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Selective synthesis and multinuclear magnetic resonance study of 2-sila- and 2-stanna-indolines

The intriguing behaviour of the *N*,*C*-dilithio-reagent obtained from *ortho*-*N*- trimethylsilyltoluidine

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Abstract

Dilithiation of *ortho*-*N*-trimethylsilyltoluidine gives the *N*,*C*-dilithio-reagent **2**. The main product from the reaction of **2** in diethyl ether with dimethyltin dichloride is the *N*-trimethylstannyl-2-silaindoline derivative **4** rather than the expected *N*-trimethylsilyl-2-stannaindoline **3**. Mixtures of **3** and **4** are obtained if **2** is prepared in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), whereas the target compound (**3**) can be made if no donor solvent is present. A mechanism involving pentacoordinate silicon is proposed on the basis of $\delta(^{29}Si)$ NMR data for **2** in various solvents. The ^{13}C, ^{15}N, ^{29}Si and ^{119}Sn NMR data of **3**, **4**, and of *N*-trimethylsilyl-*N*-trimethylstannylarylamines (**1**) are reported.

Introduction

The reactivity of the tin–nitrogen bond in stannylamines is of interest for many useful transformations [1,2]. *N*-Trimethylstannylamines can be conveniently prepared by various routes [2,3], and these procedures can also be used to make the arylamines of type **1** that have been studied by multinuclear magnetic resonance spectroscopy in this work. Treatment of the *N*-lithio derivatives with Me_3SnCl gives **1** in yields of ~ 80%, and it was hoped that the reaction of the *N*,*C*-dilithio reagent **2** with Me_2SnCl_2 would give the 2-stannaindoline derivative **3**, since there is obvious interest in comparison NMR data for the compounds **1** and **3**. The synthesis of **2** and its reaction with Me_3SiCl has been described [4], and we were surprised to find that the reaction of **2** with Me_2SnCl_2 is by no means straightforward, and that compound **4** was obtained rather than **3** when the literature procedure [4] for the in

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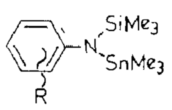
situ preparation of **2** was used. This prompted us to present an account of our attempts to synthesise **3**. The results are discussed, and a complete set of ^{13}C, ^{15}N, ^{29}Si and ^{119}Sn NMR data presented.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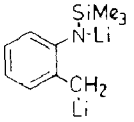
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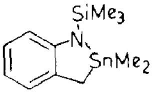
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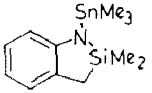
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1	a	b	c	d
R	H	2-Me	4-Me	2,6-Me_2

Results and discussion

Synthesis

The conditions used for the synthesis of the *N,C*-dilithio reagent **2** are given in Table 1, together with information on the product distribution in the distillate which was finally obtained after addition of Me_2SnCl_2 to the reaction mixture. The literature procedure (A) did not give the desired product **3**, but surprisingly the

Table 1

Experimental conditions for the preparation of **2** (from *ortho-N*-trimethylsilyltoluidine and two equivalents BuLi), and details of the products isolated from its reaction with Me_2SnCl_2

Experiment	Solvent(s)	Metalation Time (h) Temperature	Colour	Reaction with Me_2SnCl_2	Isolated [a] Yield (%)	Product **3** (%)	Distribution **4** [%]
A	Et_2O	48–60/25 °C	yellow	5 h reflux, stirring overnight	35	–	90 [b]
B	Et_2O/hexane (1/1)	60/25 °C	yellow	5 h reflux, stirring overnight	23	–	40 [c]
C	Et_2O/hexane (1/1) TMEDA [d]	22/reflux	light brown (suspension)	4 h reflux, stirring 2 h at 25 °C	36	70 [e]	15 [e]
D	hexane/TMEDA [f]	27/reflux	orange (suspension)	5 h reflux, stirring overnight	15	45 [g]	45 [g]
E	hexane	24/reflux	brown (suspension)	2 h reflux, stirring 2 h	25	90 [h]	–

[a] Based on tin in Me_2SnCl_2. [b] Impurities: ~ 5% of **1b** and ~ 5% of unknown compounds (see text). [c] Contains ~ 30% **1b** and ~ 30% of unidentified products (see text); according to $\delta(^{29}Si)$ data the residue contains mostly compounds with the 2-silaindoline ring. [d] TMEDA/BuLi 1/1. [e] Contains ~ 5% of **1b** and ~ 10% unknown products (see text). [f] TMEDA/BuLi 1.5/1. [g] Contains ~ 10% of unknown compounds (see text). [h] Contains ~ 3% of **1b** and ~ 7% of other materials (see text).

