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# A PROTON NMR INVESTIGATION OF METAL—METAL BONDING IN TRIMETHYLTIN-ALUMINIUM, -GALLIUM, -INDIUM AND -THALLIUM ORGANOMETALLIC COMPOUNDS

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## Summary

Proton NMR data for the Group III methyl derivatives, $MMe_3$ and $LiMMe_4$ are compared with NMR data for the novel tin—Group III-metal bonded species, $Li[Me_3SnMMe_3]$ (M = Al, Ga, In and Tl) and for $Li[(Me_3Sn)_n\text{-}TlMe_{4-n}]$ ($n$ = 0 to 4), reported here for the first time.

The presence of tin—metal bonding in these derivatives is established by the observed tin-across-metal coupling constants and for the thallium derivatives by the additional observation of thallium-across-tin coupling.

The variation in the magnitudes of $^2J(SnCH)$, $^2J(TlCH)$, $^3J(SnMCH)$ and $^3J(TlSnCH)$ are reported as a function of M and as a function of the number of $Me_3Sn$ groups bound to thallium in the $[(Me_3Sn)_nTlMe_{4-n}]^-$ anions. Proposals concerning the factors governing the changes in these coupling constants and the chemical shifts are presented.

## Introduction

The study of the structure, spectra and bonding present in organometallic compounds containing metal—metal bonds is of significant interest and has been the subject of many reports, but few examples are known in which these compounds contain bonds between main group metals outside of the simple catenated species of silicon, germanium and tin or the more complex systems such as derivatives of boron hydrides or carboranes.

Some early reports which deal with the formation of simple boron—silicon or boron—germanium bonds include that of Seyferth et al. [1] who reported the formation of the species $Li[Ph_3BSiPh_3]$ and $Li[Ph_3BGePh_3]$ by the direct reaction between $Ph_3B$ and the appropriate lithium salt, $LiEPh_3$ (E = Si, Ge).

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Somewhat analogous attempts by Burg and Spielman [2] to form boron—tin bonds by reaction of $Me_3B$ of $Me_nBF_{3-n}$ with $NaSnMe_3$ gave mainly polymeric materials and hexamethylditin, but no evidence was obtained for the formation of a boron—tin bond. In several subsequent studies Nöth et al. [3—5] have reported the formation of boron—tin bonded species such as $(Me_2N)_2BSnEt_3$ in which the materials obtained are stabilized by some functional group such as the dimethylamino group, but a stabilizing influence is also exerted when the Group IV derivative is bound to a complex borohydride species [6].

Aside from such boron compounds, there had been essentially no reports relating to tin—Group III bonding until recently, as indicated in the reviews by Vyazankin et al. [7] and Newlands [8]. Kruglaya and coworkers found that while $Tl(GeEt_3)_3$ could be prepared in 90% yield by the reaction of $Et_3GeH$ and $TlEt_3$ at 100°C, the reaction between $Et_3SnH$ and $TlEt_3$ proceeded readily at —20°C but only thallium metal, hexaethylditin and ethane were observed as major products [9]. Since that time the same research group reported that tin—thallium compounds can be prepared from $TlEt_3$ and $(Me_3SiCH_2)_3SnH$ [10]. However, the first evidence for metal—metal bonding between tin and aluminum, gallium, indium and thallium was presented by us for compounds of the type $Li[Me_3SnMMe_3]$ (M = Al, Ga, In and Tl) [11, 12]. In our studies we found no evidence for the formation of tin—boron bonded species, even though the early reports of Group III—tin bonding described formation of the B—Sn bond. In addition, our evidence indicates that the stability of Group III—tin bonded species which we have studied increases as one proceeds down Group III from boron to thallium.

In order to provide some basis for understanding the stability, the bonding and the structure of the $Li[Me_3SnMMe_3]$ species, we have studied the proton NMR spectra of a number of these derivatives. We also provide evidence for the formation of the entire series of compounds, $Li[(Me_3Sn)_nTlMe_{4-n}]$ ($n = 0$ to 4). Special emphasis is placed on the observed metal-across-metal and long range metal—proton coupling which occurs in these thallium compounds as well as in the series of the form $Li[Me_3SnMMe_3]$ (M = Al, Ga, In and Tl). These results are discussed in terms of the implications which they have concerning the structure and bonding in these metal—metal bonded systems.

## Experimental

We have previously described the basic experimental techniques used in this study [11, 12] and have also discussed the synthesis and NMR spectra of $LiSnMe_3$ [13]. Compounds containing Sn—M bonds (M = Al, Ga and In) may be prepared in a quite pure form by the direct reaction of the Group III alkyl, $MR_3$, and $LiSnR_3$ in 1,2-dimethoxyethane (DME) at —60° C. When the same method was used in an attempt to prepare $Li[Me_3SnTlMe_3]$, it led to the formation of a variety of mixed species, $Li[(Me_3Sn)_nTlMe_{4-n}]$. The same type of species may also be obtained by reaction of $LiTlMe_4$ with $Sn_2Me_6$ [12].

