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Through-Space Transmission of Polar Substituent Effects in the Bicyclo[1.1.1]pentane Ring System as Monitored by ^{119}Sn NMR Chemical Shifts: a ^{13}C and ^{119}Sn NMR Study of 3-Substituted-(X)bicyclo[1.1.1]pent-1-yltrimethylstannanes

William Adcock* and Alexander R. Krstic
Department of Chemistry, The Flinders University of South Australia, Adelaide, Australia 5001

A series of 3-substituted(X)bicyclo[1.1.1]pent-1-yltrimethylstannanes (3) were synthesized and their ^{119}Sn and ^{13}C NMR spectra were recorded. The ^{119}Sn substituent chemical shifts (SCS) and the one-bond carbon–tin coupling constants [$^1J(^{13}C,^{119}Sn)$] were analyzed in terms of possible substituent–probe interactions. The study clearly reveals that the ^{119}Sn NMR parameters of 3 are remarkably sensitive to modulation of the through-space back- or rear-lobe interactions between the bridgehead bond molecular orbitals by the electronic character of the substituent. An extraordinarily large four-bond tin–tin coupling constant in 3 ($X = SnMe_3$) highlights the significance of through-space bridgehead–bridgehead interactions in this system. © 1997 John Wiley & Sons, Ltd.

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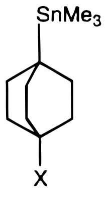
INTRODUCTION

Tin-119 NMR chemical shifts are very responsive to structural changes and their large range has made ^{119}Sn NMR a useful analytical tool.[1,2] Attempts to rationalize these shift variations are generally based on the assumption that the paramagnetic term (σ_p) to the shielding constant is dominant.[1,2] This contribution is generally expressed in a simplified form as shown in the equation

$$\sigma_A{}^p \propto \langle r^{-3}\rangle_{np}\,\Delta E^{-1}\sum Q_{AB} \qquad (1)$$

for an atom A [where r = mean orbital radius term (related to effective nuclear charge), ΔE = mean excitation energy and Q_{AB} = bond-order electron density matrix term]. For a series of structurally similar compounds, it is generally assumed that ΔE remains constant and, therefore, the charge dependence of chemical shifts resides either in the $\langle r^{-3}\rangle_{np}$ or $\sum Q_{AB}$ terms, or both. However, this simplified approach is often inadequate, hence there is a need for a better understanding of the elements underpinning these shifts. Consequently, given the complexities of shift theory of heavy nuclei,[1–3] empirical studies involving systematic structural variations on chemical shifts in model systems are most appropriate as this may assist the theoretical approach by delineating some of the important underlying factors. Remote substituent effects in rigid systems, which avoid ambiguities associated with proximity phenomena and conformational uncertainty, provide the most subtle and finely tuned responses of a nucleus to structural change. Hence studies of this kind in particular are essential for a proper appreciation of the relationship between chemical shift and molecular structure.

In previous studies,[4] we have shown by use of saturated polycyclic model systems (**1** and **2**) that ^{119}Sn NMR chemical shifts respond sensitively to remote (beyond two bonds) polar substituent influences. For example, the ^{119}Sn substituent chemical shifts (SCS) of 4-substituted(X)bicyclo[2.2.2]oct-1-yltrimethylstannanes (**1**) cover an impressive range of *ca.* 20 ppm (between I and $SnMe_3$). Regression analysis of the ^{119}Sn SCS of **1**, however, indicated a poor correlation with electrostatic field parameters (σ_F values). By means of polar-field susceptibility parameters (ρ_F) determined by a noncorrelative technique, some insight into the nature of the polar influence in **1** was achieved by factorization of the SCS into polar field ($\rho_F\sigma_F$) and residual contributions (SCS $- \rho_F\sigma_F$). The latter contributions, which are dominant, were ascribed to a through-three-bond electron delocalization mechanism (or double



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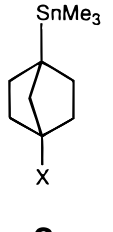

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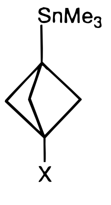

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* *Correspondence to*: W. Adcock.
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hyperconjugation). This proposal was subsequently confirmed by further model system studies.[5] However, a comparison of the ^{119}Sn SCS for a series of 4-substituted(X)bicyclo[2.2.1]hept-1-yltrimethylstannanes (**2**) with the corresponding data for **1** revealed not only that the total range of shifts for the former (*ca.* 6 ppm) is less than one third of that (20 ppm) for the latter but also that there is a striking and puzzling contrast,[4] namely that the signs of the SCS of **2** for every substituent are diametrically opposite to those observed for **1**! Since there was evidence to suggest that through-three-bond delocalization can be antagonistic to both through-two-bond and through-space interactions,[6,7] we argued largely by default that the shift trends in **1** and **2** are sensible only if through-space (back-lobe interactions) and through-three-bond contributions have shielding (or deshielding) effects which act in opposite directions.

In order to shed some light on this speculative proposal, we decided to initiate a ^{119}Sn and ^{13}C NMR study of a series of 3-substituted(X)bicyclo[1.1.1]pent-1-yltrimethylstannanes (**3**). Recent synthetic developments have made 1,3-disubstituted bicyclo[1.1.1]pentanes the archetypal model substrates for examining cross-cage interactions in polycyclic alkanes. These molecules have the unique feature that the non-bonded bridgehead carbon atoms are very close together (1.85 Å).[8,9] Hence the mandatory interaction between the back- or rear-lobes of the bridgehead bond MO orbitals is strong and can have profound physical and chemical consequences. For example, very large long-range NMR coupling constants between various nuclei at the bridgehead carbons of this system have been reported (18 Hz for H—H,[10] 71 Hz for H—F,[11] 30–60 Hz for H—P,[12] 156–226 Hz for H—Sn,[12b,13] and 22–38 Hz for C—F[14]) and, in addition, some of the largest ^{19}F SCS[14] yet observed for remote substituents in rigid aliphatic or aromatic systems. Studies of bridgehead radicals[8,9,15] and cations[8,16,17] of the bicyclo[1.1.1]pentane system also suggest strong bridgehead–bridgehead interactions.

We report here the syntheses of a limited series of **3** together with their ^{13}C and ^{119}Sn NMR spectra. Unfortunately, because of synthetic difficulties, a diverse range of substituents of the kind examined in **1** and **2** was precluded.