Table 2

^{13}C, ^{15}N, ^{29}Si and ^{119}Sn NMR parameters [a,b] for the arylamines **1**, **3**, **4**

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	MeSi	MeSn	Ar–Me	$\delta(^{15}N)$	$\delta(^{29}Si)$	$\delta(^{119}Sn)$
1a	152.4 [13.1]	129.1 [14.7]	129.0 [7.0]	122.1 [7.6]	129.0 [7.0]	129.1 [14.7]	2.5 [< 3] (56.7)	−4.0 [385.8]	–	−326.4 [22.1] (11.8)	+3.5 [21.0]	+66.0 [c]
1b	150.4 [16.8]	136.4 [12.0]	130.6 [6.6]	123.1 [8.1]	126.6 [7.0]	130.9 [12.5]	2.3 [< 3] (56.3)	−4.4 [383.7]	19.5 [< 3]	−332.4 [21.4] (11.9)	+2.9 [21.5]	+64.4
1c	149.5 [13.6]	129.5 [15.2]	130.0 [6.5]	131.1 [8.2]	130.0 [6.5]	129.5 [15.2]	2.5 [< 2] (56.7)	−4.1 [384.2]	20.9 [< 2]	−329.2 [20.0] (12.1)	+3.3 [22.6]	+64.5
1d	149.2 [18.0]	136.6 [12.5]	128.6 [8.7]	122.8 [9.8]	128.6 [8.7]	136.6 [12.5]	2.9 [4.4] (56.2)	−4.9 [380.9]	20.4 [< 2]	−338.2 [18.7] (12.8)	+2.7 [22.8]	+63.4
	C(7a)	C(4a)	C(4)	C(5)	C(6)	C(7)			C(3)			
3	154.9 [40.9]	130.3 [7.6]	132.2 [75.7]	116.5 [8.2]	126.7 [< 2]	117.1 [40.3]	1.9 [4.4] (56.1)	−2.8 [364.0]	15.3 [384.6]	−310.0 [25.7] (13.0)	+1.9 [14.0]	+136.8
4	156.8 [< 2]	130.6 [29.4]	129.9 [6.0]	116.6 [< 2]	126.8 [< 3]	113.6 [23.4]	2.3 [< 2] (54.5)	−5.7 [398.4]	18.0 [11.5] (54.5)	−313.5 [23.9] (10.1)	+24.2 [14.0]	+42.8

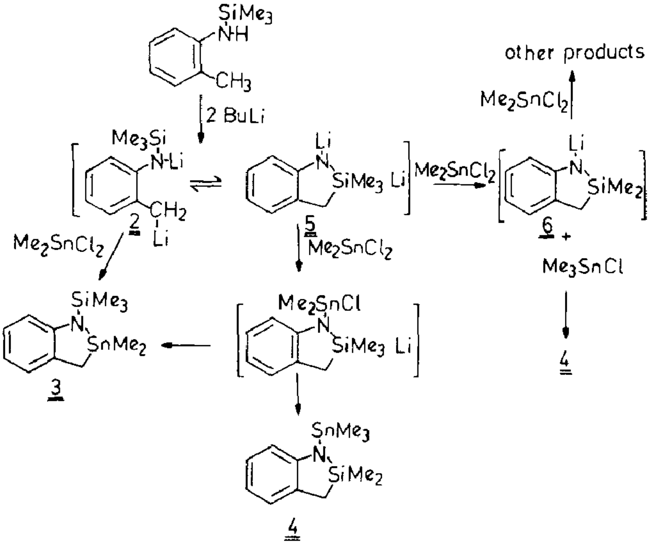
[a] In C_6D_6 (ca. 30%) in 5 mm (o.d.) tubes at 27° C; the δ values are given with respect to $\delta(^{13}C_{(C_6D_6)})$ 128.0 ($\delta(^{13}C_{(SiMe_4)})$ 0), $\delta(^{15}N_{(MeNO_2,neat)})$ 0, $\delta(^{29}Si_{(SiMe_4)})$ 0 and $\delta(^{119}Sn_{(SnMe_4)})$ 0; the values in square bracketts refer to $^{n}J(^{119}Sn^{13}C)$, $^{1}J(^{119}Sn^{15}N)$ and $^{2}J(^{119}Sn^{29}Si)$ in Hz (± 0.5); values in parentheses refer to $^{1}J(^{29}Si^{13}C)$ and $^{1}J(^{29}Si^{15}N)$ in Hz (± 0.5). [b] NMR parameters for the starting materials for comparison: *ortho*-N-trimethylsilyltolylamine; $\delta(^{13}C)$ 145.8 (C^1), 123.8 (C^2), 130.9 (C^3), 118.3 (C^4), 127.3 (C^5), 115.2 (C^6), 17.6 (Me), 0.2 (57.2) (MeSi); $\delta(^{15}N)$ −316.9; $\delta(^{29}Si)$ +2.5; 2,6-dimethyl-*N*-trimethylsilylaniline: 143.7 (C^1), 131.8 (C^2), 128.6 (C^3), 122.1 (C^4), 19.8 (Me), 1.1 (57.2) (MeSi); $\delta(^{15}N)$ −328.4; $\delta(^{29}Si)$ +4.4. [c] In reasonable agreement with the data obtained by $^{1}H\text{-}\{^{119}Sn\}$ NMR ($\delta(^{119}Sn)$ +64.0 [27]).

distillate contained another compound in ~ 90% purity, subsequently identified as **4** (vide infra). In an ether/hexane mixture (experiment B) the lithiation appears to be incomplete, as indicated by the presence of a considerable amount of **1b** in the distillate. Addition of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) [5] (experiments C and D) gave mixtures of **3** and **4**, and finally, when no donor solvent was present, **3** was obtained in 25% yield, and no **4** was observed under these conditions.

