Metalloidalmethyl Substituent Effects by ^{13}C and ^{19}F NMR : Electron

Release in the Neutral Ground State.

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Summary

^{13}C and ^{19}F chemical shift studies of a series of $CH_2M(CH_3)_3$ and

$CH_2M(C_6H_5)_3$ (M = Si, Ge, Sn, Pb) - substituted aryl derivatives (phenyl;

1-naphthyl; 2-naphthyl) have established unambiguously that the order of

hyperconjugative electron release in the neutral ground state is

Pb~Sn>Ge~Si.   This order is clearly at variance with the commonly

accepted order (Pb>Sn>Ge>Si) based on studies of electron deficient

substrates.   The phenomenon is discussed in terms of current theories

on σ-π interactions.   In addition, substituent parameters (σ_I and σ_R^o)

for the $Pb(CH_3)_3$ group have been derived utilizing new data from the

fluorophenyl tag.   These new constants are compared with those previously

reported.

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Introduction

Although experimental evidence regarding the hyperconjugative

(σ-π) nature of electron donation by $CH_2M(CH_3)_3$ or $CH_2M(C_6H_5)_3$ (M = Si,

Ge, Sn, Pb) in the neutral ground state of aromatic systems is now quite

definitive,[1-8] a discrepancy exists concerning the order of electron

release.   Some time ago we reported[3] that, as judged by a ^{19}F substituent

chemical shift (SCS)* study of a series of triphenylmetalloidalmethyl-

substituted fluoroaryl derivatives ($FArCH_2M(C_6H_5)_3$; M = Si, Ge, Sn, Pb;

Ar = phenyl; 1-naphthyl; 2-naphthyl), hyperconjugative electron release

from the C-Sn bond appears to be slightly greater than that from the

C-Pb bond i.e. Sn>Pb>>Ge~Si.   This order is clearly at variance with

the commonly accepted order (Pb>Sn>Ge>Si)[+] which has been unambiguously

defined from studies of model systems where the C-M bond interacts with

an adjacent electron-deficient substrate.[9-11]   At the time, we viewed

the result as not being a manifestation of the general intrinsic electron-

donating capabilities of the various C-M bonds in the neutral ground state

and, thus, we put forward two very tentative explanations based on the

likelihood of varying electronic and symmetry factors at the metal and

carbon centres respectively due to the metalloidal-attached phenyl groups.

More recently, we reported[6] that a ^{13}C chemical shift study of a

series of benzyltrimethylmetalloidal derivatives ($PhCH_2M(CH_3)_3$;

M = Si, Ge, Sn, Pb) indicates a more "normal" order of electron release

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* [19]F substituent chemical shifts (SCS) are defined as the difference

between the chemical shift of the unsubstituted fluoroaromatic and the

substituted fluoroaromatic compound.

+ σ^+ values are as follows (10): $CH_2Si(CH_3)_3$, -0.62;

$CH_2Sn(CH_3)_3$, -0.92; CH_2SiPh_3, -0.4; CH_2GePh_3, -0.6; CH_2SnPh_3, -0.75;

CH_2PbPh_3, -1.0.

(Pb>Sn>Ge>Si) in the neutral ground state. However, because the ^{13}C

nmr spectra were obtained at 15.086 MHz in the CW mode[12] at concentration

levels now known to be unacceptable for measuring ^{13}C chemical shifts

accurately in substituent effect studies,[13] these results must now be

considered suspect.

Herein we report further studies which we deemed essential in order

to unambiguously define the order of hyperconjugative electron release in

the neutral ground state from C-M bonds (M = Si, Ge, Sn, Pb) to an

adjacent aromatic substrate. Firstly, we have re-synthesized the

benzyltrimethylmetalloidal derivatives (I-IV) and re-measured their proton-

decoupled ^{13}C nmr spectra in dilute solutions. Secondly, we have

synthesized 1- and 2-naphthylmethyltrimethylplumbane (VI and VIII respectively)

and measured their proton-decoupled ^{13}C nmr spectra for comparison with the

recently reported[7] data for the corresponding 1- and 2-naphthylmethyltrimethyl-

stannes (V and VII respectively). Thirdly, we have synthesized a series

of $CH_2M(CH_3)_3$-substituted fluoronaphthalene derivatives in the formally

conjugated 4α (IX-XII) and 6β (XIII-XVI) dispositions* and measured their

^{19}F nmr spectra. A similar investigation of these substituents was also

carried out in the formally unconjugated 7β disposition (XVII-XX) together

with the corresponding $CH_2M(C_6H_5)_3$ groups (XXI-XXIV) which were previously[3]

examined in the 4α and 6β dispositions. The 7β disposition was investigated

since recent studies[14,15] have disclosed that ^{19}F SCS data from this

disposition, coupled with the corresponding data in the 6β disposition, can

be usefully employed for dissecting electronic effects by substituting

in the appropriate dual substituent parameter (DSP) correlative equations

and solving them. This method for computing substituent parameters

circumvents certain factors (substituent-induced structural effects,

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* The Greek letter indicates the position of the fluorine atom, the numeral
that of the other substituents.

through-space and through-bond substituent-probe interactions, and

σ- and π-electron effects)which can bedevil the fluorophenyl tag used

in the Taft approach.[16]

Finally, we have synthesized meta- and para-benzyltrimethylplumbane

(XXV and XXVI respectively) in order to complement the previously

published[17] results for this system.   In addition, although somewhat

unrelated to the problem at hand, we have synthesized and properly

characterized meta- and para-fluorophenyltrimethylplumbane. .Their

^{19}F nmr spectra have been recorded to check data previously obtained[17]

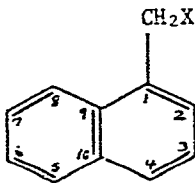from incompletely characterized samples.
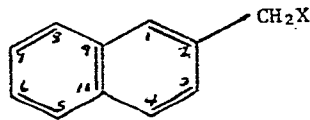

(I)   X = Si(CH$_3$)$_3$ (V)   X = Sn(CH$_3$)$_3$ (VII)   X = Sn(CH$_3$)$_3$

(II)   X = Ge(CH$_3$)$_3$ (VI)   X = Pb(CH$_3$)$_3$ (VIII)   X = Pb(CH$_3$)$_3$
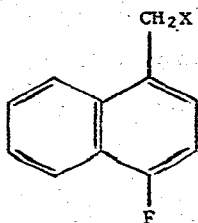
(III) X = Sn(CH$_3$)$_3$

(IV)   X = Pb(CH$_3$)$_3$

Experimental

Synthesis of compounds.

