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Proton Magnetic Resonance and Basicity Studies of Linear and Cyclic *gem*-Diamine Derivatives of Elements in Group IV

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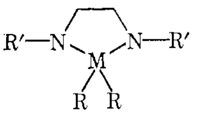
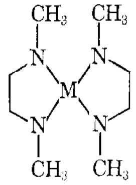
The basicities of bis(diethylamino)dialkyl derivatives of elements in group IV, and of imidazolidine derivatives, have been investigated by a variety of current methods. Nmr shifts and coupling constants both for the base and for chloroform in the presence of the base have been used. Changes in infrared stretching frequencies for chloroform have also been measured. Discussion and application of these methods reveal serious limitations for each one which is reflected in a disparity of conclusions. General agreement is reached, however, in establishing that the silicon derivative is very different from the germanium and is the least basic member for each series of compounds studied.

The nature of the bonding in silylamines has been a matter of great interest since the striking discovery that trisilylamine is nonbasic[2] and has a planar structure.[3] With the recent advent of synthetic techniques for germanium and tin amines, various series of nitrogen compounds in which one or more carbon atoms attached to nitrogen are replaced by silicon, germanium, or tin are now available.

We report a study on two such series: one open-chain and one cyclic series of *gem*-diamines where M is an element in group IV. The parameters used have been nmr chemical shifts and coupling constants and infrared stretching frequencies.

$R_2M[N(C_2H_5)_2]_2$





In addition to the changes wrought by substitution of one cogener of group IV for another, we have investigated the interaction of each compound with chloroform as reference Lewis acid by a study of the same parameters for chloroform.

Experimental Section

The preparations of the carbon,[4] silicon,[5] and germanium[6] imidazolidines, the spiro-silicon and germanium imidazolidines,[7] and bis(diethylamino)dialkylgermanes[4,6] have been reported previously. Preparation of bis(diethylamino)dimethylsilane and -stannane followed procedures reported by Henglein and Lienhard[8] and Jones and Lappert,[9] respectively.[10]

Infrared spectra of compounds as liquid smears or in Nujol mulls were examined in the 3000–2700 cm^{-1} range with a Perkin-Elmer Model 337 grating Infracord. These spectra were calibrated with polystyrene. Deuteriochloroform solutions of the amines (10% mole:mole) were examined in a sodium chloride solution cell on a Perkin-Elmer Model 521 spectrometer operating at 10-fold scale expansion in the 2300–2170 cm^{-1} region. Benzene absorptions at 2326 and 2208 cm^{-1} were used to calibrate the spectra.[11] Shifts in ν(C–D) were determined relative to the value reported for gaseous deuteriochloroform (2264 cm^{-1}).[12]

Nmr spectra were recorded on a Varian A-60 spectrometer. The temperature in the magnet gap was determined from the peak separation in either ethylene glycol or methanol. Under ambient operating conditions the gap temperature was *ca.* 37°.

Parameters determined to within ±0.3 cps were obtained by standard side-banding techniques using a Hewlett-Packard (Model 200AB) audio oscillator and Model 521C electronic counter. Recorded values are the averages of at least three tracings through each resonance. Carbon-13 satellites were observed at spectrum amplitudes 10–15 times greater than ordinarily used.

Chloroform used as a solvent in nmr studies was shaken three times with alumina (to remove ethanol) and decanted into a lightproof, capped bottle where it was stored for no more than 1 day. Tetramethylsilane was added as an internal standard (1% v/v).

Results

Table I lists the nmr chemical shift parameters in cps for the cyclic derivatives as neat liquids and 33% solutions in chloroform. The methylene bridge resonance was a single sharp line in each case[5,7] as has been noted previously.[13] Chemical shift values for the N-ethyl derivatives are gathered in Table II. The C^{13}–H^1 coupling constants for the *gem*-diamines are presented in Table III. The C^{13} satellites of the Si–methyl group of silyl imidazolidine are quartets, with a coupling of 0.5 cps. This is absent (or less than *ca* 0.3 cps) in the bis(diethylamino) analog or in 1,1-dimethylsilacyclopentane.[14]

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[1] Department of Chemistry, Queen Mary College, University of London, London, E. 1, England.

[2] A. B. Burg and E. S. Kuljian, *J. Am. Chem. Soc.*, **72**, 3103 (1950).

[3] K. Hedberg, *ibid.*, **77**, 6491 (1955).

