Analogous to the silicon case,[10] the Ge–N bond is cleaved by aluminum chloride to give Ge–Cl (see below); however, concerted displacement of dimethylamide ion appears to take precedence over that of chloride ion for the reasons discussed below. After the "push–pull" step, the transient, π-stabilized tetracoordinate germonium ion undergoes rearrangement to the ferrocene exocyclic σ complex to produce the germylated ferrocene on loss of a proton.[12]

The lower proportionate yield of tertiary product obtained in the case of germanium (see above equations) prompted an examination of the effect on that reaction of doubling the amount of aluminum chloride. No significant change in yields occurred, demonstrating that the paucity of tertiary product was *not* due to a shortage of catalyst as a result of greater utilization in the formation of secondary product. In the light of the following relative bond strengths, Ge–Cl > Si–Cl[13] > Si–N[14] > Ge–N,[11] the result is explainable on the basis that with germanium the concerted displacement of amide ion occurs rather than the displacement of chloride ion. This was supported by the finding that tetrakis(N,N-dimethylamino)germane gave tertiary products in a combined yield of 46%.

$$4FcH + [(CH_3)_2N]_4Ge \xrightarrow[(H_2O)]{4AlCl_3} \underset{21\%}{Fc_3GeCl} + \underset{25\%}{(Fc_3Ge)_2O}$$

Isolation of triferrocenylchlorogermane from this reaction demonstrated that aluminum chloride is capable of cleaving Ge–N to give Ge–Cl, and at the same time provided an explanation for the fact that no quaternary germane was obtained. Such ferrocene π-stabilized germonium species as $[(CH_3)_2N]_3Ge^+$, $[(CH_3)_2N]_2Ge^+Fc$, and $(CH_3)_2NGe^+Fc_2$ or $ClGe^+Fc_2$ are considered to be generated from the tetraminogermane in a stepwise process, $(CH_3)_2NGe^+Cl_2$, $FcGe^+Cl_2$, and Fc_2Ge^+Cl[15] (as well as analogous species in the silicon case), from the diaminodichlorogermane.

Reactions in this work were performed (0.05 mole of germane or silane; 20 hr of reflux in 350 ml of *n*-octane) similarly to those previously reported for the silylation of ferrocene.[10] Products[16] were isolated *via* chromatography on silica gel: $(Fc_2GeO)_3$, orange crystals from benzene, mp 338–340°; $(Fc_3Ge)_2O$, golden-tan platelets from ethanol, mp 205–206°; Fc_3GeCl, golden platelets from *n*-heptane, mp 224–226° dec (heating 10°/min); $Fc_2Si(OH)_2$, yellow-orange powder from *n*-heptane, mp 167–168.5°; Fc_3SiOH, short orange-brown needles from *n*-heptane, mp 193.5–195°.

For the most part, organogermanium compounds are prepared by means of organometallic reagents.[17] The few previously reported germanium derivatives of ferrocene have been prepared in this manner.[18] The germylation of ferrocene under Friedel–Crafts conditions offers a new, facile method of establishing bonds between germanium and ferrocene carbon without the need to prepare an intermediate metallic derivative of ferrocene. Investigations are in progress to determine the scope, and to verify several aspects of the mechanism.

[12] *Cf.* silylation of ferrocene.[10]

[13] H. A. Skinner, *Trans. Faraday Soc.*, **41**, 645 (1945).

[14] A. E. Beezer and C. T. Mortimer, *J. Chem. Soc., Sect. A*, 514 (1966).

[15] This species is questionable, however, since it requires cleavage of the Ge–Cl bond. The small quantity of tertiary product isolated may have been generated *via* disproportionation.

[16] Satisfactory analytical data including molecular weights were obtained; infrared spectra taken with Nujol mulls were consistent with assigned structures.

[17] O. H. Johnson, *Chem. Rev.*, **48**, 259 (1951); D. Quane and R. S. Bottei, *ibid.*, **63**, 403 (1963); F. Glockling, *Quart Rev.* (London), **20**, 45 (1966); F. Glockling and J. R. C. Light, *J. Chem. Soc., Sect. A*, 623 (1967).

[18] D. Seyferth, H. P. Hofman, R. Burton, and J. F. Helling, *Inorg. Chem.*, **1**, 227 (1962); H. Rosenberg and R. V. Schenk, Abstracts of Papers, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 8–13, 1963, p 76Q.

