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(MAIN-GROUP)-METALLOMETHYL SUBSTITUENT EFFECTS BY ^{19}F RESONANCE: EFFECT OF ARYL RING SIZE

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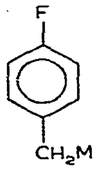
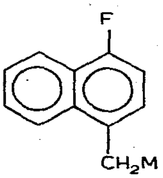
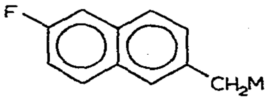
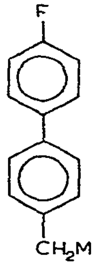
SUMMARY

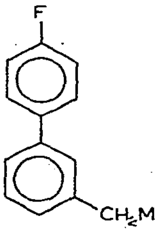
The following series of metallomethyl substituted [$(C_6H_5)_3M{-}CH_2$, where M=Si, Ge, Sn, Pb] fluoroaromatic compounds have been synthesised and characterised.











The ^{19}F spectra of these compounds have been measured (DMF solution) and the chemical shifts compared with those for the unsubstituted and methyl-substituted compounds. These comparisons are correlated with a theoretical model of $ArCH_2^-$ (for which π-charge densities and other parameters have been calculated (by an SCFMO approach), using a fractional charge model. The model reproduces the trends in the data for the various ring systems and dispositions, and adds support to the thesis that $-CH_2M$ substituents act hyperconjugatively when attached to an aryl system. A β-silylethyl substituent appears to exert no greater effect than the ethyl group. Data for the CH_2Br substituent suggest that this group is a hyperconjugative electron-withdrawing group (compared with methyl).

INTRODUCTION

Considerable evidence concerning the magnitude and origin of the electron-releasing effect of metallomethyl groups has accumulated[1,2,3], and there now seems

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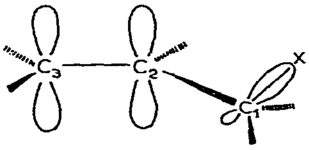
to be general agreement that the most important mechanism is hyperconjugative in nature. This is particularly in harmony with the stereo-electronic dependence of $-CH_2M$ substituent effects, established largely for Group IVB elements by charge-transfer frequencies[4] and ^{19}F substituent chemical shift measurements[3]. Hence these recent disclosures are to be viewed as extensions of the original theory of hyperconjugation developed by Mulliken[5] (for C–C and C–H systems) from which it is clear that as the electronegativity difference $|\Delta\chi|$ between C_1 and X (in the figure below) increases, σ–π conjugation (assuming proper orbital orientation) will be promoted, due to increased π-bonding capability between C_1 and C_2.



Experimental approaches to provide evidence on $-CH_2M$ substituent effects have ranged from reactivity studies to spectroscopic techniques, such as nuclear magnetic resonance and electronic spectroscopy[6]. However it is important to remember what is involved in each approach, and whether information is provided on the ground state, or some spectroscopically excited state. A full assessment of the relevance of these approaches has been provided by Dewar[7]. Processes resulting in positive charge generation in an excited or transition state, are expected to elicit a greater response from potentially electron-releasing groups, so that measurements of ΔE (by transition frequencies or rate constants) are expected to be particularly sensitive to the nature of such groups[1,7]. In the ground states of neutral molecules, however, demand for electron release is much lower and techniques (for furnishing parameters) of great sensitivity to structure are required *e.g.* NMR and NQR.

In this latter connection, we have reported[8,9,10] the unexpectedly large positive ^{19}F substituent chemical shifts (SCS) in *p*-fluorobenzyl derivatives of mercury and Group IVB metalloids, and we speculated on the generality of the phenomenon[10].

With the determination of the stereo-electronic requirements of this metallomethyl–aryl interaction[4,3], pointing to hyperconjugative electron release, it seemed to us a useful exercise, to determine the dependence of the transmission of this conjugation, on the nature of the attached aryl system. Some calculations were already available demonstrating large changes in π-charge densities (q_{ij}) at formally *para* positions in $ArCH_2^-$ systems[11]. If $-\overset{\sigma-}{C}H_2-\overset{c+}{M}$ groups did indeed act as hyperconjugative electron donors, similar differences, in formally *para*-^{19}F chemical shifts should be manifested, since such shifts are due chiefly to π-polarisation, which is determined by the electric field along the C–F bond, and the π-charge density in the region of the attached aryl-carbon[12]. To provide support for these ideas, a number of fluoroarylmethyl derivatives of Si, Ge, Sn, Pb have been synthesised and studied.

RESULTS AND DISCUSSION

(*a*) *Synthesis of compounds*

Although details are located in the experimental section, some general comments are in order since difficulties were encountered on some occasions.

General plan. Initially the aim was to synthesise the $(CH_3)_3M$ compounds via Grignard reactions, since the products would be liquids and present no problems for ^{19}F spectral measurements. For the benzyl system, this approach had already worked[10], but extension to the 4α- and 6β-naphthyl* systems potentially introduced the problem of serious (and intolerable) coupling reactions of the fluoronaphthylmethyl Grignard reagents. Some initial experiments indicated this to be the case and the coupled product (*i.e.* of the type $F\text{–}ArCH_2\text{–}CH_2Ar\text{–}F$) appeared to heavily predominate, although the standard techniques for minimising this problem were employed. Separation of the coupled product from the desired organometallic was also difficult, although their coexistence was confirmed by PMR examination of the $-CH_2-$ region of the spectrum. (Particularly when $M\text{–}^1H$ coupling was present). The Grignard approach was abandoned for the larger ring systems, and the reaction of an organometallic lithium reagent with an organic halide was chosen, *viz.*:

$$R_3MLi + F\text{–}Aryl\text{–}CH_2Br \longrightarrow R\text{–}Aryl\text{–}CH_2MR_3 + LiBr$$

The $(C_6H_5)_3MLi$ reagents were well known for M = Si, Ge, Sn and Pb[13,14,15] whereas the $(CH_3)_3MLi$ reagents (except for Sn[16] and more recently Ge[17]) seemed far less attractive, for our purposes. Hence our general approach was to treat the $(C_6H_5)_3MLi$ reagent (in THF) with the fluoroarylmethyl bromide. This approach worked well for the Ge, Sn and Pb systems, and the required organometallics could be obtained in pure form. $(C_6H_5)_3SiLi$, on reaction with the bromide did form significant amounts of coupled product (which was difficult to remove) and we presumed electron transfer processes were competing with direct displacement. The $F\text{–}Aryl\text{–}CH_2M(C_6H_5)_3$ compounds are crystalline solids, and fortunately presented no solubility problems in dimethyl formamide (DMF). Details regarding the synthesis of organic bromide precursors, analytical, m.p. and PMR data, are located in the Experimental Section.

(*b*) ^{19}*F Chemical shift data*

The data for the metallomethyl substituted fluorobenzenes (DMF solvent) are assembled in Table 1.