RESULTS AND DISCUSSION

Chemicals shifts

The ^{119}Sn SCS for **3** in CDCl$_3$, together with a dissection into polar field ($\rho_F \sigma_F$) and residual contributions (^{119}Sn SCS $- \rho_F \sigma_F$), are given in Table 1.

Regression analysis revealed that the SCS correlate poorly ($r = 0.56$, $n = 13$) against electric field parameters (σ_F),[18] as was the case for **1**. Excluding X = H, OCH$_3$ and Sn(CH$_3$)$_3$ from the data set notably improves the fit ($r = 0.86$, $n = 10$), but the precision is still poor. No attempt was made to affect multiple regression by including a group electronegativity (or σ-inductive[19]) parameter as the substituent set is not sufficiently diverse to ensure a meaningful exercise.

Table 1. ^{119}Sn substituent chemical shifts (SCS)[a,b] of 3-substituted (X) bicyclo[1.1.1]pent-1-yltrimethylstannanes (3): polar field ($\rho_F\sigma_F$) and residual contributions

X	SCS	$\rho_F\sigma_F$ [c]	Residual[d]
CN	14.39	5.03	9.36
CF$_3$	15.90	3.09	12.81
COOCH$_3$	12.83	2.01	10.82
CON(CH$_3$)$_2$	11.49	1.93	9.56
Ox[e]	11.38	1.93	9.45
COOH	13.14	2.47	10.67
OCH$_3$	32.20	2.01	30.19
C$_6$H$_5$	10.86	1.31	9.55
p-FC$_6$H$_4$	11.32	1.78	9.54
C(CH$_3$)$_3$	9.55	0.15	9.40
CH$_3$	5.67	0.23	5.44
Sn(CH$_3$)$_3$ [f]	−22.83	0.15	−22.68

[a] Chemical shifts (ppm) in CDCl$_3$ relative to parent system **3** (X = H). Accurate to ±0.1 ppm.

[b] Parent system (X = H) relative to internal Sn(CH$_3$)$_4$ (TMT): −46.92 ppm (CDCl$_3$). Downfield shifts are positive.

[c] ρ_F(CDCl$_3$) = 7.73. See Ref. 18 for σ_F values.

[d] Observed ^{119}Sn SCS $- \rho_F\sigma_F$ in ppm.

[e] 4,4-Dimethyl-2-oxazolinyl group; see Ref 14a for σ_F value.

[f] $J_{^{119}Sn-^{119}Sn} = 1611$ Hz. The ^{119}Sn–^{117}Sn coupling constant was multiplied by 1.046 to obtain $J_{^{119}Sn-^{119}Sn}$.

Factorization of the SCS was achieved by calculating the ρ_F value for **3** [$\rho_F = 7.73$(CDCl$_3$)] by dividing the chemical shift difference between **3** (X = *p*-FC$_6$H$_4$) and **3** (X = C$_6$H$_5$) by $\Delta\sigma_F$ for *p*-FC$_6$H$_4$ and C$_6$H$_5$ (0.06 for CDCl$_3$), as described previously for **1**.[4]

An examination of the data (Table 1) reveals that all the SCS are positive (downfield shifts) except for Sn(CH$_3$)$_3$, which is negative (upfield shift). This is in accord with the largely intuitive idea that electron-withdrawing and electron-donating substituents induce downfield and upfield shifts, respectively. A similar situation was observed for **1** but not for **2**.[4] The signs of the SCS for the latter system are diametrically opposite to those of **1** and **3** for the corresponding groups. It is noteworthy that the SCS of **3** cover a much wider range than those of **1** [*ca.* 55 *vs.* 14 ppm, between X = OCH$_3$ and Sn(CH$_3$)$_3$]. Accepting the idea that the electric field effect of remote substituents on NMR screening constants can be ascribed to differential polarization of the bonds about the magnetic nucleus,[20] the fairly similar ρ_F values for **3** and **1** (7.73 and 7.00 for CDCl$_3$, respectively) is surprising given that the distance factor ($1/R^3$) is significantly more favourable for the former than the latter system (the internuclear distance between the bridgehead carbons in bicyclo[1.1.1]pentane and bicyclo[2.2.2]octane is 1.85 Å[8,9] and 2.59 Å,[21] respectively). A possible compensating factor is that the Sn—C1 bond in **3** is significantly less polarizable than the corresponding bond in **1** as a result of the skeletal framework of the bicyclo[1.1.1]pentyl system being more rigid and highly strained. An alternative view is that distortion of the electron cloud surrounding the Sn nucleus by an electric field may be more difficult in **3** than **1** owing to the significantly different hybridization states of Sn in the two systems (see later).

It is significant that there is a distinct linear trend ($r = 0.907$, $r^2 = 0.823$; $n = 11$) between the SCS of **3** and **1**. This linear relationship is improved slightly

($r = 0.930$, $r^2 = 0.865$; $n = 10$) if the correlation is between the residuals (SCS $- \rho_F \sigma_F$). The corollary is that the dominant through-space and through-three-bond (double hyperconjugation) contributions to the ^{119}Sn SCS of **3** and **1**, respectively, roughly parallel one another. This is not entirely unexpected since both electronic mechanisms are largely controlled by the same pertinent molecular parameters (coefficients and energies) of the substrate–substituent and –probe (Sn) bond MOs. A major difference between them is that whereas the orbital interactions underlying the through-space effect are direct those governing the through-three-bond effect are indirect. Hence the lack of a precise relationship between the residuals is probably understandable in terms of a variable mix of energy and matrix element (coefficients) control for the two types of orbital interactions.[22]

