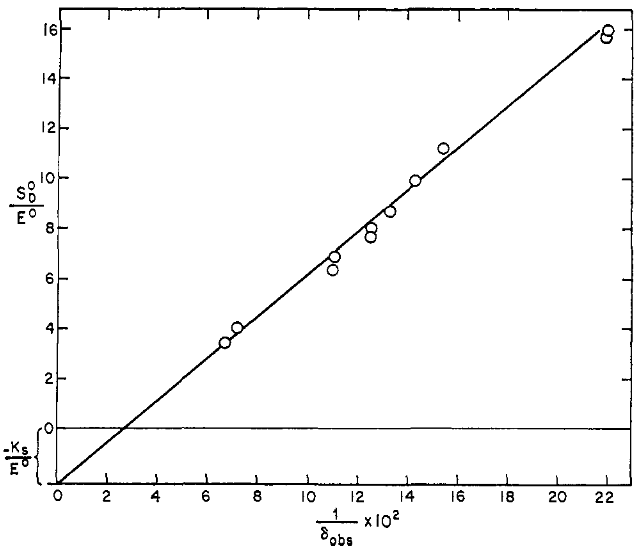

Figure 2. Plot of S_D^0/E^0 *vs.* $1/\delta_{obsd}$ for N-acetyl-*p*-fluorophenylalanine; E^0 = 0.003 *M* in pD 6 citrate. Shift of D isomer.

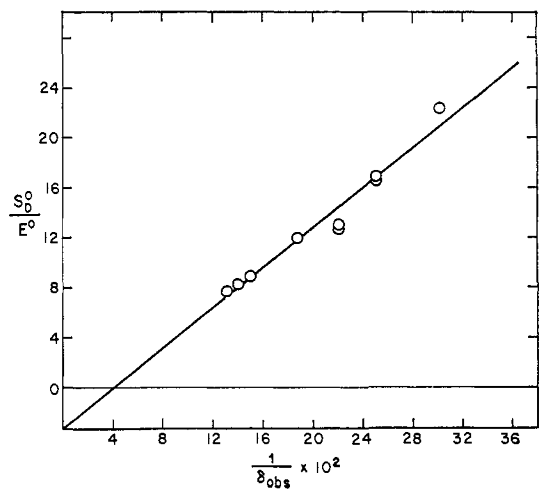

Figure 3. Plot of S_D^0/E^0 *vs.* $1/\delta_{obsd}$ for N-acetyl-*m*-fluorophenylalanine; E^0 = 0.003 *M* in pD 6 citrate. Shift of D isomer.

plify previously suggested models for the binding site[5,6] and should also be compared with the recently published map at 2-A resolution of tosyl-α-chymotrypsin.[7]

The dissociation constant for other substances which compete with N-acetyl-D-*m*-fluorophenylalanine for the active site can also be determined by this method. The appropriate expression is then

$$\frac{1}{\delta} = \frac{1}{\Delta E^0}\left(K_s + S_s^0 + \frac{K_s}{K_I}S_I^0\right)$$

where K_s and S_s^0 refer to the constants and concentrations of N-acetyl-D-*m*-fluorophenylalanine and K_I and S_I^0 to those of the competing substance. For N-acetyl-D-tryptophan and N-acetyl-L-tryptophan values of approximately 4 × 10^{-3} are obtained, in fair agreement with that of (2 ± 1) × 10^{-3} obtained by equilibrium dialysis.[8]

In these calculations we have assumed that chymotrypsin is present as the monomer. Though there is evidence for dimerization at concentrations lower than those used here,[9] there is also evidence that in the presence of substrate[10] the dimer dissociates. In our work the substrate is present in excess and virtually all the enzyme should be present as the ES complex.

Acknowledgment. We wish to thank Mr. F. W. Dahlquist and Professors M. A. Raftery and S. I. Chan for useful discussions, Mr. G. Thompson and G. Swanson for early experimental assistance, and the U. S. Public Health Service for financial support (GM-10218).

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(4) Differences in chemical shift of the order of 0.03 ppm for D and L isomers of trifluoromethylcarbinol in an optically active solvent have been observed: W. H. Pirkle, *J. Am. Chem. Soc.*, **88**, 1837 (1966); T. G. Burlingame and W. H. Pirkle, *ibid.*, **88**, 4294 (1966).