*Preparation of Li[TlMe₄].* $Li[TlMe_4]$ was prepared in a manner similar to that used by Mach to prepare $Li[AlMe_4]$ and $Li[GaMe_4]$ [14], but because of its sensitivity to light, it was always handled in subdued light or darkness. Thus, an ether solution of $TlMe_3$ was added to excess lithium metal contained in an evacuated Schlenk tube which had been fitted previously with a high vacuum stopcock, a teflon-coated stirring bar and which had been covered with aluminum foil to keep the light out. The reaction was allowed to proceed for 2 h at 0°C. The bulk solvent then was stripped off leaving a white solid (somewhat grey due to small amounts of thallium metal) which was freed of ether by pumping for several hours under high vacuum. Based on the stoichiometry indicated in eqn. 1, a 70% yield of $Li[TlMe_4]$ was obtained. Our observations

$$3Li + 4\,TlMe_3 \rightarrow Tl + 3LiTlMe_4 \qquad (1)$$

led us to believe that yields were reduced because thallium metal generated in the course of the reaction formed a protective coating on the surface of the lithium chips used. We suggest, therefore, that use of lithium having a large surface area, such as lithium dispersion, should lead to increased yields under the same reaction conditions.

The isolated product was stored in vacuo at room temperature in the dark for 2 months with no obvious decomposition. Since $TlMe_3$ is known to detonate at 90°C, no attempt was made to determine the melting point of $LiTlMe_4$ [15]. Anal. Found: C, 18.1; H, 5.07; Li, 2.70; Tl, 75.31. $C_4H_{12}LiTl$ calcd.: C, 17.70; H, 4.45; Li, 2.56; Tl, 75.29%.

*Preparation of* $Li[(Me_3Sn)_nTl_{4-n}]$. These products are readily prepared by reaction of $LiTlMe_4$ with $Sn_2Me_6$ in DME as solvent. The value of $n$ is determined by the ratio of reactants and increases as the concentration of $Sn_2Me_6$ is increased according to eqn. 2. By way of example, the preparation of $Li[Tl(SnMe_3)_4]$ is given here.

$$LiTlMe_4 + n\,SnMe_6 \rightarrow Li[(Me_3Sn)_nTlMe_{4-n}] + n\,SnMe_4 \qquad (2)$$

A solution of $LiTlMe_4$ (0.70 g, 2.6 mmol) in 10 ml of DME was prepared in a stopcock-fitted, evacuable vessel containing an attached NMR tube. In a darkened dry box pure $Sn_2Me_6$ (2.3 ml, 11.0 mmol) was added dropwise to the solution at room temperature over a period of 5 minutes. A black suspension developed within minutes. The reaction mixture was then stored at 0° overnight. Approximately 50% of the solvent was removed on the vacuum line in order to reduce the relative concentration of the more volatile $SnMe_4$ in the remainder which was then decanted into the NMR tube and sealed off. The NMR spectrum of this sample indicated that no methylthallium species were present; the principal product was inferred to be $Li[Tl(SnMe_3)_4]$ together with traces of $SnMe_4$ and $Sn_2Me_6$.

## Results and discussion

We have commented on some aspects of the spectra of the methyltin species and on the products they formed in their reaction with Group III methyl derivatives [11, 12]. We have also dealt specifically with the solvent and temperature dependence of the NMR spectra of alkali metal—tin species such as $LiSnMe_3$ [13]. We now wish to discuss the spectra of some of the simpler species since they are important for identifying the new products. Such discussions may also begin to develop the necessary background to better understand the factors which result in the stabilization of the metal—metal bonds formed in these systems.

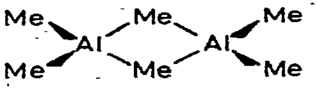
*Group III methyl derivatives.* Pertinent data for the NMR spectra of the Group III methyl derivatives involved in this study are listed in Table 1. First, for spectra recorded in hydrocarbons the chemical shifts of the simple trimethyl compounds vary inversely with the electronegativity of M, increasing with decreasing electronegativity. Second, in the presence of the basic solvent, DME, the chemical shifts of all of these species are moved upfield, with the magnitude of the change related approximately to the stability of the complex formed between the ether and the Group III alkyl. This shift is not wholly an inductive effect since a number of different terms enter in, including the change in local geometry and the introduction of additional groups into the local proximity of the methyl groups. Both the latter effects lead to changes in the chemical shifts of the methyl groups due to the modification of the local anisotropic fields associated with chemical bonds. Finally, the tetramethylmetalates are found at highest field because the addition of $CH_3^-$ to the trialkylmetal raises the electron density and leads to increased shielding of the methyl groups on the metal. The variation in the proton chemical shifts for the metalates, with the exception of boron, are again approximately inversely proportional to the electronegativity of the metal (M = Al, Ga, In and Tl). There are additional changes in chemical shifts of these species associated with contact ion pair solvent-separated ion pair equilibria. Such phenomena have been discussed for $LiBMe_4$ [19, 20] and for $LiAlMe_4$ [19—22]. The values reported here for $LiGaMe_4$ and $LiInMe_4$ are comparable to those reported by Wilkie [20] again with no metal—proton coupling observable in these systems.