The *ortho* compounds, although not directly connected with the theme of the present work were examined for two reasons. While recognising the possible complications of *ortho* effects on ^{19}F SCS values[12], we felt that the proximity of a polarised carbon–metal system could have dramatic effects. This effect, if significant, is overshadowed by a general deshielding mechanism for *ortho* groups, since the SCS values are uniformly smaller than for the *para* substituents. We were also interested in the possible detection of the four bond $M\text{–}^{19}F$ spin coupling ($M = {}^{199}Hg$, ^{207}Pb, ^{119}Sn) but none was observed under our conditions. In *o*-trifluoromethylphenylmercury systems, McFarlane[18] has recently provided evidence for a "through-space" contribution to $^{199}Hg\text{–}^{19}F$ coupling, occasioned by the abnormally small atomic separation, but the approach of fluorine to M in *o*-fluorobenzylmetallics is apparently inadequate.

For the *meta* and *para* compounds, the large difference in SCS values indicates

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* α or β refer to the disposition of fluorine, the numerals to the locations of CH_2M.

TABLE 1

^{19}F SUBSTITUENT CHEMICAL SHIFTS (SCS) OF METALLOMETHYL SUBSTITUTED FLUORO BENZENES[a]

Substituent	*ortho*	*meta*	*para*
$CH_2Si(C_6H_5)_3$	+4.30[b]	+1.12	+6.29
$CH_2Ge(C_6H_5)_3$	+2.85	+1.05	+6.20
$CH_2Sn(C_6H_5)_3$	+2.82	+0.83	+6.91
$CH_2Pb(C_6H_5)_3$	+2.98	+0.81	+6.44
CH_2HgCl	+2.77	+1.80[c]	+6.80[c]
$-CH_2Br$		−0.14	+0.38
CH_3	+4.75	+1.13	+5.45
$CH_2CH_2Si(CH_3)_3$			+5.23[d]
CH_2CH_3			+5.00

[a] Compared with fluorobenzene=0. [b] $(CH_3)_3Si$ derivative. [c] DMSO solvent. [d] +5.18 in benzene.

the donor effect of CH_2M substituents, and parallels the results reported previously for $-CH_2M(CH_3)_3$ substituents[10]. The above results serve as a basis for comparisons with the other ring systems (*vide infra*).

The result for the $-CH_2CH_2Si(CH_3)_3$ substituent does indicate that field effect is probably minor for $-CH_2Si(CH_3)_3$ and by implication for CH_2M groups presently under study. This is based on the very large attenuation (or fall-off) factor on going from $-CH_2Si(CH_3)_3$ (1.75) to $-CH_2CH_2Si(CH_3)_3$ ($\sim$0.2), relative to $-CH_3$ and $-CH_2CH_3$ respectively. Given that the field effect[19] is approximately proportional to $\cos\theta/R^2$, since θ will be very similar and small for both groups (in any case $\cos\theta$ is a slowly changing function when θ is small) and R will be increased only by the interposition of a CH_2 group, the dramatic fall-off in the effect is too large to be accommodated by the field effect, and points strongly to some conjugative mechanism. Basically the same conclusion has been reached by Hanstein, Berwin and Traylor[6] from considerations of σ^+ values of Ph_3PbCH_2- and $Ph_3PbCH_2CH_2-$ groups from charge transfer spectra.

TABLE 2

SCS VALUES OF METALLOMETHYL SUBSTITUTED FLUORONAPHTHALENES AND FLUOROBIPHENYLS[a].

Substituent	*Naphthalene*		*Biphenyl*[b]	
	4α[c]	6β	4,4′	4,3′
$CH_2Si(C_6H_5)_3$	4.09	1.91	+0.59	
$CH_2Ge(C_6H_5)_3$	4.03	1.86		
$CH_2Sn(C_6H_5)_3$	4.73	2.21	+0.66	+0.23
$CH_2Pb(C_6H_5)_3$	4.11	2.06	+0.66	+0.23
CH_2Br	−2.66	−1.00	−0.46	−0.46
CH_3	2.94	1.48	0.43	0.12

[a] Compared with fluoro-aromatic=0. [b] Fluoro at 4-position. [c] In 4α position, SCS of $-CH_2HgCl$=4.00. This compound was seriously contaminated with the coupled product from the Grignard reagent (see Experimental).

The chemical shift data for substituted fluoronaphthalenes and fluorobiphenyls are presented in Table 2.

Compared with the data for 4-benzyl systems in Table 1, it is clear that replacement of hydrogen in the 4α position of naphthalene by CH_2M leads to a comparable (but significantly reduced) positive shielding of the fluorine probe. The effect at 6β, and in 4,4′- and 4,3′-biphenyl systems is greatly reduced.

However, quantitative evaluation of these CH_2M substituent effects for the various ring systems and dispositions requires comparison with the corresponding methyl group SCS value, since these are quite dependent on ring system and disposition. Hence the effect of replacement of a benzyl-type hydrogen with a metal or metalloid is assessed by the difference: (^{19}F chemical shift of metallomethyl aromatic compound) − (^{19}F chemical shift of methyl aromatic compound).

These results are presented in Table 3.

TABLE 3

METALLO-SUBSTITUENT EFFECTS (CH_3=O)

Substituent	*4-Benzyl*	*Disposition naphthalene*		*Biphenyl*	
		4α	6β	4,4′	4,3′
$Si(C_6H_5)_3$	0.84	1.15	0.44	0.16	
$Ge(C_6H_5)_3$	0.75	1.09	0.38		
$Sn(C_6H_5)_3$	1.46	1.79	0.73	0.23	0.11
$Pb(C_6H_5)_3$	1.00	1.17	0.58	0.23	0.11
Br	−5.07	−5.6	−2.48	−0.89	−0.58

Qualitatively, the order of increasing shielding for all of the metalloids is 4α > 4-benzyl > 6β > 4,4′-biphenyl > 4,3′-biphenyl, while for Br (*i.e.* substituent CH_2Br) the order is 4,3′ > 4,4′ > 6β > 4-benzyl > 4α *i.e.* the reverse since compared with methyl, CH_2Br is an electron-withdrawing group.

THE THEORETICAL MODEL

Since available results[1,3,4] on the stereo-electronic dependence of CH_2M substituent effects pointed strongly to a predominantly σ–π conjugative mode of action, we decided to develop a conjugative theoretical model to explain the trends evident in Table 3*. Considering that the hyperconjugative effect is due to interaction of aryl ring MO's with the (polarised) C–M σ-bonding MO[7], an extreme approach would be to use $ArCH_2^-$ as the model, and obtain a measure of the transmission of mesomeric effects from CH_2(i) to positions (j) in the ring systems. The ^{19}F shift data

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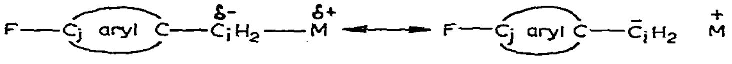
* Qualitative aspects of the σ–π conjugative model, and factors considered to be important have been summarised by Traylor and co-workers[1]. A quantitative approach to σ–π conjugation effects in allylmercury compounds has been reported by Bach and Scherr[2] employing extended Hückel MO calculations, and incorporating the mercury atom. In this connection, see however ref. 20, especially p. 442–443. Very recently, photo-electron spectroscopy results and CNDO/2 calculations have been interpreted in terms of σ–π conjugation in allyltrimethylsilane[43].