(5) G. E. Hein and C. Niemann, *ibid.*, **84**, 4487, 4495 (1962).

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(9) M. S. N. Rao and G. Kegeles, *J. Am. Chem. Soc.*, **80**, 5724 (1958).

(10) F. J. Kézdy and M. L. Bender, *Biochemistry*, **4**, 104 (1965).

Thomas McL. Spotswood, Josephine M. Evans, John H. Richards
Contribution No. 3496
Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California 91109
Received June 23, 1967

Silylation of Ferrocene by Chloro- and Aminosilanes under Friedel–Crafts Conditions

Sir:

Halosilanes have not been known to undergo reactions analogous to Friedel–Crafts alkylation of aromatic compounds.[1-3] Indeed, the formation of siliconium ions by heterolytic cleavage of silicon–halogen bonds with Lewis acids is virtually unknown.[4-7] Triphenylsiliconium ion, derived from the iodo- and bromosilanes but not the chlorosilane, has been detected only as the bipyridyl-stabilized ion.[8]

We report here that ferrocene can be silylated by chloro- and aminosilanes under Friedel–Crafts conditions. This constitutes the first successful use of halosilanes in reactions analogous to Friedel–Crafts alkylation and provides evidence that siliconium ion, probably in the form of a ferrocene-complexed intermediate, can be generated *via* cleavage of silicon–halogen bonds under these conditions. Some of our results are listed in Table I.

The observed reactivity is in part the result of enhancement of the catalytic activity of aluminum chloride by complexing with donor species, *viz.*, the aminosilane or triethylamine. The concept of a dimolar aluminum chloride complex of a tertiary amine, proposed as a catalytic species for aromatic alkylation,[9] has been found applicable to phosphorus(III) and

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(1) H. Gilman and G. E. Dunn, *Chem. Rev.*, **52**, 77 (1953).

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(3) F. A. Drahowzal in "Friedel-Crafts and Related Reactions," Vol. II, Part 1, G. A. Olah, Ed., Interscience Publishers, London, 1964, p 466, and references therein.

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(5) Reference 4, pp 205 and 206.

(6) J. Y. Corey and R. West, *J. Am. Chem. Soc.*, **85**, 2430 (1963).

(7) G. A. Russell, *ibid.*, **81**, 4831 (1959).

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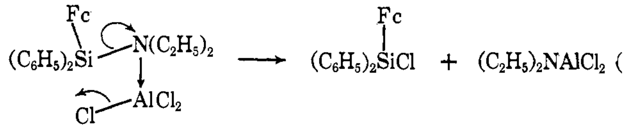
(9) Reference 3, pp 419, 420, and 444, and references cited therein.

Table I. Silylation of Ferrocene (FcH)

Silane	Molar ratio, FcH:silane: $AlCl_3$	Solvent[a]	Products[b] (yield, %[c])		Recovered FcH, %
$(C_6H_5)_2SiCl_2$	2:1:1	*n*-Octane	$FcSi(OH)(C_6H_5)_2$[d] (<1)		81
$(C_6H_5)_2Si(Cl)N(C_2H_5)_2$	2:1:1	*n*-Octane	$FcSi(OH)(C_6H_5)_2$[d] (26);	$(Fc)_2Si(C_6H_5)_2$[e] (4)	54
$(CH_3)_2Si(Cl)N(CH_3)_2$[f]	2:1:1	*n*-Heptane	$FcSi(OH)(CH_3)_2$[g] (7);	$[FcSi(CH_3)_2]_2O$[h] (27)	75
$(CH_3)_2Si(Cl)N(CH_3)_2$[f]	2:1:2	*n*-Heptane	$FcSi(OH)(CH_3)_2$[g] (53);	$[FcSi(CH_3)_2]_2O$[h] (16)	38
$(C_6H_5)_3SiCl$	1:1:1[i]	*n*-Octane	$FcSi(C_6H_5)_3$[j] (6)		62
$(C_6H_5)_3SiN(CH_3)_2$	1:1:1	*n*-Octane	$FcSi(C_6H_5)_3$[j] (8)		32