TABLE 1

NMR DATA FOR GROUP IIIA METHYL DERIVATIVES

| M | *E.N.*[a] | $MMe_3$ in hydrocarbon $\delta^b$ | $MMe_3$ in DME $\delta^b$ | $LiMMe_4$ in DME $\delta^b$ |
|---|---|---|---|---|
| B | 2.04 | 0.71[c] | 0.83 | 2.22<br>($J(^{10}BCH)$ 1.88,<br>$J(^{11}BCH)$ 3.80) |
| Al | 1.61 | 1.82[c]<br>(b 1.20,<br>t 2.10)[d] | 2.45 | 2.83<br>($J(^{27}AlCH)$ 6.34) |
| Ga | 1.81 | 1.50[e] | 2.05 | 2.58 |
| In | 1.78 | 1.56[c] | 1.93 | 2.68 |
| Tl | 2.04 | 0.99[c]<br>($J$(TlCH) 251)[f] | 1.17<br>($J$(TlCH) 266)[f] | 2.01<br>($J$(TlCH) 223.1)[f] |

[a] *E.N.*, Pauling electronegativity as found in ref. 16. [b] Chemical shift δ is given in ppm above internal cyclopentane at 38°C. [c] Data taken from ref. 17 for spectra at ambient temperature. [d] Data taken from ref. 17 for hydrocarbon spectrum of trimethylaluminum at —70°C indicating the cessation of methyl exchange where b indicates bridge and t indicates terminal positions for methyl groups in



[e] Data taken from ref. 18. [f] Coupling constants reported here are the average of $^2J(^{203}TlCH)$ and $^2J(^{205}TlCH)$ since in DME coupling is observed for $TlMe_3$ only at low temperature (—70°C) and individual coupling constants due to $^{203}Tl$ and $^{205}Tl$ cannot be resolved. For $LiTlMe_4$, $^2J(^{203}TlCH)$ 222.2 and $^2J(^{205}TlCH)$ 224.1, however are observed at +38°C.

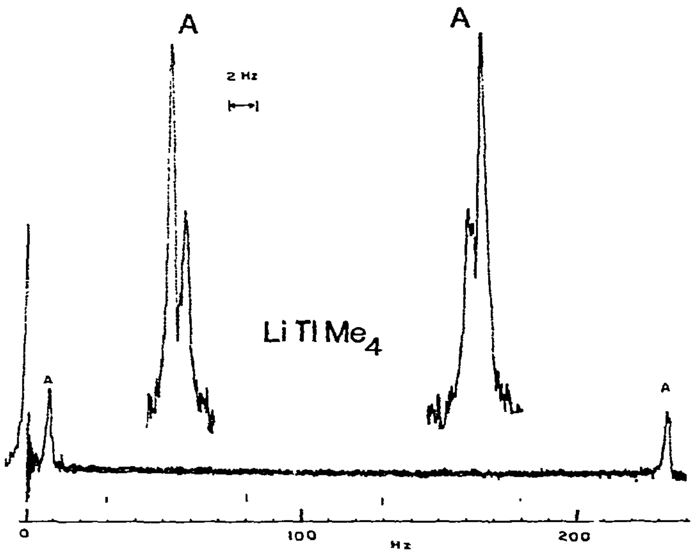


Fig. 1. The 60 MHz NMR spectrum of $LiTlMe_4$ in DME solution showing both $^3J(^{203}TlCH)$ 222.2 and $^3J(^{205}TlCH)$ 224.1 Hz, with cyclopentane at δ 0.

We first reported NMR data for $LiTlMe_4$ in our earlier communication [11] and now discuss its spectrum which is provided in Fig. 1. Since thallium has two isotopes of spin $I$ ½, $^{203}$Tl (29.50%, $\mu$ 1.5960) and $^{205}$Tl (70.50%, $\mu$ 1.6116), spectra of methylthallium compounds should show two sets of closely spaced lines. The separation between the inner lines of these two sets corresponds to $^2J(^{203}Tl—H)$ while the separation between the outermost lines is due to $^2J(^{205}Tl—H)$ and appears for the more intense set as seen in the expansion in Fig. 1. The ratio of $J(^{205}Tl)/J(^{203}Tl) = \mu(^{205}Tl)/\mu(^{203}Tl) = 1.0098$ and because of the closeness in the magnitudes of the two coupling constants, only an average value is observed if the lines are broadened for any reason or if the coupling constants are small.