(F attached to C_j) are then taken as a quantitative reflection of the π-charge in the vicinity of the attached carbon (C_j), since ^{19}F shielding appears to be largely determined by C–F π-polarisation[12].



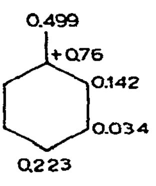
(I) (II)

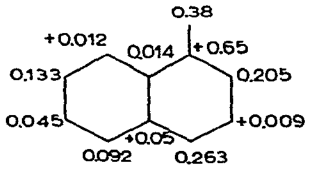
Although form (I) above is a more realistic description of the situation than (II) (II would be appropriate to cases where M was very electropositive, *e.g.* Na), calculations are far easier for arylmethyl carbanions ($ArCH_2^-$) and π-charge densities (I – atom charge) have been calculated on this basis. Application of these parameters to the situation implied by (I) is valid, granted the operation of a fractional charge (and fractional transmission factor) approach, since we are concerned with comparisons (for the same metalloid) for the different ring systems and dispositions. The basis of this approach has been set out by Dewar[7].

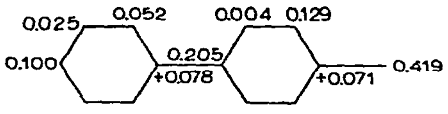
CALCULATION OF TRANSMISSION FACTORS (q_{ij}) FOR $ArCH_2^-$

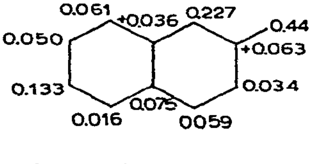
Some time ago Longuet-Higgins[11] demonstrated a very simple method for calculating π-charge densities in odd alternate hydrocarbon anions (or cations), based on the Hückel method.

However in view of the known deficiencies of the HMO method[20], and the problems in treating hydrocarbon ions, it was considered desirable to obtain π-charges (q_{ij}) by an SCFMO method. A program was already available[21] for such calculations for $ArCH_2^-$ systems in which the exocyclic C–C bond was assigned the fully conjugated benzene bond length of 1.39 Å. This procedure has had impressive success in correlating other spectral parameters[22,23] and details of the method can be found elsewhere[20,24]. For the biphenyl case, the molecular geometry was assumed to be planar, and the inter-annular bond was assigned a length of 1.39 Å. The data for q_{ij} are presented below.









Values of q_{ij} calculated by both methods are shown in Table 4, although the SCF values are employed in the analysis.

TABLE 4

COMPARISON OF MEASURES OF MESOMERIC TRANSMISSION FACTORS; q_{ij} AND ^{19}F CHEMICAL SHIFT DATA

Entry	*Method*	*Mesomeric transmission factor q_{ij} disposition*			
		4-benzyl	*4α*	*6β*	*4,4′ biphenyl*
1	HMO	0.143	0.200	0.058	0.032
2	SCFMO	0.223	0.263	0.133	0.100
	^{19}F data				
3 Metalloid =	Si	0.84	1.15	0.44	0.16
4	Ge	0.75	1.09	0.38	
5	Sn	1.46	1.79	0.73	0.23
6	Pb	1.00	1.17	0.58	0.23
7	CH_2Br	−5.07	−5.60	−2.48	−0.89

In Table 4 the values of q_{ij} for the various dispositions are presented, together with the corresponding ^{19}F SCS data, as detailed in Table 3.

It is apparent that the order of ^{19}F shieldings parallels the charge densities calculated by either approach (entries 1 and 2). *i.e.* for the metalloids 4α > 4-benzyl > 6β > 4,4′-biphenyl. The data for the metalloids are reproduced in Fig. 1 where q_{ij} (SCFMO values) is plotted against the corresponding value of Δ shown in Table 4. Δ = (^{19}F SCS of fluoroarylmetallomethyl compound − ^{19}F SCS of fluoroarylmethyl compound). The 6β- and 4α-naphthyl and 4-benzyl data are exceptionally well

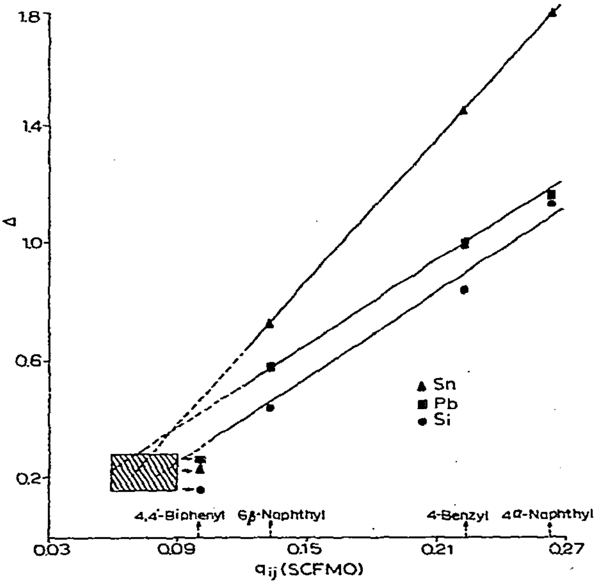


Fig. 1. Plot of Δ(= ^{19}F chemical shift of fluoroarylmetallomethyl compound − ^{19}F chemical shift of fluoroarylmethyl compound) against the mesomeric transmission factor or π-charge density (q_{ij}) at formally *para* positions in the indicated aryl systems. The data for the CH_2Ge substituent have not been plotted. The hatched area indicates a more reasonable value of q_{ij} for the 4,4′-biphenyl case (see Text).

correlated for Sn and Pb and tolerably well for Si and Ge. The data for the 4,4′ disposition in biphenyl are seen to deviate considerably from the correlation lines drawn in Fig. 1, and suggest that the value of q_{ij} for this system (0.100) is exalted. There are good reasons for this exaltation, to be found in the geometry assumed for the biphenyl system in the calculations. Firstly, the interannular bond length is known[25] to be 1.48 Å and this is accepted for $sp^2-sp^2\,\sigma$ bonds[25]. The value of 1.39 Å used in the program would overestimate interannular conjugation and hence q_{ij} at 4-position. Secondly the assumption of a planar biphenyl system (D_{2h}) is almost certainly wrong. Although biphenyl is planar in the solid[25], there is evidence that in solution and the gas phase, θ (angle of twist from planarity about C_1–$C_{1'}$ bond) may be as large as 43° [27,28]. Since the overlap integral S is proportional to $\cos\theta$,

$$S^- = S^{\circ} \cos\theta$$

and since the resonance integral β is approximately proportional to the overlap integral[5],

$$\beta^- = \beta^{\circ} \cos\theta$$

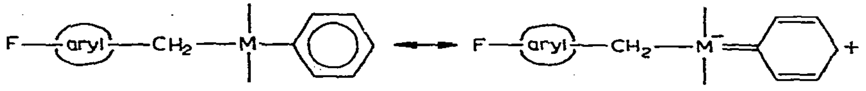
resonance interactions for $\theta = 43$ would be seriously reduced and hence the SCFMO value of $q_{ij} = 0.100$ at the 4′ position is certainly too large.