Some insight into the nature of the orbital interactions governing the through-space effect in **3** is gained by examining the results of some high-level *ab initio* molecular orbital calculations reported by Wiberg and McMurdie.[16,23] These results indicate that removing electron density from the carbon bridgehead orbitals of bicyclo[1.1.1]pentane by σ-electron-withdrawing groups (electronegative substituents) significantly reduces the 1,3-non-bonded repulsion which appears to be the principal source of strain in the ring system. The converse situation holds for σ-electron donors (electropositive substituents). Thus, we ascribe the dominant orbital interactions governing the through-space contribution to the SCS of **3** (SCS $- \rho_F \sigma_F$; Table 1) to the bonding bridgehead orbitals (σ_{CX}–σ_{CSn}). Surprisingly, as we shall see later in connection with the one-bond coupling constants of **3**, σ^*_{CX}–σ_{CSn} orbital interactions (homohyperconjugation) appear relatively unimportant. The results for **3**, therefore, leave the origin of the 'reverse' SCS observed for **2** as somewhat of a conundrum. Interestingly, in connection with another study,[24] we have inadvertently discovered that the triflate group (X = OSO_2CF_3) provides the first example of a 'normal' SCS (positive sign for an electron-withdrawing group) for system **2**. The SCS($CDCl_3$) for OSO_2CF_3 in **2** is +1.97 ppm *vs.* −4.02 ppm for OH. The σ_F values ($CDCl_3$) of these groups are 0.67 and 0.29, respectively {derived from the appropriate ^{19}FSCS($CDCl_3$)of 1-X-4-(*p*-fluorophenyl)bicyclo[2.2.2]octanes}.[18] Thus, if we assume that the ρ_F value of **2** is similar to that of **1** [ρ_F($CDCl_3$) = 7.00], then approximately half of the downfield shift (*ca.* 6.0 ppm) on converting OH to OSO_2CF_3 can be ascribed to an enhanced electrostatic field influence. The remaining contribution must be a manifestation of the perturbed electron delocalization influence (possibly a through-two-bond interaction) as a result of a significant change in the electronegativity of O.

Coupling constants

Table 2. One-bond carbon–tin coupling constants ($^1J_{^{13}C-^{119}Sn}$) of compound 3[a]

X	$^1J_{^{13}C-^{119}Sn}$ (Hz)	$^1J_{^{13}CH_3-^{119}Sn}$ (Hz)	Σ[b]
H	371.3	319.2	1432.0
CN	356.7	342.3	1402.0
$COOCH_3$	371.3	331.7	1445.6
Ox	375.5	330.7	1457.2
COOH	368.4	333.2	1438.4
OCH_3	404.7	339.0	1553.1
C_6H_5	386.3	324.4	1483.3
p-FC_6H_4	384.1	325.7	1478.0
CH_3	391.2	319.4	1493.0
$C(CH_3)_3$	390.3	318.3	1489.2
$Sn(CH_3)_3$	298.6	299.9	1195.7

[a] Solvent, $CDCl_3$.
[b] Σ = sum of one-bond carbon–tin coupling constants.

The one-bond carbon–tin coupling constants [$^1J(^{13}C, ^{119}Sn)$] of **3** are given in Table 2. Before examining these data in detail, it is instructive briefly to revisit the $^1J(^{13}C,^{119}Sn)$ parameters of **1**, for which a diverse range of substituents are available.[4,25] Linear regression analysis indicates that an excellent correlation exists between $^1J(^{13}CH_3,^{119}Sn)$ and σ_F[18,26] for system **1**:

$$^1J(^{13}CH_3,^{119}Sn) = 27.20\sigma_F + 296.22 \tag{2}$$

(system 1; $r = 0.992$, $r^2 = 0.985$, $n = 17$)

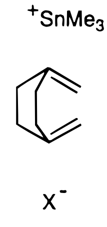
The precision of fit of the corresponding correlation for $^1J(^{13}C,^{119}Sn)$ is substantially less but still demonstrates a strong linear trend:

$$^1J(^{13}C,^{119}Sn) = -64.83\sigma_F + 473.49 \tag{3}$$

(system 1; $r = 0.920$, $r^2 = 0.847$, $n = 17$)

Accepting that the Fermi contact term is the dominant determinant of one-bond coupling,[1,2] we have interpreted these trends[4b] as being consistent with a redistribution of s character in the binding hybrid orbitals of tin as a result of the dominant polar-field influence of the substituent. Overlaid on this effect is the double hyperconjugative interaction[4,5,18a,c,25] of the substituent as depicted by canonical structure **4** (illustrated for only one of the three ethano bonds). The latter electronic mechanism impacts directly on the bond order of the C-1—Sn bond[25b] and, hence, is believed to be responsible for the less than perfect fit of the correlation between $^1J(^{13}C,^{119}Sn)$ and σ_F [Eqn (3)]. The fact that $\sum J$ (Hz) about Sn is fairly constant, however, highlights the dominance of the polar-field induced hybridization changes at the Sn atom in system **1**. Thus, the results for this system are an excellent benchmark against which corresponding data from other systems can be compared and interpreted.

A poor correlation ($r = 0.845$) exists between $^1J(^{13}CH_3,^{119}Sn)$ for system **3** (Table 2) and σ_F.



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However, excluding X = H, OCH_3 and $Sn(CH_3)_3$ from the data set leads to a very good linear relationship:

$$^1J(^{13}CH_3,^{119}Sn) = 44.68\sigma_F + 317.87 \qquad (4)$$

$$(\text{system } 3;\ r = 0.982,\ r^2 = 0.965,\ n = 10)$$

which is similar to the situation for **1**. The intercept of the correlation [Eqn (4)] provides a fairly accurate estimate of the $^1J(^{13}CH_3,^{119}Sn)$ value of the parent system (X = H, Table 2). This appears to confirm that there is no significant additional polar effect other than an electrostatic field influence perturbing $^1J(^{13}CH_3,^{119}Sn)$ when H is replaced by weakly electronegative carbon-based substituents in **3**. It is of interest to note that the slopes of the correlations for the two systems [44.68 (**3**) *vs.* 27.20 (**1**)] are significantly different. In terms of the hybridization model, the relative magnitude of these polar susceptibility parameters suggests that the Sn atom in **3** is considerably more responsive to polar field-induced rehybridization than that in **1**. The shorter distance in the former system compared with the latter is undoubtedly a major contributing factor as well as the differential polarizability of the bonds about the Sn nucleus in both systems. However, the fact that the calculated values of $^1J(^{13}CH_3,^{119}Sn)$ for OCH_3 and $Sn(CH_3)_3$ (329.5 and 318.8 Hz, respectively) derived from Eqn (4) (using σ_F values of 0.26[18a] and 0.02,[18b] respectively) deviate markedly from the observed values (see Table 2) clearly implicates an additional significant factor for very electronegative and electropositive substituents (see below).

