temperature factors, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates and temperature factors, and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Reactions of Trimethylchlorosilane with Various Nucleophiles in the Gas Phase Using the Flowing Afterglow Technique

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Summary: The reactivity of methyl iodide and trimethylchlorosilane with a number of different nucleophiles has been studied by using the flowing afterglow technique. The reactivity of various nucleophiles with methyl iodide generally varies with their basicity with the more basic nucleophiles reacting most rapidly. On the other hand, trimethylchlorosilane reacts with these nucleophiles in a very different manner; essentially it reacts either at the collision rate with nucleophiles giving exothermic reaction or not at all with nucleophiles giving endothermic reaction. Such results are consistent with a concerted nucleophilic substitution for methyl iodide and the intermediate formation of a pentacoordinate species for trimethylchlorosilane.

Although a covalent, pentacoordinate intermediate is probably involved in many reactions of silicon compounds, most notably in reactions involving retention of configuration at silicon,[1,2] the question of whether such an *intermediate* (1) or a related *transition state* (2) is formed in displacement reactions of chlorosilanes has been explored only rarely.[2,3] As a natural outgrowth of our studies of pentacoordinate silicon anions in the gas phase,[4] we have investigated this problem for S$_N$2 reactions by measuring the rates of reaction of a series of nucleophiles with both trimethylchlorosilane and methyl iodide. The response of these two halides to changes in the basicity of the nucleophiles is so dramatically different that we believe widely different mechanisms operate in the two systems. Indeed, the results are in full accord with the intervention of a pentacoordinate intermediate corresponding to 1 formed in each encounter between the chlorosilane and nucleophile.

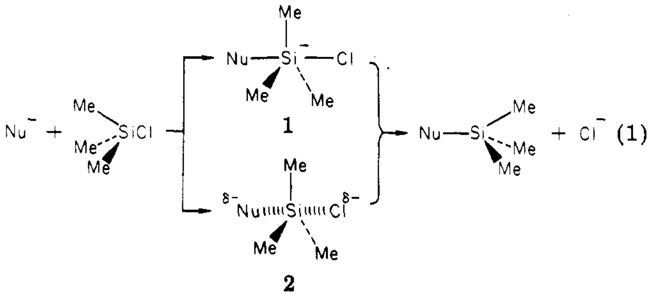

Table I. Rate Constants for Reaction of Nucleophiles (Nu$^-$) with Methyl Iodide and Trimethylchlorosilane

Nu$^-$	proton affinity, kcal/mol	k_{CH_3I}, 10^{-10} cm^3 molecule^{-1} s^{-1}	k_{Me_3SiCl}, 10^{-10} cm^3 molecule^{-1} s^{-1}
H$_2$N$^-$	404	31	34
HO$^-$	391	30	28
F$^-$	371	26	21
H$_2$P$^-$	370	13	18
HS$^-$	353	8.9	21
NC$^-$	353	1.8	19
N$_3^-$	344	1.3	18
NSO$^-$	344 ± 5	0.28	20
NCO$^-$	344	0.13	21
Cl$^-$	333	2.1	5.7
NCS$^-$	325 ± 5	<0.002	<0.03

