Group IVB Metalloidal Substituent Effects by Fluorine-19 Resonance

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Abstract: Possible effects of substituents of the MR_3 type (M = a group IVB metalloid, R = CH_3 or C_6H_5) attached to an aryl system are evaluated and tested by examination of ^{19}F substituent chemical shifts (SCS) of appropriate m- and p-fluorophenyl and 4,4'-fluorobiphenyl systems. (The extent to which a substituent electronically perturbs the C-F neighborhood is indicated by the substituent chemical shift (SCS), which is defined as the difference between the chemical shift of the unsubstituted fluoroaromatic and the substituted fluoroaromatic.) The $(CH_3)_3Si$ substituent engages in conjugative electron withdrawal in both p-fluorophenyltrimethylsilane and 4-fluoro-4'-trimethylsilylbiphenyl, while the $(CH_3)_3Ge$ group produces net electron withdrawal in 4-fluoro-4'-trimethylgermylbiphenyl. Overall, the evidence suggests that all the $M(CH_3)_3$ substituents participate in $d\pi-p\pi$ electron withdrawal, but this may be masked by shielding mechanisms. Replacement of CH_3 in $M(CH_3)_3$ by electronegative groups such as phenyl and vinyl leads to more negative SCS values, since the effective electronegativity of the metalloidal center is increased. Comparisons are also drawn with results from pentafluorophenyl systems. Substituents of the type CH_2MR_3 (M and R as above) produce large positive SCS values when *para* to fluorine, and metallomethyl substituents generally are probably quite effective *ortho-para* donors. The pertinence of the present results to scales of electronegativities of the group IVB metalloids is presented.

As part of a general program on metallo substituent effects, we recently pointed out that mercuri substituents only feebly perturb the π-electron system in aryl mercurials as judged by ^{19}F substituent chemical shifts (SCS), whereas the same technique indicated substantial C–Hg bond polarization in benzyl mercurials.[2] We have extended this approach to certain aryl derivatives of group IVB elements, as there is great current interest in examples of $d\pi-p\pi$ bonding interactions involving aryl and vinyl derivatives of silicon and germanium.[3] Since the magnetic energy necessary to bring about the resonance condition in a nucleus is too small to have any significant effect on the thermodynamic and electronic properties of a molecule,[4] the observed substituent chemical shifts (SCS) are a reflection of ground-state interactions. Previous conclusions concerning (p → d) π bonding have been extracted from chemical reactivity data[3b,c] as well as electronic[3c] and vibrational spectra,[3d] and are therefore invalid in the present context. Chemical methods really depend on the free energy difference between two chemically different states, whereas electronic and vibrational spectra provide an energy difference between ground and excited states, thus, gross assumptions are necessary to equate these measurements with the ground state.

In order to provide ^{19}F nuclear magnetic resonance

data pertinent to the question of group IVB metalloidal-aryl interactions, we have synthesized a number of phenyl, benzyl, and biphenyl derivatives of group IVB elements, strategically fluoro substituted so that ^{19}F SCS values would provide evidence for ground-state conjugation.

Results and Discussion

The sensitivity of ^{19}F chemical shifts of aryl fluorides to perturbations of the local environment has been well documented.[5] Recently, Dewar, *et al.*,[6] have made the important suggestion that this can be attributed to the polarization of the C–F π bond which, because of the electronegativity of fluorine, involves orbitals largely concentrated on fluorine. The extent of this polarization is determined by the magnitude of the electric field along the C–F bond, which in turn is mainly due to the π charge density at the ring carbon atom adjacent to fluorine (mesomeric effect) and the inductive contribution from the substituent (direct field effect). Before examining in detail the effects of metalloidal

(a) deshielding   (b) shielding

substituents on ^{19}F chemical shifts, it is instructive to consider the proposed mechanisms by which alkyl substituents can perturb an adjacent aromatic substrate. On the basis of a localized bond model it has been possible to invoke three mechanisms by which alkyl groups can release electrons when attached to multiply bonded carbon atoms[7a] (i) the inductive

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(2) (a) W. Adcock, B. F. Hegarty, W. Kitching, and A. J. Smith, *J. Organometal. Chem.*, 12, 21 (1968); (b) W. Kitching, W. Adcock, and B. F. Hegarty, *Aust. J. Chem.*, 21, 2411 (1968).

(3) (a) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, 1, 112 (1955); (b) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 4403 (1954); (c) D. G. Anderson, J. R. Chipperfield, and D. E. Webster, *J. Organometal. Chem.*, 12, 323 (1968), and references cited therein; (d) J. M. Angelelli, R. T. C. Brownlee, A. R. Katritzky, R. D. Topsom, and L. Yakhontov, *J. Amer. Chem. Soc.*, 91, 4500 (1969), and references cited therein; (e) R. West, *J. Organometal. Chem.*, 3, 314 (1965).

