and other silicon compounds.

Inter- vs. Intramolecular Exchange. The fact that all exchange stops at +34 °C as soon as intermolecular silyl exchange has been stopped implies that any intramolecular process must be of much higher activation energy. In that case, an intramolecular process may be more favorable at higher temperatures because of the large and negative entropy of activation of hydrolysis and intermolecular exchange. Such an explanation readily accounts for the observation of O'Brien and Hrung,[4] who obtained consistent activation energies of 24–32 kcal/mol for intramolecular silyl exchange in *N*-(trimethylsilyl)pyrazoles, provided the activation energies were determined above coalescence temperatures in the range 91–130 °C. At lower temperatures in dilute solutions of diphenyl ether the activation energies were low (3–6 kcal/mol) and the latter process is presumably due to hydrolysis and intermolecular silyl exchange as found for **1** and **2**.

Acknowledgment. The financial assistance of the National Research Council of Canada is gratefully acknowledged.

Registry No. **1**, 18156-74-6; **2**, 60498-72-8; Me_3SiCl, 75-77-4; 2-methylimidazole, 693-98-1; ^{13}C, 14762-74-4.

References and Notes

(1) F. A. Cotton and D. J. Ciappenelli, *Synth. Inorg. Met.-Org. Chem.*, 197 (1972).
(2) H. Noth and B. Wrackmeyer, *Chem. Ber.*, **107**, 3070 (1974).
(3) V. N. Torocheshnikov, N. M. Sergeyev, N. A. Viktorov, G. S. Goldin, V. G. Poddubny, and A. N. Koltsova, *J. Organomet. Chem.*, **70**, 347 (1974).
(4) D. H. O'Brien and C.-P. Hrung, *J. Organomet. Chem.*, **27**, 185 (1971).
(5) Yu. K. Grishin, N. M. Sergeyev, and Yu. A. Ustynyuk, *Org. Magn. Reson.*, **4**, 377 (1972); C. H. Cambell and M. L. H. Green, *J. Chem. Soc. A*, 3282 (1971).
(6) A. Davison and P. E. Rakita, *Inorg. Chem.*, **9**, 289 (1970). For a review see L. M. Jackman and F. A. Cotton, *Dyn. Nucl. Magn. Reson. Spectrosc.*, 377 (1975).
(7) A. Davison and P. E. Rakita, *J. Organomet. Chem.*, **23**, 407 (1970); P. E. Rakita and G. A. Taylor, *Inorg. Chem.*, **11**, 2136 (1972).
(8) J. A. Gibson, D. G. Ibbott, and A. F. Janzen, *Can. J. Chem.*, **51**, 3203 (1973); D. G. Ibbott and A. F. Janzen, *ibid.*, **50**, 2428 (1972).
(9) R. K. Marat and A. F. Janzen, paper presented at the 59th Chemical Conference and Exposition, London, Ontario, Canada, June 6–9, 1976.
(10) J. A. Gibson and A. F. Janzen, *Can. J. Chem.*, **50**, 3087 (1972).
(11) A. F. Janzen and L. J. Kruczynski, paper presented at the EUCHEM Conference on Synthesis in Organic Chemistry, Menton, France, June 27–30, 1976.
(12) A. F. Janzen, submitted for publication.
(13) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970).
(14) L. Birkofer, P. Richter, and A. Ritter, *Chem. Ber.*, **93**, 2804 (1960).
(15) M. R. Grimmett, *Adv. Heterocycl. Chem.*, **12**, 104 (1970).
(16) I. R. Beattie, *Q. Rev., Chem. Soc.*, **17**, 382 (1963).
(17) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, Calif., 1967, p 476.