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Chemical Shift Anisotropies from Nuclear Magnetic Resonance Studies in Liquid Crystals

Sir:

The anisotropy in the nuclear magnetic shielding in a molecule can be determined from the shift in the nuclear magnetic resonance signal that arises from partial molecular alignment in a magnetic field.[1] Such alignment can be easily achieved for liquid crystals[2] and for molecules dissolved in liquid crystals.[3] In order to determine a chemical shift anisotropy, two pieces of experimental information are required: (1) the degree of alignment of the molecule and (2) the shift of the magnetic resonance between the partially aligned state and the isotropic state of the molecule. In a nematic liquid crystal, the degree of alignment is obtained from measurements of the direct nuclear dipole–dipole interactions which appear in the spectrum as averages over the anisotropic motion of the molecule. The spectral shift between the partially aligned and the isotropic states is usually obtained by measuring the shift of the observed spectrum as the liquid-crystal solvent changes from the nematic state to the isotropic state.

The position of the spectrum is determined with respect to some reference compound. TMS has generally been used as an internal reference for proton chemical shift anisotropies with the assumption that bulk susceptibility and solvent contributions to the proton magnetic shielding will be the same for a partially aligned molecule as for a nonaligned molecule. These contributions were originally thought to be small because it was found that the proton chemical shift anisotropy appeared to be -23 ± 4 ppm when internally referenced with TMS, while it changed to an apparent -28 ± 3 ppm when externally referenced with TMS.[4]

Recently it has been pointed out[5] that the bulk susceptibility of the liquid-crystal solvent and other environmental effects that change when the nematic to isotropic phase transition occurs are not negligible and would account for the unusually large shift anisotropy reported for CH_3F externally referenced with TMS.[6]

[1] A. D. Buckingham and E. G. Lovering, *Trans. Faraday Soc.*, **58**, 2077 (1962).

[2] R. D. Spence, H. A. Moses, and P. L. Jain, *J. Chem. Phys.*, **21**, 380 (1953).

[3] A. Saupe and G. Englert, *Phys. Rev. Letters*, **11**, 462 (1963).

[4] B. J. Lavery, Ph.D. Thesis, The Pennsylvania State University, 1967.

[5] A. D. Buckingham and E. E. Burnell, *J. Am. Chem. Soc.*, **89**, 3341 (1967).

While these effects do not change the conclusions of the earlier work, namely, that J_{HF} is absolutely positive in CH_3F,[6] it seemed desirable to carefully examine the question of chemical shift referencing in liquid-crystal solvents.

Remeasurement of the proton chemical shift anisotropy of CH_3F in *p,p'*-di-*n*-hexyloxyazoxybenzene at 80° internally referenced with TMS gave $(\sigma_{\parallel} - \sigma_{\perp})^H = -12.9 \pm 1.3$ ppm. The concentration of TMS was roughly equal to that of CH_3F, while in the previous measurement, where a larger value was obtained, the TMS was present in excess. Measurement of the proton chemical shift anisotropy at 80° internally referenced with CH_4 gave the surprising result that $(\sigma_{\parallel} - \sigma_{\perp})^H = -0.6 \pm 0.5$ ppm. Moreover, it was found that when CH_4 and TMS were both dissolved in *p,p'*-di-*n*-hexyloxyazoxybenzene the signal due to TMS was 0.172 ± 0.005 ppm upfield from CH_4 in the isotropic state and 0.278 ± 0.003 ppm upfield in the nematic state, while the signal of gaseous TMS is 0.138 ± 0.004 ppm upfield from gaseous CH_4. We believe these differences are mainly due to what has been called "solvent anisotropy effects."[7] There is at present no definite prescription for deciding which of the two compounds is the best reference to use in a particular situation, although TMS does exhibit a small direct dipolar splitting in a nematic solvent,[8] indicating that it may possibly be exhibiting a small shift anisotropy.

The fluorine chemical shift anisotropy is $(\sigma_{\parallel} - \sigma_{\perp})^F = -159.3 \pm 0.7$ ppm internally referenced with CF_4.