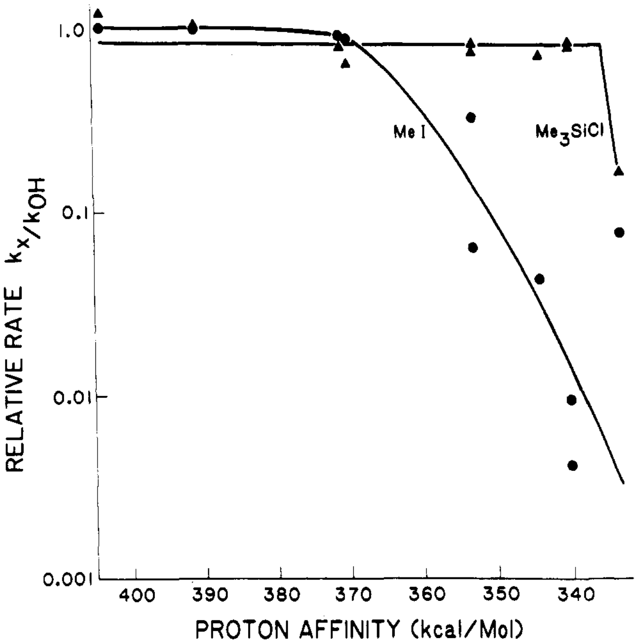

Figure 1. Relative rates of various nucleophiles reacting with methyl iodide and trimethylchlorosilane.

Our experiments were carried out in a flowing afterglow (FA) apparatus[5,6] in which H$_2$N$^-$, HO$^-$, F$^-$, and Cl$^-$ are produced by electron impact on NH$_3$, N$_2$O/CH$_4$, NF$_3$, and CCl$_4$ in a helium stream (flow velocity 80 m/s, 0.3 torr of He) in a 100 × 8 cm stainless-steel tube. The tube is equipped with moveable and fixed inlets and terminates in a quadrupole mass filter detection system. Reaction rates are measured by adding the halides through the moveable inlet and measuring the decrease in reactant ion intensity as a function of reaction distance. Other nucleophiles are synthesized in the flow tube. All ions are allowed to reach thermal equilibrium with the helium buffer gas before reaction with halides commences.

The results are collected in Table I and displayed in Figure 1. Both trimethylchlorosilane and methyl iodide[7]

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[1] Corriu, R. J. P.; Henner, B. J. L. *J. Chem. Soc., Chem. Commun.* **1973**, 116.

[2] Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231.

[3] Chauviere, G.; Corriu, R. J. P.; Henner, B. J. L. *J. Organomet. Chem.* **1975**, *86*, Cl.

[4] Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480.

[5] DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146.

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react at every encounter with sufficiently basic anions. As the reactivity of the nucleophile (as measured by its strength as a base) decreases, so does its rate of reaction with methyl iodide. Although this change in rate is not a linear function of nucleophile basicity, it is clear that basicity is a major factor in determining rate. By contrast, trimethylchlorosilane reacts at each encounter with these nucleophiles until reaction abruptly ceases when the displacement becomes endothermic. Indeed, the only measureable rate less than the collision rate is that with $^{37}Cl^-$. Here the loss of $^{37}Cl^-$ is approximately one fourth of the collision rate and moderate amounts of the stable adduct 1 (Nu = ^{37}Cl) are formed.

These results are those expected for the formation of 1 at every encounter for reactive nucleophiles. Since there is little solvent present to remove the collision energy, simple adduct formation between ions and neutral molecules is inefficient in the gas phase. Therefore, 1 will decompose in the thermodynamically favorable direction, generating chloride ion. For unreactive nucleophiles we, of course, cannot tell if an intermediate corresponding to 1 forms, whether it reverts to starting material, or if no reaction at all occurs. However, for the thermoneutral reaction with $^{37}Cl^-$, displacement is very rapid and the intermediate has a sufficiently long lifetime ($>10^{-7}$ s) for some of it to be stabilized by collision with helium. In contrast, Cl^- reacts quite slowly with methyl chloride in the gas phase.[8]

In the analogous reactions with methyl iodide, a highly ordered transition state (**2**) is required for displacement. Brauman and co-workers,[8,9] have discussed the relationship between this transition state and barrier height in gas phase S_N2 reactions. That no similar effects are observed for silicon strongly suggests that silicon and carbon compounds react by distinctly different mechanisms.[10]

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Registry No. H_2N^-, 17655-31-1; HO^-, 14280-30-9; F^-, 16984-48-8; H_2P^-, 13937-34-3; HS^-, 15035-72-0; NC^-, 57-12-5; N_3^-, 14343-69-2; NSO^-, 56971-19-8; NCO^-, 71000-82-3; Cl^-, 16887-00-6; NCS^-, 1111-68-8; Methyl iodide, 74-88-4; trimethylchlorosilane, 75-77-4.