The benzyltrimethylmetalloidal   derivatives were prepared as

previously indicated[6] while the 6β- series of CH$_2$M(C$_6$H$_5$)$_3$-substituted

3-fluoronaphthalenes were available from a previous study.[3]

1-Bromomethyl-4-fluoronaphthalene was prepared as previously described.[3]

2-Fluoro-6-methylnaphthalene and 2-fluoro-7-methylnaphthalene, which

were previously obtained in limited amounts by rather tedious procedures[18],

CH₂X structures:

(IX)   X = Si(CH₃)₃   (XIII)   X = Si(CH₃)₃   (XVII)   X = Si(CH₃)₃
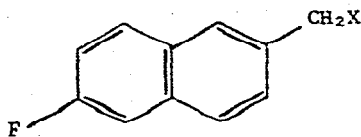
(X)   X = Ge(CH₃)₃   (XIV)   X = Ge(CH₃)₃   (XVIII)   X = Ge(CH₃)₃
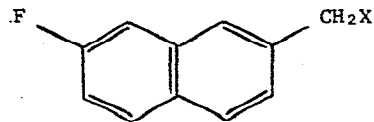
(XI)   X = Sn(CH₃)₃   (XV)   X = Sn(CH₃)₃   (XIX)   X = Sn(CH₃)₃

(XII) X = Pb(CH₃)₃   (XVI)   X = Pb(CH₃)₃   (XX)   X = Pb(CH₃)₃

(XXI)   X = Si(C₆H₅)₃

(XXII)   X = Ge(C₆H₅)₃

(XXIII)   X = Sn(C₆H₅)₃

(XXIV)   X = Pb(C₆H₅)₃

CH₂Pb(CH₃)₃   XXV
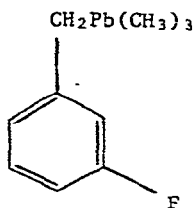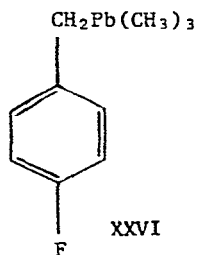
CH₂Pb(CH₃)₃   XXVI

were readily prepared in good yields (~80%) from p-fluorobenzylmagnesium chloride and m-fluorobenzylmagnesium chloride respectively according to the procedure outlined by Ulolinska-Mocydlavz et al[19] for the synthesis of 2,7-dimethylnaphthalene with some minor modications.   Whereas the hydroxy-acetal derivative from p-fluorobenzylmagnesium chloride and 4,4-dimethoxy-butan-2-one was cyclized to 2-fluoro-7-methynaphthalene by heating on a steam bath for 2 hours in glacial acetic acid and aqueous hydrogen bromide[19], the corresponding hydroxy-acetal from m-fluorobenzyl-magnesium chloride was cyclized to 2-fluoro-6-methylnaphthalene by heating in 10% aqueous sulphuric acid at reflux for 2 days[20].   The methyl compounds were then converted to the appropriate bromomethyl derivatives[3,18] by a standard procedure using N-bromosuccinimide[3,21].

2-Deuterio-6-methylnaphthalene 2-Chloro-6-methylnaphthalene was prepared

from p-chlorobenzylmagnesium chloride and 4,4-dimethoxy-butan-2-one by a similar procedure to that outlined above for 2-fluoro-6-methylnaphthalene. Sublimation followed by recrystallization from hexane afforded white plates, m.p. 128-130°. PMR : δ 2.45 (3H, singlet, CH_3) and δ 7.1-7.8 (6H, multiplet, aromatics); m/e 176.45.

To magnesium turnings (1.2g; 0.05g atm) in di-n-butylether (10 ml) at reflux under nitrogen was added rapidly a solution of 2-chloro-6-methyl-naphthalene (5.2g; 0.029 mol) in di-n-butylether (20 ml)/tetrahydrofuran (10 ml). The mixture was heated at reflux until all the 2-chloro-6-methylnaphthalene was consumed as indicated by g.l.p.c. After cooling, the mixture was quenched with deuterium oxide (2 ml) and then worked up in the standard manner. The crude product was distilled under vacuum (60°/0.1 mm Hz) to afford 2-deuterio-6-methylnaphthalene (2.9g; 70% yield), m.p. 33-35°. PMR : δ 2.39 (3H, singlet, CH_3) and δ 7.0-7.8 (multiplet, aromatics). Deuterium incorporation was approximately 40% on the basis of PMR and mass spectrometry.

Method A: General *in situ* Grignard procedure[22] for trimethyl- and triphenyl-metalloidalmethyl substituted fluoronaphthalenes.

To magnesium turnings (0.36g; 0.015 atom) in dry ether (10 ml) in a 100 ml three-necked flask equipped with condenser, pressure-equalising dropping funnel, magnetic stirring-bar and nitrogen inlet was added a crystal of iodine followed by the dropwise addition of a solution of 1,2-dibromoethane (0.1 ml) and dry ether (5 ml). After the evolution of ethylene had ceased, the appropriate quantity of $(CH_3)_3MX$ or $(C_6H_5)_3MX$ (0.025 mol) was added followed by the dropwise addition of a solution of the bromomethylfluoronaphthalene (3g; 0.0125 mol) in ether (20 ml) at a rate sufficient to maintain gentle reflux. After the addition was complete, the reaction mixture was heated at reflux for 30 minutes before workup in the usual way. The compounds were generally purified by Kugelrohr

distillation (Büchi GKR 500) and then recrystallization where appropriate.
Yields varied from 70-90%. Purity was checked by g.l.p.c. and all PMR
spectra were in accord with the assigned structures.

4-Fluoro-1-naphthylmethyltrimethylsilane (IX) Method A.

B.p. 80°C/0.1 mm Hg n_D^{22} 1.5592. PMR (CDCl$_3$, from (CH$_3$)$_3$Si at δ 0.00):
2.50 (2H, singlet, CH$_2$) and 6.9-8.2 (6H, multiplet, aromatics); m/e 232.38.
Anal. Found: C, 72.69; H, 7.30. C$_{14}$H$_{17}$FSi calcd: C, 72.36; H, 7.37%.

4-Fluoro-1-naphthylmethyltrimethylgermane (X) Method A.

B.p. 80°C/0.1 mm Hz. n_D^{21} 1.5745. PMR (CDCl$_3$, from (CH$_3$)$_3$Ge at δ 0.00):
2.55 (2H, singlet, CH$_2$) and 6.8-8.2 (6H, multiplet, aromatics); m/e 276.88.
Anal. Found: C, 60.90; H, 6.20. C$_{14}$H$_{17}$FGe calcd: C, 60.73; H, 6.19%.

4-Fluoro-1-naphthylmethytrimethylstannane (XI) Method A.

B.p. 80°C/0.1 mm Hg. n_D^{23} 1.5992. PMR (CDCl$_3$, from (CH$_3$)$_3$ Sn at δ 0.00;
J(Sn-CH$_3$)52 Hz): 2.73(2H, singlet, CH$_2$) and 6.9-8.2 (6H, multiplet,
aromatics); m/e 322.98. Anal. Found: C, 52.29; H. 5.27. C$_{14}$H$_{17}$FSn calcd:
C, 52.06; H, 5.31.

4-Fluoro-1-naphthylmethyltrimethylplumbane (XII) Method A.

A sample for analysis was not obtained due to the lability of the compound
towards heat and oxygen. The crude material was stored under a nitrogen
atmosphere. PMR (CDCl$_3$, from (CH$_3$)$_4$Si at δ 0.00): 0.55 (9H, singlet,
(CH$_3$)$_3$Pb; J(Pb-CH$_3$) 56Hz), 2.31 (2H, singlet, CH$_2$) and 6.8-8.1
(6H, multiplet, aromatics).

6-Fluoro-2-naphthylmethyltrimethylsilane (XIII) Method A.

M.p. 51-53°C. PMR (CDCl$_3$, from (CH$_3$)$_3$Si at δ 0.00): 2.19 (2H, singlet, CH$_2$)
and 6.95-7.7 (6H, multiplet, aromatics); m/e 232.38. Anal. Found:
C, 72.71; H, 7.34. C$_{14}$H$_{17}$FSi calcd: C, 72.36; H, 7.37%.

