*Journal of Organometallic Chemistry*, 255 (1983) 279–285
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# ON THE RELATION BETWEEN ELEMENT NMR CHEMICAL SHIFTS IN THE FOURTH MAIN GROUP

T.N. MITCHELL
*Abteilung Chemie, Universität Dortmund, Postfach 500 500, 4600 Dortmund 50 (F.R.G.)*

(Received May 23rd, 1983)

## Summary

Regression analyses of representative chemical shift data for the isotopes carbon-13, silicon-29, tin-119 and lead-207 show a reasonable carbon–silicon shift correlation ($r = 0.825$) and very good silicon–tin ($r = 0.990$) and tin–lead ($r = 0.975$) correlations. In the latter two cases the observed shift ratios correspond fairly closely to the $\langle r^{-3} \rangle_{np}$ ratios for the element pairs. Pentacoordination at silicon may be more important than previously realised.

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A recent paper by Olah and Field [1], which deals with the correlation of carbon-13 and silicon-29 NMR shifts in analogous compounds, prompted us to investigate whether a correlation between silicon-29 and tin-119 chemical shifts or between the latter and lead-207 chemical shifts is observed.

As the basis for his C/Si correlation (which was however not placed on a numerical basis) Olah took a total of 35 compounds, the carbon chemical shifts of five of these being estimated from Grant's additivity rule [2]. We have used only literature values for a total of 43 compounds; for our Si/Sn correlation data on 48 compounds were used, for the Sn/Pb correlation 35 values were taken. The graphical results of these correlations are shown in Figs. 1–3, while the complete data used are given in Table 1. It should be noted that the coordination number of compounds of the Group IV elements is invariant for carbon but can increase to five or six for silicon, while even higher values are apparently possible for tin and lead: the literature data available do not permit the inclusion of compounds with coordination numbers greater than four in our analysis (we shall return to this point below).

The results of the statistical analyses afford the following relationships between the various chemical shifts:

$$\delta(\text{Si}) = 0.787\,\delta(\text{C}) - 61.7;\ r = 0.825$$

$$\delta(\text{Sn}) = 5.119\,\delta(\text{Si}) - 18.5;\ r = 0.990$$

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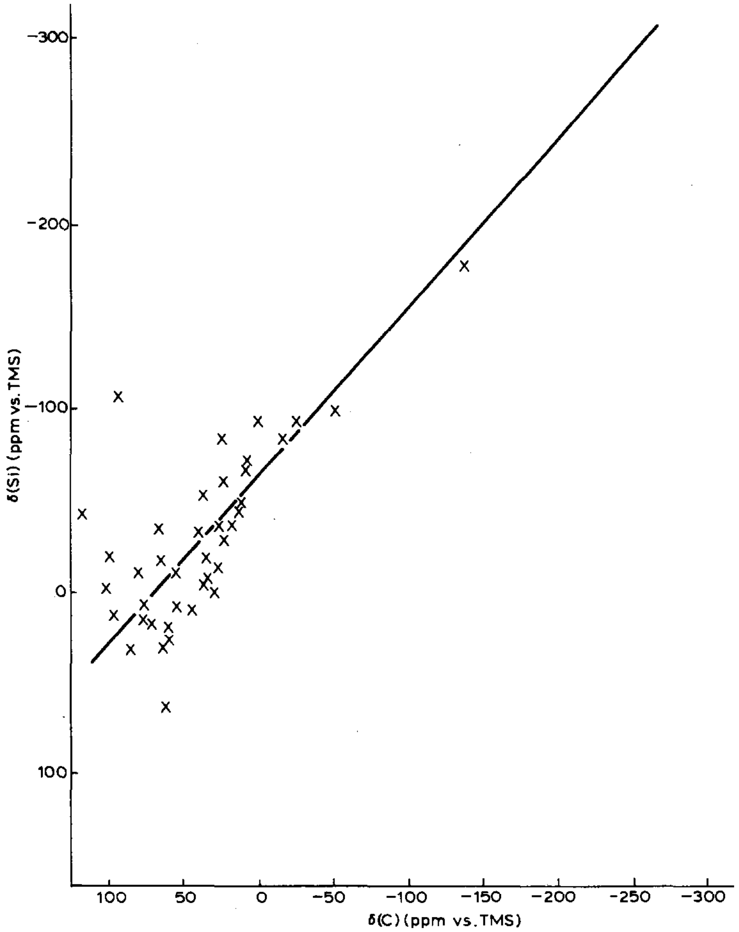