[4] C. H. Yoder and J. J. Zuckerman, *ibid.*, **88**, 4831 (1966).

[5] C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **4**, 116 (1965).

[6] C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 2170 (1966).

[7] C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **3**, 1329 (1964).

[8] F. A. Henglein and K. Lienhard, *Makromol. Chem.*, **32**, 218 (1959).

[9] K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1944 (1965).

[10] We have elsewhere pointed out the danger of explosion during distillation of bis(dialkylamino)stannanes from large-scale reaction mixtures. See E. W. Randall, C. H. Yoder, and J. J. Zuckerman, *Inorg. Nucl. Chem. Letters*, **1**, 105 (1966). We are grateful to Dr. K. Jones for correspondence on this point.

[11] C. F. Jumper, M. T. Emerson, and B. B. Howard, *J. Chem. Phys.*, **35**, 1911 (1961).

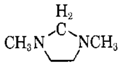
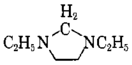
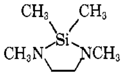
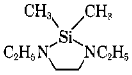
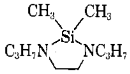
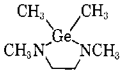
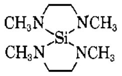
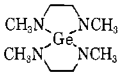
[12] E. W. Abel, D. A. Armitage, and R. G. Willey, *Trans. Faraday Soc.*, **60**, 1257 (1964).

[13] D. Kummer and J. D. Baldeschwieler, *J. Phys. Chem.*, **67**, 98 (1963).

[14] In answer to a referee's query, one of us (J. J. Z.) puts forward the following analysis based on isovalent hybridization arguments: the 118 cps coupling arises through directly bonded C^{13}–H^1 interaction where the presence of C^{13} in either silicon–methyl group gives rise to magnetic inequivalence of the attached protons and to the resulting fine structure which is a four-bond H^1–H^1 coupling. Assuming a dominant Fermi contact coupling mechanism through the intervening bonds, then the silicon–methyl bonds are more s in character in the dimethylsilylamines than in the silacyclopentane or tetramethylsilane. Moreover the closing of ∠N–Si–N in the imidazolidine ring would be expected to enhance the s character of the silicon–methyl bond and thus increase the magnitude of the four-bond $J(H^1$–$H^1)$ over the open-chain case.

TABLE I

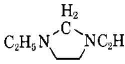
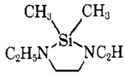
CHEMICAL SHIFTS OF CYCLIC DERIVATIVES (±0.3 CPS)[a]

Compound	M–R		/‾\		N–CH$_3$	
	Neat	33%	Neat	33%	Neat	33%
	192.3	198.8	160.2	166.5	137.0	143.0
	199.3 ± 0.5	206.0	161.0 ± 0.5	169.1		
	3.0	1.0	175.0	174.2	150.1	149.2
	0.0 ± 0.7		174.7			
	0.6	1.8				
	13.7	21.4	169.6	173.9	152.7	156.3
	176.2	177.6	145.8	148.0		
	175.2	179.3	156.3	161.2		

[a] All chemical shifts in this section will be expressed in cycles per second and were obtained at 60 Mcps.

TABLE II

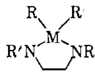
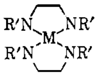
CHEMICAL SHIFTS OF ETHYL DERIVATIVES (±0.3 CPS)[a]

Compound	M–R		N–CH$_2$–CH$_3$		N–CH$_2$–CH$_3$		Δ	
	Neat	33%	Neat	33%[b]	Neat	33%[b]	Neat	33%[b]
$H_2C[N(C_2H_5)_2]_2$	180.0	183.4	57.7	58.9	153.1 ± 0.5	154.6	95.4	95.7
$(CH_3)_2Si[N(C_2H_5)_2]_2$	2.2	1.9	57.9	57.3	169.2	168.0	111.3	110.7
$(CH_3)_2Ge[N(C_2H_5)_2]_2$	15.5	17.4	58.3	58.6	171.8	171.8	113.5	113.2
$(CH_3)_2Sn[N(C_2H_5)_2]_2$	13.8		60.2		177.8		117.6	
	199.3 ± 0.5	206.0	60.7 ± 0.5	65.6	148.9 ± 0.5	155.0	88.2	89.4
	0.0 ± 0.7		63.4		167.0		103.6	

[a] All chemical shifts in this section will be expressed in cycles per second and were obtained at 60 Mcps. [b] In chloroform.