The magnitude of the Tl—H coupling may be related to the amount of *s* character used by the thallium in its bonding orbital to this group, presuming that the major coupling term is a result of the Fermi contact interaction [23, 24]. This appears to hold for a series of thallium derivatives reported by Maher and Evans [23]. An extension of their data collected in Table 2 to include

TABLE 2

RELATION BETWEEN THALLIUM—PROTON COUPLING AND THALLIUM HYBRIDIZATION

| Compound | Presumed hydridization | $^2J$(TlCH) | Relative "s" character | Relative $^2J$(TlCH) |
|---|---|---|---|---|
| $TlMe^{2+}$ | *s* | 902$^{a1}$ | 1.00 | 1.00 |
| $TlMe_2{}^+$ | *sp* | —403$^{a2}$ | 0.50 | 0.45 |
| $TlMe_3$ | $sp^2$ | —251$^{a3}$ | 0.33 | 0.28 |
| $(TlMe_4)^-$ | $sp^3$ | 224$^b$ | 0.25 | 0.25 |

[a] Data taken from ref. 22. (1) Observed in $D_2O$ solution of $MeTl(ClO_4)_2$. (2) Observed in $CHCl_3$ solution of $Me_2Tl[OCH(CH_3)_2]$. (3) Observed in $CH_2Cl_2$ solution of $TlMe_3$. In donor solvents the coupling constant is slightly larger. [b] Observed for 0.3 *M* solution of $LiTlMe_4$ in DME at 38°C, this work.

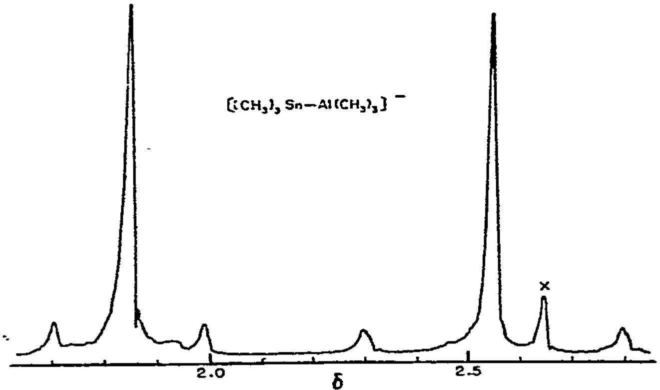


Fig. 2. The 60 MHz NMR spectrum of $[Me_3SnAlMe_3]^-$ with $^2J$(SnCH) 17.2 and $^3J$(SnAlCH) 29.6 Hz. Absorption X represents an impurity.

$LiTlMe_4$ shows excellent agreement, assuming $sp^3$ hybridization of the thallium center for this species. This observation generally supports the conclusion that the major contribution for $^2J$(Tl—H) coupling in these derivatives arises from the Fermi contact term operating across two bonds and provides a simple (although somewhat speculative) means for assigning approximate geometries and hybridizations for species which have Tl—$CH_3$ bonds.

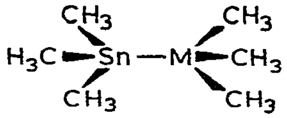
*Group III derivatives of the type Li[Me$_3$SnMMe$_3$].* The general appearance of the NMR spectra of the aluminum, gallium and indium derivatives is represented by the spectrum of $Li[Me_3SnAlMe_3]$ shown in Fig. 2. These spectra consist of two equally intense absorptions, the lowfield line due to the $SnMe_3$ moiety and the high field line to the $MMe_3$ group. Both lines are flanked by satellites with proper intensities which show that they arise from tin—proton coupling. The magnitude of the coupling varies as a function of M and is discussed below. The satellites flanking the upfield absorption are especially significant since these are due to $^3J$(SnMCH) and conclusively prove the existence of the tin—metal bond in these systems. The NMR parameters for the series of $Li[Me_3SnMMe_3]$ derivatives (M = Al, Ga, In and Tl) are listed in Table 3. These data, considered together with previous information on the $LiMMe_4$ compounds, support the proposed ethane type structure I for the anionic species $[Me_3SnMMe_3]^-$.

TABLE 3

NMR PARAMETERS FOR $Li[Me_3SnMMe_3]$ SPECIES[a]

| M | δ($MCH_3$) | $^3J$(SnMCH) | $^2J$($^{205}$TlCH) | δ($SnCH_3$) | $^2J$(SnCH) | $^3J$(TlSnCH) |
|---|---|---|---|---|---|---|
| Al | 2.55 | 29.6 | | 1.85 | 17.2 | |
| Ga | 2.28 | 34.0 | | 1.83 | 20.2 | |
| In | 2.33 | 21.0 | | 1.74 | 22.0 | |
| Tl | 1.73 | 17.2 | 223.1 | 1.68 | 24.5 | 32.0 |

[a] All data were recorded in —60°C DME solutions, coupling constants are reported in Hz and chemical shifts are reported in ppm relative to internal cyclopentane (δ(TMS) = +1.513 relative to cyclopentane).