Comparison of theoretical and experimental data for the 4-benzyl, 4α- and 6β-naphthyl systems is on safer grounds since the imponderables associated with the biphenyl system are removed, and rigid π-systems are under scrutiny.

The results in Fig. 1 for these three dispositions demonstrate a truly impressive correlation between ^{19}F data and q_{ij} values derived for $ArCH_2^-$ and strongly suggest that the CH_2M substituents are in fact operating in a conjugative fashion. Reduction in q_{ij} for the 4-position in biphenyl to that represented by the hatched area in Fig. 1 shows that these data (for Si, Sn, Pb) could be equally well correlated, if more information on the biphenyl geometry were available, permitting a more realistic value of q_{ij}.

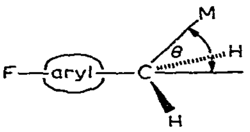
A somewhat surprising result is that on the basis of the present ^{19}F data, hyperconjugative electron-release from the C–Sn bond appears to be greater than that from the C–Pb bond. This is apparent either from Table 4, or from the slopes of the correlation lines in Fig. 1. Other data, derived from charge-transfer frequencies[1], and rates of carbonium ion formation[1] from hydride abstraction reactions of $(CH_3CH_2)_4$Sn and $(CH_3CH_2)_4$Pb, are consistent with the opposite order[29]. There seem to be at least two possible explanations of this difference, but it must be recognised that the difference between tin and lead, while real, is reproduced consistently for the 4-benzyl, 4α- and 6β-naphthyl systems (Table 4). Thus any explanation of this phenomenon cannot depend on orientation of substituent and fluorine-probe, but must be based on a real effect operative in the CH_2–$M(C_6H_5)_3$ part of the molecule.

Firstly, the resultant of the mesomeric (d_π–p_π) and inductive effects between tin and directly attached phenyl groups is known[10,30] to be greater than for lead *i.e.* in the sense of greater π-charge removed from the phenyl ring. This is indicated by the structures drawn below.



Hence in the compounds under study, tin is more effective in transferring π-charge from the attached aryl groups to the region of the CH_2–M bond, and thence to the fluoro-aryl ring system, leading to increased p-F shielding. In other words, the effective electropositivity of tin is increased relative to lead, and the CH_2–Sn bond is a more powerful σ–π electron-releasing group, Replacement of the three phenyl groups by methyl, for example, would greatly reduce or essentially completely remove this complication, but synthetic difficulties already alluded to, prevented this*.

The other possibility is that deviations from tetrahedral symmetry about the methylene carbon are more severe for tin than for lead, in the sense that θ (below) is greater in the tin compounds:



Since the σ–π interaction between the C–M bond and the fluoro-aryl system will be a function of sin θ[7], this interaction will be promoted in the tin compounds. However, C–Pb bond lengths are only about 0.1 Å greater than similar C–Sn bond lengths, and there seems to be no reason to believe that non-bonded effects are so different in the tin compounds that θ will be significantly different. It is worth noting, however, that in the solid-state structure of tetrabenzylzirconium[31], the average angle at the methylene carbon is unexpectedly small (92°) (*i.e.* corresponds to $180° - \theta$) leading to $\theta = 88°$. For tetrahedral symmetry, $\theta = 71°$. The significance of this result to benzylmetal compounds generally is unclear due to a general paucity of structural data**.

Given that either or both of the above effects are operative in the present series of compounds, it is clear that the magnitude of Δ for the metalloids (*i.e.* slopes of correlation lines) cannot be taken as a relative measure of the electron-releasing effect of these C–M bonds. However, for a particular metalloidal series (*e.g.* Sn) constancy in the degree of π-charge transfer from the attached phenyl groups (as well as a constant geometry about the metalloids and methylene centers) can be assumed, so that correlations with q_{ij} will be expected for a hyperconjugative interaction. This is what is observed.

Data for the CH_2Br group were also collected and are presented above. In Table 4, the effectiveness of this group as an electron-withdrawing group follows the sequence predicted for a conjugatively acting group. In Fig. 2 correlation of Δ (previously defined) and q_{ij} is impressive (given the vagaries of the biphenyl case) and

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* In this context, we have established[44] that the *para*-^{13}C chemical shift in benzyltrimethyllead is slightly to higher field than that in benzyltrimethyltin. The discussion above also applies to the silicon and germanium systems (See Table 3).

** However, significant differences in preferred crystal structures for the tetrabenzyls of Ti, Zr and Hf and Sn have been observed. *d*-Orbitals incorporated in the bonding schemes of the former metals have been suggested as partly responsible for the differences, but crystal packing effects also appear significant. In tetrabenzyltin, the angles at methylene carbons were normal (111°), and non-bonded effects appeared to be important in determining the preferred solid-state conformation. In this connection see the structure of tribenzyltinacetate[45].

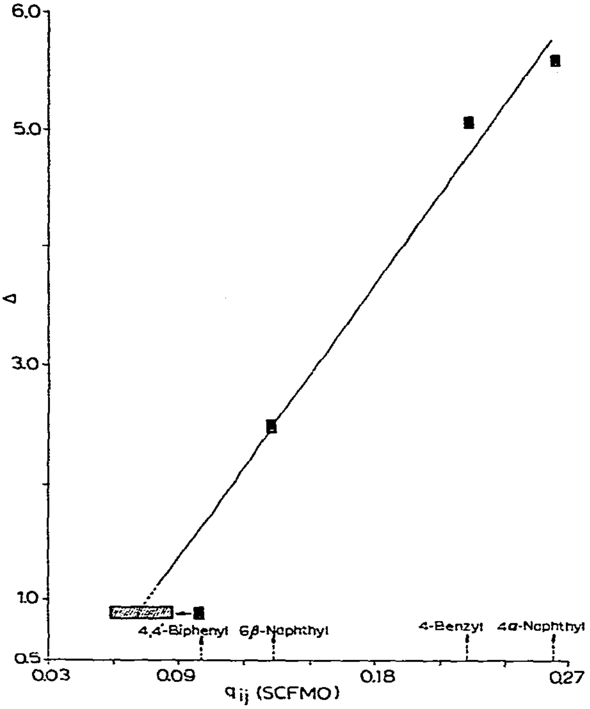


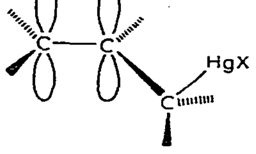
Fig. 2. Plot of $\Delta(={}^{19}F$ chemical shift of fluoroarylmethyl compound $-{}^{19}F$ chemical shift of bromofluoroarylmethyl compound) against the mesomeric transmission factor or π-charge density (q_{ij}) at formally *para* positions in the indicated aryl systems. The hatched area indicates a more reasonable value of q_{ij} for the 4,4'-biphenyl case (see Text).

