that a 1,2-phenyl shift cannot compete with the ready migration of the trimethylsilyl group.[8] However, the formation of **5** as the principal rearrangement product is, at first consideration, explicable in more than one way: (a) **5** could be formed directly from **3** by way of metalation at one of the six CH_3Si groups,[9] followed by 1,3-trimethylsilyl shift (path a); or (b) **5** could be formed indirectly from **3** by way of **4** in which either **6** or **4** undergoes metalation at one of the six CH_3Si groups and subsequently undergoes a 1,4-trimethylsilyl shift to yield anion **8** (path b). If path b obtains, anion **8** would have to be subsequently transformed into anion **9**, in order to fit the finding that the isolated, deuterated **5** is only the 1-deuterio isomer.

Subsequent experiments strongly favor the principal formation of **5** by a 1,4 shift, rather than a 1,3 shift. First of all, treatment of **4** in TMEDA with butyllithium leads, upon hydrolysis, exclusively to **5**; at no time during the reaction did withdrawn aliquots reveal any trace of **3**. Hence, it is improbable that **4** reverts to the anion of **3**, in order to yield **5** by a 1,3 shift. Secondly, a time study of the reaction of **3** in TMEDA with butyllithium shows that **3**, **4**, and **5** are all present throughout the reaction; as conversion to **5** reaches >98%, small traces of **3** and **4** persist. From the foregoing, we cannot as yet rule out that some of the rearrangement of **3** to **5** does occur *via* a 1,3 shift,[10] but there is no doubt that a considerable portion of the reaction involves a 1,2 shift, converting **3** into **4**, followed by a relatively more rapid 1,4 shift, converting **4** into **5**. Ongoing research aims at defining the relative importance of such novel competing 1,*n* anionic shifts in carbosilanes.

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[10] NOTE ADDED IN PROOF. Subsequent experiments with α,α-bis-(trimethylsilyl)ethylbenzene and butyllithium in TMEDA have now shown that a 1,3-trimethylsilyl shift can occur in such a system. In this case, the observed formation of α-[dimethyl(trimethylsilylmethyl)-silyl]ethylbenzene cannot be reasonably ascribed to consecutive 1,2 and 1,4 shifts.

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Formation and Relative Stability of Chloride Ion Clusters in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

Sir:

High-pressure mass spectrometry has been extensively used in recent years by Kebarle to study positive and negative ions "solvated" by neutrals in the gas phase.[1-5] For example, the relevant thermodynamic quantities have been obtained for Cl^- clustered by hydrogen bonding neutrals[4] and by CH_3CN.[5] Such studies are of extreme importance in relating the intrinsic chemical behavior of ionic species under solvent-free conditions (gas phase) with that usually observed in condensed phases. Such traditional concepts as acidities and basicities are by now well illustrated examples of significant differences between gas-phase and solution chemistry.[6-10]

The advantages of ion cyclotron resonance spectroscopy have been used in our present investigations to introduce a new and general method for the formation of chloride ion clusters in the gas phase. This method is based on the reaction of $COCl^-$ with neutral species according to reaction 1 at pressures as low as 5×10^{-6}

$$COCl^- + M \longrightarrow Cl^-(M) + CO \qquad (1)$$

Torr.[11] This reaction has been initially studied with a series of alkyl halides, and related compounds, to yield $Cl^-(CH_3Cl)$, $Cl^-(C_2H_5Cl)$, $Cl^-(i\text{-}C_3H_7Cl)$, $Cl^-(t\text{-}C_4H_9Cl)$, $Cl^-(CH_3F)$, $Cl^-(CH_2F_2)$, $Cl^-(CHF_3)$, $Cl^-(CF_4)$, $Cl^-(CH_3Br)$, $Cl^-(CH_3OH)$, $Cl^-(CH_3NO_2)$, $Cl^-(CH_3CN)$, and $Cl^-(CH_3CF_3)$.[12]

Several binary mixtures of neutrals were studied in the presence of $COCl^-$ to determine relative clustering ability. Since $COCl^-$ was found to react completely above 10^{-5} Torr, reaction 2 was probed under these conditions

$$Cl^-(A) + B \rightleftharpoons A + Cl^-(B) \qquad (2)$$

by pressure dependence of the relative intensities of the cluster ions and pulsed double resonance in both directions to establish the preferred "solvent" molecule. This technique is analogous to that used for relative proton affinities.[8] For example, at pressures above 3×10^{-5} Torr the species $Cl^-(CH_3NO_2)$ clearly predominates over $Cl^-(C_2H_5Cl)$ in an approximately equimolar mixture of CH_3NO_2 and C_2H_5Cl, although at lower pressures the intensities are roughly the same. On the other hand, no appreciable relative variation is observed with pressures up to 8×10^{-5} Torr for $Cl^-(CH_3OH)$ and $Cl^-(CH_3NO_2)$ in a CH_3OH and CH_3NO_2 mixture with phosgene. Pulsed double resonance experiments with fields as low as 0.01 V/cm establish that reaction 3 proceeds in both directions under the conditions present in the experiment

$$Cl^-(CH_3NO_2) + CH_3OH \rightleftharpoons Cl^-(CH_3OH) + CH_3NO_2 \qquad (3)$$

Experiments of this nature performed on selected pairs of compounds yield the following relative gas phase "solvating" ability: (a) $CH_3Cl < C_2H_5Cl < (CH_3)_2$-

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[11] Experiments were carried out in a Varian V-5900 ICR spectrometer provided with a dual inlet system. The reacting ion, $COCl^-$, was obtained by electron impact of phosgene at 25 eV. The pressure of phosgene was kept constant in the experiments at 2.5×10^{-6} Torr.