TABLE III

C^{13}–H^1 COUPLING CONSTANTS (±0.3 CPS) IN GROUP IV *gem*-DIAMINES

M	R	R′	M–CH$_3$	N–CH$_3$	N–CH$_2$–CH$_3$
			$R_2M[N(C_2H_5)_2]_2$		
C	H				131.6 ± 0.5
Si	CH$_3$		117.3		130.8 ± 0.5
Ge	CH$_3$		125.8 ± 0.5		130.0 ± 0.5
Sn	CH$_3$		129.8 ± 0.5		129.7 ± 0.5
					
C	H	CH$_3$		133.8	
Si	CH$_3$	CH$_3$	118.0 (quartet)	131.8	
Si	CH$_3$	C$_2$H$_5$	118.0 (quartet)		
Si	CH$_3$	C$_3$H$_7$	119.0 (quartet)		
Ge	CH$_3$	CH$_3$	126.6	130.0	
					
Si		CH$_3$		133.6	
Ge		CH$_3$		134.0	

The following are listed in Table IV: changes in the C–D stretching frequency of deuteriochloroform solutions relative to the gaseous value [Δν(C-D)]; the proton chemical shifts of chloroform at infinite dilution of chloroform in the base; and C^{13}–H couplings for solutions of chloroform (0.15 mole fraction) in the base.

Figure 1 shows the 3000–2700 cm^{-1} region of several carbon, silicon, and germanium imidazolidines for comparison of the C–H stretching frequencies.

Discussion

(A) Nmr Parameters for the *gem*-Diamines. (1) Chemical Shifts. (i) N–Alkyl Group.—Table II lists the methyl and methylene shifts and their differences ($\Delta = \delta_{CH_3} - \delta_{CH_3}$) in the N–ethyl derivatives examined. Internal chemical shifts (Δ) of various ethyl derivatives have been related to the electronegativities of the substituents,[15] and it has been shown that if the electro-

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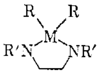
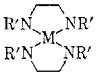
[15] Recently Δ values for the disilanyl group (SiH_3SiH_2–) have been determined. No simple correlation between Δ and the electronegativity of the substituent was found [C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 1071 (1964)].

TABLE IV

BASICITY OF GROUP IV *gem*-DIAMINES TOWARD CHLOROFORM

M	R	R′	$\nu_{C-D\cdots N}$ ($\pm$2 cm^{-1})	$\Delta\nu$ ($\pm$2 cm^{-1})	δ_0 ($\pm$3 cps)	$J(C^{13}-H^1)$ ($\pm$1 cps)
			$R_2M[N(C_2H_5)_2]_2$			
C	H		2189	75	455	209.5
Si	CH_3		2224 2144	40 69.5	439.5	208.5
Ge	CH_3		2188	76	441	209.0
						
C	H	CH_3	2187	77	502	214.0
C	H	C_2H_5	2183	81	511	215.4
Si	CH_3	CH_3	2194	70	477	211.2
Si	CH_3	C_2H_5	2193	71	470.5	210.3
Si	CH_3	C_3H_7	2193	71	452	209.4
Ge	CH_3	CH_3	2176	88	502.5	212.8
						
Si		CH_3	2207	57	452.5	209.6
Ge		CH_3	2197	67	473	210.6

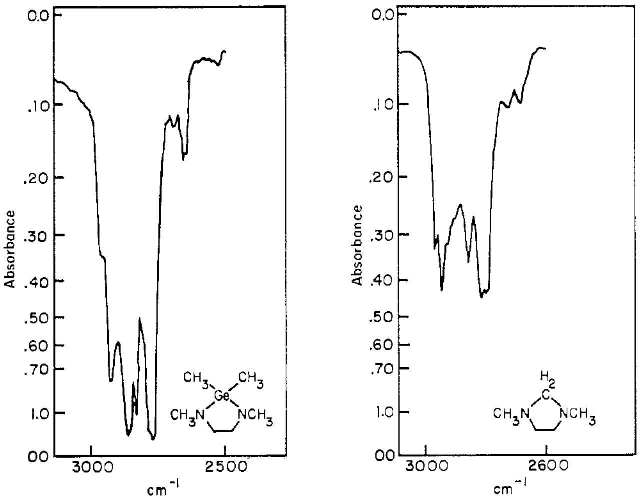


Figure 1.

negativity of the substituent falls below 1.7, the positions of the methyl and methylene resonances are reversed [$\Delta < 0$]. This has been tested for $Al(C_2H_5)_3$, $Pb(C_2H_5)_4$ [$\Delta \sim 0$],[16] and $Na^+B(C_2H_5)_4^-$.[17] Deviation from expected Δ values can arise through anisotropy and dispersion effects.