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

(5) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 85, 709, 3146 (1963).

(6) (a) T. G. Squires and M. J. S. Dewar, *ibid.*, 89, 379 (1967); (b) W. Adcock and M. J. S. Dewar, *ibid.*, 89, 379 (1967).

effect (direct field mechanism and σ-inductive effect), (ii) the π-inductive or inductomesomeric effect, and the (iii) mesomeric effect or hyperconjugation. The relative importance of these processes has been impossible to assess experimentally or theoretically, although it has been suggested[7] that hyperconjugation is probably unimportant in the ground state of neutral molecules, the so-called "hyperconjugation" of alkyl groups being due to the π-inductive or inductomesomeric effect. Thus, it is probably unnecessary to invoke σ-π conjugation to rationalize ground-state measurements.

In presenting a rationalization of our SCS data (ground state) we have tentatively adopted the simple inductive model[7] by assuming that hyperconjugation is negligible and that the magnitude of the SCS is determined by the inductive field effect and the π-inductive or inductomesomeric effect. It is obvious that both these mechanisms will operate to shield the ^{19}F nucleus when the alkyl substituent is located in the para position, and this is confirmed by an observed large positive SCS (Table I). Since it is not

Table I. Substituent Chemical Shifts (SCS) (ppm) of Substituted Fluorobenzenes

Substituent	Cyclohexane	DMF
m-CH$_3$	+1.27 (+1.15)[a]	+1.13 (+1.18)[a]
p-CH$_3$	+5.48 (+5.40)[a]	+5.45
m-(CH$_3$)$_3$C	+0.55	+0.65
p-(CH$_3$)$_3$C	+5.60	+5.51
m-CF$_3$	−2.10[a]	−2.48[a]
p-CF$_3$	−5.05[a]	−5.90[a]

[a] Taken from ref 5.

known whether the π-inductive effect will operate to reinforce or oppose the shielding inductive field effect from a nonconjugative positive,[6b,8] no a priori prediction can be made when the alkyl group is in the meta position. The observed smaller positive SCS in the meta position (Table I) indicates that a shielding mechanism predominates. Some support for the adopted inductive model can be obtained by examining the SCS values listed in Table I for the t-butyl and trifluoromethyl substituents (replacement of the hydrogen atoms in methyl by methyl and fluorine, respectively). The sign and magnitude of the observed SCS for these two groups relative to methyl can be successfully predicted from the inductive model. Recently,[9] chemical reactivity data have been rationalized in terms of an inductive model without recourse to the concept of fluorine double bond–no bond resonance (hyperconjugation).

The congeners in group IVB differ from carbon in that the nd orbitals are not greatly higher in energy than the ns and np orbitals; therefore, the possibility of nd orbital population exists. Therefore, the aryl–metalloidal bond may be considered to comprise a σ component on which is superimposed a π component of unknown magnitude, although some estimates of

this π-bond order have been given for anion radicals.[10] The metalloid, being the positive end of the dipole (more electropositive than an sp^2 carbon), will perturb the adjacent aryl system by the same types of mechanisms described for the alkyl groups (inductive field effect and π-inductive effect). The net results of the processes in the para position will be to shield the ^{19}F nucleus, since both effects obviously operate to reinforce one another in a conjugated position. Similar to the alkyl substituents, no such a priori prediction can be made for the meta position, it being known that substituents meta to fluorine exert anomalous effects.[6b,8] As the electropositivity of the metal increases (e.g., Sn) this polarization phenomenon will be more important, but electronegative groups attached to the metal (i.e., other than the fluoroaryl group) may override and reverse the direction of the polarization (cf. CF$_3$).

Superimposed on the π-inductive effect of the metalloid is the possible conjugative electron withdrawal via dπ–pπ interaction. This mesomeric interaction (−M) in conjugated positions should lead to deshielding of the ^{19}F nucleus, i.e., the −M effect reduces the π-electron density in the ortho and para positions. Although resonance structures imply no conjugative interaction in the meta position, recent SCF. MO treatments[6b,8] suggest that there is an effect opposite to that experienced in the ortho and para positions. This possible interaction makes evaluation of the meta SCS more complex. Unambiguous qualitative conclusions can only be extracted from the para SCS data.

(a) Phenyl Systems. The SCS values obtained are assembled in Table II.

Complete data are only available for the solvent cyclohexane. Since solvents of donor character may compete for available central atom (M) d orbitals and thereby reduce the need for $\pi \rightarrow$ d interaction, cyclohexane was the first solvent explored. However, to probe the question of solvent effects (particularly strong oxygen donors) measurements were also performed for N,N-dimethylformamide (DMF) and dimethyl sulfoxide solutions. The positive meta SCS values for the metalloidal substituents are consistent with the electropositive nature of the central atom (M), the inductive field effect apparently being the predominating mechanism. Variations in the meta SCS are small and it would not be valid to account for any slight trends in terms of variation in polarization of the M–C$_{aryl}$ bond. Such bonds vary in length, and these variations together with other effects (polarization of π electrons) could account for the differences.