6-Fluoro-2-naphthylmethyltrimethylgermane (XIV) Method A.

M.p. 49-51°C. PMR (CDCl$_3$, from (CH$_3$)$_3$Ge at δ 0.00): 2.22 (2H, singlet, CH$_2$)
and 6.9-7.7 (6H, multiplet, aromatics); m/e 276.88. Anal. Found:

C, 60.52; H, 6.07. $C_{14}H_{17}FGe$ calcd: C, 60.73; H, 6.19%.

6-Fluoro-2-naphthylmethyltrimethylstannane (XV) · Method A.

M.p. 44-46°C. PMR ($CDCl_3$, from $(CH_3)_3Sn$ at δ 0.00; J(Sn-CH$_3$) 52 Hz):
2.40 (2H, singlet, CH_2) and 7.0-7.7 (6H, multiplet, aromatics); m/e 322.98.
Anal. Found: C, 52.28; H, 5.30. $C_{14}H_{17}FSn$ calcd:C, 52.06; H, 5.31%.

6-Fluoro-2-naphthylmethyltrimethylplumbane (XVI) Method A.

Similar problems were encountered with this compound as described
above for the corresponding 4α isomer. PMR ($CDCl_3$, from $(CH_3)_4Si$ at
δ 0.00): 0.55 (9H, singlet, $(CH_3)_3Pb$; J(Pb-CH$_3$) 56 Hz), 2.95 (2H,
singlet, CH_2) and 6.8-7.7 (6H, multiplet, aromatics).

7-Fluoro-2-naphthylmethyltrimethylsilane (XVII) Method A.

M.p. 41-42°C. PMR ($CDCl_3$, from $(CH_3)_3Si$ at δ 0.00): 2.14 (2H, singlet,
CH_2) and 6.85-7.7 (6H, multiplet, aromatics); m/e 232.38. Anal. Found:
C, 72.72; H, 7.26. $C_{14}H_{17}FSi$ calcd: C, 72.36; H, 7.37%.

7-Fluoro-2-naphthylmethyltrimethylgermane (XVIII) Method A.

M.p. 38-40°C. PMR ($CDCl_3$, from $(CH_3)_3Ge$ at δ 0.00): 2.23 (2H, singlet, CH_2)
and 6.85-7.7 (6H, multiplet, aromatics); m/e 276.88. Anal. Found: C, 60.55;
H, 6.06. $C_{14}H_{17}FGe$ calcd: C, 60.73; H, 6.19%.

7-Fluoro-2-naphthylmethyltrimethylstannane (XIX) Method A.

M.p. 43-44°C. PMR ($CDCl_3$, from $(CH_3)_3Sn$ at δ 0.00; J(Sn-CH$_3$) 52Hz);
2.40 (2H, singlet, CH_2) and 6.9-7.7 (6H, multiplet, aromatics); m/e 322.98.
Anal. Found: C, 51.82; H, 5.15. $C_{14}H_{17}FSn$ calcd.: C, 52.06; H,5.31%.

7-Fluoro-2-naphthylmethyltrimethylplumbane (XX) Method A.

Similar problems were encountered with this compound as described above
for the corresponding 4α isomer. PMR ($CDCl_3$, from $(CH_3)_4Si$ at δ 0.00):
0.57 (9H, singlet,, $(CH_3)_3Pb$; J(Pb-CH$_3$) 56Hz), 2.92 (2H, singlet, CH_2) and
6.8-7.3 (6H, multiplet, aromatics).

7-Fluoro-2-naphthylmethyltriphenylsilane (XXI) Method A.

M.p. 114-115°C. PMR ($CDCl_3$, from $(CH_3)_4Si$ at δ 0.00): 3.00 (2H, singlet,

CH$_2$) and 7.33 (21H, multiplet, aromatics); m/e 418.59. Anal. Found: C, 83.08;

H, 5.66. C$_{29}$H$_{23}$FSi calcd.: C, 83.21; H, 5.54%.

7-Fluoro-2-naphthylmethyltriphenylgermane (XXII) Method A.

M.p. 103-106°C. PMR (CDCl$_3$, from (CH$_3$)$_4$Si at δ 0.00): 3.07 (2H, singlet,

CH$_2$) and 7.25 (21H, multiplet, aromatics); m/e 463.10. Anal. Found:

C, 75.26; H, 5.10. C$_{29}$H$_{23}$FGe calcd.: C, 75.22; H, 5.01%.

7-Fluoro-2-naphthylmethyltriphenylstannane (XXIII) Method A.

M.p. 93.5-94.5°C. PMR (CDCl$_3$, from (CH$_3$)$_4$Si at δ 0.00): 3.00 (2H, singlet,

CH$_2$) and 7.08 (21H, multiplet, aromatics); m/e 509.20. Anal. Found: C, 68.51;

H, 4.71. C$_{29}$H$_{23}$FSn calcd.: C, 68.41; H, 4.55%.

7-Fluoro-2-naphthylmethyltriphenylplumbane (XXIV) Method A.

M.p. 81-83°C. PMR (CDCl$_3$, from (CH$_3$)$_4$Si at δ 0.00): 3.46 (2H, singlet, CH$_2$)

and 7.25 (21H, multiplet, aromatics); m/e 597.70. Anal. Found: C, 58.50;

H, 3.82. C$_{29}$H$_{23}$FPb calcd.: C, 58.28; H, 3.88%.

Method B: General procedure for trimethylplumbylmethyl substituted

naphthalenes.

1 or 2-Naphthylmethylpotassium was prepared by Schlosser and Hartmann's

procedure[23] as follows:

A dry hexane solution (10 ml) of 1 or 2-methylnaphthalene (1.42g; 0.01 mol)

and potassium tert-butoxide (twice sublimed; 1.12g; 0.01 mol) contained

under nitrogen in a 100 ml centrifuge tube was treated dropwise with

n-butyllithium (6.25 ml; 1.6M in hexane; 0.01 mol) with stirring and

allowed to stir for 10 minutes. The reaction mixture was then centrifuged

at 2,200 r.p.m. for 5 minutes to precipitate the potassium salt. The

supernatant was removed through a stainless steel tube under nitrogen

pressure before fresh dry hexane (25 ml) was added and the potassium salt

resuspended with vigorous stirring. The suspension was centrifuged again

and the washing process repeated once more. Dry ether (25 ml) was added and

the potassium salt resuspended with vigorous stirring. The suspension was

centrifuged again and the washing process repeated once more. Dry ether

(25 ml) was then added to the potassium salt followed by trimethyllead chloride

(2.78g; 0.01 mol) under a stream of nitrogen and the mixture allowed to stir

for 10 minutes. The ether solution was washed with water (2 x 10 ml) and

dried over anhydrous $MgSO_4$ before the solvent was removed under reduced

pressure. The crude material was twice distilled under high vacuum to

yield a pale yellow oil (1.67g; 42% yield). Appropriate handling and

storage procedures were taken as these compounds were sensitive to air,

moisture, and light.

<u>1-Naphthylmethyltrimethylplumbane</u> (VI) Method B.