(I)

A plot of the chemical shifts, δ($MMe_4$) in $LiMMe_4$ vs. δ($Me_3SnMMe_3$) in Li[$Me_3SnMMe_3$] (Fig. 3), shows a linear relationship. This implies that the factors which determine the chemical shifts in the two cases are similar but does not provide a specific answer as to the nature of these factors. As Shaw and Allred concluded for the structurally similar series, $Me_3SnEMe_3$, (E = C, Si, Ge and Sn) one of the major terms which contributes to the change in chemical shifts is the change in the anisotropy of the M—C and Sn—M bonds in the series [25]. In our series of compounds the chemical shifts of the methyl groups associated with the tin do not show as much variation, nor do they vary in such a linear fashion. Another parameter often shown to correlate well with chemical shifts is the electronegativity of the substituent, in this case, M (M = Al, Ga, In and Tl). Figure 4a and 4b show plots of the chemical shifts δ(MMe) and δ(SnMe) vs. the electronegativity of M for the Li[$Me_3SnMMe_3$] compounds. There are clear trends established between δ(MMe) and electronegativity of M, but certainly the scatter shown in these figures demonstrates that other factors are of major importance in influencing the chemical shifts of the protons. Without doubt, changes in the anisotropy of the bonds and small changes in geometry resulting from the elongation of the Sn—M and M—C bonds as M is varied must also contribute to the changes in the chemical shifts of the methyl protons.

Parameters listed in Table 3 can be compared with those which we obtained for DME solutions of hexamethylditin. The value of $^2J$(SnCH) of 49.1 Hz in $Sn_2Me_6$ is very much larger than that of $^2J$(SnCH) in any of the tin—Group III com-

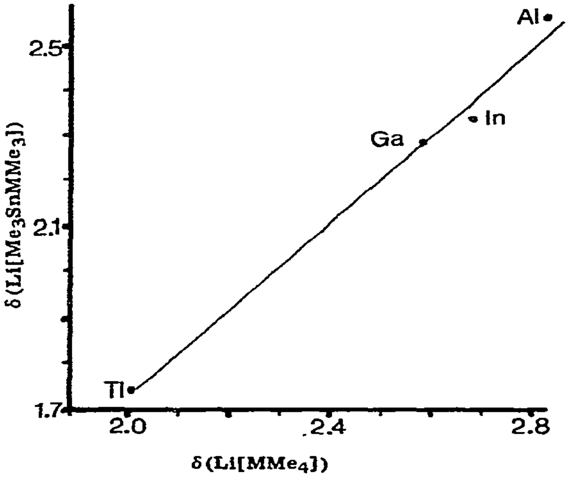


Fig. 3. Correlation between chemical shifts δ(Li[$Me_3SnMMe_3$]) and δ(Li[$MMe_4$]) of analogous methyl metal protons for M = Al, Ga, In and Tl. All δ values are in ppm upfield of cyclopentane.

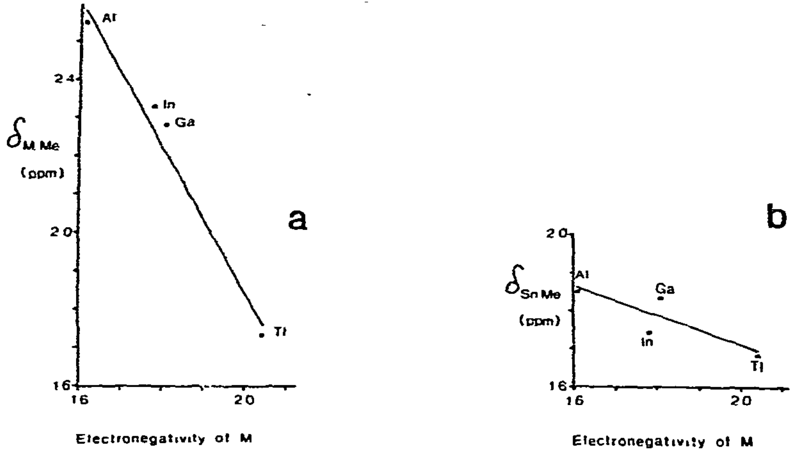


Fig. 4. Correlation between electronegativity of M in Li[Me$_3$SnMMe$_3$] compounds. (a) δ(MMe) in ppm vs. electronegativity of M where M = Al, Ga, In and Tl. (b) δ(SnMe) in ppm vs. electronegativity of M where M = Al, Ga, In and Tl.