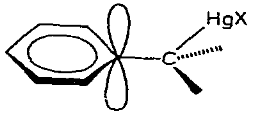
leads to the suggestion that CH_2Br acts predominantly by a hyperconjugative mechanism, and it would be most useful to know the preferred conformations of $ArCH_2Br$ systems *i.e.* whether C–Br σ-MO and ring π-MO's maximised their interaction. The correlation with the same q_{ij} values for both hyperconjugatively electron-withdrawing and -donating groups is to be expected, since only the sign of q_{ij} would be altered (to a first approximation) for $ArCH_2^-$ and $ArCH_2^+$ [11].

Very recently, McBee, Serfaty and Hodgins[32] disclosed detailed calculations and measurements on a series of side-chain halogenated toluenes, $ArCH_2X$, $ArCHX_2$ and $ArCX_3$ where Ar = phenyl and *meta*- and *para*-fluorophenyl. Employing Taft's σ_I/σ_R^0 analysis and CNDO/2 calculations, they concluded that a resonance interaction, hyperconjugative in nature, was operating between the halogenated methyl group, and the π-system, with π-charge transfer from the latter. In addition, there is a further piece of evidence[33], generally overlooked, that pertains to the ground state of benzyl chloride. The NQR frequency of ${}^{35}Cl$ in benzyl chloride (33.6 mc/sec) is actually lower than in methyl chloride (34.2 mc/sec), and is consistent with a hyperconjugative transfer of π-charge from the π-system to the C–Cl σ bond.

Examination of the data in Table 3 for the 4,4'- and 4,3'-biphenyl derivatives shows the substituent effect of $-CH_2M$ or $-CH_2Br$ to be much reduced (by a factor of ca. $\frac{1}{2}$) in the 4,3' orientation. This reduction seems too large for a field effect[12] (rotation around the inter-annular bond does not affect the situation) and supports the conclusion already arrived at from the data on the fluoro–phenethyl system (*vide supra*) that field effects are of minor importance.

In the case of CH_2M groups, there is direct physical evidence that the conformation maximising σ–π conjugation is predominant. Detailed vibrational spectral studies[34] of allyl- and benzylmercury systems, both in the solid and solution, indicate the predominance of the conformers, drawn below. These are indicated as favored structures by the calculations of Bach and Scherr[2].





The X-ray structure of tetrabenzylzirconium[31] reveals that the plane of the ring is essentially perpendicular to the C–C(H_2)–Zr plane analogous to the situation illustrated above for benzylmercuric halide. More structural data (particularly pertaining to solution) on benzyl- and allylmetallics will be required to gauge the general conformational control exercised by σ–π interactions*. There are several aspects of the interpretation of ^{19}F SCS data that require comment.

In our present treatment, we have neglected to allow for the mesomeric field effect on the ^{19}F shifts, although Dewar[35] has demonstrated that such allowance can be made and leads to an improved treatment and understanding of substituent effects on side chain reactions (FMMF treatment). In the present cases, it seems fairly certain that the mesomeric field effect would not grossly alter the picture, since in conjugated positions the π-charge at carbon directly attached to fluorine is so dominant. It is however, quite pronounced in unconjugated positions, where the charge at the carbon attached to fluorine is small or zero. These latter cases, however do not concern us here.

In addition mutual conjugation between substituent and fluorine probe has been ignored, although it is not clear that it would be significant anyway. Such resonance interactions would be most serious for 4-benzyl and 4α-naphthyl and certainly tiny in 6β-naphthyl. The experimental data show no wild deviations for these two dispositions, and we conclude that such effects are not operative to the extent that our basic conclusions are in jeopardy. It now seems indicated that geometrical distortions[35,36] of aromatic systems by substituents can produce a chemical shift, apart from any specific electronic effect. Statistical analysis of data for 6β substituted naphthalenes[35], shows that while the sensitivity of ^{19}F SCS is greatest in this disposition ($\rho = -30.6$!), the SCS attributable to geometrical distortion is zero. Since our data for the 6β series correlate well with the 4-benzyl and 4α-naphthyl data, where significant "residual" ^{19}F shifts are indicated[35], we conclude that such distortion effects are essentially constant in each of our dispositions, due to the very close structural similarity of the CH_2M substituents. A further conclusion from Dewar's work in this area[35] is that effects of substituents on ^{19}F shifts cannot be treated in

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* σ–π conjugative effects also appear to be important in alkyl radicals with β-Si, Ge, Sn and Br substituents. See for example ref. 46 and references therein. Also ref. 47.

the same fashion as substituent effects on other chemical properties. The Hammett equation seems to fail miserably in correlating ^{19}F SCS, yielding ρ values that not only depend on the aryl system and disposition, but are quite unreal chemically. This simply means that while both NMR and other measurements of substituent–substrate interactions, are separately useful, great caution needs to be exercised in correlations of results from the two approaches.

In summary we believe that the correlation between the theoretical conjugative model and the ^{19}F data is consistent with recent demonstrations of the stereo-electronic dependence of CH_2M substituent effects[1,3,4], and that such groups act hyperconjugatively when attached to aryl (and possibly other unsaturated) systems. Preliminary ^{13}C chemical shift data for systems of this type are consistent with the above conclusions, and will be reported soon[37].

EXPERIMENTAL

Synthesis of compounds

Benzyl compounds. The Ge, Sn, Pb and Hg compounds were synthesised by standard Grignard reactions, using the appropriate metal or organometal halide. These compounds were stable and crystalline with sharp melting points. The reaction of $(C_6H_5)_3SiCl$ with the Grignard reagents was very sluggish, even in boiling THF, and the reaction of $(C_6H_5)_3SiLi$ with *m*- and *p*-fluorobenzyl halides proved satisfactory. The synthesis of *o*-fluorobenzyltriphenylsilane, was difficult by either route, and eventually *o*-fluorobenzyltrimethylsilane was prepared.

The information regarding analysis, m.p.'s and PMR data is shown in Table 5.

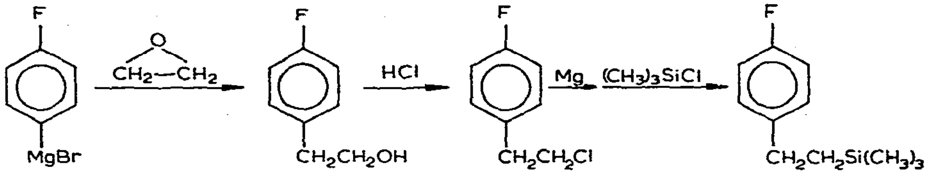
TABLE 5[a]

Formula *$FC_6H_4CH_2M$*	*Found*		*Calcd.*		*m.p. (°C)*	*PMR ($\delta(CH_2)$)*
	C	*H*	*C*	*H*		
ortho						
$M=Si(CH_3)_3$[b]	66.22	8.72	65.93	8.24	b.p. 93°/46 mm	2.05
$GePh_3$	72.16	5.17	72.70	5.09	71	2.9
$SnPh_3$	64.57	4.68	65.31	4.58	61.5	2.8 ($J=64$ Hz)
$PhPh_3$	54.83	3.97	54.84	3.84	49.5	3.23 ($J=72$ Hz)
HgCl	24.11	1.74	24.34	1.73	114	3.13 ($J=246$ Hz)
meta						
$M=SiPh_3$	81.29	6.05	81.30	5.69	87	2.8
$GePh_3$	72.55	5.21	72.70	5.09	94–95	3.0
$SnPh_3$	65.38	4.84	65.31	4.58	97–98	2.97 ($J=65$ Hz)
$PbPh_3$			Ref. 4			
HgCl			Ref. 3			
para						
$M=SiPh_3$	81.54	5.91	81.30	5.69	88.5	2.7
$GePh_3$	72.74	5.38	72.70	5.09	92–93	2.99
$SnPh_3$	64.08	4.69	65.31	4.58	89–90	2.8 ($J=66$ Hz)
$PbPh_3$			Ref. 4			
HgCl			Ref. 3			

[a] *J* values refer to M–^{1}H spin coupling. In the *o*-fluorobenzylmetallics $J(o\text{-}F\text{–}CH_2)=2.5$ Hz. [b] $\delta[(CH_3)_3Si]=0$.