In striking contrast to the reasonable correlation of the one-bond coupling constants to the bridgehead carbon in **1** [see Eqn (3)], the corresponding data for **3** exhibit no linear relationship whatsoever ($r = 0.04$, $n = 11$) against σ_F and, moreover, only a weak linear trend ($r = 0.822$) when X = H, OCH_3 and $Sn(CH_3)_3$ are excluded from the data set. Thus, the $^1J(^{13}C,^{119}Sn)$ trends for **3** demonstrate more markedly than the corresponding $^1(J^{13}CH_3,^{119}Sn)$ variations (see above) that an additional factor (or factors) overlays polar-field induced hybridization changes at the Sn atom in this system. A further demonstration of this point is that in contrast to **1**, $\sum J$ (Hz) about Sn for **3** varies significantly particularly for X = OCH_3 and $Sn(CH_3)_3$.

Based on the $^1J(^{13}C,^{119}Sn)$ trends of **1** (Eqn (3)), the electrostatic field effect of electron-withdrawing groups should act to reduce substantially the coupling constant (relative to X = H) to the bridgehead carbon of **3**. Furthermore, it was expected that this trend would be reinforced by a significant cross-cage interaction (homohyperconjugation, $\sigma_{C\text{–}Sn}\text{–}\sigma^*_{C\text{–}X}$; denoted by structure **5**) which would decrease the C—Sn bond order and, therefore, the one-bond coupling constant.

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It can be seen (Table 2) that only CN displays the expected trend. This particular substituent is endowed with a large polar field influence ($\sigma_F = 0.56$)[18a] but a feeble σ-electron-withdrawing effect. Note, however, that for the OCH_3 group, which has a moderate polar field influence ($\sigma_F = 0.26$)[18a] but is the strongest σ-electron withdrawer in the data set,[19] the one-bond coupling to C-1 is markedly *increased*! Furthermore, even the relatively weak σ-electron withdrawing alkyl groups [CH_3 and $C(CH_3)_3$], which exert virtually no electrostatic field influence,[18a] also increase $^1J(^{13}C,^{119}Sn)$. The converse situation holds for the very electropositive $Sn(CH_3)_3$ group ($\sigma_F \approx 0$),[18a,b] namely, a significant decrease in $^1J(^{13}C,^{119}Sn)$. We believe that these trends are a manifestation of substituent-induced changes in the 1,3-non-bonded repulsion between the bridgehead carbons[16,23] (see above). In the case of electronegative substituents, the repulsion is reduced and, hence, the electronic ground state is stabilized which translates into a strengthening of the C-1—Sn bond. The associated increase in the bond order leads to an increase in $^1J(^{13}C,^{119}Sn)$. On the other hand, the repulsion is increased on substitution with the electropositive $Sn(CH_3)_3$ group which destabilizes the electronic ground state and leads to consequential changes diametrically opposite to the σ-electron withdrawers, namely, a decrease in $^1J(^{13}C,^{119}Sn)$. It is important to note that direct experimental evidence for this phenomenon has recently emerged from an electrochemical study of 1-halo- and 1,3-dihalobicyclo[1.1.1.]pentanes.[27] This study revealed a significant increase in the strength of the bridgehead C—Br and C—I bonds when H at the other bridgehead is replaced by fluorine. More recently, high-level *ab initio* calculated bond dissociation energies of bicyclo[1.1.1]pentanes indicates that the C-1—H bond is increased by *ca.* 4 kcal mol^{-1} (1 kcal = 4.184 kJ) for a 3-fluoro substituent.[9] Perhaps the most surprising feature of the trends of $^1J(^{13}C,^{119}Sn)$ for **3** is that these parameters appear to offer no evidence for the importance of homohyperconjugative interactions ($\sigma_{CSn}\text{–}\sigma^*_{cx}$; see structure **5**). The dominant cross-cage orbital interaction appears to be clearly $\sigma_{CSn}\text{–}\sigma_{cx}$.

Finally, we wish to draw attention to the large coupling $^4J(^{119}Sn,^{119}Sn)$ between the tin nuclei in the ditin compound of **3** [X = $Sn(CH_3)_3$; see footnote f in Table 1). The extraordinary value of 1611 Hz for this coupling is to be compared with the much smaller coupling constants between similarly disposed tin nuclei in **2** [X = $Sn(CH_3)_3$][4] and 1,3-bis(trimethylstannyl)adamantane[28] (20.7 and 123.6 Hz, respectively). Because of the considerable internuclear distance between the bridgehead carbons in the latter compound (2.49 Å in adamantane; AM1 calculation),[29] it seems reasonable to assume that the coupling mechanism in this system is dominated by through-four-bond transmission and that the through-space contribution is negligible. Thus, assuming additivity of through-bond transmission of spin information,[30] the three equivalent through-four-bond pathways available in **3** should lead to a $^4J(^{119}Sn,^{119}Sn)$ value of *ca.* 371 Hz, which is considerably less than the observed value (see above). This suggests that the through-space component involving direct orbital interactions between the bridgehead carbon atoms dominates the coupling mechanism. Depending on whether the contributing through-bond and through-space components have the same or opposite sign, the latter contribution in **3** to $^4J(^{119}Sn,^{119}Sn)$ is estimated to be *ca.* 1240 or 1982 Hz, respectively. We favour the latter determination because of the very small value (20.7 Hz) of $^4J(^{119}Sn,^{119}Sn)$ in **2** [X = Sn(CH$_3$)$_3$]. In this system the bridgehead carbons are sufficiently proximate (2.27 Å in norbornane, AM1 calculated)[29] to allow significant through-space transmission of the spin information. Furthermore, the bridgehead C—Sn bonds are poorly aligned with the two ethano bridging bonds, hence only a minor contribution by $^5J(^{119}Sn,^{119}Sn)$ to the net tin–tin coupling in **2** [X = Sn(CH$_3$)$_3$] is to be expected. Spin transmission via the five-bond pathway is optimized in **1** [X = Sn(CH$_3$)$_3$; $^5J(^{119}Sn,^{119}Sn) = 120$ Hz[4]] because the three ethano bonds are optimally aligned in an antiperiplanar relationship with the bridgehead C—Sn bonds. The internuclear distance between the bridgehead carbons in this latter system (2.56 Å in bicyclo[2.2.2]octane, AM1 calculated)[29] ensures that a through-space contribution is negligible.[7]