pounds, whereas the value of $^3J$(SnSnCH) of 16.1 Hz in hexamethylditin is smaller than corresponding $^3J$(SnMCH) values in the tin—Group III species. Closer examination of the coupling constants for the LiMe$_3$SnMMe$_3$ shows that there is a regular increase in the magnitude of $^2J$(SnCH) as one proceeds down the series from aluminium. This roughly parallels the increase in size and electronegativity for the M substituent. In contrast to this, $^3J$(SnMCH) is larger in absolute magnitude than $^2J$(SnCH) and shows much more marked changes. However, these are not regular, first increasing from aluminum to gallium and then falling sharply to indium and thallium. In comparison with the analogous tin—Group IV series examined by Shaw and Allred [25] such changes suggest that different factors may govern the magnitude of the coupling constants in the two systems since these investigators observed only small irregular changes in $^2J$(SnCH), but a significant and regular decrease in the magnitude of $^3J$(SnECH) with increase in the size of E. These observations, along with those which we have reported, emphasize the complexity and multiplicity of factors which determine metal—proton and long range metal-across-metal—proton coupling.

The fact that no other metal—proton coupling can be resolved for M = Al, Ga and In is not surprising. Because of the large quadrupole moment of the aluminum nucleus, aluminum—proton coupling has been observed only for highly symmetrical species, such as solvated LiAlMe$_4$ [19—22]. Metal—proton coupling has never been observed for gallium and indium species, including LiGaMe$_4$ and LiInMe$_4$ [20].

*Li[(Me$_3$Sn)$_n$TlMe$_{4-n}$].* The unique nature of these metal—metal bonded species may best be appreciated by consulting the recent compilation on the chemistry of thallium, which includes a discussion on thallium—metal bonded compounds [26].

Following our initial efforts [11] we established that the reaction of LiTlMe$_4$ with Sn$_2$Me$_6$ [12] could produce desired Sn—Tl bonded species. We have since shown that all of the derivatives from $n = 1$ to 4 can be prepared by this route. Data derived from the NMR spectra of these species are presented

TABLE 4

NMR DATA FOR $Li[(Me_3Sn)_nTlMe_{4-n}]$

| Compound | $\delta(TlCH_3)^{a,b}$ | $^2J(^{205}TlCH)^{b,c}$ | $^3J(SnTlCH)^c$ | $\delta(SnCH_3)^a$ | $^2J(SnCH)^a$ | $^3J(TlSnCH)^c$ |
|---|---|---|---|---|---|---|
| A $LiTlMe_4$ | 2.01 (2.01) | 224.1 (220.8) | | | | |
| B $Li[Me_3SnTlMe_3]$ | 1.71 (1.73) | 227.8 (223.1) | 17.0 | 1.68 | 24.5 | 32.0 |
| C $Li[(Me_3Sn)_2TlMe_2]$ | 1.49 (1.49) | 220.2 (214.8) | 20.0 | 1.59 | 28.3 | 39.0 |
| D $Li[(Me_3Sn)_3TlMe]$ | 1.23 | 213.8 | 22.8 | 1.53 | 32.0 | 44.0 |
| E $Li[(Me_3Sn)_4$ | | | | 1.46 | $35.0^d$ | 47.4 |

[a] δ is given in ppm above internal cyclopentane for DME solutions (δ(TMS) = + 1.513 ppm relative to cyclopentane). [b] Values in parentheses were determined at —60° C in DME, others at 38° C. [c] Coupling constants are reported in Hz and are average values for $^{117}Sn$ and $^{119}Sn$ and for $^{203}Tl$ and $^{205}Tl$ since separate satellites could not be resolved for such relatively small values. [d] In $Li[(Me_3Sn)_4Tl]$ the individual coupling constants $J(^{117}SnCH)$ 34.3 Hz and $J(^{119}SnCH)$ 35.7 Hz could be resolved.

in Table 4. The spectrum obtained for a mixture of both $Li[(Me_3Sn)_2TlMe_2]$ and $Li[(Me_3Sn)_3TlMe]$ in the same solution is shown in Fig. 5. The preparation of these species by means of eqn. 2 also leads to the formation of $SnMe_4$, labelled X. Typically, these spectra consists of three regions. The central region (region 2) consists of methyltin absorption lines. It is flanked by two areas (labelled 1) which arise from methyl groups directly bound to thallium. For clarity, region 2 and the upfield portion of region 1 have been expanded in Fig. 5 in order to point out relevant features.