Fig. 1. Correlation of $^{13}C$ chemical shifts in carbon compounds with $^{29}Si$ chemical shifts in their silicon analogues.

$$\delta(\mathrm{Pb}) = 2.424\,\delta(\mathrm{Sn}) + 74.8;\ r = 0.975$$

These three correlations will be discussed separately below: however, the following general comments are in order. The slopes of the straight lines (see Figs. 1–3) reflect the relative chemical shift dispersion of the elements. The assumption that the paramagnetic term dominates the chemical shift would suggest that the slopes will be approximately proportional to the $\langle r^{-3}\rangle_{np}$ ratios for the element pairs. The $\langle r^{-3}\rangle_{np}$ values given by Jameson and Gutowsky [3] give ratios as follows: δ(Si)/δ(C) 2.0, δ(Sn)/δ(Si) 4.5, δ(Pb)/δ(Sn) 1.9. Thus the agreement with the experimental slopes is good for the Sn/Si and Pb/Sn pairs, but poor for the Si/C pair. Other authors quote values of $\langle r^{-3}\rangle_{np}$ which give ratios corresponding more closely to the experimental results: thus those of Barnes and Smith [4] give a ratio of 1.9, while those quoted by Webb [5] give one of 1.2. Apart from $\langle r^{-3}\rangle_{np}$, effects of $\Delta E$ and of the *d*-orbitals also influence the chemical shifts, but in particular the effect of $\Delta E$ has not as yet been found quantifiable.

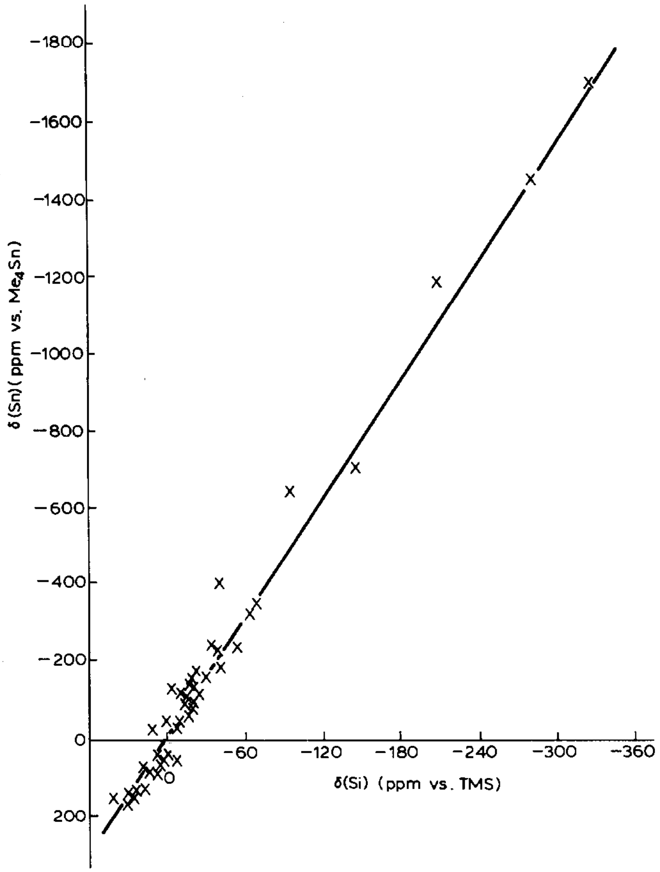


Fig. 2. Correlation of $^{29}$Si chemical shifts in silicon compounds with $^{119}$Sn chemical shifts in their tin analogues.

## $\delta$(Si) vs. $\delta$(C)

The main body of data refers to hydrides, halides and hydride halides of the elements. Though the overall statistical correlation is fair, large deviations are observed for various groups of compounds (see Fig. 1): thus for $Me_nXH_{4-n}$, the data points lie on a straight line which passes through the "origin" ($\delta$(Si) = 0, $\delta$(C) = 29.7) for $Me_4X$), but has a much larger slope (2.943, $r = 0.996$). Similarly for $Ph_nXH_{4-n}$, a straight line can be drawn but with an intermediate slope (1.212, $r = 0.981$). As has previously been pointed out by other authors, the limited number of oxygen compounds shows a completely different behaviour to the remaining compounds in that a low-field shift of $\delta$(C) corresponds to a high-field shift of $\delta$(Si). Anomalous behaviour is also shown by the compounds $XF_4$. In spite of the partial success of Engelhardt et al. [6] in interpreting carbon and silicon chemical shifts and in view of the behaviour observed for $^{119}$Sn (see below), it is perhaps worthwhile to consider the possibility that the silicon alkoxides, fluorides and (to a lesser extent) chlorides are to some extent associated in solution. Exclusion of the methoxides and $XF_4$ from the regression analysis improves $r$ to 0.945, yielding the expression:

$$\delta(\mathrm{Si}) = 0.947\,\delta(\mathrm{C}) - 57.5$$

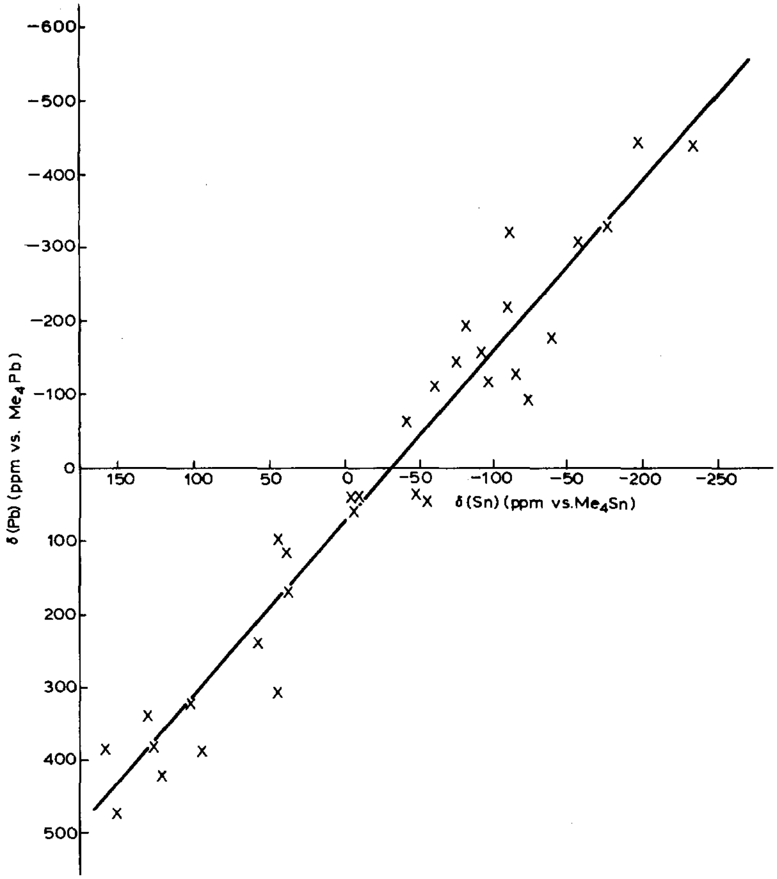


Fig. 3. Correlation of $^{119}$Sn chemical shifts in tin compounds with $^{207}$Pb chemical shifts in their lead analogues: values for $X(OAc)_4$ and $X(C{\equiv}CMe)_4$ are not included.

An expansion of the data base for both carbon and silicon is obviously required before the true limitations of a statistical correlation of this type can become apparent.

### δ(Sn) vs. δ(Si)

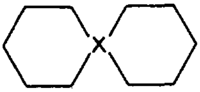
A larger variety of compounds is covered in this correlation, the main body of data referring to element halides and compounds with an element-*sp*$^2$- or -*sp*-carbon bond. The correlation yields a straight line which passes very near the origin: $\delta(Si) = 0$ corresponds to $\delta(Sn) = -14$ ppm, $\delta(Sn) = 0$ to $\delta(Si) = 2.8$ ppm. However, interpretation of the individual data shows that the values for element hydrides, element halides and tetraalkyl (or aryl) derivatives yield lines with somewhat increased slopes. Values for compounds **14**, **31** and **35** lie well away from the overall line: however, the tin alkoxides are known to be associated in solution, the monomeric $Me_2Sn(O\text{-}t\text{-}Bu)_2$ and $MeSn(O\text{-}t\text{-}Bu)_3$ having shifts of $-2$ and $-177$ ppm respectively, very close to the line if one assumes that the shifts of the corresponding silicon methoxides and t-butoxides are similar.