EXPERIMENTAL

Synthesis of compounds

Except for the ditin compound (**3**, X = SnMe$_3$), which was prepared by lithiation of [1.1.1]propellane followed by treatment with trimethyltin chloride, all the tin compounds [**3**, X = H, CN, CF$_3$, CON(CH$_3$)$_2$, COOCH$_3$, Ox (4,4-dimethyl-2-oxazolinyl), COOH, OCH$_3$, C$_6$H$_5$, *p*-FC$_6$H$_4$, CH$_3$ and C(CH$_3$)$_3$] were prepared from the appropriate 3-substituted(X)bicyclo[1.1.1]pent-1-yl bromide or iodide by one or more of the following methods: (i) treatment with (trimethylstannyl) lithium (Me$_3$SnLi) in THF at 0 °C (direct trimethylstannylation; method A); (ii) treatment with *tert*-butyllithium in diethyl ether (lithium–halogen exchange) followed by the addition of trimethyltin chloride (method B); or (iii) irradiation (450 W medium-pressure Hg vapour lamp) in the presence of excess hexamethylditin (method C). A variation of method C is to irradiate (300 W tungsten lamp) a mixture of the appropriate *O*-acyl-*N*-hydroxy-2-thiopyridone derivative (Barton PTOC ester)[31] with hexamethylditin in dry benzene.[32] It should be noted that four of the tin compounds (**3**, X = H,[13] C$_6$H$_5$,[32] COOCH$_3$ [32] and COOH[32]) are known. Literature procedures were followed in the preparation of 1-bromobicyclo[1.1.1]pentane,[33] 1,3-diiodobicyclo[1.1.1]pentane,[34] 1-iodo-3-phenylbicyclo[1.1.1]pentane,[34] 1-iodo-3-methoxybicyclo[1.1.1]pentane,[35] 1-iodo-3-trifluoromethylbicyclo[1.1.1]pentane,[35b] 3-carbomethoxybicyclo[1.1.1]pentane-1-carboxylic acid,[36] methyl 3-bromobicyclo[1.1.1]pentane-1-carboxylate[32] and 3-bromobicyclo[1.1.1]pentane-1-carboxylic acid.[32] Some of the precursor halogen compounds {1-bromo-3-(4,4-dimethyl-2-oxazolinyl)bicyclo[1.1.1]pentane,[9] 1-bromo-3-fluorobicyclo[1.1.1]pentane,[9] 1-iodo-3-fluorobicyclo[1.1.1]pentane[37] and 1-iodo-3-methylbicyclo[1.1.1]pentane[38]} were available from other studies. A sample of 1-iodo-3-*p*-fluorophenylbicyclo[1.1.1]pentane was obtained by irradiation of a mixture of [1.1.1]propellane and 1-fluoro-4-iodobenzene following the procedure of Kaszynski *et al.*[34] for the preparation of the corresponding phenyl derivative. Following procedures recently described for the preparation of 1-chloro-3-iodoadamantane from 3-chloroadamantane-1-carboxylic acid,[28] 3-chlorobicyclo[1.1.1] pentane-1-carboxylic acid[32] and 3-*tert*-butylbicyclo[1.1.1]pentane-1-carboxylic acid[32] were converted into 1-chloro-3-iodobicyclo[1.1.1] pentane and 1-iodo-3-*tert*-butylbicyclo[1.1.1]pentane, respectively. The physical and spectral properties of the last two compounds were identical with those reported.[39] The remaining precursor halogen derivatives {3-bromobicyclo[1.1.1]pentane-1-carbonitrile[32] and *N*,*N*-dimethyl 3-bromobicyclo[1.1.1]pentane-1-carboxamide (m.p. 82–83 °C)} were prepared from 3-bromobicyclo[1.1.1]pentane-1-carboxylic acid[32] by the use of established functionalization procedures.

In most instances hexamethylditin was found to be a contaminant of the tin compounds. However, because its presence did not interfere with the ^{13}C and ^{119}Sn NMR measurements and, moreover, because of the general instability of the bridgehead stannanes (**3**), no determined effort was made to obtain most of the compounds in an analytically pure form. All the tin compounds (**3**) were unambiguously characterized by ^{13}C NMR spectroscopy (Table 3).

To highlight the instability of the stannanes, we draw attention to the fact that the ditin derivative (**3**, X = SnMe$_3$) decomposed completely within 4 weeks even though stored in the dark under nitrogen at 0 °C. In addition, an attempt to purify the methoxytin derivative by chromatography [basic alumina column (activity −2)] led to its rapid decomposition. The instability of the parent compound (**3**, X = H) has also been noted.[13]

Finally, we should mention that our attempts to prepare halogen derivatives of **3** (X = F, Cl and I) were unsuccessful. Trimethylstannylation (method A) of 1-bromo-3-fluoro-,[9] 1-iodo-3-fluoro-[37] and 1,3-diiodobicyclo[1.1.1]pentanes[34] gave only [1.1.1]propellane as the primary product. Tin substitution is not observed. Presumably the initial step in the reaction involves the formation of a bridgehead carbanion which collapses rapidly via an intramolecular S_N2-type substitution to the propellane.[25,28,40] Failure was also encountered when the aforementioned dihalo precursors (including 1-chloro-4-iodobicyclo[1.1.1]pentane) were irradiated in the presence of hexamethylditin (method C). It should be noted that we recently reported[9] on the unusual and unprecedented abstraction of fluorine and chlorine atoms by the triethylsilyl radical from the 3-fluoro- and 3-chlorobicyclo[1.1.1]pent-1-yl radicals, respectively. We suspect that facile termination steps of this sort by the trimethylstannyl radical are responsible for the failure of method C to effect tin substitution when applied to the 1,3-dihalobicyclo[1.1.1]pentanes.

Bicyclo[1.1.1]pent-1-yltrimethylstannane (3, X = H): method A. A solution of trimethylstannylsodium[28] in tetrahydrofuran (6 ml, 4.90 mmol, 2.4 mol equiv.) was added dropwise to a well stirred solution of 1-bromobicyclo[1.1.1]pentane (300 mg, 2.04 mmol) in THF (3 ml) maintained at 0 °C under nitrogen. After allowing the reaction mixture to warm to room temperature and then stirring overnight, the solvent was removed *in vacuo* (75 °C/720 mmHg) through a short column packed with glass helices followed by careful Kugelrohr distillation (75 °C/0.01 mmHg) to give the known[13] parent stannane as a colourless oil. ^{1}HNMR (CDCl$_3$), δ 2.76 (1H, s, CH), 1.82 (6H, s, CH$_2$), −0.11 (9H, s, SnMe$_3$; $^2J_{^{119}Sn-H} = 53.28$ Hz, $^2J_{^{117}Sn-H} = 51.0$ Hz, $^4J_{^{119}Sn-H} = 195.03$ Hz, $^4J_{^{117}Sn-H} = 186.58$ Hz). Exact mass spectrum: calculated for (M$^{+\cdot}$ − CH$_3$), 217.0039; found, 217.0043.