The para SCS values are particularly interesting, since only in the case of silicon is an unambiguous deshielding effect clearly operative. This is opposite to what is expected from simple inductive effects emanating from the comparatively electropositive silicon. It should be pointed out that the observed deshielding effect (−0.50 ppm is the resultant of the shielding effect (inductive and π inductive) and the deshielding effect (−M). Thus dπ–pπ electron withdrawal seems unquestionably indicated for silicon,[5,11] while the small shielding influences indicated for (CH$_3$)$_3$Ge, (CH$_3$)$_3$Sn, and (CH$_3$)$_3$Pb compared with the t-butyl substituent

(7) (a) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962; (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(8) M. J. S. Dewar and A. P. Marchand, J. Amer. Chem. Soc., 88, 3318 (1966).

(9) C. L. Liotta and D. F. Smith, Chem. Commun., 416 (1968), and references cited therein.

(10) A. L. Allred and L. W. Bush, J. Amer. Chem. Soc., 90, 3352 (1968).

(11) J. Maire and J. Angelelli, Bull. Soc. Chim. Fr., 1311 (1969).

Table II. Substituent Chemical Shifts (SCS) (ppm) of Substituted Fluorobenzenes in Various Solvents

Substituent	Cyclohexane meta	para	DMF meta	para	DMSO meta	para	Dioxane meta	para	CCl₄ meta	para
$(CH_3)_3C$	+0.55	+5.60	+0.65	+5.50						
$(CH_3)_3Si$	+0.85	−0.50 (−0.50)[a]	+0.45	−0.60 (−0.60)[a]	+1.45	−0.10	+0.80	−0.55	+0.83[b]	−0.51[b] (−0.50)[a]
$(CH_3)_3Ge$	+0.70	+0.55	+0.60	+0.50					+0.75[b]	+0.56[b]
$(CH_3)_3Sn$	+0.60	+0.20	+0.60	+0.30	+1.10	+0.85	+0.65	+0.30	+0.55[b]	+0.15[b]
$(CH_3)_3Pb$	+0.40	+0.20								

[a] Taken from ref 5.   [b] Taken from J. Maire and J. Angelelli, *Bull. Soc. Chim. Fr.*, 1311 (1969).

strongly suggest that $d\pi$–$p\pi$ interactions may also be significant for these groups. In the absence of a −M effect for these substituents we should expect a shielding effect at least as large as that observed for the alkyl substituents. This interpretation is based on the simple inductive model and may be erroneous if hyperconjugation is significant.

The overall conclusion here is in agreement with the earlier proposal of Chatt and Williams,[3b] although the $d\pi$–$p\pi$ bonding does appear to be a sensitive function of d-orbital size. Apparently the vacant d orbitals of the smaller silicon atom can conjugate more effectively with the adjacent phenyl system. Concurrence with Chatt and Williams' analysis must be considered fortuitous, since a recent investigation[12] of the thermodynamics of metalloidal acid dissociations has revealed that no recourse to $d\pi$–$p\pi$ effects is necessary and that other explanations may readily account for the observed trend. This is not surprising, since it is well known that equilibrium constants are often controlled by factors other than the internal energy difference between the two states.[13]

Solvent effects are definitely important, as judged by the data for the silicon and tin systems. Dioxane and DMF parallel cyclohexane, but the strong oxygen donor DMSO causes significant perturbations in the SCS values. The increased shielding of the ¹⁹F nucleus by $(CH_3)_3Si$ and $(CH_3)_3Sn$ on changing the solvent from cyclohexane to DMSO (evidenced by more positive *para* SCS) could be due to a combination of two effects: (a) strong coordination reduces the requirement for $\pi \rightarrow d$ bonding, and (b) strong coordination could promote polarization of the M–C$_{aryl}$ bond by stabilization of the positive charge.

We have also explored the effect of replacing a methyl group (or groups) in the $(CH_3)_3M$ substituent by either a vinyl, allyl, or phenyl group (or groups),[14] since the electronic influence of the trimethylmetalloidal substituent might be expected to be modified in two distinct ways.

(1) The three groups, being electronegative relative to methyl, should increase the effective electronegativity

of the metalloid by an electron-withdrawing σ-inductive effect, thereby decreasing the shielding mechanisms (inductive field effect and π-inductive effect) and increasing the deshielding mechanism (−M). The latter effect would be due to the contraction of the d orbitals, thereby enhancing the $d\pi$–$p\pi$ interaction. It is obvious that both these effects would be synergic and inseparable, the net result being a more negative (or less positive) SCS.

(2) The groups may compete with the *p*-fluorophenyl groups for the $\pi \rightarrow d$ interaction so that a decrease in the deshielding mechanism (−M) would be expected, *i.e.*, the net result being a more positive (or less negative) SCS.