[12] For species like $Cl^-(CCl_4)$ see: P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *Advan. Mass Spectrom.*, 4, 621 (1968).

$CHCl$; (b) $CH_3F < CH_3Cl \sim CH_3Br$; (c) $C_2H_5Cl < CHF_3$; (d) $CH_3Cl < CH_3CF_3$; (e) $C_2H_5Cl < CH_3NO_2 \sim CH_3CN \sim CH_3OH$. The cluster $Cl^-(CF_4)$ is the least stable of these series.

A direct quantitative comparison with the results of Kebarle[4,5] shows that our trends are at least compatible with those established by high-pressure mass spectroscopy, where ions are presumably thermalized. Following the procedure outlined by Bowers,[9] equilibrium constants determined for reaction 4 were found

$$Cl^-(CH_3CN) + CH_3OH \rightleftharpoons CH_3CN + Cl^-(CH_3OH) \quad (4)$$

$$\Delta G^\circ = -0.2 \pm 0.3 \text{ kcal/mol}$$

to be independent of pressure in the range of 6×10^{-5} to 4×10^{-4} Torr. The resulting ΔG° compares very favorably with the calculated value of -0.5 kcal/mol.[4,5] Thus, the above trends can be regarded as truly representative of the relative clustering ability of the neutrals.

The fact that CH_3CF_3, CH_3NO_2, and CH_3CN form very stable cluster ions can be accounted for by their relatively large dipole moments[13] resulting in a favorable ion–permanent dipole interaction. For compounds with similar dipole moments as in (a) and (b), the increasing stability follows the increase in polarizability of these compounds.[14] This polarizability trend is thus similar to that previously observed in our work with "solvated" alkoxide ions.[15] Such an observation points out again the relevant role of ion-induced dipole interactions in determining the behavior of ions in the gas phase.[6,8] The high relative stability of $Cl^-(CHF_3)$ suggests a hydrogen bonding type of interaction in this case, similar to that in CH_3OH and $CHCl_3$.[4]

A preliminary investigation on the structural aspects of an ion like $Cl^-(CH_3Cl)$ indicates that the chlorines in this moiety are not equivalent. Such a conclusion is based on a triple resonance experiment performed by observing the behavior of reactions 5 while ejecting one of the precursor ions obtained from phosgene.

$$(CH_3{}^{35}Cl^{37}Cl)^- + CH_3CF_3 \longrightarrow {}^{35}Cl^-(CH_3CF_3) + CH_3{}^{37}Cl \quad (5a)$$

$$(CH_3{}^{35}Cl^{37}Cl)^- + CH_3CF_3 \longrightarrow {}^{37}Cl^-(CH_3CF_3) + CH_3{}^{35}Cl \quad (5b)$$

Conventional pulsed double resonance shows that reaction 5a and 5b are equally probable. Ejecting $CO^{37}Cl^-$ continuously, reaction 5b is affected, but no appreciable effects take place in reaction 5a. The opposite behavior is observed when $CO^{35}Cl^-$ is ejected continuously. Thus, the chlorine originally present in the precursor ion is transferred preferably in the secondary reaction.

The method introduced in this communication can be used to produce other cluster ions of interest. Thus, esters, ketones, benzene, acetylene, and phosgene itself have been found to yield cluster ions by reaction 1. Studies on these species are presently in progress. It is interesting to note that reaction 1, with CO acting as a convenient energy sink for the bimolecular clustering reaction at low pressures, is very reminiscent of the alkoxide–alkyl formate reaction used in the study of alkoxide ion clusters.[15]

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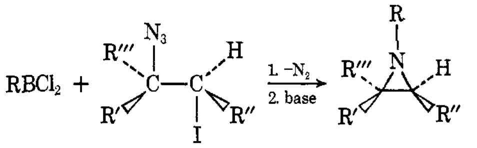
Facile Reaction of Alkyl- and Aryldichloroboranes with 2-Iodoalkyl Azides. A Stereospecific Synthesis of *N*-Alkyl- and *N*-Arylaziridines

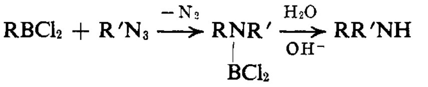
Sir:

2-Iodoalkyl azides, now readily available,[1] undergo a facile reaction with aryl-[2] and alkyldichloroboranes[3,4] to produce β-iodo secondary amines. These amines, without isolation, undergo ring closure with base to provide the corresponding *N*-aryl- and *N*-alkylaziridines in good yields (73–94%). Significantly, the stereochemistry of the original 2-iodoalkyl azide is maintained, providing for the first time a synthesis of *N*-aryl- and *N*-alkylaziridines with known stereochemistry (eq 1).



(1)

Recently, we established that aryl- and alkyldichloroboranes react readily with organic azides[5] to provide a convenient synthesis of the corresponding secondary amines in high yield (eq 2). These results suggested



$$RBCl_2 + R'N_3 \xrightarrow{-N_2} \underset{\displaystyle BCl_2}{\underset{|}{RNR'}} \xrightarrow[OH^-]{H_2O} RR'NH \quad (2)$$

the possibility that 2-iodoalkyl azides might react with organodichloroboranes to give the corresponding β-iodo-*sec*-amines. If so, these amines should undergo ring closure with base to give the corresponding N-substituted aziridines. Dropwise addition of 1-azido-2-iodoethane to phenyldichloroborane in benzene results in vigorous evolution of nitrogen, complete within

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