The observed order of Δ, *viz.*, Sn > Ge > Si >> C, in the *gem*-diamines corresponds, if these factors are ignored, to effective electronegativities at nitrogen which show the same sequence. The Pauling electronegativity values for tin, germanium, and silicon, on the other hand, are all less than that for carbon. The above order could be produced by the onset of $(p \rightarrow d)\pi$ bonding with silicon and an increase in the π bonding from germanium to tin. The π bonding would presumably decrease the electron density at nitrogen and result in an increase in the Δ value.[18] Correlation of the Δ values in these terms, however, assumes that neighbor anisotropy and dispersion effects are absent, constant, or vary linearly with electronegativity of the nitrogen. If anisotropy or dispersion effects increase C < Si < Ge < Sn according to the size of the nitrogen substituent, then the observed Δ values could correspond to the electronegativity order usually assumed: C > Si $\sim$ Ge $\sim$ Sn. The N-methyl resonances of both monocyclic and spiro derivatives follow the same order as the Δ values.

(ii) **M-Alkyl Groups.**—The first columns of Tables I and II list the $M(CH_3)_2$ or CH_2 resonances. The order of M-methyl shifts, Ge > Sn > Si, is followed by all the compounds studied by us as well as by the tetramethyl derivatives and methyl-substituted fourth group halides and chalcogens.[19] Allred and Rochow utilized this order, as obtained by them for the tetramethyl derivatives, to evaluate the electronegativities of the fourth-group elements.[20] Although it is true that the electron distribution about M in $M(CH_3)_4$ has tetrahedral symmetry, the electron distribution about carbon in these molecules is anisotropic since the local symmetry at this atom is C_{3v} rather than T_d. Therefore, the proton resonances under consideration here may also be influenced by anisotropy effects.[21]

(2) **C^{13}-H Coupling Constants.**—The Hamiltonian for the spin interaction is the sum of four terms, one of which is for the spin contact interaction. This was first discussed by Fermi and is considered to be the predominant term in most systems. Various theoretical treatments utilizing this term alone have related the magnitude of the coupling constant to bonding parameters.[22] Grant and Litchman recently expressed $C^{13}-H^1$ coupling constants by

$$J(K) = \left(\frac{E_{CH_4}}{E_K}\right)\left(\frac{N_K}{N_{CH_4}}\right)^2\left(\frac{\alpha_K}{\alpha_{CH_4}}\right)^2\left(\frac{Z_K}{\alpha_{CH_4}}\right)^3 J(CH)_4 \quad (1)$$

which relates the coupling constant, $J(K)$, of the Kth C-H bond of a substituted methane to the coupling constant, $J(CH_4)$, of methane itself, where E is the average excitation energy (does not vary greatly for C-H bonds), N is the bond normalization constant defined by Karplus and Grant,[23] α^2 is directly proportional to the amount of s character in the C-H bond, and Z is the effective nuclear charge which appears in the radial part of the wave function of the 2s orbital. It was demonstrated that coupling constants for 15

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[16] E. B. Baker, *J. Chem. Phys.*, **26**, 960 (1957).

[17] A. G. Massey, E. W. Randall, and D. Shaw, *Spectrochim. Acta*, **20**, 379 (1964).

[18] Δ in triethylamine is 85.2 cps, which changes to 118 cps in tetraethylammonium bromide.[17]

[19] A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958); (b) M. P. Brown and D. E. Webster, *J. Phys. Chem.*, **64**, 698 (1960); (c) H. Schmidbauer, *J. Am. Chem. Soc.*, **85**, 2336 (1963); (d) H. Schmidbauer and I. Ruidisch, *Inorg. Chem.*, **3**, 599 (1964); (e) H. Schmidbauer in "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1965, p 185.

[20] A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 269 (1958).

[21] R. S. Drago and N. A. Matwiyoff, *J. Organometal. Chem.* (Amsterdam), **3**, 62 (1965).

[22] J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, and references therein.