It can be seen that these effects (1 and 2) are opposing. The appropriate SCS data are assembled in Table III (solubility problems were encountered).

Table III. Substituent Chemical Shifts (SCS) (ppm) of Substituted Fluorobenzenes in Various Solvents

Substituent	Cyclohexane meta	para	DMF meta	para	HMPA[a] meta	para
$C_2H_3(CH_3)_2Si$		−0.85		−1.00		
$C_3H_5(CH_3)_2Si$		−0.95		−0.90		
$(C_6H_5)_3Sn$				−1.55		−1.77
$(C_6H_5)_3Pb$				−1.00	−0.80	

[a] Hexamethylphosphoramide or hexamethylphosphoric triamide (tris(dimethylamino)phosphine oxide).

It is clear from the data in Table III that the SCS values become more negative, suggesting that the first effect described is the predominating modification of the electronic behavior of a trimethylmetalloidal substituent.

Certain characteristics of the biphenyl system have been investigated, and quite interesting results were obtained, which are set out below in Table IV.

Table IV. Substituent Chemical Shifts (SCS) (ppm) of 4′-Substituted Fluorobiphenyls

Substituent	DMF	HMPA[a]
$(CH_3)_3Si$	−0.18	−0.28
$(CH_3)_3Ge$	−0.11	−0.14
$(CH_3)_3Sn$	+0.10	

[a] Hexamethylphosphoramide.

An unambiguous conjugative interaction between the trimethylsilyl substituent and the aryl system is indicated by an observed negative SCS, a result in agreement with observations already made from the phenyl system. However, the negative SCS for the trimethyl-

(12) J. M. Wilson, A. G. Briggs, J. E. Sawbridge, P. Tickle, and J. Zuckerman, Abstracts of Papers, 4th International Conference on Organometallic Chemistry, University of Bristol, Aug 1969.

(13) M. J. S. Dewar, Symposium on Linear Free Energy Relationships, Durham, N. C., 1964. The entropies of ionization of carboxylic acids vary over a wide range and gross assumptions are necessary to disentangle the electronic response of the substituent from the ΔpK_a ($\equiv \log K − \log K_0$). It is generally assumed that compensating changes in H and S within a series of structurally similar compounds allows us to interpret changes in K in terms of internal energy differences. Therefore, it is not surprising to have conflicting conclusions from chemical reactivity data. For example, Anderson, Chipperfield, and Webster's[3c] conclusions from the enhanced basicities of some substituted pyridines that the metalloidal substituents donate electrons to the adjacent substrate is contrary to the conclusion of Chatt and Williams.[3b]

(14) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 688 (1956).

germyl substituent is contrary to the result obtained from the phenyl system. This negative SCS for the $(CH_3)_3Ge$ groups confirms the prediction already made from the simple inductive model, i.e., $d\pi-p\pi$ interaction occurs for all the metalloids. This effect becomes apparent in the biphenyl system (compared to the phenyl system) for two reasons. (a) Conjugative electron withdrawal ($-M$) by a substituent would be expected to increase on lowering the ionization potential of the aromatic substrate. (b) The inductive effect is more effectively "dampened" by distance than is the mesomeric effect.[15] Both these factors enhance the mesomeric effect relative to the inductive effect.

The situation may be summarized as follows: $(CH_3)_3Si$, (a) phenyl system, mesomeric effect $>$ inductive effect, (b) biphenyl system, mesomeric effect $>$ inductive effect; $(CH_3)_3Ge$, (a) phenyl system, inductive effect $>$ mesomeric effect, (b) biphenyl system, mesomeric effect $>$ inductive effect; $(CH_3)_3Sn$, (a) phenyl system, inductive effect $>$ mesomeric effect, (b) biphenyl system, inductive effect $>$ mesomeric effect.

The results from the biphenyl system strongly suggest that negative SCS cannot be attributed to mutual conjugation between fluorine and the substituent (electromeric effect), since this effect would have been expected to be more important in the phenyl system.

It seemed of interest at this stage to compare the SCS computed from the metallo-substituted pentafluoro moiety with those determined from the fluorophenyl system. Because ^{19}F chemical shifts are sensitive to ortho substituents possessing unshared electron pairs,[16] the use of the pentafluoro moiety for experimentally assessing the electronic interactions of substituents is questionable. Certainly we should not expect any correspondence between the SCS derived from this system (Table V) and those determined from

Table V. Substituent Chemical Shifts[a] (SCS) (ppm) Derived from the Pentafluorophenyl System

Substituent	meta	para
$(CH_3)_3Si$	-0.50^b $(-0.70)^c$	-1.40^b $(-1.60)^c$
F_3Si	-2.80^b	-10.90^b
$(C_6H_5)_3Ge$	-2.10^d	-2.80^d
$(CH_3)_3Sn$	-2.00 $(-1.20)^b$	-1.40 $(-0.80)^b$
$(CH_3)_3Pb$	-1.60^d	$+0.80^d$
$(C_6H_5)_3Pb$	-3.30^d	-1.70^d