The anisotropy in the magnetic susceptibility of *p,p'*-di-*n*-hexyloxyazoxybenzene, $\Delta\chi$, is of interest since it must be known to evaluate the change in the bulk susceptibility correction for the nematic to isotropic phase transition.[5] This can be determined from the width of the nmr signal of nuclei in the annulus of a coaxial sample cell containing the liquid crystal in the central region. The nematic phase has a smaller diamagnetic susceptibility than the isotropic phase and will produce a smaller signal width of the nuclear resonance of material in the annulus. This width has been discussed previously[9–11] and is given by[9]

$$\Delta H = 4\pi H_0\left[(\chi_1 - \chi_2)\frac{a^2}{r^2} + (\chi_2 - \chi_3)\frac{b^2}{r^2}\right]$$

where *a* and *b* are the inner and outer radii of the inner tube of the coaxial cell, *r* is the mean radius of the annulus, and χ_1, χ_2, and χ_3 are the magnetic susceptibilities of the contents of the inner tube, the glass, and the contents of the annulus, respectively. The anisotropy in the magnetic susceptibility is then given by

$$\Delta\chi = \frac{3}{8\pi}\frac{r^2}{a^2}\left[\frac{\Delta H^{\text{iso}} - \Delta H^{\text{nem}}}{H_0}\right]$$

neglecting the small contributions from the volume change accompanying the phase transition. In Table I values of ΔH are given for hexafluorobenzene in the annulus of a coaxial cell containing CF_4 dissolved in *p,p'*-di-*n*-hexyloxyazoxybenzene. The value of a^2/r^2 was 0.545, and the fluorine resonance frequency was 94.075 MHz. The values of $\Delta\chi$ compare favorably to the value of 0.158 ppm found for *p*-azoxyanisole.[12]

Table I. Measured Widths, ΔH,[a] Magnetic Susceptibility Anisotropies, $\Delta\chi$,[b] Downfield Chemical Shifts, δ_{CF_4},[c] and Estimated Change in Solvent Anisotropy Contributions to the Magnetic Shielding, σ_a, for the Isotropic to Nematic Phase Transition[d]

Temp, °C	ΔH, ppm	$\Delta\chi$, ppm	δ_{CF_4}, ppm	$\Delta\sigma_a$
80	2.74	0.177	105.28	−0.50
100	2.86	0.151	105.27	−0.45
130	3.55	0	105.03	. . .

[a] Of the ^{19}F resonance of C_6F_6 in the annulus of a coaxial cell containing CF_4 dissolved in *p,p'*-di-*n*-hexyloxyazoxybenzene. [b] For *p,p'*-di-*n*-hexyloxyazoxybenzene. [c] From C_6F_6. [d] The liquid crystal is isotropic at 130°, nematic at the other two temperatures.

It is also seen from Table I that there is a downfield shift of the ^{19}F resonance of CF_4 when the solvent changes from isotropic to nematic. This is opposite to what would be expected if the anisotropy in bulk susceptibility were the only environmental effect present. Attributing this behavior to changes in the solvent anisotropy shielding, we find for the change in shielding in going from the isotropic to nematic solvent

$$\Delta\sigma = \Delta\sigma_b + \Delta\sigma_a = \frac{4\pi}{9}\Delta\chi + \Delta\sigma_a$$

The values of $\Delta\sigma_a$ required to produce the observed shifts in CF_4 are listed in Table I.

Assuming that the magnitude of the correction is the same for CH_3F, the chemical shift anisotropies are $(\sigma_{\parallel} - \sigma_{\perp})^H = -6.1$ ppm and $(\sigma_{\parallel} - \sigma_{\perp})^F = -157$ ppm, obtained from the externally referenced spectrum.[4] The agreement for the fluorine chemical shift anisotropy obtained when internally referenced with CF_4 is quite reasonable.

In conclusion, we believe that the determination of ^{19}F magnetic shielding anisotropies by internal referencing or by external referencing with bulk susceptibility anisotropy corrections leads to reasonably accurate values. However, proton shielding anisotropies are sharply dependent upon the techniques and references used. Until these various effects are well understood, consistent and well-described experimental technique is suggested.

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(6) R. A. Bernheim and B. J. Lavery, *J. Am. Chem. Soc.*, **89**, 1279 (1967).

(7) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

(8) L. C. Snyder and S. Meiboom, *ibid.*, **44**, 4057 (1966).

(9) C. A. Reilly, H. M. McConnell, and R. G. Meisenheimer, *Phys. Rev.*, **98**, 264A (1955).

(10) M. G. Morin, G. Paulett, and M. E. Hobbs, *J. Phys. Chem.*, **60**, 1594 (1956).

(11) J. R. Zimmerman and M. R. Foster, *ibid.*, **61**, 282 (1957).

(12) G. Föex, *Trans. Faraday Soc.*, **29**, 958 (1933).

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The Formation and Reactions of Monovalent Carbon Intermediates. I. The Photolysis of Diethyl Mercurybisdiazoacetate

Sir:

The chemistry of carbon atom as well as di- and trivalent carbon intermediates has been thoroughly explored. Little, however, is known about the monovalent carbon intermediates. Methyne (CH) has been detected spectroscopically in numerous energetic reac-