[23] M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U.S.*, **45**, 1269 (1959).

haloalkanes over a 100-cps range could be accounted for by assuming constant angular behavior in the wave functions and by considering only the variation in Z_{eff}.[24]

Since, however, an increase in s character in the C–H bond, or an increase in effective nuclear charge, changes J(K) in the same direction and, further, since both these factors are related to the substituent's electronegativity through isovalent hybridization arguments,[25] it appears valid to relate an increase in coupling constant to an increase in effective electronegativity of the substituent.

(i) **N–C^{13}–H Coupling Constants.**—The C^{13}–H^1 coupling constants of the fourth-group *gem*-diamines are presented in Table III, where the variation for both open-chain and cyclic systems is C > Si > Ge. This can be reasonably interpreted as a variation of the effective electronegativity of nitrogen in the same order. These data indicate that the nitrogens of the spiroheterocycles are appreciably more electronegative than those in the monocyclic derivatives. Variation in effective electronegativity of nitrogen in these compounds is probably determined by two main factors: (1) the σ electronegativity of M, and (2) π overlap between M and N. One could choose to estimate the first factor from numerous electronegativity scales and, since all scales agree that the electronegativities of silicon and germanium are very similar, attribute the difference to a larger amount of (p → d)π bonding in the silicon compounds or, alternatively, the difference could simply be ascribed to a difference in σ electronegativities.

(ii) **M–C^{13}–H Coupling Constants.**—The M–C^{13}–H coupling constants are also listed in Table III. The magnitudes of these couplings vary in the order Sn > Ge > Si—the same order observed in tetramethyl[21,26] and trimethylhalo group IV derivatives as well as trimethylsilyl, -germyl, and -stannyl chalcogens.[19c,d] This pattern has been rationalized by Drago and Matwiyoff[21] in terms of the dependence of the variation in orbital overlap with s character upon the size of M.[27] Goldstein and Reddy[28] and Matwiyoff and Drago[29] have argued that there should be a linear correlation between chemical shifts and C^{13}–H^1 coupling constants for compounds in which neighbor anisotropy effects are absent, constant, or vary linearly with electronegativity of substituent. The data of Tables I, II, and III clearly show that such a relationship does not exist for the compounds we have studied.

(B) **Basicity Studies.**—One can envisage two types of parameters related to base strength. One type is characteristic of the free base and measures what may be called the "intrinsic basicity." The second type is an interaction parameter either for the base in the presence of a Lewis acid, or for a given reference Lewis acid in the presence of the base, which measures the actually realized basicity. The interaction parameter is a differential quantity referred to the free base or the free Lewis acid. In this view the sequences of intrinsic basicities would resemble the realized sequences of basicity only if interaction energies (*e.g.*, free energies of rehybridization of the bases) and steric effects follow the intrinsic parameter.

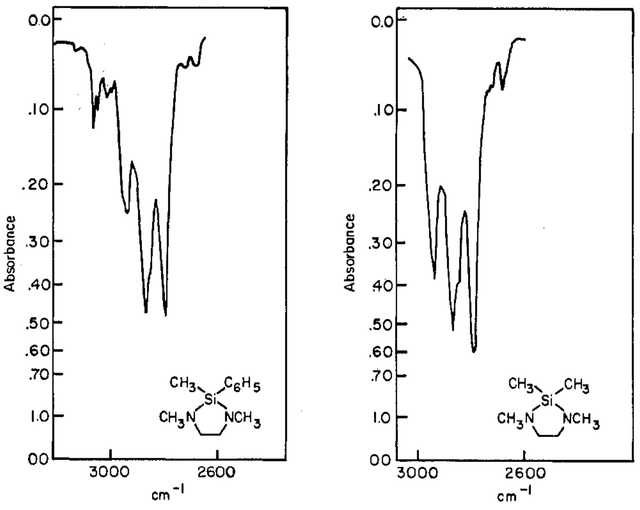

Figure 2.

The interaction parameters studied here are all for chloroform (or deuteriochloroform) as reference Lewis acid: $\Delta\nu$, the change in the C–D stretching frequency; δ_0, the C–H proton chemical shift at infinite dilution; and the change in the proton–carbon-13 coupling constant, J(CHCl$_3$). Two parameters which may conceivably be considered intrinsic parameters, J(C^{13}–H) for the carbon adjacent to the nitrogen atom of the base and the infrared stretching frequency of the C–H bonds in the N–CH$_3$ groups, have been studied.