[a] The definition of the SCS (ref 6b, 8) was strictly adhered to. [b] Solvent benzene; taken from M. G. Hogben and W. A. G. Graham, J. Amer. Chem. Soc., 91, 283 (1969), and A. J. Oliver and W. A. G. Graham, J. Organometal. Chem., 19, 17 (1969). [c] Solvent benzene; this work. [d] Solvent CCl_4; taken from K. W. Jolly and L. H. Sutcliffe, Spectrochim. Acta, Part A, 24, 1191 (1968), and I. J. Lawrenson, J. Chem. Soc., 1117 (1965).

the mono-substituted phenyl fluorides. This is found to be the case (cf. Table II).

Another factor that probably contributes to the poor correspondence is that the effective electronegativity of the metalloids in both systems is not the same; consequently, the inductive and mesomeric contributions will be different. The substituted fluorophenyl system has the advantage that it is less complex, and no

(15) M. J. S. Dewar and P. J. Grisdale, J. Amer. Chem. Soc., 84, 3539 (1962).

(16) M. J. S. Dewar and J. Keleman, J. Chem. Phys., 49, 499 (1968).

complications are likely due to a varying "ortho" effect within the series. It is of interest to note that replacing the methyl CH_3 group with C_6H_5 in the pentafluoro system affects the SCS in the same way that was observed in the fluorophenyl system, i.e., the shielding mechanisms decrease while the deshielding effect ($-M$) probably increases. Converting $(CH_3)_3Si$ to F_3Si changes the direction of the dipole between the substrate and the substituent, which is reflected by the magnitude of the SCS in Table V [cf. H_3C and F_3C (ref 17), similar mechanisms operating].

(b) Benzyl Systems. We reported recently that the mercurimethyl substituent appeared to be a relatively good ortho-para donor, and speculated that this might be a property of metallomethyl groups generally.[2] We have obtained data, listed in Table VI, which seem to be in line with this view.

It can be seen (Table VI) that there is a large difference in the meta and para SCS values, in agreement with our report on the mercury systems, and such a difference indicates strong polarization of the benzyl-metalloid bond, resulting in increased shielding and more positive para SCS values. meta SCS values would be expected to be much less positive for an effect of this sort. This large "hyperconjugative $\sigma-\pi$" interaction of metallo-type substituents[18] is probably entirely due to the enhanced inductive and π-inductive effects (inductive model, previously described for the alkyl substituents): the adjacent electropositive metal increases the effective electropositivity of the carbon by a σ-inductive effect, thereby enhancing the polarity of the M^+-CH_2 bond. This leads to increased shielding of the fluorine nucleus, i.e., SCS more positive than for corresponding alkyl substituent.

There seems to be no general agreement[19] on the respective electronegativities of the elements Si, Ge, Sn, and Pb. Pauling's electronegativity values for group IV (C $>$ Si $\sim$ Ge $\sim$ Sn $\sim$ Pb) have been disputed by a number of workers who have put forward a new scale based essentially on chemical methods. The order is C $>$ Ge $>$ Si $\sim$ Sn $>$ Pb. Allred and Rochow[20a] have suggested an alternation of electronegativities, C $>$ Pb $>$ Ge $>$ Sn $>$ Si, on the basis of the proton chemical shifts of the tetramethyl derivatives. However, it is now known that proton chemical shifts are likely to be complicated by magnetic perturbations to the extent that it is virtually impossible to disentangle the electronic influence. Since long-range magnetic interactions are much less important in the case of fluorine,

(17) I. J. Lawrenson, J. Chem. Soc., 1117 (1965).

(18) A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, J. Organometal. Chem., 20, 49 (1969), concluded that strong release of the $(Me_3Si)_xCH_{3-x}$ groups arises mainly from hyperconjugative electron release from the Me_3Si-C bonds, rather than from inductive effects. However, the analysis which led to this conclusion did not consider the probable change in the hybridization state of carbon by steric phenomena. Distortion of the tetrahedral symmetry around carbon will occur on replacing the small hydrogen atoms with large trimethylsilyl groups. This will be particularly pronounced when all three hydrogens are replaced. To accommodate the new geometry the hybridization state of carbon becomes more sp^2 in character, i.e., structural distortions increase the effective electronegativity of carbon. It should be noted that this will oppose any change in electronegativity caused by the σ-inductive effect.

(19) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966.

(20) (a) A. L. Allred and E. G. Rochow, J. Inorg. Nucl. Chem., 5, 269 (1958); 20, 167 (1961); (b) H. H. Huang and K. M. Hui, J. Organometal. Chem., 2, 288 (1964); J. Nagy, J. Reffy, A. Kauszmann-Borbély, and K. Pálossy-Becker, ibid., 7, 393 (1967).