3-Cyanobicyclo[1.1.1]pent-1-yltrimethylstannane (3, X = CN): method A. A solution of trimethylstannyllithium[28] in THF (5 ml, 2.78 mmol, 2.4 mol equiv.) was added dropwise to a well stirred solution of 1-bromo-3-cyanobicyclo[1.1.1]pentane (200 mg, 1.16 mmol) in THF (2 ml) maintained at 0 °C under nitrogen. After allowing the reaction mixture to warm to room temperature and then stirring overnight, the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (15 drops). Commercial pentane fraction (50 ml) was then added to the reaction mixture. After drying (MgSO$_4$), the solvent was removed *in vacuo* and the residue submitted to Kugelrohr distillation to afford the desired compound as a colourless solid, m.p. 55–56 °C. ^{1}H NMR (CDCl$_3$), δ 2.24 (6H, s, CH$_2$), 0.02 (9H, s, SnMe$_3$; $^2J_{^{119}Sn-H} = 55.14$ Hz, $^2J_{^{119}Sn-H} = 52.62$ Hz). Exact mass spectrum: calculated for (M$^{+\cdot}$ − CH$_3$), 241.9992; found, 242.0036.

3-(4,4-Dimethyl-2-oxazolinyl) bicyclo[1.1.1]pent-1-yltrimethylstannane (3, X = Ox). Prepared from the corresponding bromide via method A as described above for the cyano derivative (**3**, X = CN). ^{1}H NMR (CDCl$_3$), δ 3.76 [2H, s, CH$_2$(Ox)], 2.00 (6H, s, CH$_2$), 1.13 [6H, s, CH$_3$(Ox)], −0.08 (9H, s, SnMe$_3$; $^2J_{^{119}Sn-H} = 54.12$ Hz, $^2J_{^{117}Sn-H} = 52.08$ Hz). Exact mass spectrum: calculated for (M$^{+\cdot}$ − CH$_3$), 314.0567; found, 314.0615.

3-Phenylbicyclo[1.1.1]pent-1-yltrimethylstannane (3, X = C$_6$H$_5$). Prepared from the corresponding iodide via method A as described above for the cyano derivative (**3**, X = CN). This is a known compound.[32] ^{1}H NMR (CDCl$_3$), δ 7.24 (5H, bs, C$_6$H$_5$), 2.12 (6H, s, CH$_2$), 0.05 (9H, s, SnMe$_3$; $^2J_{^{119}Sn-H} = 54.48$ Hz, $^2J_{^{117}Sn-H} = 52.02$ Hz).

3-(p-Fluorophenyl)bicyclo[1.1.1]pent-1-yltrimethylstannane (3, X = p-FC$_6$H$_4$). Prepared from the corresponding iodide via method A as

Table 3. ^{13}C NMR chemical shifts[a–d] of 3-substituted(X)bicyclo[1.1.1]pent-1-yltrimethylstannanes (3)

X	C-1	C-2	C-3	$Sn(CH_3)_3$	Other
H	30.77	55.01	38.20	−11.27	
	(371.3)		(134.9)	(319.2)	
	(355.0)		(129.0)	(304.9)	
CN	35.14	56.98	31.28	−11.11	115.8 (C⟨N)
	(356.7)	(6.6)	(172.7)	(342.3)	(119.2)
	(340.9)		(165.1)	(327.1)	(114.3)
CF_3	27.28	51.10	44.47	−11.53	119.8 (CF_3)
			[36.5]	(335.0)	[279.1]
				(320.3)	
$COOCH_3$	28.88	54.78	46.39	−11.15	168.4 (CO), 51.37 (CH_3)
	(371.3)		(137.0)	(331.7)	(115.6)
	(355.0)		(131.0)	(317.1)	(110.5)
$CON(CH_3)_2$	49.14	56.04	29.60	−11.20	168.3 (CO), 35.89 (CH_3)
				(329.2)	37.26 (CH_3)
				(314.7)	
Ox	29.65	54.81	43.02	−11.25	161.5 (CNO), 78.93 (CO)
	(375.5)		(144.6)	(330.7)	(109.2), 67.00 (CN)
	(359.0)		(138.2)	(316.2)	(104.4), 28.37 (CH_3)
COOH	28.86	54.59	46.12	−11.20	173.5 (CO)
	(368.4)	(7.60)	(136.6)	(333.2)	(112.8)
	(352.2)		(130.6)	(318.6)	(107.8)
OCH_3	14.61	53.85	68.23	−10.65	52.58 (CH_3)
	(404.7)		(201.0)	(339.0)	
	(386.2)		(192.0)	(324.6)	
C_6H_5	26.92	55.68	51.22	−11.05	141.9 (i), 125.6 (*o*)
	(386.3)		(138.0)	(324.4)	(92.2), 128.2 (*m*)
	(369.3)		(131.9)	(310.0)	(88.2), 126.1 (*p*)
p-FC_6H_4	26.78	55.74	52.53	−11.06	137.76 (*i*), 127.2 (*o*)
	(384.1)		(138.3)	(325.7)	(93.4), [7.8]
	(367.2)		(132.2)	(311.0)	(89.3), 114.9 (*m*)
					[3.3], [21.2]
					161.61 (*p*)
					[244.2]
CH_3	27.88	56.06	46.44	−11.23	20.31
	(391.16)		(135.94)	(319.35)	(96.69)
	(373.76)		(129.94)	(305.19)	(92.49)
$C(CH_3)_3$	24.07	50.27	57.68	−11.26	30.66, 25.61
	(390.3)		(123.8)	(318.3)	(81.8)
	(372.9)		(118.3)	(304.3)	(78.2)
$Sn(CH_3)_3$	42.97	60.21	42.97	−11.36	
	(298.6)		[92.7]	(299.9)	
	(284.5)		[89.0]	(286.7)	

[a] Chemical shifts for $CDCl_3$ solution relative to $(CH_3)_4Si$. Accurate to ±0.05 ppm. Positive shifts indicate decreased shielding.