Only the chemical shifts of the CH_2 protons are shown, since the aromatic proton resonances were unexceptional. All compounds integrated correctly in their PMR spectra for the assigned structures.

p-(β-Trimethylsilylethyl)fluorobenzene was prepared by the following sequence:



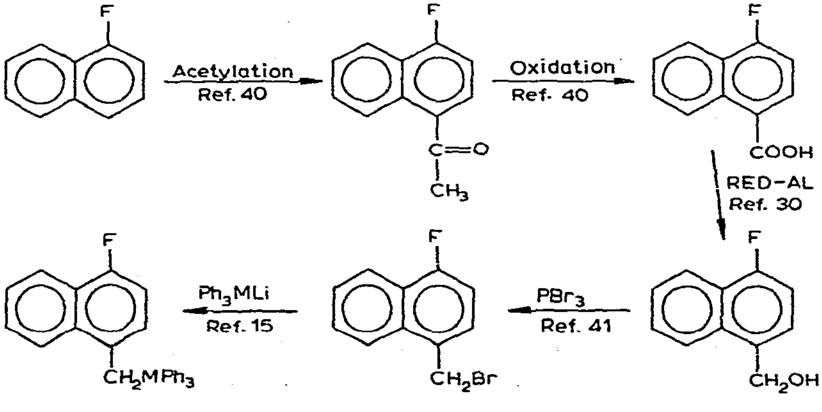
β-(*p*-Fluorophenyl)ethanol was based on the procedure described by Huston and Agett[38] for β-phenyl. The required compound distilled as a colorless liquid b.p. 110–120°/16 mm in 57% yield (mol. wt. found: 140. C_8H_9OF calcd.: 140). PMR: δ-$CDCl_3$ from TMS) 2.51 (1H singlet) OH; 2.8 (2H triplet) $ArCH_2$; 3.8 (2H, triplet) CH_2OH; 7.02 (4H, multiplet) aromatics.

This compound was converted to β-(*p*-fluorophenyl)ethyl chloride by the procedure of Norris and Taylor[39]. A colorless liquid distilling at 82–87°/16–18 mm in 75% yield was obtained (mol.wt. found: 160. C_8H_8FCl calcd.: 158.5). PMR: $\delta(CDCl_3)$ 3.01 (2H, triplet) $ArCH_2$; 3.68 (2H, triplet) CH_2Cl; 7.03 (4H, multiplet), aromatics.

p-(β-Trimethylsilylethyl)fluorobenzene. Trimethylsilyl chloride (5.45 g; 0.05 mole) was added slowly to the Grignard reagent prepared from the above chloride (4.75 g; 0.03 mole) and magnesium turnings (0.8 g; 0.033 mole) in dry THF (100 ml). After 7 h reflux, the reaction mixture was cooled, acidified with ammonium chloride solution, and worked up in the normal manner to yield the title compound as a colorless liquid (3.8 g, 65%) b.p. 99–101°/17 mm. (Found: C, 66.49; H, 8.91; *m/e* 197. $C_{11}H_{17}FSi$ calcd.: C, 67.30; H, 8.73%; mol.wt., 196.3.) PMR: $\delta(CDCl_3)$ 0.0 (9H singlet) $(CH_3)_3Si$, 0.82 (2H multiplet) CH_2Si; 2.57 (2H, multiplet) $ArCH_2$; 6.93 (4H, multiplet), aromatics: n_D^{20} 1.4745.

Fluoronaphthylmethyl metallics

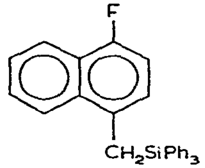
4α *Series.* The sequence shown below was employed in the synthesis of 1-



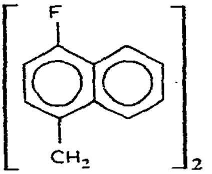
fluoro-4-bromomethylnaphthalene. This compound was converted into the required organometallics by reaction with the appropriate Ph_3MLi solution (THF)[15]. Work-up in the normal way, and recrystallisation from ethanol yielded the germanium, tin and lead compounds as nicely crystalline colorless compounds. The reaction of Ph_3SiLi with 1-fluoro-4-bromomethylnaphthalene was not straightforward, and yielded a mixture of (apparently) two compounds as judged by a duality in the CH_2 region of the PMR spectrum. Integration of this region against the aromatic region indicated the Ph_3Si derivative was one of these compounds. Recrystallisation from ethanol failed to effect separation and a sample of m.p. 118–124° was examined and the ^{19}F spectrum showed two signals, at +4.09 and +2.25 ppm (relative to α-fluoronaphthalene), the former signal being appropriate for a CH_2SiPh_3 substituent, by comparison with the shifts for the pure Ge, Sn and Pb compounds. The +2.25 ppm shift was in the range expected for an alkyl substituent. The impurity was suspected to be the coupled product, 1,2-bis(1-fluoro-4-naphthyl)ethane. Confirmation of this was effected as follows. In an attempted preparation of 1-fluoro-4-chloromercurimethylnaphthalene by a Grignard reaction, a considerable amount of by-product poorly soluble in ethanol was obtained. This was recrystallised from ethanol–acetone, m.p. 155–156° and analysed correctly for the coupled product. (Found: C, 82.88; H, 4.82. $C_{22}H_{16}F_2$ calcd.: C, 83.01; H, 5.03%.)

The PMR spectrum integrated correctly, with three sets of two-proton absorptions in the aromatic region at δ 7.1, 7.6 and 8.1 and CH_2 absorption at δ 3.45, exactly coincident with one of the resonances in the product mixture described above. The ^{19}F resonance of this pure compound was also coincident with one of the resonances in the ^{19}F spectrum of the mixture. Analysis of the mixture gave the following results.

Found for the mixture: C, 82.97; H, 5.63.



calcd.: C, 81.52; H, 5.71%;



calcd.: C, 83.01; H, 5.03%.

Consideration of these data must lead to the assignment of the other signal in the ^1H ($\delta=3.33$) and ^{19}F ($\delta=4.09$ ppm) spectra to the required silicon compound.