Table VI. Substituent Chemical Shifts (SCS) (ppm) of Substituted Fluorobenzenes in Various Solvents

Substituent	Cyclohexane		DMF		DMSO		Dioxane		HMPA[c]	
	meta	para	meta	para	meta	para	meta	para	meta	para
$(CH_3)_3SiCH_2$	1.05	7.05	1.10	7.20	1.15	7.75	1.15	7.15		
		(6.95)[a]								
$(CH_3)_3GeCH_2$	0.90	7.05	1.10	7.30						
$(CH_3)_3SnCH_2$	0.85	7.75	1.00	8.15	1.60	8.70	0.95	8.00		
$(C_6H_5)_3PbCH_2$[b]									0.80	6.40

[a] Taken from ref 5. [b] The instability and decomposition problems encountered with the liquid trimethylbenzylplumbanes necessitated examination of the crystalline triphenylbenzyl compounds. [c] Hexamethylphosphoramide.

[19]F SCS data from a suitable model may provide a scale of electronegativities. The fact that the *para* SCS for the benzyl system is determined essentially by the electronegativity of the metalloid suggests that these values (in cyclohexane to avoid solvent effects) should be a valuable and reliable empirical guide to their relative electronegativities. From the data in Table VI it is seen that a new scale can be put forward based on ^{19}F SCS (a gound-state measurement), *i.e.*, C > Si ~ Ge > Sn. Results from dipole moment studies suggest a similar sequence.[20b] The *meta* SCS from the phenyl system (Table II) requires a scale of electronegativities (decreasing), $R_3Pb > R_3C > R_3Sn > R_3Ge > R_3Si$. However, we have already pointed out that *meta* SCS's are determined by other factors besides the inductive effect and so this order is expected to be anomalous.[21]

From the data in Table VI it can also be seen that changing the solvent from cyclohexane to strongly coordinating solvents (DMSO and DMF) causes a pronounced shift of the *para* SCS values. For $(CH_3)_3Sn$, the change from cyclohexane to DMSO is associated with a 1-ppm change in the *para* SCS. This change is reasonably ascribed to solvation of and hence stabilization of the positive metalloidal pole $(CH_2{}^{\delta-}$--$M{}^{\delta+}$-$(CH_3)_3)$.

We have also explored the effect of replacing a methyl group in *p*-fluorobenzyltrimethylsilane by a vinyl or an allyl group, and the results are listed in Table VII.

The effect is seen to be a modest but definite one, producing a less positive SCS. This effect can be attributed to an increase in the effective electronegativity of silicon (*cf.* $(C_6H_5)_3Pb$ in Table VI).

Table VII

Compound	Solvent	
	Cyclohexane	DMF
p-FC$_6$H$_4$CH$_2$Si(CH$_3$)$_3$	+7.05	+7.20
p-FC$_6$H$_4$CH$_2$Si(CH$_3$)$_2$C$_2$H$_3$	+6.85	+7.10
p-FC$_6$H$_4$CH$_2$Si(CH$_3$)$_2$C$_3$H$_5$	+6.75	+7.05

(21) NOTE ADDED IN PROOF. Stewart and Treichel [R. P. Stewart and P. M. Treichel, *J. Amer. Chem. Soc.*, **92**, 2710 (1970)] have recently utilized the ^{19}F SCS's of substituted *m*-fluorobenzyl derivatives, *m*-FC$_6$H$_4$CH$_2$X, to compute relative group electronegativities for seven transition metal groups. The method involved the use of an empirical relationship between the ^{19}F nmr chemical shift, δ(CH$_2$X), and the group electronegativity, χ(X), of the substituent X. However, the same order was obtained using the SCS's themselves or derived σ_I parameters for the CH$_2$X groups. The *meta* SCS from the *m*-fluorobenzyl metalloidal derivatives (in cyclohexane) requires a scale of electronegativities decreasing Sn > Ge > Si > C, which is in direct *contrast* to the order based on the SCS from the *p*-fluorobenzyl derivatives. This is not at all surprising, since we have already pointed out

Experimental Section

Proton nmr spectra of all compounds were obtained for carbon tetrachloride solutions using a Varian A-60 spectrometer. All spectra integrated for the assigned structures and resonance patterns were of the expected multiplicity and chemical shift.

The ^{19}F spectra were obtained at either 56.4 or 94.1 MHz using Varian DP60 and HA100 spectrometers. The former instrument had been modified to obtain spectra in the HA mode which were calibrated using a "Racal" SA535 universal counter-timer. Except for one compound, pentafluorophenyltrimethylsilane, all the flourine nmr spectra were obtained for 15% (w/w) solutions containing 5% (w/w) of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluoro-cyclobutane as internal calibrant. Hexafluorobenzene was used as an internal reference for pentafluorophenyltrimethylsilane and chemical shifts were corrected to CFCl$_6$ by adding 163.0 ppm to the chemical shift from C$_6$F$_6$. This allowed the calculation of the SCS for the (CH$_3$)$_3$Si substituent using the chemical shift data of Graham, *et al.*,[22] for pentafluorobenzene.