Thus, in region 1 two methylthallium species are present (labelled C and D as in Table 4) and both show tin satellites (due to $^3J$(SnTlCH)). The relative intensity of the satellites on compound D is greater than that on C, indicating a higher degree of tin substitution on thallium in species D. In region 2 the spectrum is somewhat more complicated due to the presence of $SnMe_4$ (X) and its satellites. In this region, species D appears as an intense doublet, due to

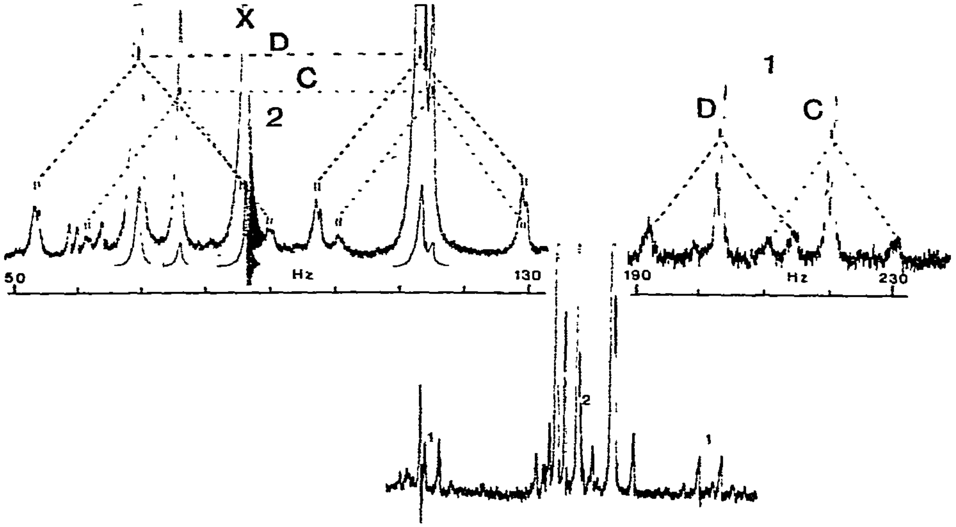


Fig. 5. The 60 MHz NMR spectrum of a mixture of $Li[(Me_3Sn)_2TlMe_2]$ (C), $Li[(Me_3Sn)_3TlMe]$ (D) and $SnMe_4$ (X). Region 2 consists of absorptions associated with methyltin groups while the regions labelled 1 are associated with methylthallium absorptions. The central region and the upfield region have been expanded for clarity with calibration relative to internal cyclopentane.

$^3J$(TlSnCH), each branch of which is flanked by tin satellites, due to $^2J$(SnCH). Species C exhibits a similar pattern with reduced intensity and at a more upfield chemical shift. By investigation of the relative magnitude of tin satellites in the methylthallium region and by comparison of the intensity of the absorption peaks in region 2 to those in region 1, the assignments given in Table 4 were made.

The spectrum of Li[(Me$_3$Sn)$_4$Tl] is presented in Fig. 6. Again, an absorption due to SnMe$_4$ is apparent; but, in addition, one due to Sn$_2$Me$_6$ is present since the stannylthallate is formed in the presence of excess Sn$_2$Me$_6$. The doublet nature of the spectrum arises from $^3J$(TlSnCH) and each of these peaks is flanked by tin satellites as indicated. Within the Li[(Me$_3$Sn)$_n$TlMe$_{4-n}$] series the chemical shift of protons on both tin and thallium decreases as $n$ increases. The magnitude of the coupling constants $^3J$(SnTlCH), $^2J$(SnCH) and $^3J$(TlSnCH) all increase as $n$ increases, whereas $^2J$(TlCH) increases with substitution of the first tin moiety and then decreases regularly.

Of major importance in the discussion of trends in coupling constants is the Fermi contact mechanism. A corrolary of this mechanism is that coupling interactions between nuclei depend upon the "s" character in the bonds connecting the nuclei since electrons in s orbitals have a finite probability of interacting with nuclei. The magnitude of metal—proton coupling should depend, therefore, on both the effective nuclear charge of the metal and hybridization or "s" character of metal orbitals involved in bonding. It has been shown for both thallium [23, 24] and tin [27—29] compounds, as well as for mercury compounds [30], that the magnitude of metal—proton coupling over two bonds can be satisfactorily related by means of such Fermi interaction. Of special interest is the fact that this mechanism appears to hold well for mercury—proton coupling over three bonds ($^3J$($^{199}$HgSiCH)) in trimethylsilylmercury derivatives [31, 32].

The values of $^2J$(TlCH) observed in the stannylthallates deviate only slightly from the value observed in LiTlMe$_4$, suggesting relatively little difference in the nature of the metal—carbon bond in these species. By comparison, values of $^2J$(SnCH) for these compounds exhibit larger variations. The fact that these values all lie well below that observed in SnMe$_4$ ($^2J$($^{119}$SnCH) 54.5 Hz) is indicative of the increased negative charge on tin in these species and may also re-