TABLE 1

CHEMICAL SHIFTS USED IN CORRELATIONS (in ppm vs. TMS ($^{13}$C and $^{29}$Si), $Me_4Sn$ or $Me_4Pb$)

| No. | Compound | $\delta$(C) | $\delta$(Si) | $\delta$(Sn) | $\Delta$(Pb) |
|---|---|---|---|---|---|
| **1** | $Me_4X$ | 27.9 | 0.0 | 0 | 0 |
| **2** | $Me_3XH$ | 25.2 | −15.5 | −105 | |
| **3** | $Me_2XH_2$ | 16.1 | −37.3 | −227 | |
| **4** | $MeXH_3$ | 5.9 | −65.2 | −346 | |
| **5** | $XH_4$ | −2.1 | −93.1 | | |
| **6** | $XF_4$ | 91.0 | −109 | | |
| **7** | $Me_3XCl$ | 65.3 | 30.3 | 160 | 382 |
| **8** | $Me_2XCl_2$ | 85.2 | 32.2 | 140 | |
| **9** | $MeXCl_3$ | 95.0 | 12.5 | 20 | |
| **10** | $XCl_4$ | 96.7 | −20 | −150 | |
| **11** | $Me_3XBr$ | 60.7 | 26.4 | 128 | 379 |
| **12** | $Me_2XBr_2$ | 58.3 | 19.9 | 70 | |
| **13** | $MeXBr_3$ | 31.5 | −19.2 | −170 | |
| **14** | $XBr_4$ | −28.5 | −92.7 | −638 | |
| **15** | $Me_3XI$ | 42.0 | 8.9 | 39 | 171 |
| **16** | $MeXI_3$ | | −144 | −700 | |
| **17** | $XI_4$ | −292.3 | −346.2 | −1700 | |
| **18** | $H_3XF$ | 75.4 | 17.4 | | |
| **19** | $H_3XCl$ | 25.1 | −36.1 | | |
| **20** | $H_2XCl_2$ | 54.2 | −11.0 | | |
| **21** | $HXCl_3$ | 77.7 | −36.1 | | |
| **22** | $H_3XBr$ | 10.2 | −49.0 | | |
| **23** | $H_2XBr_2$ | 21.6 | −30.4 | | |
| **24** | $HXBr_3$ | 12.3 | −43.3 | | |
| **25** | $H_3XI$ | −20.5 | −83.3 | | |
| **26** | $H_2XI_2$ | −53.8 | −99.6 | | |
| **27** | $HXI_3$ | −139.7 | −175.9 | | |
| **28** | $Cl_3XBr$ | 67.8 | −34.3 | | |
| **29** | $Cl_2XBr_2$ | 35.0 | −50.7 | | |
| **30** | $ClXBr_3$ | 5.1 | −69.8 | | |
| **31** | $Br_2XI_2$ | | −212.3 | −1190 | |
| **32** | $BrXI_3$ | | −280.1 | −1450 | |
| **33** | $Me_3XOMe$ | 72.1 | 17.5 | 129 | 331 |
| **34** | $Me_2X(OMe)_2$ | 100.0 | −2.0 | −126 | |
| **35** | $MeX(OMe)_3$ | 115.0 | −40.5 | ca. −430 | |
| **36** | $X(OMe)_4$ | 121.9 | −79.2 | | |
| **37** | $Me_3XO$-t-Bu | 76.3 | 8.5 | 91 | |
| **38** | $Me_3XOAc^a$ | | 21.9 | 129 | 428 (in $H_2O$) |
| **39** | $X(OAc)_4$ | | −95.1 | | −1869 |
| **40** | $Me_3XSMe$ | | 16.2 | 90 | 239 |
| **41** | $Me_2X(SMe)_2$ | | 28.1 | 144 | |
| **42** | $MeX(SMe)_3$ | | 34 | 167 | |
| **43** | $Me_3XSeMe$ | | | 46 | 98 |
| **44** | $Me_3XNEt_2$ | | 3.7 | 58 | 242 |
| **45** | $Me_3XPPh_2$ | | | −4 | 40 |
| **46** | $(Me_3X)_3P$ | | 0.3 | 36 | |
| **47** | $Me_3XSiMe_3$ | | −19.8 | −127 | |
| **48** | $Me_3XSnMe_3$ | 21.1 | −10.3 | −110 | −324 |
| **49** | $Me_2X(SnMe_3)_2$ | 10.1 | | −262 | |
| **50** | $X(SnMe_3)_4$ | −25.7 | | −806 | |
| **51** | $(Me_3X)_2Hg$ | 59.5 | 62 | | |
| **52** | $Me_3X \cdot Re(CO)_5$ | | −14.4 | −89 | |
| **53** | $Me_3X \cdot Mn(CO)_5$ | | −4.5 | 63 | |