The compounds studied (Table VIII) were synthesized either by a standard Grignard procedure or *via* the appropriate lithio derivative unless otherwise stated.

Standard Grignard Procedure. *p*-Fluorophenyltrimethylgermane. About one-tenth of a solution of *p*-fluorobromobenzene (4.3 g, 0.025 mol) in anhydrous ether (20 ml) was added to a well-stirred suspension of magnesium (0.62 g, 0.03 mol) and anhydrous ether (10 ml). Reaction was initiated by the addition of 1 drop of bromine, and the remaining *p*-fluorobromobenzene was then added to the vigorously stirred mixture. When all visible action had ceased the mixture was stirred for 30 min followed by the dropwise addition of trimethylgermanium bromide (5 g, 0.025 mol). The mixture was refluxed overnight and then, after cooling, quenched by the addition of an excess of iced ammonium chloride solution. The reaction mixture was extracted with ether, and the combined ether extracts were dried over calcium chloride. The dark-colored liquid remaining after removal of drying agent and ether was distilled. with excess frothing, to yield a colorless liquid, bp 186° [lit.[11] 35° (1 mm)].

Lithiation Procedure. 4-Fluoro-4'-trimethylsilylbiphenyl. *n*-Butyllithium (0.01 mol, 2.35 *M* in hexane) was added to a solution of 4-fluoro-4'-bromobiphenyl in dry hexane (75 ml) under nitrogen. The reaction mixture was stirred for 6 hr and then trimethylchlorosilane (1.1 g, 0.001 mol) was added; stirring was maintained overnight. The reaction mixture was then quenched with excess dilute sulfuric acid and extracted with hexane. Removal of solvent yielded crude 4-fluoro-4'-trimethylsilylbiphenyl. Recrystallization from methanol gave lustrous flaky crystals, mp 95-96.5°.

Pentafluorophenyltrimethylsilane was prepared according to the method of Glemser.[23] Distillation afforded a colorless liquid, bp 60° (14 mm).

p-Fluorophenyltrimethyltin was kindly donated by H. H. Huang, Singapore.

(see Discussion) that substituents *meta* to fluorine exert "anomalous" effects, the ^{19}F SCS being the result of a polar effect (inductive effect) and a mesomeric effect, the latter being a combination of two effects, a mesomeric field effect and a true *meta* mesomeric interaction; *i.e.*, the *meta* SCS's are not *pure* inductive parameters and no *a priori* prediction can be made whether the inductive and mesomeric effects oppose or reinforce one another. The advantage of ^{19}F SCS's from the *p*-fluorobenzyl derivatives is that they are easier to interpret since the inductive and mesomeric effects obviously operate to reinforce one another.

(22) M. G. Hogben and W. A. G. Graham, *ibid.*, **91**, 283 (1969); A. J. Oliver and W. A. G. Graham, *J. Organometal. Chem.*, **19**, 17 (1969).

(23) M. Fild, O. Glemser, and G. Christoph, *Angew. Chem., Int. Ed. Engl.*, **3**, 801 (1964).

Table VIII.