[b] ^{13}C–$^{117,119}Sn$ coupling constants (in Hz) are given in parentheses.

[c] The number of the ring carbon atoms is shown in the structure.

[d] ^{13}C–^{19}F coupling constants (in Hz) are given in square brackets.

described above for the cyano derivative (3, X = CN). Kugelrohr distillation (150 °C/0.01 mmHg) gave the desired compound as an oil. ^1H NMR ($CDCl_3$), δ 7.80–6.92 (4H, m, *p*-FC_6H_4), 2.17 (6H, s, CH_2), −0.01 (9H, s, $SnMe_3$; $^2J_{^{119}Sn-H} = 53.60$ Hz, $^2J_{^{117}Sn-H} = 51.0$ Hz). Exact mass spectrum: calculated for ($M^{+\cdot} - CH_3$), 311.0328; found, 311.0258.

3-Trifluoromethylbicyclo[1.1.1]pent-1-yltrimethylstannane (3, X = CF_3). Prepared from the corresponding iodide via method A as described above for the cyano derivative (3, X = CN) except that the reaction mixture was worked up similarly to the parent stannane (3, X = H). After removing the solvent by distillation (760 mmHg) through a short column packed with glass helices, the bulk residues were Kugelrohr distilled (125 °C/0.1 mmHg). Further fractionation by Kugelrohr distillation (50 °C/150 mmHg) gave the title compound as an oil. ^1H NMR ($CDCl_3$), δ 1.84 (6H, s, CH_2), 0.00 (9H, s, $SnMe_3$; $^2J_{^{119}Sn-H} = 54.48$ Hz, $^2J_{^{117}Sn-H} = 52.44$ Hz); ^{19}F NMR ($CDCl_3$, relative to $CFCl_3$), δ − 76.23. Exact mass spectrum: calculated for ($M^{+\cdot} - CH_3$), 300.0148; found, 300.0197.

A sample of this compound was also obtained by method C as described below for the methoxy derivative (3, X = OCH_3).

3-*tert*-Butylbicyclo[1.1.1]pent-1-yltrimethylstannane [3, X = $C(CH_3)_3$] Prepared from the corresponding iodide as outlined above for the trifluoromethyl derivative (3, X = CF_3). Kugelrohr distillation (50 °C/0.01 mmHg) afforded the compound as an oil. ^1H NMR ($CDCl_3$), δ 1.69 (6H, s, CH_2), 0.82 [9H, s, $C(CH_3)_3$], 0.03 (9H, s, $SnMe_3$; $^2J_{^{119}Sn-H} = 53.40$ Hz, $^2J_{^{117}Sn-H} = 51.00$ Hz). Exact mass spectrum: calculated for ($M^{+\cdot} - CH_3$), 273.0665; found, 273.0697.

N,N-Dimethyl 3-trimethylstannylbicyclo[1.1.1]pentane-1-carboxamide [3, X = $CON(CH_3)_2$]. Prepared from the corresponding bromide via method A as described above for the cyano derivative (3, X = CN). ^1H NMR ($CDCl_3$), δ 3.05 [3H, s, $N(CH_3)_2$], 2.84 [3H, s, $N(CH_3)_2$], 2.15 (6H, s, CH_2), 0.00 (9H, s, $SnMe_3$; $^2J_{^{119}Sn-H} = 53.04$ Hz,

$^2J_{^{117}Sn-H} = 51.00$ Hz). Exact mass spectrum: calculated for ($M^{+\cdot} - CH_3$), 288.0410; found, 288.0375.

3-Methylbicyclo[1.1.1]pent-1-yltrimethylstannane (3, X = CH_3): method B. A solution of 1-iodo-3-methylbicyclo[1.1.1]pentane (900 mg, 4.3 mmol) in dry diethyl ether (10 ml) was cooled to −80 °C and treated dropwise with 4.5 ml of 1.94 M *tert*-butyllithium in pentane under an atmosphere of nitrogen. The reaction mixture was stirred for 15 min at this temperature before a solution of trimethyltin chloride (917 mg, 4.6 mmol) in diethyl ether (5 ml) was added dropwise. After stirring for a further 15 min at −80 °C, the reaction mixture was allowed to warm to room temperature. After removing the solvent by distillation (760 mmHg) through a short column packed with glass helices, the crude residue was Kugelrohr distilled (85 °C/30 mmHg) to give a clear, colourless liquid. ^{1}H NMR ($CDCl_3$), δ 1.73 (6H, s, CH_2), 1.055 (3H, s, CH_3), −0.006 (9H, s, $SnMe_3$; $^2J_{^{119}Sn-H} = 53.23$ Hz, $^2J_{^{117}Sn-H} = 50.85$ Hz). Exact mass spectrum: calculated for ($M^{+\cdot} - CH_3$), 231.0196; found, 231.0190.

Methyl 3-(trimethylstannyl)bicyclo[1.1.1]pentane-1-carboxylate (3, X = $COOCH_3$): method C. An NMR tube was charged with a solution of methyl 3-iodobicyclo[1.1.1]pentane-1-carboxylate (100 mg, 0.40 mmol), dry, degassed hexadeuterobenzene (1.2 ml), hexamethyldistannane (1.5 mol equiv.) and benzene (two drops; an internal integration standard and reference). The tube was exposed to radiation from a Hanovia 450 W medium-pressure mercury vapour lamp at a distance of 10 cm. Monitoring of several runs by ^{1}H and ^{13}C NMR spectroscopy indicated that the reaction was complete and the yield was optimized after irradiation for 2 min 45 s. After removing the solvent by distillation (760 mmHg) through a micro Vigreux column, the residue was Kugelrohr distilled (125 °C/0.10 mmHg) to give the tin ester as a colourless oil. ^{1}H NMR ($CDCl_3$), δ 3.64 (3H, s, $COOCH_3$), 2.11 (6H, s, CH_2), 0.06 (9H, s, $SnMe_3$; $^2J_{^{119}Sn-H} = 53.88$ Hz, $^2J_{^{117}Sn-H} = 51.60$ Hz). Exact mass spectrum: calculated for ($M^{+\cdot} - CH_3$), 275.0094; found, 275.0128.