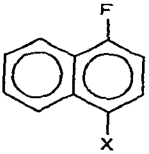
An attempt mentioned above to prepare the analogous mercury compound by a Grignard route was thwarted by the extensive formation of the coupled product. Direct examination of the mixture did yield a value of +4.00 ppm for the substituent chemical shift of 1-fluoro-4-chloromercurimethyl naphthalene, although this value is not employed in an analysis of the results.

The analytical and PMR data for the 4α series are assembled in Table 6.

6β-Naphthyl series. 2-Fluoro-6-methylnaphthalene was prepared as previously described[30].

2-Fluoro-6-bromomethyl naphthalene. A solution of 2-fluoro-6-methylnaphthalene (3.2 g, 0.02 moles) in carbon tetrachloride (75 mol) was heated under reflux with *N*-bromosuccinimide (3.9 g, 0.022 mole) for 24 h. The solution was filtered and solvent removed under reduced pressure to yield crude 2-fluoro-6-bromomethyl-

TABLE 6

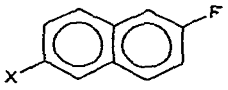


X	*Found*		*Calcd.*		*m.p. (°C)*	*PMR δ(CH₂)*
	C	*H*	*C*	*H*		
CH_2GePh_3	75.19	5.20	75.22	4.97	117–118	3.38
CH_2SnPh_3	68.26	4.76	68.37	4.51	92–93	3.35 ($J=64$ Hz)
CH_2PbPh_3	58.25	3.94	58.29	3.85	90–91	3.30 ($J=72$ Hz)
CH_2Br	55.67	3.64	54.81	3.34	66–67	4.92

naphthalene, which was crystallised from petroleum ether (b.p. 40–60°) in colorless needles (3.8 g, 80%) m.p. 52–52.5°. (Found: C, 55.42; H, 3.35, *m/e* 240. $C_{11}H_8FBr$ calcd.: C, 55.25; H, 3.37%; mol. wt., 239.) PMR ($CDCl_3$): δ 4.63 (2H) CH_2Br; aromatics (6H) centered δ 7.45.

Conversion to the organometallic derivatives was again effected by reaction with the appropriate $(C_6H_5)_3MLi$ solution in THF[15]. Work-up in the normal way and recrystallisation from n-hexane yielded crystalline compounds having the characteristics shown in Table 7.

TABLE 7



X	*Found*		*Calcd.*		*m.p. (°C)*	*δ(CH₂)*
	C	*H*	*C*	*H*		
CH_2SiPh_3	80.9	5.54	81.52	5.71	92–94.5	3.05
CH_2GePh_3	74.49	5.06	75.22	4.97	104.5–106	3.11
CH_2SnPh_3	68.51	4.44	68.37	4.51	88–89	3.08 ($J=66$ Hz)
CH_2PbPh_3	58.34	3.86	58.29	3.85	77–77.5	3.5 ($J=76$ Hz)

Some coupled product was again formed in the synthesis of the above silicon compound, and probably accounts for the broader melting point range. In the ^{19}F spectrum of the crude material, a resonance at +1.13 ppm (compared with 2-fluoronaphthalene) is assigned to this coupled product.

Biphenyl series

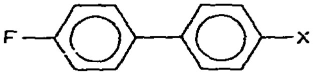
4,4′ Series. Reaction of *p*-fluorophenyl Grignard reagent with 4-methylcyclohexanone, followed by elimination of water and subsequent aromatisation with sulfur yielded 4-fluoro-4′-methylbiphenyl in good yield. Details of these reactions have been given previously[42].

Reaction of the title compound with *N*-bromosuccinimide in the manner outlined above effected conversion of CH_3 to CH_2Br in good yield. Recrystallisation from pentane yielded 4-fluoro-4'-bromomethylbiphenyl as lustrous colorless crystalline flakes m.p. 77–78°. (Found: C, 58.95; H, 3.90. $C_{13}H_{10}FBr$ calcd.: C, 58.86; H, 3.7%.) PMR: $\delta(CH_2)$ at 4.66, aromatics (complex) centered at δ 7.40.

Conversion of the above bromomethyl compound to the Sn and Pb compounds was straightforward with $(C_6H_5)_3MLi$. Again reaction of $(C_6H_5)_3SiLi$ led to a two components mixture, as judged by ^1H and ^{19}F spectra. Separation by recrystallisation was not successful, and again integration and chemical shift considerations for both spectra left no doubt that the contaminant was the coupled product. (In the ^1H spectrum, $\delta(CH_2)$ 3.0). (This is in line with behaviour for the 4α silicon compound, where the identity of the coupled product was established). Analysis of the mixture (m.p. broad about 140°) is shown below and is consistent with the presence of the required Si compound and coupled product. (Found for mixture: C, 81.61; H, 5.80. $C_{31}H_{25}SiF$ calcd.: C, 83.59; H, 5.61. $C_{26}H_{20}F_2$ (coupled product) calcd.: C, 84.32; H, 5.40%.) The CH_2 resonances of the Si compound and coupled product were nearly coincident with δ 3.0.

It is difficult to visualize any compound (other than the coupled product) having the analytical, and spectral properties found. The ^{19}F resonance assigned to the required Si compound is in the expected region, since data for the analogous pure Sn and Pb compounds were obtained (Table 8).

TABLE 8



X	*Found*		*Calcd.*		*m.p. (°C)*	*δ(CH₂)*
	C	*H*	*C*	*H*		
CH_2SnPh_3	70.19	4.90	69.53	4.67	118–119	3.08 (J=68 Hz)
CH_2PbPh_3	60.64	4.20	59.71	4.01	100–102	3.42 (J=75 Hz)

4,3' Series. Reaction of 4-fluorophenyl Grignard reagent with 3-methylcyclohexanone, followed by elimination of water and aromatisation in the reported manner, yielded 4-fluoro-3'-methylbiphenyl[42].

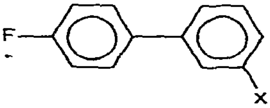
Reaction with *N*-bromosuccinimide (in the manner outlined for the 4,4' isomer) appeared complicated, and direct PMR examination revealed that the initially formed bromomethyl ($\delta(CH_2)$ 4.35) compound was reacting further at a surprisingly fast rate to yield the dibromomethyl compound (δ(CH) 6.51). Hence the required 4-fluoro-3'-bromomethylbiphenyl was formed in poor yield, and contaminated with the dibromomethyl and starting methyl compounds ($\delta(CH_3)$ 2.3).

The procedure then was to deliberately form the $CHBr_2$ compound, which was isolated in moderate yield, and which was hydrolysed to the aldehyde, and then oxidised to the acid[42]. This was reduced[30] with RED-AL to the alcohol, which was isolated as a crude material m.p. 39–41°, having the expected ^1H spectrum ($\delta(CH_2)$ 4.7, aromatics centered at δ 7.2).

This material was converted to the bromomethyl compound (with PBr_3)[41] which was fully characterised. The compound crystallised from pentane as lustrous flakes, m.p. 62°. (Found: C, 59.36; H, 3.94. $C_{13}H_{10}FBr$ calcd.: C, 58.86, H, 3.7%.) $\delta(CH_2)$ 4.56, aromatics (complex) centered δ 7.4.