Compound	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Mp [bp (mm)], °C
m- and p-FC$_6$H$_4$C(CH$_3$)$_3^a$	C$_{10}$H$_{13}$F	78.94	8.55	78.90	8.62	[171–173]
p-FC$_6$H$_4$Si(CH$_3$)$_3^b$	C$_9$H$_{13}$SiF	64.24	7.73	64.24	7.83	[91–94 (60)] [91–94 (60)]^f
m-FC$_6$H$_4$Si(CH$_3$)$_3^b$	C$_9$H$_{13}$SiF	64.24	7.73	64.74	7.76	[70–74 (60)] [63 (14)]^g
p-FC$_6$H$_4$Ge(CH$_3$)$_3^b$	C$_9$H$_{13}$GeF	50.79	6.11	50.56	6.44	[186] [35 (1)]^g
m-FC$_6$H$_4$Ge(CH$_3$)$_3^h$	C$_9$H$_{13}$GeF	50.79	6.11	50.50	6.01	[187] [35 (1)]^g
p-FC$_6$H$_4$Sn(CH$_3$)$_3^c$	C$_9$H$_{13}$SnF	41.74	5.02	41.79	5.00	
m-FC$_6$H$_4$Sn(CH$_3$)$_3^b$	C$_9$H$_{13}$SnF	41.74	5.02	42.15	5.19	[120–125 (60)] [83 (9)]^g
p-FC$_6$H$_4$CH$_2$Si(CH$_3$)$_3^b$	C$_{10}$H$_{15}$SiF	65.89	8.23	65.73	8.35	[115–120 (60)]
m-FC$_6$H$_4$CH$_2$Si(CH$_3$)$_3^b$	C$_{10}$H$_{15}$SiF	65.89	8.23	65.34	7.95	[108–110 (60)]
p-FC$_6$H$_4$CH$_2$Ge(CH$_3$)$_3^b$	C$_{10}$H$_{15}$GeF	52.95	6.61	52.88	6.51	[53–55 (1)]
m-FC$_6$H$_4$CH$_2$Ge(CH$_3$)$_3^b$	C$_{10}$H$_{15}$GeF	52.95	6.61	52.80	6.47	[54–57 (1)]
p-FC$_6$H$_4$CH$_2$Sn(CH$_3$)$_3^b$	C$_{10}$H$_{15}$SnF	44.00	5.50	44.29	5.38	[127–134 (40)]
m-FC$_6$H$_4$CH$_2$Sn(CH$_3$)$_3^{b,e}$	C$_{10}$H$_{15}$SnF	44.00	5.50	45.03	5.50	[130–134 (60)]
p-FC$_6$H$_4$Si(CH$_3$)$_2$C$_3$H$_5^b$	C$_{11}$H$_{15}$SiF	68.00	7.70	68.10	7.64	
p-FC$_6$H$_4$Si(CH$_3$)$_2$C$_2$H$_3^b$	C$_{10}$H$_{13}$SiF	66.63	7.19	66.31	7.11	[101–105 (52)]
p-FC$_6$H$_4$CH$_2$Si(CH$_3$)$_2$C$_3$H$_5^b$	C$_{12}$H$_{17}$SiF	69.03	8.16	69.25	8.06	[64–74 (1.8)]
p-FC$_6$H$_4$CH$_2$Si(CH$_3$)$_2$C$_2$H$_3^b$	C$_{11}$H$_{15}$SiF	68.00	7.70	68.37	7.65	[60–68 (1.8)]
p-FC$_6$H$_4$Pb(C$_6$H$_5$)$_3^{b,e}$	C$_{24}$H$_{19}$PbF	54.00	3.56	54.91	3.31	174–176
m-FC$_6$H$_4$Pb(C$_6$H$_5$)$_3^b$	C$_{24}$H$_{19}$PbF	54.00	3.56	54.23	3.48	176
p-FC$_6$H$_4$CH$_2$Pb(C$_6$H$_5$)$_3^b$	C$_{25}$H$_{21}$PbF	54.82	3.83	54.75	3.93	96–97
m-FC$_6$H$_5$CH$_2$Pb(C$_6$H$_5$)$_3^b$	C$_{25}$H$_{21}$PbF	54.82	3.83	54.69	3.91	96–97
p-FC$_6$H$_4$Sn(C$_6$H$_5$)$_3^b$	C$_{24}$H$_{19}$SnF	64.76	4.27	64.51	4.22	170–172
p-FC$_6$H$_4$C$_6$H$_4$Si(CH$_3$)$_3^d$	C$_{15}$H$_{17}$SiF	73.74	6.96	73.81	6.97	95–96.5
p-FC$_6$H$_4$C$_6$H$_4$Ge(CH$_3$)$_3^d$	C$_{15}$H$_{17}$GeF	62.37	5.89	62.40	5.91	105–106
p-FC$_6$H$_4$C$_6$H$_4$Sn(CH$_3$)$_3^d$	C$_{15}$H$_{17}$SnF	53.77	5.07	54.02	5.00	99–100

^{a} m-FC$_6$H$_4$C(CH$_3$)$_3$, 54.5°, 10 Torr; p-FC$_6$H$_4$C(CH$_3$)$_3$, 53.5–54.4°, 10 Torr [C. Ruchart and S. Eichler, *Chem. Ber.*, **95**, 1921 (1962)]; synthesized *via* a Friedel–Crafts reaction. ^{b} Synthesized *via* a Grignard procedure. ^{c} Donated. ^{d} Lithio derivative. ^{e} Although the C analyses are not good, the proton and fluorine nmr spectra were in accordance with the assigned structures. ^{f} J. D. Roberts and E. A. McElhill, *J. Amer. Chem. Soc.*, **71**, 2923 (1949). ^{g} Reference 11.

m- and *p*-Fluoro-*t*-butylbenzene. Aluminum chloride (0.12 mol) was added in increments over 1 hr to a well-stirred solution of *t*-butyl alcohol (0.1 mol) and fluorobenzene (0.6 mol) at 0°. The mixture was stirred overnight and allowed to come to room temperature. The mixture was distilled and the fraction boiling at 171–173° collected. This fraction, a mixture of the *meta* and *para* isomers of fluoro-*t*-butylbenzene could not be separated by refractionation (24-in. column, packed with glass helices) or by vapor-phase chromatography.