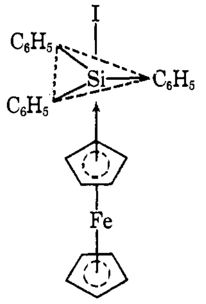
[a] Reflux time: 20 hr. [b] Satisfactory analytical data were obtained for all new compounds. Infrared spectra were taken with Nujol mulls and are consistent with assigned structures. [c] Based on the silane. [d] Yellow-orange crystals from *n*-heptane, mp 159–161°. [e] Yellow-orange platelets from *n*-heptane, mp 181–182°. [f] The products could not be isolated when $(CH_3)_2SiCl_2$ was used. [g] Orange rhombs from 30–60° petroleum ether, mp 62–63°. [h] Yellow-orange needles from methanol, mp 76–76.5°. [i] Triethylamine (0.5 equiv) was included in the reaction mixture. [j] Yellow-orange needles from *n*-heptane, mp 141–142° [lit. 142–143°: R. A. Benkeser, D. Goggin, and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954)].

arsenic(III),[10] and now silicon (*cf.* I, for example). In common with its behavior toward P^{III}–N and As^{III}–N compounds, aluminum chloride in coordinating nitrogen of the aminosilanes likely cleaves the Si–N bond generating Si–Cl (*e.g.*, eq 1), at least in those cases in which the quaternary silanes are produced (Table I). Silylamines are known to undergo such cleavage with BCl_3 and BF_3.[11]



(1)

Observations made on solutions of ferrocene and triphenyliodosilane serve to shed some light on the role of ferrocene itself in the generation of siliconium ion. The ultraviolet spectrum of ferrocene in the presence of 1 equiv of the iodosilane in either *n*-heptane or dichloromethane shows the disappearance of the ferrocene rising end absorption at 220 mμ,[12] although no comparable effect is perceptible with 0.5 equiv of the iodosilane. In the former case a new band appears at 226.5 mμ (ε 18,000). It undergoes a gradual shift to shorter wavelength (224 mμ) on dilution, does not obey Beer's law, and thus cannot be attributed to iodide ion. Unlike bipyridyl,[8] ferrocene does not produce a stabilized siliconium ion with triphenyliodosilane. This was confirmed when values of the equivalent conductance of less than 2×10^{-6} mho were determined for solutions of ferrocene and the iodosilane (1:1 and 2:1 molar ratios; 7×10^{-3} *M* in iodosilane) in dichloromethane, as compared to $\sim 2.5 \times 10^{-3}$ mho for bipyridyl[8] in place of ferrocene. Ferricinium ion or unpaired electron could not be detected by ultraviolet[13] or esr[14] spectroscopy. The results indicate the existence, in solution, of a molecular entity which may be represented as a ferrocene π complex of the iodosilane, in which the Si–I bond has little ionic character and silicon is pentacoordinate.[15] The following depicts one of several possible structures of the trigonal bipyramid.



A probable mechanism for the aluminum chloride catalyzed reaction includes, as a first step, 180° or 90°-flank[16] nucleophilic attack of ferrocene on silicon *via* the ring π system,[17] in a concerted-type displacement involving the catalyst [*e.g.*, I; R′ = $(C_6H_5)_2SiCl$–]. The transient, π-stabilized tetracoordinate siliconium ion[15] then undergoes rearrangement to the exocyclic σ complex, II, which loses a proton to give the silanol precursor, III.

A similar sequence can be visualized for the silylation of ferrocene by the chlorosilane generated from III by Si–N bond cleavage (*cf.* eq 1), leading to the final product, diferrocenyldiphenylsilane. The importance of species IV[18] and V[19] in the stabilization of the α-ferrocenylsiliconium ion can be minimized on the basis that there is no possibility that analogous species are involved in the formation of III.

Generally, in performing these reactions, ferrocene, anhydrous aluminum chloride, and the silane (0.05 mole) were refluxed under nitrogen in a suitable solvent

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(10) Manuscripts are in preparation by the authors; presented in part at the Second International Symposium on Organometallic Chemistry, University of Wisconsin, Madison, Wis., Aug 30–Sept 3, 1965, Abstracts of Proceedings, p 41. A preliminary communication has appeared: G. P. Sollott and W. R. Peterson, Jr., *J. Organometal. Chem.* (Amsterdam), 5, 491 (1965).

(11) A. B. Burg, "Fluorine Chemistry," J. H. Simons, Ed., Academic Press Inc., New York, N. Y., 1950, p 109; R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961), and references therein.