(1) **Interaction Parameters.**—The changes in frequency ($\Delta\nu$) of the stretching vibration for an H–A group upon formation of a hydrogen-bonded complex have been correlated with a wide variety of factors[30] including the enthalpy, ΔH, of the hydrogen bond.[31] The Badger–Bauer postulate relating $\Delta\nu$ and ΔH has been refuted[30,32] and restated[33] numerous times. Its validity is still questioned in many quarters.

The nmr chemical shift of an acidic proton is also affected by association of the acid with a base: a shift to low field is produced. The observed shift is a weighted average of the shifts of the hydrogen-bonded species and of the pure donor and thus depends on the equilibrium constant, K (as well as upon the characteristic chemical shift, Δ_c, for the complex). Although in theory K can be evaluated from a knowledge of the variation of nmr shifts with concentration, it

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[24] D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc.*, **87**, 3994 (1965).

[25] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

[26] G. W. Smith, *J. Chem. Phys.*, **39**, 2031 (1963).

[27] N. Muller and D. E. Pritchard, *ibid.*, **31**, 1471 (1959).

[28] J. H. Goldstein and G. S. Reddy, *ibid.*, **36**, 2644 (1962).

[29] N. A. Matwiyoff and R. S. Drago, *ibid.*, **38**, 2583 (1963).

[30] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960.

[31] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937); R. M. Badger, *ibid.*, **8**, 288 (1940).

[32] D. L. Powell and R. West, *Spectrochim. Acta*, **20**, 983 (1964).

[33] M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).

has been shown by Berkeley and Hanna[34] that K measured in this way does not correlate well with the basicity of the acceptor. Reasonable correlations involving Δ_0 were obtained, however. If K is large δ_0 should also parallel base strength since δ_0 will then be approximately proportional to Δ_0. Eyman and Drago have recently employed δ in conjunction with changes in infrared stretching frequency of the O–H band of phenyl as reference acid in a variety of bases to study enthalpies of formation of the Lewis complexes.[35]

The magnitude of proton–carbon-13 coupling, $J(\mathrm{HCCl_3})$, for chloroform is another indication of interaction between chloroform and a base. Evans[36] observed enhancement of this coupling in donor solvents. $J(\mathrm{CHCl_3})$, like the chemical shift, should be a weighted average of the values for free and complexed chloroform and so should depend on the association constant. It would constitute a good quantitative measure of the base strength, however, only if the characteristic value for each complex was known or was nearly independent of the nature of the base.

Figure 3 shows that a reasonable correlation between δ_0 and $J(\mathrm{CHCl_3})$ is obtained in this study. On the other hand, it may be seen from Figure 4 that $\Delta\nu$ does not correlate well with δ_0, nor hence with $J(\mathrm{CHCl_3})$. A large number of rationalizations based on violation of any of the assumptions outlined could be invoked. For example, entropy factors neglected in the use of $\Delta\nu$ to derive base strengths could be cited. Steric factors (the deviates shown in Figure 4 are the most sterically hindered amines) might also be held responsible. Such an exercise, however, is not only precarious, but is hardly warranted since the over-all conclusion that the silylamines are definitely the least basic of the compounds studied here is permitted without it.

(2) **Intrinsic Parameters.** (i) **C–H Vibrations in the N–CH$_3$ Group.**—Study of the C–H stretching region can provide information about bonding in amines since bases containing the N-methyl group give rise to characteristic bands in the 2800 cm^{-1} region said to be sensitive to the state of the nitrogen lone pair.[37,38]

Examination of the 3000–2700 cm^{-1} region of the spectra of several carbon, silicon, and germanium imidazolidines reveals that the sharp absorption which is observed at 2840 ± 5 cm^{-1} in the carbon derivative and at 2830 cm^{-1} in the germanium derivative is not observed as a prominent band, but appears as a shoulder at 2850 cm^{-1} in the silaimidazolidines. These data may be interpreted in terms of the silicon derivatives having a lower intrinsic basicity than the carbon or germanium analogs.