B.p. 80°C/0.01 mm Hg.; n_D^{22} 1.6617. PMR ($CDCl_3$, from $(CH_3)_4Si$ at δ 0.00):

0.58 (9H, singlet, $(CH_3)_3Pb$; J(Pb-CH_3) 56 Hz), 2.38 (2H, singlet, CH_2;

J(Pb-CH_3) 63 Hz) and 6.8-7.7 (7H, multiplet, aromatics). Anal. Found:

C, 42.76; H, 4.59. $C_{14}H_{18}Pb$ calcd.: C, 42.73; H, 4.61%. The 4-deuterio

analogue was obtained similarly from 1-deuterio-4-methylnaphthalene.[24]

A sample of 1-naphthylmethyltrimethylstannane (V), which had previously

been prepared by treating 1-bromomethylnaphthalene with $(CH_3)_3SnLi$,[7] was

also obtained by Method B.

<u>2-Naphthylmethyltrimethylplumbane</u> (VIII) Method B.

B.p. 80°C/0.01 mm Hg. M.p. 46-49°. PMR ($CDCl_3$, from $(CH_3)_4Si$ at δ 0.00):

0.67 (9H, singlet, $(CH_3)_3$ Pb; J(Pb-CH_3) 56 Hz), 2.97 (2H, singlet,

CH_2; J(Pb-CH_3) 54 Hz) and 6.9-7.7 (7H, multiplet, aromatics). Anal. Found:

C, 43.01; H, 4.60. $C_{14}H_{18}Pb$ calcd.: C, 42.73; H, 4.61%.

The 6-deuterio analogue was obtained similarly from 2-deuterio-6-methylnaph-

thalene (vide supra). A sample of 6-deuterio-2-naphthylmethyltrimethylstannane

(m.p. 54-56°) was also obtained by this method.[7]

<u>Method C: General Grignard procedure for trimethylplumbyl- and</u>

<u>trimethylplumbylmethyl substituted fluorobenzenes.</u>

Trimethyllead chloride (5.8g, 0.02 mol) was added to the Grignard

reagent prepared from the appropriate fluorobenzylchloride or fluorobromo-benzene (0.03 mol) and magnesium turnings in dry diethyl ether as solvent. The reaction mixture was allowed to stir at room temperature for 20 hours before quenching with a saturated solution of ammonium chloride. The ether layer was dried, evaporated and the crude oily product purified by distillation (yield 50%). All the compounds were sensitive to air, moisture and light. Storage in the dark under a dry nitrogen atmosphere was essential.

p-Fluorobenzyltrimethylplumbane (XXVI) Method C.

B.p. 76-79°C/0.4 mm Hg. PMR (CDCl$_3$, from (CH$_3$)$_4$Si at δ 0.0):0.69 (9H, sing., (CH$_3$)$_3$Pb; J(Pb-CH$_3$)57 Hz), 2.8 (2H, singlet, CH$_2$) and centred at 6.92 (4H, multiplet, aromatic protons). Anal. Found: C, 34.8; H, 4.2. C$_{10}$H$_{15}$FPb calcd.: C, 33.23; H, 4.18%.

m-Fluorobenzyltrimethylplumbane (XXV) Method C.

B.p. 60°C/0.1 mm Hg. n$_D^{23}$1.5808. PMR (CDCl$_3$, from (CH$_3$)$_4$ Si at δ 0.0): 0.70 (9H, singlet, (CH$_3$)$_3$Pb; J(Pb-CH$_3$) 57 Hz), 2.77 (2H, singlet, CH$_2$; J(Pb-CH$_2$) 62 Hz) and 6.3-7.1 (4H, multiplet, aromatic protons). Anal. Found: C, 34.13; H, 4.2.C$_{10}$H$_{15}$FPb calcd.: C, 33.23; H, 4.18%.

p-Fluorophenyltrimethylplumbane Method C.

B.p. 60°/1 mm Hg (lit.[25] 80°/15 mm Hg). n$_D^{22}$ 1.5640. PMR (CDCl$_3$, from (CH$_3$)$_4$Si at δ 0.0): 0.92 (9H, singlet, (CH$_3$)$_3$Pb; J(Pb-CH$_3$) 64 Hz) and 6.75-7.5 (4H, multiplet, aromatic protons).

m-Fluorophenyltrimethylplumbane Method C.

B.p. 60°/1 mm Hg. n$_D^{23}$ 1.5650. PMR (CDCl$_3$, from (CH$_3$)$_4$Si at δ 0.0): 0.93 (9H, singlet, (CH$_3$)$_3$Pb; J(Pb-CH$_3$) 65 Hz) and 7.2 (4H, multiplet, aromatic protons). Anal. Found: C, 31.30; H, 3.79. C$_9$H$_{13}$FPb calc.: C, 31.12; H, 3.77%.

Spectra

Most of the fluorine nmr spectra were obtained at 56.4 MHz using a Varian DP60 spectrometer which had been modified to obtain spectra in

Table 1

^{13}C NMR PARAMETERS[a]

Compound	X	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	CH$_2$	M-CH$_3$
Chemical Shifts of benzyl derivatives[b]													
I	Si(CH$_3$)$_3$	140.45	128.08	128.14(-0.20)[c]	123.90(-4.44)[c]							27.04	-1.94
II	Ge(CH$_3$)$_3$	141.37	127.61	128.18(-0.18)[c]	123.84(-4.50)[c]							26.29	-2.57
III	Sn(CH$_3$)$_3$	143.14	126.79	128.35(0.00)[c]	123.15(-5.20)[c]							20.16	-10.14
IV	Pb(CH$_3$)$_3$	144.44	126.72	128.22(-0.16)[c]	123.21(-5.17)[c]							25.19	-2.28
Chemical shifts of naphthylmethyl derivatives[d]													
V[e]	Sn(CH$_3$)$_3$	139.57 (43.6)	123.55 (25.0)	125.57 (15.7)	123.96 (6.0)	128.62 (4.2)	125.21 (4.2)	124.91 (4.5)	123.80 (10.2)	130.77 (16.7)	133.79 (11.7)	17.68 (235)	-9.3 (327)
VI[e]	Pb(CH$_3$)$_3$	140.71 (70.5)	123.56 (57.0)	125.48 (27)	123.96 (36)	128.78	125.26	125.02	123.82	130.66 (31.5)	133.71 (22.5)	22.97 (194)	-1.20 (194)
VI[b]	Pb(CH$_3$)$_3$	140.79	123.60	125.51	123.96	128.81	125.51	125.07	123.96	130.71	133.74	22.99	-1.17
VII[e]	Sn(CH$_3$)$_3$	123.25 (25.0)	140.74 (40.8)	126.93 (~19)	127.69 (12.6)	127.50	123.90	125.70	126.68	133.98 (13.6)	130.55 (9.1)	20.54 (287)	-9.97 (342.7)
VIII[e]	Pb(CH$_3$)$_3$	123.06 (55.5)	142.07 (65)	126.84 (33)	127.58[f] (~18)	127.42	123.93	125.65	126.76	133.85 (28)	130.60 (24.75)	25.55 (196)	-2.02 (202)
VIII[b]	Pb(CH$_3$)$_3$	123.09	142.16	126.87	127.61	127.50	123.96	125.70	126.87	133.87	130.66	25.58	-1.99
Chemical shifts of fluoronaphthylmethyl derivatives[g,h]													
XI	Sn(CH$_3$)$_3$	135.40 (~4-5)	122.68 (7.4)	109.07 (20.35)	156.02 (247.84)	121.16 (5.55)	125.95	125.62 (broad)	124.23 (3.7)	131.78 (~4)	126.42 (20.34)	17.22	-9.34
XIX	Sn(CH$_3$)$_3$	122.72 (5.55)	142.35	126.27 (broad)	127.77	129.91 (9.25)	114.16 (24.04)	160.93 (244.14)	109.75 (20.35)	134.90 (9.25)	127.66	20.80	-9.60
Calc. chemical shifts of V and VII from XI and XIX respectively using ^{13}C SCS values for fluorine derived from 1- and 2-fluoronaphthalene[i]													
V	Sn(CH$_3$)$_3$	139.66	122.92	125.49	125.07	128.53	125.3	124.97	124.61	130.34	134.43		
VII	Sn(CH$_3$)$_3$	123.29	141.34	127.02	127.82	127.52	123.74	126.09	126.79	134.20	131.59		