(12) D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516 (1961), have assigned the ferrocene absorption band at 202.5 mμ to an allowed transition from a bonding level to an antibonding level between π orbitals, similar to the 184-mμ band of benzene.

(13) Absorption at 619 mμ, characteristic of the ferricinium ion [M. Rosenblum, R. W. Fish, and C. Bennett, *J. Am. Chem. Soc.*, **86**, 5166 (1964)], was not present in the spectrum.

(14) The authors thank Dr. Maurice Codell for this determination.

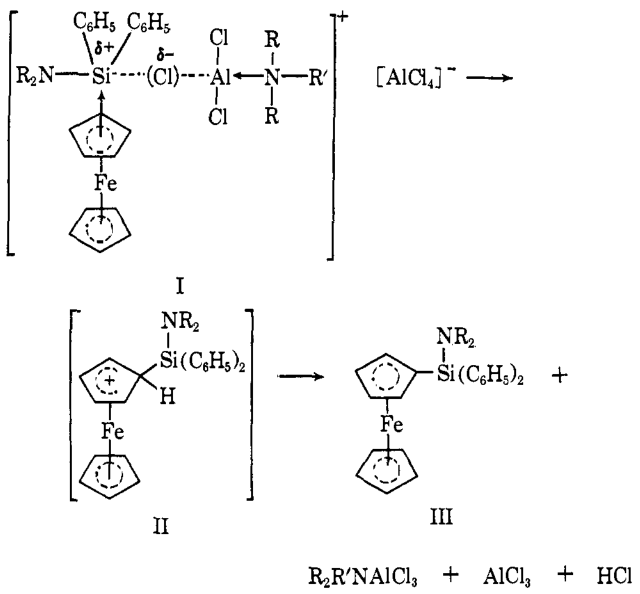
(15) The bipyridyl-stabilized siliconium ion of Corey and West[8] was pentacoordinate.

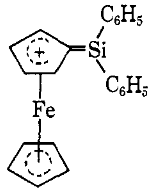
(16) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(17) M. Rosenblum and F. W. Abbate, *J. Am. Chem. Soc.*, **88**, 4178 (1966), have reported that the iron atom is not an essential participant in the acylation of ferrocene.

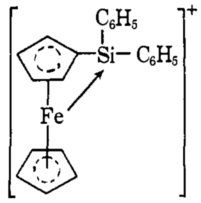
(18) Examples of silicon doubly bonded to carbon are unknown. In contrast to $(C_6H_5)_3C^+$, $(C_6H_5)_3Si^+$ is not stabilized by dative π bonding from the attached benzene rings.[1,8]

(19) The role of the nonbonding 3d electrons of iron in the stabilization of α-ferrocenylcarbonium ions is currently the subject of considerable debate: T. T. Tidwell and T. G. Traylor, *J. Am. Chem. Soc.*, **88**, 3442 (1966), and references therein; T. G. Traylor and J. C. Ware, *ibid.*, **89**, 2304 (1967).





IV



V

(150 ml; Table I). After evaporation of the solvent and treatment of the residue with water, products were isolated *via* chromatography on activated alumina. The products, usually obtained initially as oils, were crystallized from appropriate solvents (Table I).

This work makes available a new route to silicon compounds of ferrocene and is facile compared to methods previously available for the synthesis of such compounds.[20] The scope of the new process is under further investigation.

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(20) E. A. Mailey, C. R. Dickey, G. M. Goodale, and V. E. Matthews, *J. Org. Chem.*, 27, 616 (1962), and references therein.

Gilbert P. Sollott, William R. Peterson, Jr.
Pitman-Dunn Research Laboratories, U. S. Army, Frankford Arsenal
Philadelphia, Pennsylvania 19137

Received June 12, 1967

Dipole–Dipole Interactions of a Spin-$^1/_2$ Nucleus with a Quadrupole-Coupled Nucleus[1]

Sir:

In recent nmr experiments, the dipolar broadening of the proton resonance in solid $HMn(CO)_5$ and $HCo(CO)_4$ has been used to estimate the metal–hydrogen bond distance.[2,3] The M–H bond distances thus obtained are exceptionally short, 1.28 A for Mn–H and 1.42 A for Co–H. However, the analyses were based on the Van Vleck[4] second moment expression which assumes that the nuclei are quantized in the direction (z) of the static magnetic field H_0 and which therefore neglects any quadrupole coupling effects at the metal nucleus. This communication describes a theoretical analysis and numerical calculations for a two-spin ($^1/_2$, $^7/_2$) system, having axial symmetry about the internuclear vector **r** and quadrupole coupling at the spin-$^7/_2$ nucleus. It is found that the second moment M_2 of the spin-$^1/_2$ nucleus may be as much as 1.84 times its value in the absence of the quadrupole coupling. Therefore, the M–H bond distances reported previously[2,3] may be as much as 11% too small.