TABLE 1 (continued)

| No. | Compound | δ(C) | δ(Si) | δ(Sn) | Δ(Pb) |
|---|---|---|---|---|---|
| **54** | $Me_3X\cdot Co(CO)_4$ | | 44.0 | 151 | |
| **55** | $(Me_3X)_2CN_2$ | | −0.1 | 38 | |
| **56** | $Me_3XCH{=}CH_2$ | 33.7 | −7.6 | −40 | −65 |
| **57** | $Me_2X(CH{=}CH_2)_2$ | | −13.7 | −84 | |
| **58** | $MeX(CH{=}CH_2)_3$ | | −20.6 | −124 | |
| **59** | $X(CH{=}CH_2)_2$ | | −28.5 | −162 | |
| **60** | $Me_3XCH{=}CHMe$ [b] | | −10.6 | −58 | −110 |
| **61** | $Me_2X(CH{=}CHMe)_2$ [b] | | −22.0 | −116 | −220 |
| **62** | $MeX(CH{=}CHMe)_3$ [b] | | −38.9 | −175 | −330 |
| **63** | $X(CH{=}CHMe)_4$ [b] | | −51.2 | −234 | −440 |
| **64** | $Me_3XC{\equiv}CMe$ | | | −74 | −140 |
| **65** | $Me_2X(C{\equiv}CMe)_2$ | | | −156 | −305 |
| **66** | $X(C{\equiv}CMe)_4$ | | | −284 | −686 |
| **67** | $Me_3XC{\equiv}CXMe_3$ | | −19.3 | −81 | −159 |
| **68** | $Et_4X$ | 37.1 | | −6 | 71 |
| **69** | $Et_3XCl$ | | | 153 | 472 |
| **70** | $Et_3XI$ | | | 39 | 303 |
| **71** | $Et_3XOAc$ | | | 102 | 317 |
| **72** | $Bu_4X$ | 36.9 | | −7 | 40 |
| **73** | $Bu_3XOAc$ | | | 96 | 383 |
| **74** | $Bu_2X(OAc)_2$ | | | −195 | −448 |
| **75** | $(Me_3CCH_2)_4X$ | | | −53 | 47 |
| **76** | $Ph_3XH$ | 62.0 | −17.0 | −148 | |
| **77** | $Ph_2XH_2$ | 37.0 | −33.0 | −234 | |
| **78** | $PhXH_3$ | 21.0 | −60.0 | −320 | |
| **79** | $Ph_3XCl$ | 81.2 | 1.3 | −48 | 33 |
| **80** | $Ph_3XI$ | | | −115 | −131 |
| **81** | $Ph_3XOAc$ | | | −121 | −93 |
| **82** | $Ph_4X$ | 65.0 | | −137 | −179 |
| **83** | $Ph_3XMe$ | 53.6 | −12.5 | −93 | −119 |
| **84** | $Ph_2XMe_2$ | | −9.4 | −60 | |
| **85** | $PhXMe_3$ | 34.5 | −5.1 | −28 | |
| **86** |  | | | 121 | 416 |
| **87** |  | | | −80 | −199 |

[a] HOAc = $CH_3COOH$. [b] = *cis*-configuration at the double bond.

### δ(Pb) vs. δ(Sn)

As in the former correlation, the main types of compound included are halides and derivatives with a metal-$sp^2$-carbon bond. Though the overall correlation is good, the straigth line does not pass so close to the origin; however, consideration of only the vinyl and ethinyl derivatives yields a line with a somewhat lesser slope (2.232) and which passes much closer to the origin (δ(Pb) = 26.5 for δ(Sn) = 0, δ(Sn) = −11.8 for δ(Pb) = 0 ppm). However, the accumulation of more data on lead compounds is required. It should be noted that lead chemical shifts show a much larger dependence on solvent than do tin shifts, and it is thus important to have data on solutions in "neutral" solvents: $CHCl_3$ should perhaps be taken as the standard solvent for Group IV compounds for comparison purposes, possibly at a standard concentration wherever possible.

## Data sources

The carbon data are mainly those quoted by Olah [1], with additional values from the compilation by Bremser and co-workers [7]. Silicon chemical shifts were mostly obtained from Marsmann's review [8] and the majority of the tin data from the review by Smith and Tupciauskas [9]. No corresponding review article exists for lead chemical shifts: data were taken from our own work [10] as well as papers by Cox [11], van Beelen et al. [12], Cooper et al. [13], Maciel and Dallas [14], Wrackmeyer [15], Lorberth [16] and Kennedy et al. [17]. Where two or more shifts are available for the same compound, either the average value or (if large deviations are reported) the "most probable" value (i.e. a purely subjective one) was taken. It should be noted that the data used were not obtained under standard conditions: for conditions of measurement the reader is referred to the primary literature.

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