a. Chemical shifts in chloroform-d referred to TMS (± 0.1 ppm). Positive values indicate decreased shielding relative to TMS. The carbon-numbering system is as shown in the structural formulas. b. Dilute solutions, conc[n] 5 mole %. c. Substituent chemical shifts (SCS), i.e. chemical shifts relative to internal benzene as standard. Negative values indicate increased shielding. d. ^{13}C-117,119Sn and ^{13}C-217Pb coupling constants (Hz) are given in brackets. e. Concentrated solutions, conc[n] 20 mole %.

f. Uncertain due to signal overlapping. g. Conc[n] 10 mole %. h. ^{13}C-19F coupling constants (Hz) are given in brackets.

i. Taken from ref. 27.

the HA mode. The spectra were calibrated using a "Racal" SA535 universal counter timer. The spectra were obtained on solutions containing 5-10% (W/W) of the fluoro compound together with 3-5% (W/W) of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFB) as internal standard. Some fluorine nmr spectra were also obtained at 84.66 MHz on a Bruker WH-90 Fourier transform nmr spectrometer. The proton broad-band decoupled spectra were recorded at 6000 and 600 Hz spectra widths with 16K/8K data points.

^{13}C spectra were recorded in the pulse Fourier transform mode at 22.625 MHz or 67.89 MHz on Bruker spectrometers. All samples were prepared in deuteriochloroform with $(CH_3)_4Si$ as an internal standard. Concentrated solutions were employed for acquisition of ^1H coupled spectra and proton-decoupled spectra for observing metal-carbon coupling constants. However, fairly dilute solutions (5 mole %) were used for accurate chemical shift determinations. It is of interest to note that concentration effects on the ^{13}C shifts were very small for the naphthalene derivatives.

^1H NMR were measured with a Varian A-60 spectrometer.

Results and Discussion.

^{13}C NMR Spectra

The ^{13}C nmr data for compounds I-VIII, XI, and XIX are listed in Table 1 together with the calculated spectra for V and VII. The spectra for compounds I-IV were assigned in the manner previously outlined[6,7]. Compound V was previously[7] assigned on the basis of deuterium-substitution at C4,[24,26,27] off-resonance noise decoupling, ^{13}C-$^{117,119}Sn$ satellite information, intensity and chemical shift considerations. The calculated spectrum listed in Table 1 derived from fluoro-substitution[8,27,28] at C(4) (compound XI); Table 1) confirms most of the assignments. However, a re-examination of V at 67.89 MHz revealed ^{13}C-$^{117,119}Sn$ coupling to the resonance peak at 123.8 ppm. The magnitude of this coupling (10.2 Hz)

suggests that the previous assignments listed for C(6) and C(7) should be transposed. Previous[7] spectral assignments for compound VII were arrived at by methyl-substitution at C(6), ^{13}C-^{117,119}Sn satellite information, off-resonance noise decoupling, intensity and chemical shift considerations. In this study, deuterio-[24,26,27] and fluoro-substitution[8,27,28] at C(6) and C(7) respectively confirmed most of the assignments except those for C(1) and C(3). The calculated spectrum for VI (Table 1) by the fluorine ^{13}C SCS method[8,27,28] indicates unambiguously that the previous[7] assignments for these carbons should be reversed.

The unambiguous spectral assignments listed in Table 1 for compounds VI and VIII were arrived at on the basis of ^{2}H effects on the spectra[24,26,27] (deuterio-substitution at C(4) and C(6) in VI and VIII respectively), details of the fully ^{1}H coupled spectra,[29] ^{13}C-^{207}Pb satellite information, off-resonance noise decoupling, intensity and chemical shift considerations. It is of interest to note that in compound VI ^{13}C-^{207}Pb coupling to C(4) (36Hz) is greater than the coupling to C(3) (27Hz), a phenomenon previously observed[6] for the corresponding benzyllead derivative (IV). This contrasts markedly with our recent observation[7] that the relative magnitude of ^{13}C-^{117,119}Sn coupling to C(4) and C(3) in compound V is the reverse of that observed for the benzyltin derivative (III). A full discussion of the coupling constants in these compounds, together with details of analogous ^{13}C-^{199}Hg coupling in benzyl and naphthylmethyl derivatives, will be the subject of a future publication after further studies have been completed.

An examination of the chemical shift trends for C(4) in compounds I-IV (Table 1) and in particular, the substituent chemical shift (SCS) values listed for this carbon, indicates quite clearly that the order of electron release from the C-M bonds by the ^{13}C probe in the neutral ground state is Pb~Sn>Ge~Si. Thus, the previously[6] inferred order from the chemical shifts of these compounds was in error due to concentration effects.

Further corroborative evidence for the similar electronic effect of

$CH_2Sn(CH_3)_3$ and $CH_2Pb(CH_3)_3$ is displayed by the chemical shift patterns

for the naphthalene derivatives (V-VIII; Table 1).   Note that the aromatic

spectral region of VI and VIII are almost facsimiles of the corresponding

regions for compounds V and VII respectively except for the very

proximate carbon centres, C(1) and C(2).   In particular, it should be

noted that the chemical shifts for the non-proximate strongly conjugated

dispositions (C(4) in V and VII;   C(6) and C(10) in VI and VIII), which are

the most sensitive probe centres in naphthalene for unambiguously

discriminating electronic differences[27], are virtually identical.

Substituent parameters (σ_I = 0.00; σ_R^O = -0.24) for $CH_2Sn(CH_3)_3$ or

$CH_2Pb(CH_3)_3$ can be derived from the ^{13}C SCS* of C(6) and C(7) in the

2-substituted naphthalene derivatives (-1.83 and -0.08 ppm respectively)

by employing eq. 1 and 2:   the dual substituent parameter (DSP) correlative

equations of the ^{13}C SCS (C(6) and C(7)) from 2-substituted naphthalenes.[27]

This method for obtaining substituent parameters is analogous to that

$$SCS = 4.01 \sigma_I + 7.74 \sigma_R^O \quad (C(6); CDCl_3) \qquad (1)$$

$$SCS = 2.85 \sigma_I + 0.37 \sigma_R^O \quad (C(7); CDCl_3) \qquad (2)$$

recently described for ^{19}F SCS data from these two dispositions.[14,15]

The resonance parameter (σ_R^O) for these weakly polar groups can also

be obtained by substituting (C(10)SCS = -2.81 ppm) in the DSP equation

for C(10) from 2-substituted naphthalenes (eq. 3)[27] and ignoring the small

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* The ^{13}C substituent chemical shift (SCS) is defined as the difference

(ppm) between the ^{13}C chemical shift of the substituted compound and that

of the appropriate carbon in the parent hydrocarbon (naphthalene (DCCl_3;

relative to TMS):   127.85 (C1); 125.78 (C2); 133.47 (C9).