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(7) Methyl iodide was used in this study because it gave the widest range of rates as a function of the nucleophile's basicity. Methyl chloride and bromide showed similar trends, but the rate of reaction with various nucleophiles was in too narrow a range.

(8) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

(9) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993.

(10) Strictly speaking the results do not require that the pentavalent anion (1 or 2) be at a local minimum. However, if there is a barrier to reaction at silicon, it must be substantially smaller than that at carbon.

Book Reviews

Gmelin Handbook of Inorganic Chemistry. 8th Edition. Fe. Organoiron Compounds. Part B6, Mononuclear Compounds 6. A. Slawisch, volume author and editor-in-chief. 1981. ii + 425 pages. DM 998, $453.60. Part C5. Binuclear Compounds 5. U. Behrens and B. Lubke, volume authors. U. Krüerke, volume editor. 1981. ii + 172 pages. DM 501, $213.20. Gmelin Institut für Anorganische Chemie der Max-Planck-Gesellschaft zur Förderung der Wissenschaften and Springer-Verlag, Berlin/Heidelberg/New York (in English).

It is no exaggeration to say that one cannot open an issue of any major journal which covers organometallic and/or inorganic chemistry without encountering at least one paper which deals with organoiron compounds. Thus it is no surprise that the three-part Gmelin organoiron series (A, ferrocene derivatives; B, mononuclear Fe compounds; C, di- and polynuclear Fe compounds), with the present two books, already numbers 17 volumes (with more to come)—by far the largest of the various Gmelin organometallic series.

Part B6, one of the larger Gmelin volumes, continues the coverage of mononuclear organoiron compounds and is devoted entirely to iron complexes which contain organic ligands bonded to iron by four carbon atoms. For the most part, η^4-diene ligands, cyclic and acyclic, are involved, and, with the exception of the compounds on the first 24 pages of the book, the complexes contain one, two, or (mostly) three CO ligands as well. Thus most of the book deals with (η^4-butadiene)iron tricarbonyl and its C-substituted derivatives. All available information about these compounds is detailed: preparation, properties, structure, spectroscopy, chemical reactions. Much information is provided in tabular form. The many formulas and figures throughout the book are essential in the presentation of this material. The coverage is thorough and backed up by references (up to the end of 1980) to the original and review literature, as well as to patents, theses, and conference reports. A formula index is not provided (Part B7 will contain one for both B6 and B7), but the table of contents serves as a general ligand-type index. Of particular value is the 2-page collection of reviews and monographs which are devoted either generally or specifically to compounds with ligands bonded by four carbon atoms.

Part C5 of the organoiron compound series concludes the description of binuclear iron compounds with coverage of such compounds with ligands bonded to the iron atoms by six to twelve carbon atoms. The majority of the complexes are of the type $^6LFe_2(CO)_n$ and$^8LFe_2(CO)_n$ (n = 4–7). A perusal of the book with its many formulas and figures shows that the ^{6}L and ^{8}L ligands are, for the most part, complicated cyclic (often bi- or polycyclic) organic molecules or groups of great diversity. In many cases the two $Fe(CO)_n$ (usually with n = 3) units contained in the complex are connected by a Fe–Fe σ bond, but this is not a requirement for inclusion in this volume. In other complexes the two Fe(CO)n units are not bonded in any way and at times are in widely separated parts of the molecule.

The literature coverage in Part C5 is complete through the end of 1978, with some material from the literature of 1979 and 1980 included as well. The volume contains an empirical formula index and a ligand formula index. These make the rather complicated material in this much more easily accessible to the reader.

Chemists interested and/or active in organoiron chemistry will welcome these excellent new additions to the Gmelin organoiron series.

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