The reaction of the above bromomethyl compound with Ph_3SnLi and Ph_3PbLi proceeded smoothly and the products had the characteristics shown in Table 9.

TABLE 9



X	*Found*		*Calcd.*		*m.p. (°C)*	*δ(CH₂)*
	C	*H*	*C*	*H*		
CH_2SnPh_3	69.32	4.93	69.53	4.67	68–69	3.05 (J=64 Hz)
CH_2PbPh_3	59.15	4.17	59.71	4.01	79–79.5	3.5 (J=74 Hz)

^1H NMR spectra were recorded (for $CDCl_3$ solutions) at 60 MHz (Varian A60) or 100 MHz (Jeolco-Minimar). ^{19}F spectra were recorded at 56.4 MHz (Varian DP60) for DMF solutions, and spectra were calibrated using a "Racal" SA535 universal counter-timer. All the ^{19}F spectra were obtained for 15% (w/w) solutions containing 5% (w/w) of 1,1,2,2′-tetrachloro-3,3,4,4-tetrafluorocyclobutane as internal calibrant.

All ^1H spectra integrated for the assigned structures.

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REFERENCES

1 T. G. Traylor, W. Hanstein, H. G. Berwin, N. A. Clinton and R. S. Brown, *J. Amer. Chem. Soc.*, 93 (1971) 5715, and references therein. J. M. Jerkunica and T. G. Traylor, *J. Amer. Chem. Soc.*, 93 (1971) 6278 and references therein.
2 R. D. Bach and P. A. Scherr, *J. Amer. Chem. Soc.*, 94 (1972) 220, and references therein.
3 W. Adcock, S. Q. A. Rizvi and W. Kitching, *J. Amer. Chem. Soc.*, 94 (1972) 3657.
4 W. Hanstein, H. F. Berwin and T. G. Traylor, *J. Amer. Chem. Soc.*, 92 (1970) 7476. See also C. G. Pitt, *J. Organometal. Chem.*, 23 (1970) 35.
5 R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.*, 63 (1941) 41.
6 See, for example refs. 1 and 2 and also W. Hanstein, H. J. Berwin and T. G. Traylor, *J. Amer. Chem. Soc.*, 92 (1970) 829.
7 M. J. S. Dewar, *Hyperconjugation*, The Ronald Press Company, New York (1962).
8 W. Adcock, B. F. Hegarty, W. Kitching and A. J. Smith, *J. Organometal. Chem.*, 12 (1968) 21.
9 W. Kitching, W. Adcock and B. F. Hegarty, *Aust. J. Chem.*, 21 (1968) 2411.

10 A. J. Smith, W. Adcock and W. Kitching, *J. Amer. Chem. Soc.*, 92 (1970) 6140.
11 H. C. Longuet-Higgins, *J. Chem. Phys.*, 18 (1950) 265.
12 See, for example, M. J. S. Dewar and T. G. Squires, *J. Amer. Chem. Soc.*, 90 (1968) 210; G. L. Anderson and L. M. Stock, *J. Amer. Chem. Soc.*, 90 (1968) 212; 91 (1969) 6804. M. J. S. Dewar and J. Keleman, *J. Chem. Phys.*, 49 (1968) 499.
13 H. Gilman, D. J. Peterson and D. Wittenberg, *Chem. and Ind.*, 8 (1958) 1479.
14 H. Gilman and C. W. Gerow, *J. Amer. Chem. Soc.*, 78 (1956) 5435.
15 C. Tamborski, E. F. Ford and E. J. Soloski, *J. Org. Chem.*, 28 (1963) 181.
16 C. Tamborski, E. F. Ford and E. J. Soloski, *J. Org. Chem.*, 28 (1963) 237.
17 E. J. Bulten and J. G. Noltes, *J. Organometal. Chem.*, 29 (1971) 397.
18 W. McFarlane, *Chem. Commun.*, (1971) 609.
19 M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, 84 (1962) 3548, and subsequent papers.
20 M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill Book Co., New York, 1969.
21 Program of T. Peacock and G. Feeman of Department of Chemistry, University of Queensland.
22 T. E. Peacock and P. T. Wilkinson, *Proc. Phys. Soc.*, 83 (1964) 525.
23 L. J. Johnston and T. E. Peacock, *Mol. Phys.*, 20 (1971) 849.
24 T. E. Peacock, *Electronic Properties of Aromatic and Heterocyclic Molecules*, Academic Press, New York, 1965.
25 J. Dahr, *Indian J. Phys.*, 7 (1932) 42; *Proc. Natl. Inst. Sci. India*, 15 (1949) 11.
26 M. J. S. Dewar and H. N. Schmersing, *Tetrahedron*, 11 (1960) 96. C. A. Coulson, *Chem. Soc. Spec. Publ.*, 12 (1958) 89ff.
27 H. Suzuki, *Bull. Chem. Soc. Japan*, 32 (1959) 1340.
28 See, for a discussion, H. H. Jaffe and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, John Wiley, New York, 1962. Especially p. 389–407.
29 See also C. Eaborn, *J. Chem. Soc.*, (1956) 4858, R. W. Bott, C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.*, 2 (1964) 154.
H. Bock and H. Alt, *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 942.
H. Bock, H. Alt and H. Seidl, *J. Amer. Chem. Soc.*, 91 (1969) 355.
30 W. Adcock, S. Q. A. Rizvi, W. Kitching and A. J. Smith, *J. Amer. Chem. Soc.*, 94 (1972) 369.
31 G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn and A. J. P. Pioli, *Chem. Commun.*, (1971) 677.
32 E. T. McBee, I. Serfaty and T. Hodgins, *J. Amer. Chem. Soc.*, 93 (1971) 5711.
33 See ref. 7 p. 79–86.
34 J. Mink and Yu. A. Pentin, *J. Organometal. Chem.*, 23 (1970) 293.
35 M. J. S. Dewar, R. Golden and J. M. Harris, *J. Amer. Chem. Soc.*, 93 (1971) 4187.
36 W. Adcock, J. Alste and A. Zeb, to be published.
37 D. Doddrell, W. Kitching and W. Adcock, to be published.
38 R. C. Huston and A. H. Agett, *J. Org. Chem.*, 6 (1941) 123.
39 J. F. Norris and H. B. Taylor, *J. Amer. Chem. Soc.*, 46 (1924) 753.
40 T. L. Jacobs, S. Winstein, J. W. Rallo and J. H. Robson, *J. Org. Chem.*, 11 (1946) 27.
41 R. L. Gay and C. R. Hauser, *J. Amer. Chem. Soc.*, 89 (1967) 2297.
42 M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, 88 (1966) 3318.
43 U. Weidner and A. Schweig, *Angew. Chem. Intern. Ed. Engl.*, 11 (1972) 146.
44 D. Doddrell, B. D. Gupta, W. Kitching and W. Adcock, to be published.
45 N. W. Alcock and R. E. Timms, *J. Chem. Soc. C*, (1968) 1873.
46 T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 94 (1972) 648.
47 A. R. Lyons and M. C. R. Symons, *Chem. Commun.*, (1971) 1086.