Negative signs imply shielding.

inductive component in this disposition. The value $(\sigma_R^0 = -0.25)$

$$SCS = 0.41\ \sigma_I + 11.23\ \sigma_R^0\ (C(10);\ DCl_3)\quad (3)$$

is in excellent agreement with that derived from eq.1 and 2. Similarly, the DSP equation for the <u>para</u> position of mono-substituted benzenes[13] (eq.4) can be employed by ignoring the inductive component and utilizing

$$SCS = 4.73\ \sigma_I + 20.98\ \sigma_R^0 \quad\quad\quad (4)$$

the appropriate ^{13}C SCS (Table 1). The σ_R^0 values are : $CH_2Si(CH_3)_3$, -0.21; $CH_2Ge(CH_3)_3$, -0.21; $CH_2Sn(CH_3)_3$, -0.25; $CH_2Pb(CH_3)_3$, -0.25.

^{19}F NMR Spectra

The ^{19}F SCS for the $CH_2M(CH_3)_3$ and $CH_2M(C_6H_5)_3$ - substituted fluoro-naphthalenes are set out in Tables 2-4 together with some of the relevant ^{19}F SCS previously published for these groups. A cursory examination of the data in the strong conjugative dispositions (4α; 6β; and para) provides decisive confirmation of the order of electron release determined by the ^{13}C studies (vide supra), namely, Pb~Sn>Ge~Si. Concentration effects were eliminated as a possible factor for the trends by chemical shift studies to infinite dilution of the <u>para</u>-substituted fluorobenzene derivatives. No significant variations in the ^{19}F SCS were observed.

Substituent parameters derived from the ^{19}F SCS data for the 6β and 7β dispositions of β-fluoronaphthalene by employing the appropriate DSP equations[14] are listed in Table 5. The substituent parameters determined by Taft's methodology[16] from the ^{19}F SCS in Table 4 are listed in Table 6 together with reported[4] infra-red derived σ_R^0 values. Several comments seem appropriate. Firstly, the polar parameters (σ_I) listed in Table 5 and 6 for the substituents* are all small and reasonably constant differing little from the σ_I value generally adopted for $CH_3(-0.04)$[30].

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* Traylor et al.[10] have coined the term "isoinductive resonance substituents" to describe these groups.

Table 2. ^{19}F Substituent Chemical Shifts (SCS; ppm)^a of 4α-, 6β-, and
7β-Trimethylmetalloidalmethyl Substituted Fluoronaphthalenes

Substituent	Benzene			DMF		
	$4\alpha^b$	$6\beta^c$	$7\beta^c$	$4\alpha^b$	$6\beta^c$	$7\beta^c$
$CH_2Si(CH_3)_3$	+4.73	+2.17	+0.33	+5.03	+2.29	+0.43
$CH_2Ge(CH_3)_3$	+4.73	+2.23	+0.31	+5.04	+2.36	+0.46
$CH_2Sn(CH_3)_3$	+5.49	+2.63	+0.28	+5.99	+2.87	+0.52
$CH_2Pb(CH_3)_3$	+5.21	+2.62	+0.25	+5.78	+2.91	+0.54
CH_3	+2.96^d	+1.44 (+1.45)^d	+0.22 (+0.21)^d	+2.94^d	+1.47 (+1.48)^d	+0.23 (+0.25)^d

a. Positive values imply an upfield shift relative to the appropriate standard.

b. Relative to α-fluoronaphthalene.

c. Relative to β-fluoronaphthalene.

d. Taken from ref. 18.

The slight fluctuations observed (note change in sign for the two scales) cannot be taken at face value since these are probably artifacts of the method employed for dissection. Secondly, the resonance parameters (σ_R^o) derived by ^{19}F nmr methods are similar to those calculated from ^{13}C nmr data (vide supra) and, thus, formalize the order of hyperconjugative electron release (Pb≃Sn>Ge≃Si) suggested by the relative ^{19}F substituted chemical shifts in the various conjugated dispositions. Thirdly, the σ_R^o values for $CH_2M(C_6H_5)_3$ (Table 5) are all significantly smaller than those listed for $CH_2M(CH_3)_3$. An obvious explanation is that electron release

Table 3. ^{19}F Substituent Chemical Shifts (SCS; ppm)^a of

4α-, 6β-, and 7β- Triphenylmetalloidalmethyl Substituted

Fluoronaphthalenes.

Substituent	Benzene		DMF		
	$6\beta^b$	$7\beta^b$	$4\beta^c$	$6\beta^b$	$7\beta^b$
$CH_2Si(C_6H_5)_3$	+1.89	+0.30	+4.09^d	+1.91^d	+0.30
$CH_2Ge(C_6H_5)_3$	+1.89	+0.25	+4.03^d	+1.86^d	+0.25
$CH_2Sn(C_6H_5)_3$	+2.17	+0.13	+4.73^d	+2.21^d	+0.20
$CH_2Pb(C_6H_5)_3$	+2.01	+0.11	+4.11^d	+2.06^d	+0.18

a.   Positive values imply an upfield shift relative to the appropriate

standard.   b.   Relative to β-fluoronaphthalene.   c.   Relative

to α-fluoronaphthalene.   d.   Taken from ref. 3.

from the C-M bonds in the former groups is reduced as a consequence of

reduced polarity of the carbon-metal bond ($C^{\delta-}\!\!-\!\!M^{\delta+}$) due to the greater

electron-withdrawing inductive effect of C_6H_5 (σ_I = 0.1)[30] relative to CH_3

groups i.e. a significant indirect inductive effect is operative for these

substituents.[31]   However, a similar phenomenon is also indicated by the σ^+

values[9,10] for $CH_2M(CH_3)_3$ and $CH_2M(C_6H_5)_3$ groups.   Hence the energy

differential (ΔE) between the σ and π orbitals involved in the interaction

may also be implicated (vide infra).   Finally, it should be noted that

substituent parameters for $CH_2M(CH_3)_3$ groups derived with ^{1}H and ^{13}C nmr

data from the 4-substituted styrenes (32) also indicate hyperconjugative

electron release in the order Pb∼Sn>Ge∼Si.   However, these parameters

Table 4. ^{19}F Substituent Chemical Shifts (SCS; ppm)[a,b,c] of meta- and para- Trimethylmetalloidalmethyl Substituted Fluorobenzenes.

	Cyclohexane		DMF	
Substituent	meta	para	meta	para
$CH_2Si(CH_3)_3$	+1.05	+7.05	+1.10	+7.20
$CH_2Ge(CH_3)_3$	+0.90	+7.05	+1.10	+7.30
$CH_2Sn(CH_3)_3$	+0.85	+7.75[d]	+1.00	+8.15
$CH_2Pb(CH_3)_3$	+0.87[e,f]	+7.46[e,g]	+1.46	+8.01
CH_3	+1.27	+5.48	+1.13	+5.45

a.   Positive values imply an upfield shift relative to the appropriate standard.

b.   Relative to fluorobenzene.

c.   Taken from ref. 17.

d.   +7.79 in benzene.

e.   This study; CCl_4 solvent.

f.   This study; +0.89 in benzene.

g.   This study; +7.55 in benzene.

differ significantly in magnitude from those reported in this paper. The values are as follows : $CH_2Si(CH_3)_3$, $\sigma_I = -0.10$, $\sigma_R^o = -0.15$; $CH_2Ge(CH_3)_3$; $\sigma_I = -0.10$, $\sigma_R^o = -0.15$; $CH_2Sn(CH_3)_3$, $\sigma_I = -0.11$, $\sigma_R = -0.19$; $CH_2Pb(CH_3)_3$, $\sigma_I = -0.12$, $\sigma_R^o = 0.19$. It is of interest to compare the calculated ^{13}C SCS (para) for these groups in the phenyl system (Table 7) (determined by substituting the various parameters in the appropriate DSP equation (eq. 4)) with the observed results (Table 1).