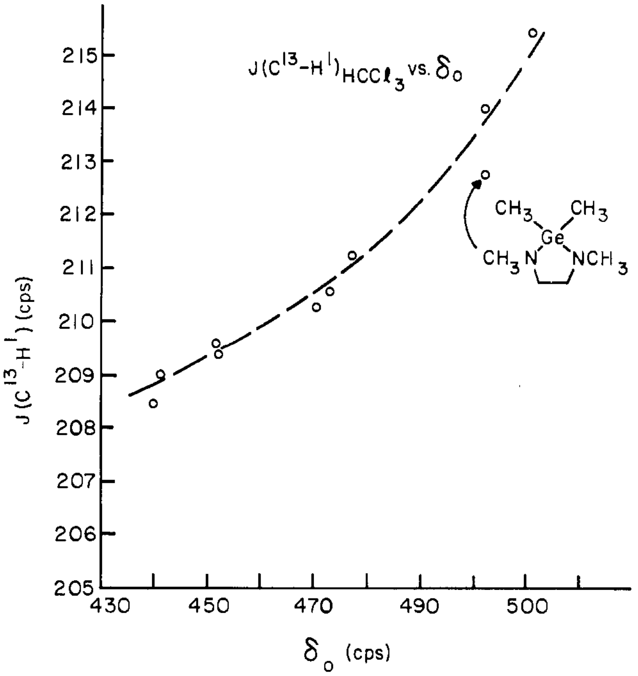

Figure 3.

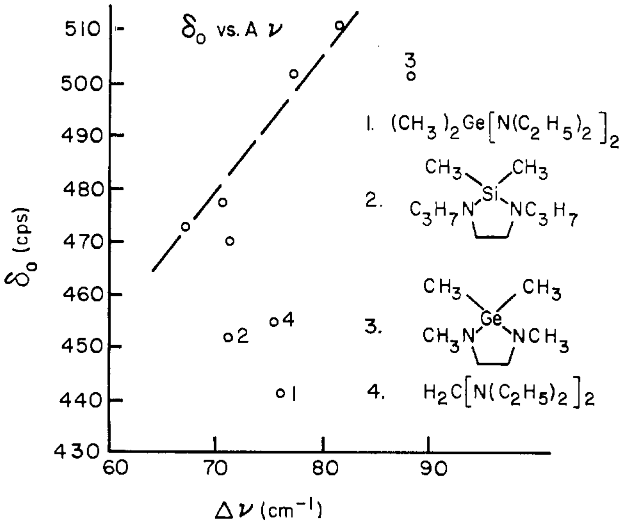

Figure 4.

(ii) **Effective Electronegativities at Nitrogen.**—It might be hoped that the effective electronegativity, X, displayed by nitrogen in the bases is related to the base strength. To a first approximation one might have expected the effective electronegativity to be related inversely to the basicity of the compounds.

On this basis since nitrogen attached to silicon appears from the N–C^{13}–H results to be more electronegative than nitrogen attached to germanium, the silicon compounds are less basic than the germanium compounds. Note, however, that this argument makes the carbon derivatives the least basic.

(C) **Conclusions.**—The detailed comparisons of the methods which have been used recently to determine relative basicities reveal a variety of limitations for each method. The application of each of these methods to the series of bases studied here gives a number of different sequences of base strength for any one series. The use of these methods is therefore cautioned

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against both on theoretical and practical grounds. All the parameters measured, however, indicate a considerable difference in effective electronegativity and basicity between silicon and germanium homologs.

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Synthesis and Structure of $(CH_3)_4Sn_3Fe_4(CO)_{16}$[2]

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The reaction of CH_3SnCl_3 and $Na_2Fe(CO)_4$ involves a facile redistribution of methyl groups to give as isolable products $[(CH_3)_2SnFe(CO)_4]_2$ and the new compound $(CH_3)_4Sn_3Fe_4(CO)_{16}$. The crystal structure of $(CH_3)_4Sn_3Fe_4(CO)_{16}$ has (monoclinic) symmetry $P2_1/c$ and a unit cell of dimensions $a = 11.04$ A, $b = 16.36$ A, $c = 19.09$ A, and $\beta = 108.5°$. There are four molecules per unit cell. The structure has been refined by least squares, using counter-measured Mo Kα diffraction data. Each $(CH_3)_4Sn_3Fe_4(CO)_{16}$ molecule contains a row of three tetrahedrally coordinated tin atoms, the central tin atom being bonded to four $Fe(CO)_4$ groups and each terminal tin atom being bonded to two $Fe(CO)_4$ groups and two methyl groups. The coordination of each iron is octahedral. The presence of almost exactly planar Sn_2Fe_2 rings causes compression of the average SnFeSn angle to 77.9° and of the FeSnFe angles within a ring to 105.2° at the terminal tin atom and 98.8° at the central tin atom. The average interatomic distances are: Fe–(terminal)Sn = 2.625 A, Fe–(central)Sn = 2.747 A, Fe–C = 1.75 A, C–O = 1.17 A, and Sn–C = 2.22 A.