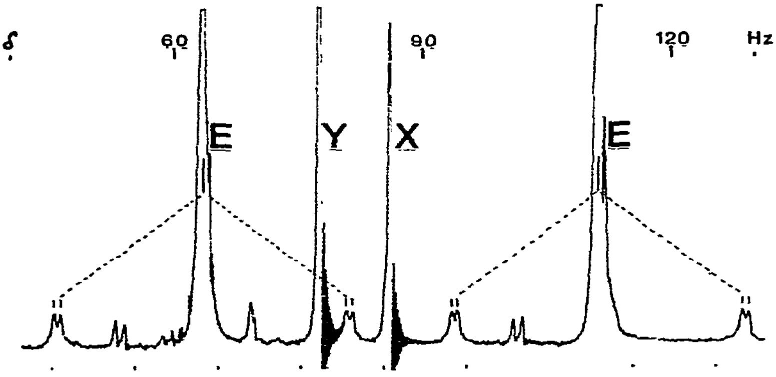


Fig. 6. The 60 MHz NMR spectrum of Li[(Me$_3$Sn)$_4$Tl] (E) with impurities of SnMe$_4$ (X) and Sn$_2$Me$_6$ (Y). Calibration is in Hz relative to cyclopentane.

flect an increase in "*p*" character in tin orbitals used in bond formation with carbon. It could also be suggested that the nature of tin—carbon bonding in the thallium complexes more closely parallels that in $\text{Li}[\text{Sn}(\text{SnMe}_3)_3]$ for which ${}^2J({}^{119}\text{SnCH})$ is 35.5 Hz.

Because of the previous correlations between observed and predicted trends in coupling constants, we had hoped in addition to relate variations in ${}^3J(\text{SnTlCH})$ and ${}^3J(\text{TlSnCH})$ to the nature of tin—thallium bonding in the $\text{Li}[(\text{Me}_3\text{Sn})_n\text{TlMe}_{4-n}]$ series. Since all the tin—thallium complexes have the same net charge (minus one), the effective nuclear charge on tin or thallium should not vary much from one compound to another in the series, and we might expect to correlate coupling constants to the hybridization of the metal orbitals. Examination of the data in Table 4 shows, however, that the contact interaction alone cannot account for all the observed trends since all coupling constants except ${}^2J(\text{TlCH})$ increase with increasing substitution of tin on thallium. Both ${}^2J(\text{SnCH})$ and ${}^3J(\text{SnTlCH})$ increase as one proceeds down the table which, making sole use of the Fermi term, suggests that the "s" character is increasing both in tin orbitals bonded to thallium and in those bound to carbon. This suggestion must be false if the total "s" character in all four tin orbitals is to remain constant. It also suggests that values of tin—proton coupling over three bonds cannot be satisfactorily related to the Fermi mechanism as opposed to values of tin—proton coupling over two bonds [27—29] and mercury—proton coupling over three bonds [31, 32].

There are several additional observations which may be made as well as some conclusions which may be drawn. The observations are that variation of the number of trimethyltin groups attached to a thallium atom gives rise to a nearly linear change in both short and long range coupling constants. This is clearly shown in Fig. 7a, 7b and 7c. It appears, therefore, that the factors which determine metal—proton coupling are all interrelated in these systems. Nonetheless, these are not compatible with the sole use of the Fermi contact description for coupling, as has been postulated for metal—proton coupling in

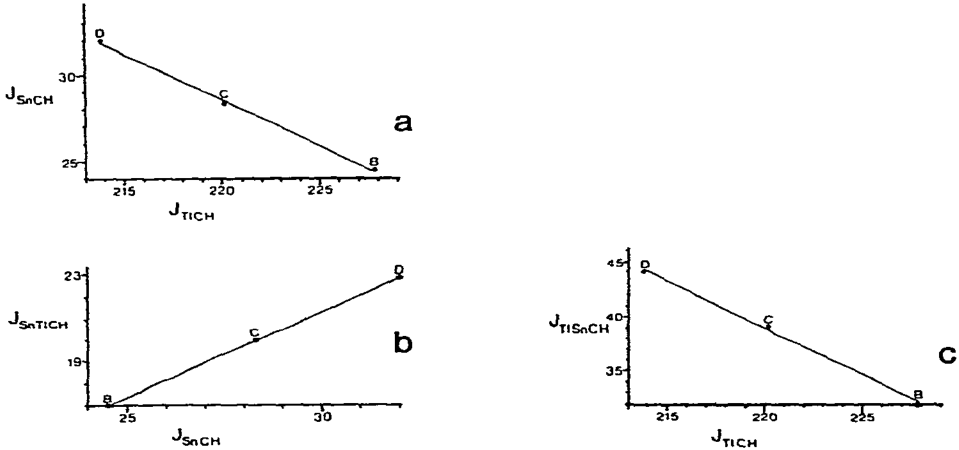


Fig. 7. Plots of data as listed in Table 4 for the $\text{Li}[(\text{Me}_3\text{Sn})_n\text{TlMe}_{4-n}]$ series for (a) ${}^2J(\text{TlCH})$ vs. ${}^2J(\text{SnCH})$, (b) ${}^3J(\text{TlSnCH})$ vs. ${}^2J(\text{TlCH})$ and (c) ${}^3J(\text{SnTlCH})$ vs. ${}^2J(\text{SnCH})$.

other systems, but appear to require some additional provision for coupling through other interactions.

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