Table 5. Substituent Parameters (σ_I and σ_R^o) Derived from ^{19}F SCS of Substituted Fluoronaphthalenes

Substituent	σ_I			σ_R^o	
	Benzene	DMF		Benzene	DMF
$CH_2Si(CH_3)_3$	+0.01	-0.01		-0.19	-0.18
$CH_2Ge(CH_3)_3$	+0.02	-0.01		-0.20	-0.18
$CH_2Sn(CH_3)_3$	+0.05	0.00		-0.25	-0.23
$CH_2Pb(CH_3)_3$	+0.06	-0.01		-0.25	-0.23
$CH_2Si(C_6H_5)_3$	+0.01	+0.01		-0.16	-0.16
$CH_2Ge(C_6H_5)_3$	+0.02	+0.03		-0.17	-0.17
$CH_2Sn(C_6H_5)_3$	+0.07	+0.06		-0.22	-0.21
$CH_2Pb(C_6H_5)_3$	+0.07	+0.06		-0.21	-0.20

Table 6. Infra-red and Fluorobenzene Derived Substituent Parameters.

Substituent	σ_R^o (ir)[a]	σ_I (NMR)	σ_R^o (NMR)
$CH_2Si(CH_3)_3$	± 0.20	-0.06	-0.20[a]
$CH_2Ge(CH_3)_3$		-0.04	-0.21
$CH_2Sn(CH_3)_3$	± 0.26	-0.04	-0.23[a]
$CH_2Pb(CH_3)_3$		-0.04	-0.22

a. Taken from ref. 4.

Table 7.   Calculated ^{13}C SCS (para) for $CH_2M(CH_3)_3$
Substituted Benzenes Utilizing DSP eq. 4.

	Calc. SCS.			Obs. SCS
$CH_2Si(CH_3)_3$	-4.47^a	-3.95^b	-3.62^c	-4.44^d
$CH_2Ge(CH_3)_3$	-4.60^a	-4.10^b	-3.62^c	-4.50^d
$CH_2Sn(CH_3)_3$	-5.02^a	-5.00^b	-4.51^c	-5.20^d
$CH_2Pb(CH_3)_3$	-4.81^a	-4.96^b	-4.51^c	-5.17^d

a.   Substituent parameters derived from fluorophenyl tag (Table 6)

b.   Substituent parameters derived from fluoronaphthyl tag (Table 5; benzene solvent).

c.   Substituent parameters derived from 4-substituted styrene system (32).

d.   Taken from Table 1.

The ^{19}F SCS determined in this study for meta- and para-fluorophenyl-trimethylplumbane are as follows: meta, 0.43 ppm (benzene); 0.86 ppm (DMF); 0.39 ppm (CCl_4);   para, 1.08 ppm (benzene); 1.57 ppm (DMF);   1.03 ppm (CCl_4). The previously reported values[17] should therefore be rejected.   Taft's methodology[16] provides the following substituent parameters: $\sigma_I = 0.03$; $\sigma_R^o = -0.02$.   These results are listed in Table 8 together with previously reported substituent parameters for the $M(CH_3)_3$ groups (M = Si, Ge, Sn, Pb). An examination of this data indicates that the various scales appear to be dependent on the aromatic system from which they are derived.   We have no explanation for this rather puzzling situation except to point out that often the electronic effects of these weakly interacting substituents are smaller than the standard deviations of the correlative equations employed to dissect the substituent parameters.   However, although the parameters

Table 8. Substituent Parameters Derived by NMR Methods for $M(CH_3)_3$ Substituents.

	Fluorophenyl tag[a]		Fluoronaphthyl tag[a,b]		Styrene System[c]	
	σ_I	σ_R^o	σ_I	σ_R^o	σ_I	σ_R^o
$Si(CH_3)_3$	-0.03	0.04	0.02(0.03)	0.05(0.04)	-0.09	0.07
$Ge(CH_3)_3$	-0.01	0.01	0.06(0.06)	0.01(-0.02)	-0.10	0.07
$Sn(CH_3)_3$	0.00	0.01	0.09(0.06)	-0.02(-0.03)	-0.11	0.05
$Pb(CH_3)_3$	0.03[d]	-0.02[d]	0.12[e](0.08)[e]	-0.08[e](-0.08)[e]	-0.12	0.05

a. Taken from ref. 14.

b. Benzene as solvent. Values in parentheses are for DMF as solvent.

c. Taken from ref. 32.

d. This study.

e. Revised values based on a re-examination of the ^{19}F nmr spectra for 2-fluoro-7-trimethylplumbylnaphthalene which yielded the following ^{19}F SCS: -0.38 ppm (benzene); -0.22 ppm (DMF). These values are slightly different from those previously reported (18).

determined with data from 4-substituted styrenes[32] appear to be more compatible with current preconceptions regarding the electronic effects of these groups (inductive electron-donation and mesomeric electron-withdrawal[4]), it is of interest to compare the observed ^{13}C SCS (para) for these groups in the phenyl system[33] with those calculated (Table 9) by substituting the various parameters (Table 7) into the appropriate DSP equation (eq. 4). Bearing in mind that structural factors resulting from ortho H-CH$_3$

Table 9. Calculated ^{13}C SCS (para) for $M(CH_3)_3$ Substituted Benzenes Utilizing DSP eq.4.

	Calc. SCS			Obs. SCS[d]
$Si(CH_3)_3$	0.70^a	1.14^b	1.04^c	0.40
$Ge(CH_3)_3$	0.20^a	0.49^b	1.00^c	-0.10
$Sn(CH_3)_3$	0.21^a	0.01^b	0.53^c	-0.20
$Pb(CH_3)_3$	-0.28^a	-1.11^b	0.48^c	-0.90

a.   Substituent parameters derived from fluorophenyl tag (Table 8).

b.   Substituent parameters derived from fluoronaphthyl tag (Table 8).

c.   Substituent parameters derived from 4-substituted styrene system (Table 8).

d.   Taken from ref. 33.

interactions are perturbing the SCS for $Si(CH_3)_3$ and probably to a lesser extent $Ge(CH_3)_3$,[21,33] it can be seen that there is a more reasonable parallel between the observed and calculated trends where the latter are determined from the fluorophenyl and fluoronaphthyl derived parameters rather than the apparently more acceptable values from the styrene system.   This strongly suggests that the $Pb(CH_3)_3$ group effects mesomeric electron-donation presumably by hyperconjugation! It is also important to note that the ^{13}C SCS for the resonance dominated C(10) position (see eq. 3) in $M(CH_3)_3$ 2-substituted naphthalenes[33] are in accord with the conclusions drawn from the σ_R^o values for these groups by the 2-fluoronaphthyl probe viz. the operation of mesomeric electron-withdrawal and - donation for Si and Pb, respectively, but no significant net conjugation for Ge and Sn.   The ^{13}C SCS for C(10) are as follows:

Si(CH$_3$)$_3$,+ 0.2 ppm; Ge(CH$_3$)$_3$, -0.1 ppm; Sn(CH$_3$)$_3$, -0.1 ppm; Pb(CH$_3$)$_3$, -0.5 ppm. For a more detailed discussion of the electronic effects of M(CH$_3$)$_3$ substituents our recent paper specifically devoted to this topic should be consulted.[33]

Conclusions

The principal conclusion from this work is that the order of electron release by CH$_2$M(CH$_3$)$_3$ or CH$_2$M(C$_6$H$_5$)$_3$ (M = metalloid) groups in the neutral ground state of aromatic systems is unambiguously Pb~Sn>Ge~Si. Further, the study has clearly shown that this order is independent of the aryl system, the orientation of substituent and probe, the nature of the ground state probe, and the group (methyl or phenyl) attached to the metalloid. Hence the observed phenomenon is a real effect operative in the C-M portion of the molecule and any attempts to explain it must be based on current theories of hyperconjugation. PMO theory, in conjunction with CNDO/2 calculations, has allowed the definition of several molecular parameters which determine the magnitude of σ-π interactions[34]: (i) the energy differential (ΔE = E(π)-E(σ)) between the σ and π orbitals involved; (ii) the electron densities (a^2(π) and a^2(σ)) in the p orbitals of the connecting atoms of the σ and π systems; and (iii) the perturbation integral P($\sigma\pi$) which includes the overlap component. Now since a^2(π), E(π), and P($\sigma\pi$) will remain constant for a given disposition in a particular arylmethyl derivative (ArCH$_2$M(CH$_3$)$_3$ or ArCH$_2$M(C$_6$H$_5$)$_3$), the observed order of electron release in the neutral ground state must be determined by E(σ) and a^2(σ). Values for E(σ) maybe reliable estimated from the ionization potentials of suitable model compounds on the basis of Koopman's theorem.[34] Further, the relative magnitude of E(σ)'s may also be inferred from bond strengths.[11,35] Hence there is no doubt that the extent of hyperconjugation from the C-M bonds will increase in the order Pb>>Sn>>Ge>Si since ΔE decreases as M changes from Si to Pb.

Unfortunately, trends in $a^2(\sigma)$ cannot be reliably defined by experiment or by current theoretical treatments. However, we believe that the order of electron release for C-M bonds in the neutral ground state suggests strongly that this parameter $(a^2(\sigma))$ offsets the order firmly dictated by ΔE. We realise that this proposal demands the acceptance that R_3Pb and R_3Ge be more electronegative than R_3Sn and R_3Si respectively $(R = CH_3$ or $C_6H_5)$ which is clearly at odds with the common preconception regarding the order of electropositivity of these congeneric groups. It is important to note, however, that this apparent unreasonable deduction is by no means new[11,36] and is supported by the Allred-Rochow electronegativity scale[37] which has been given some credence by a recently derived non-empirical scale[38]. Thus, whereas the much stronger hyperconjugative interactions in electron deficient systems are overwhelmingly determined by ΔE, the similar but much weaker interactions in the neutral ground state must be the result of a subtle balance between ΔE and $a^2(\sigma)$.

We also considered structural phenomena as a possible reason for the discrepancy between the neutral ground state order and that observed in electron deficient systems. Unfortunately, experimental or theoretical data is not available to bring to bear on this question. However, there seems no reason to believe that non-bonded effects are different for the tin and lead compounds given that the difference in the two respective bond lengths is small ($\sim0.1\text{Å}$) and that the relative magnitude of the resonance parameters is independent of the effective steric size of the group (CH_3 or C_6H_5) attached to the metalloid. It is worth noting, however, that Hoffmann et al[39] have proposed that hyperconjugative interactions will always be accompanied by geometrical adjustment depending on the extent of the interaction and the system concerned. Although this type of structural perturbation should be quite small in the neutral ground state, and thus have no effect on the observed order of electron release, it maybe

an important factor in electron deficient species where σ-π interactions
are much more powerful. However, the fact that rate data[9] from systems
in which C-M bonds hyperconjugate with electron deficient transition states
correlate extremely well with σ_R^+ values determined by the charge-transfer
technique* gives no encouragement for this idea†.

Finally, although experimental measurements of charge distribution
(^{13}C and ^{19}F SCS) do not differentiate between charge redistribution versus
charge transfer, we believe that in the light of Libit and Hoffmann's[41]
recent theoretical analysis of methyl substituent effects in neutral π
systems definite conclusions can be drawn regarding whether charge transfer
is significant. The main conclusion by Libit and Hoffmann[41] is that the
electron donating effect of the methyl group in neutral π systems is an
apparent one since there is little charge transfer from methyl to the
adjacent π substrate. The origin of the substantial π polarisation has
been traced to a mixing of π^* into π orbitals within the π system via
hyperconjugative interactions of both with the methyl group σ orbital:
the net result of this effect is akin to non-bonded repulsive interactions
between the π system and the CH_3 σ orbital at the point of attachment.[42]
A trenchant experimental result in support of this theoretical deduction is

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* The Franck-Condon principle excludes structural effects of the kind
  being considered.

† It is possible, however, that the correlation is fortuitous since in the
  complex used in the charge-transfer method a very favourable geometrical
  relationship of the CH_2-MR_3 groups with respect to the benzene ring maybe
  imposed by the acceptor substrate prior to charge-transfer occurring.
  A photoelectron spectral analysis of benzyltrimethylplumbane to compare
  with the known data for the corresponding tin derivative[40] would be of
  value to perhaps exclude this possibility.

the fact that the apparent electron donating effect of CH_3 in the 4α

disposition (formally para) of naphthalene (ground state) is substantially

less than that observed in the para position of benzene (para (^{13}C SCS) =

3.05 ppm[13]; 4α (^{13}C SCS) = 1.37 ppm[27]; para (^{19}F SCS) = 5.48 ppm[17];

4α (^{19}F SCS) = 2.96 ppm[18])[†]: Although this result is clearly discordant

with quantum mechanical models involving charge transfer (4α>para)[3], it appears

in line with expectations based on Libit and Hoffmann's[41] model since the

relative magnitude of the hyperconjugative interactions in benzene and naphthalene

should be largely determined by $a^2(\pi)$ (phenyl (0.333)>1-naphthyl (0.181))[34]

rather than ΔE. However, if we compare the enhanced electron-donating effects

(^{13}C or ^{19}F SCS) of replacing hydrogen in CH_3 with $(CH_3)_3M$ (M = Si, Ge, Sn, Pb)

in the para and 4α dispositions of benzene and naphthalene respectively,

we now find that the effects are significantly greater in the latter than

the former. This observation is clearly in line with a charge transfer

model. In this connection, it should be noted that we[3,7] have already

successfully correlated ^{19}F and ^{13}C chemical shifts relative to CH_3 for

$CH_2M(C_6H_5)_3$ (M = Si, Ge, Sn, Pb) and $CH_2Sn(CH_3)_3$ respectively with π-charges

determined by a SCFMO method for a theoretical conjugative model. Clearly,

the new data presented in this paper could also be successfully fitted in a

similar way.

Acknowledgments

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† We have drawn attention to this phenomenon in previous papers (ref 18,
21 and 43). However, because no explanation seemed feasible at the time
effects Recently, ^{13}C and ^{19}F SCS for the CH_3 group in the 5α disposition
suggests that structural factors perturb the 4α disposition by approx. 1 ppm
downfield (ref. 14 and 33).

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