Introduction

A number of compounds containing tin–transition metal bonds have been described in the literature.[4] One such compound is $[(CH_3)_2SnFe(CO)_4]_2$, which can be obtained[5] by the reaction of $(CH_3)_2SnCl_2$ with solutions of the $HFe(CO)_4^-$ anion. Since Fe–Sn bonds are quite stable and a compound, $[Fe(CO)_3NO]_4Sn$, is known,[6] in which the four iron atoms are bonded to one tin atom, the reaction of CH_3SnCl_3 and $Na_2Fe(CO)_4$ was investigated in hopes of obtaining a closed polynuclear metal cluster of iron and tin atoms. However, because of a facile redistribution of the methyl groups bonded to tin, the product was not the expected adamantane-type metal cluster, but a mixture of the known $[(CH_3)_2SnFe(CO)_4]_2$ and the new compound, $(CH_3)_4Sn_3Fe_4(CO)_{16}$. The crystal structure of the latter compound was determined to establish its geometry, in a continuing study of the bonding in polynuclear complexes.

Experimental Section

All reactions were performed in a dry, oxygen-free nitrogen atmosphere in either glass apparatus or a polyethylene dry bag.

Reagents.—$Fe_3(CO)_{12}$ was obtained from Alfa Inorganics and purified by thorough washing with 0.1 *M* HCl, methanol, and petroleum ether (bp 30–60°), followed by overnight Soxhlet extraction with *n*-hexane in a nitrogen atmosphere. The mixture was cooled to 25° and the dark green crystals were collected under nitrogen, vacuum dried, and stored in sealed glass ampoules. Pure $Fe_3(CO)_{12}$ was recovered in 90% yield. Ammonia (Matheson Co.) was distilled from sodium. Anhydrous $SnCl_2$, $(CH_3)_2SnCl_2$, and $(CH_3)_3SnCl$ were used as obtained from the Metal and Thermit Co. Tetrahydrofuran was distilled from $LiAlH_4$ in a nitrogen atmosphere and used immediately.

Preparation of CH_3SnCl_3.—The CH_3SnCl_3 was prepared[7] from $SnCl_2$ and CH_3Cl at 360°. The product was purified by recrystallization from petroleum ether at −78° followed by sublimation at 60° (1 μ). Gas chromatographic analysis showed that the purified product contained 98.2% CH_3SnCl_3 and 1.7% $(CH_3)_2SnCl_2$. The gas chromatographic analyses were made using a 1-m 20% fluorosilicon (FS 1265) on 60–80 mesh NAWFB column with a helium flow rate of 10 cc/7.1 min. The column was maintained at 100° with the vaporizer at 150°. Under these conditions the observed retention times were: CH_3SnCl_3, 5.3 min; $(CH_3)_2SnCl_2$, 8.4 min; and $(CH_3)_3SnCl$, 3.3 min. The CH_3SnCl_3 samples contained no $(CH_3)_3SnCl$.

Preparation of $Na_2Fe(CO)_4$.—The preparation of $Na_2Fe(CO)_4$ from sodium and $Fe_3(CO)_{12}$ in tetrahydrofuran[8] produces a dark red solution which contains uncertain quantities of polynuclear iron carbonyl anions as well as $Na_2Fe(CO)_4$. However, the reaction of $Fe_3(CO)_{12}$ with sodium in anhydrous liquid ammonia produces almost pure $Na_2Fe(CO)_4$.[9] The following procedure is convenient for a large-scale preparation. A 1-l. flask equipped with a Dry Ice condenser, nitrogen inlet, and magnetic stirrer was filled with dry nitrogen. $Fe_3(CO)_{12}$ (16.9 g, 0.0336 mole) and 600 ml of sodium-dried ammonia were charged into the flask, which was immersed in a Dry Ice–acetone bath. Freshly cut sodium (4.7 g, 0.20 g-atom) was added in 0.1–0.2-g portions over 0.5 hr, the sodium being maintained in a nitrogen atmosphere before addition. The reaction mixture initially became deep red, but, upon complete addition of the sodium, a white precipitate and a pale yellow supernatant liquid were obtained. The mixture was stirred at −78° for 15 min; the ammonia was then removed at 0°, and the gray residue was dried at 90° (0.1 μ)

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