We start with Slichter's expression[5] for the line shape f(ω) in the vicinity of $\omega_0 = \gamma_I H_0$ when $H_0 \gg \Delta H_{loc}$ and $kT \gg E_a$, for the spin-$^1/_2$ nucleus I. This is

$$f(\omega) = \sum_{E_a > E_b} \delta(E_a - E_b - \hbar\omega) \qquad (1)$$

with E_a and E_b the final and initial Zeeman energies of the eigenstates a and b involved in a transition of nucleus I. The function $\delta(E_a - E_b - \hbar\omega)$ has the value zero or one, respectively, when the argument is nonzero or zero. Equation 1 implies that the transition probabilities near ω_0 are constant; therefore, to find f(ω) we need only the energy differences ($E_a - E_b$).

The spin pair is heteronuclear, so the eigenfunctions, ψ_i^+, are the product functions

$$\psi_i^+ = (\pm {}^1/_2, \phi_i) \qquad (2)$$

and the ϕ_i's are eigenstates of nucleus S. We are concerned only with transitions of nucleus I, which requires that

$$(E_a - E_b)_i = \langle\psi_i^-|\mathcal{H}|\psi_i^-\rangle - \langle\psi_i^+|\mathcal{H}|\psi_i^+\rangle \qquad (3)$$

where $\mathcal{H}$ is the Hamiltonian describing spin I. To calculate energies to first order, $\mathcal{H}$ must contain the Zeeman term plus secular perturbations. However, because of the quadrupole interaction, the spin S may be quantized with nonvanishing components away from $\mathbf{H}_0$. Therefore, assuming only dipolar perturbations, we find

$$\mathcal{H} = -\gamma_I\hbar H_0 I_z + \frac{\gamma_I\gamma_S\hbar^2}{r^3}[(1 - 3\cos^2\theta)I_zS_z - (3\sin\theta\cos\theta)I_zS_x] \qquad (4)$$

where θ is the angle between $\mathbf{H}_0$ and **r**. Next, we define

$$\Delta\omega_i = -\gamma_I H_0 + (E_a - E_b)\hbar^{-1} \qquad (5)$$

which is a measure of the frequency spread around ω_0 due to dipolar interactions with spin S. Combination of eq 2–5 gives

$$\Delta\omega_i = \frac{\gamma_I\gamma_S\hbar}{r^3}[\langle S_z\rangle_i(3\cos^2\theta - 1) + 3\langle S_x\rangle_i \sin\theta\cos\theta] \qquad (6)$$

with $\langle S_{x,z}\rangle_i = \langle\phi_i|S_{x,z}|\phi_i\rangle$.

The solutions for $\Delta\omega_i$ require $\langle S_{x,z}\rangle_i$ which in turn depends on ϕ_i. To find the ϕ_i we assumed the quantization axis of nucleus S to be determined by its Zeeman and quadrupole interactions; this approximation is equivalent to $H_0 \gg \Delta H_{loc}$ employed for the I nucleus in

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(1) This research was supported in part by the U. S. Office of Naval Research and the National Science Foundation. One of us (D. L. V. H.) wishes to thank Procter and Gamble for the grant of a fellowship supporting his work.

(2) T. C. Farrer, S. W. Ryan, A. Davison, and J. W. Faller, *J. Am. Chem. Soc.*, **88**, 184 (1966).

(3) T. C. Farrar, F. E. Brinkman, T. D. Coyle, A. Davison, and J. W. Faller, *Inorg. Chem.*, **6**, 161 (1967).

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(5) C. P. Slichter, "Principles of Magnetic Resonance," Harper and Row Publishers, New York, N. Y., 1963, p 51.