3-(Trimethylstannyl)bicyclo[1.1.1]pentane-1-carboxylic acid (3, X = COOH). A solution of the corresponding ester (3, X = $COOCH_3$; 0.98 g, 3.39 mmol) in THF (15 ml) was added in one portion to a vigorously stirred solution of water (15 ml) and concentrated sulphuric acid (2.94 ml) maintained at 0 °C. The reaction mixture was then heated to 45 °C and maintained at this temperature for 48 h with stirring. After removing the THF *in vacuo*, the reaction mixture was extracted several times with dichloromethane. After drying ($MgSO_4$), the solution was concentrated *in vacuo* and the crude product loaded on to a silica column. Elution with dichloromethane removed impurities. The acid was recovered from the column by elution with methanol and, after removal of the solvent, Kugelrohr distilled (100 °C/0.05 mmHg) to afford a white solid (0.54 g, 58%), m.p. 144–147 °C; ^{1}H NMR ($CDCl_3$), δ 10.20 (1H, bs, COOH), 2.14 (6H, s, CH_2), 0.05 (9H, s, $SnMe_3$; $^2J_{^{119}Sn-H} = 53.88$ Hz, $^2J_{^{117}Sn-H} = 51.84$ Hz). Exact mass spectrum: calculated for ($M^{+\cdot} - CH_3$), 260.9938; found, 260.9932.

3-Methoxybicyclo[1.1.1]pent-1-yltrimethylstannane (3, X = OCH_3). Prepared from the corresponding methoxyiodide via method C as described above for the ester derivative (3, X = $COOH_3$). Kugelrohr distillation (125 °C/0.1 mmHg) afforded a colourless oil. ^{1}H NMR ($CDCl_3$), δ 3.26 (3H, s, OCH_3), 1.84 (6H, s, CH_2), 0.05 (9H, s, $SnMe_3$; $^2J_{^{119}Sn-H} = 54.48$ Hz, $^2J_{^{117}Sn-H} = 52.44$ Hz). Exact mass spectrum: calculated for ($M^{+\cdot} - CH_3$), 247.0145; found, 247.0158.

1,3-Bis(trimethylstannyl)bicyclo[1.1.1]pentane (3, X = $SnMe_3$). By use of a modified procedure of Szeimies and Bunz,[41] a flame-dried, argon-purged, three-necked, round-bottomed flask (1000 ml) fitted with a thermometer (−120 °C), a CO_2 condenser, a Rotaflow gas tap and a Flik-it tap was charged with 4,4′-di-*tert*-butylbiphenyl (DBB; 3.4 g, 2.80 mmol), dry THF (20 ml) and a magnetic follower. Finely cut slivers of lithium metal (2% Na) amalgam (100 mg, 14.40 mmol) were then added to the stirred solution at room temperature under argon, resulting in the formation of Li^+DBB^- within a few minutes, as evidenced by a dark blue–green coloration. The round-bottomed flask was then cooled to −100 °C and the CO_2 condenser charged with ethanol and liquid nitrogen to maintain a temperature of −80 °C. Dry dimethyl ether (150 ml) was then distilled from sodium–benzophenone into the THF solution of Li^+DBB^- and the mixture (now cloudy white in appearance) was allowed to stir at reflux (*ca.* 25 °C). After 5 h at reflux, the reaction mixture had regained its former rich blue–green colour.

By use of a modified version of a procedure outlined by Szeimies *et al.*,[42] a well stirred ethereal solution of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (4.15 g, 14.00 mmol) was cooled to −80 °C under nitrogen and treated dropwise with 14.7 ml of 2.0 M *n*-butyllithium (29.40 mmol, 2.1 mol equiv.) in cyclohexane. After stirring for 1 h at −15 °C the reaction mixture was allowed to warm to 0 °C and the [1.1.1]propellane together with diethyl ether were then distilled *in vacuo* (20 mmHg) through a short column packed with glass helices into a liquid nitrogen-cooled trap. ^{1}H NMR analysis of the condensate showed resonance signals for [1.1.1]propellane [δ($CDCl_3$) 1.98 s] and diethyl ether. It was free of 1-bromobutane.

A solution of the [1.1.1]propellane in diethyl ether (6.30 mmol, 15 ml; precooled to −25 °C) was added dropwise via a transfer line to the THF–$(CH_3)_2O$ solution of Li^+DBB^-. The reaction mixture was then stirred at reflux for a further 1 h, giving rise to the deep-red solvated 1,3-dilithiobicyclo[1.1.1]pentane.[41] A solution of trimethyltin chloride (2.51 g, 2.0 mol equiv.) in diethyl ether (2 ml) was added in one portion, causing the mixture to become instantly clear and colourless. After further reflux for 1 h, the $(CH_3)_2O$ was allowed to boil off before the THF was removed *in vacuo* by Kugelrohr distillation (50 °C/200 mmHg). Kugelrohr, distillation of the residue (75 °C/0.01 mmHg) gave the desired compound as an oil contaminated with hexamethylditin and a trace of trimethyltin chloride. The compound was further purified by Kugelrohr distillation (25 °C/0.05 mmHg). ^{1}H NMR ($CDCl_3$), δ 2.10 (6H, s, CH_2; $^3J_{^{119}Sn-H} = 4.08$ Hz), −0.01 (9H, s, $SnMe_3$; $^2J_{^{119}Sn-H} = 51.84$ Hz, $^2J_{^{117}Sn-H} = 49.80$ Hz). Exact mass spectrum: calculated for ($M^{+\cdot} - CH_3$), 378.9683; found, 378.9762.

The low yield (*ca.* 20%) of the ditin compound (3, X = $SnMe_3$) can be ascribed either to a rapid collapse of the initially formed 3-trimethylstannylbicyclo[1.1.1]pent-1-yllithium intermediate via an intramolecular S_N2-type substitution to give [1.1.1]propellane or to competing rapid electron transfer (SET) between the dilithio derivative and trimethyltin chloride. Both would lead to copious amounts of hexamethylditin, which was observed.

Spectra

Mass spectra were recorded on a Kratos MS25RF spectrometer. NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.75 MHz (^{1}H), 75.46 MHz (^{13}C) and 111.9 MHz (^{119}Sn). Proton-decoupled ^{13}C and ^{119}Sn NMR spectra were obtained on $CDCl_3$ solutions (*ca.* 0.1 M) with Me_4Si and Me_4Sn as an internal reference, respectively.

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