The NMR data for the major products **3** and **4** (Table 2) from experiments A to E prove that they are isomers. How are an Me_3Sn and an Me_2Si group formed from reagents containing Me_3Si and Me_2Sn groups? (It should be noted that we observed a small amount of **1b** in A and a considerable amount of **1b** in experiment B) We observed no indication for conversion of **3** into **4** or vice versa once they were isolated by distillation. Furthermore, we must emphasize that we did not detect any **4** when there were no donors present.

The phenomenon of association of organo- and amido-lithium compounds is well known [6] and the structures of *N,C*-dilithio reagents, in particular, are difficult to predict [7]. The product distribution obtained after reaction with an electrophile will be a function of the structure of the *N,C*-dilithio reagent and the nature of the electrophile (e.g. its Lewis acidity). The latter point is important since quenching of **2** with Me_3SiCl does not give products containing the 2-silaindoline ring [4,28*].

Our experimental observations indicate that consideration must be given to intermediates such as **5** which involves a pentacoordinate silicon atom linked to the three methyl groups, the nitrogen atom, and the CH_2 group (Scheme 1). As indicated by a preliminary ^{29}Si NMR study of solutions of **2** in benzene, ether, or toluene/TMEDA (vide infra and Table 3), the presence of a donor solvent will favour such an arrangement as it offers additional coordination sites for the lithium



Scheme 1. Proposed mechanism for the competing formation of **3** and **4**.

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* Reference number with asterisk indicates a note in the list of references.

Table 3

^{29}Si and some ^{13}C NMR data [a] for various solutions of the *N*,*C*-dilithioreagent **2**

Solvent(s)	$\delta(^{29}Si)$	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_2	MeSi
Et_2O (diluted)[b]	−11.6	–	–	–	–	–	–	–	–
C_6D_6 (sat.)[c]	+20.9	165.4	134.1	129.9	113.6	127.2	112.8[d]	19.0[e]	2.7
TMEDA/toluene[f] (2/3)	−15.9[g]	–[h]	–[h]	–[h]	–[h]	–[h]	–[h]	27.2 (broad)	4.0 (broad)

[a] For references of δ values see footnote *a* in Table 2. [b] $\delta(^1H)$: 0.19 ($SiMe_3$), 1.80 (CH_2), 6.23, 6.41, 6.75, 7.00 (aromatic protons). [c] $\delta(^1H)$: 0.34 ($SiMe_3$), 2.03 (CH_2), 6.55, 6.65, 7.05, 7.32 (aromatic protons). [d] ^{13}C resonance signal is significantly broadened. [e] *J*-modulated spectrum confirms that this ^{13}C resonance belongs to a CH_2 group. [f] $\delta(^1H)$: 0.29 ($SiMe_3$), – (CH_2) hidden underneath the toluene/CH_3 resonance, 6.1, 6.52, 6.55, 6.63 (aromatic protons). [g] Fairly broad ^{29}Si resonance signal at room temperature which sharpens at lower temperature; at −40 °C: $\delta(^{29}Si)$ −15.8 and three additional ^{29}Si resonance signals of low intensity (< 10%) with $\delta(^{29}Si)$ +18.8, −13.6, −14.9. [h] All ^{13}C resonance signals of the aromatic carbons are broad and of low intensity.

ions. If MeLi complexes in donor solvents were present both Me_3SnCl (formation which is required by the products obtained) and Me_4Sn should be formed and the latter has not been observed in the ^{119}Sn NMR spectra of the reaction solutions. If the intermediacy of **5** is assumed several pathways for the reaction can be envisaged. The first step in the reaction of **5** with Me_2SnCl_2 may be the formation of the Sn–N bond, followed by an intramolecular transfer of the CH_2 or a CH_3 group from silicon to tin to give **3** or **4**, respectively. Alternatively, **5** may react with Me_2SnCl_2 at the Si–CH_2 bond (leading directly to **3**) or at the Si–CH_3 bond to give **6** and Me_3SnCl. Of course, these may combine to give **4**, but there is also a chance that **6** (two equivalents) would react with Me_2SnCl_2 to give other high boiling products containing the 2-silaindoline unit (detected in the residue of experiment B by ^{13}C, ^{29}Si and ^{119}Sn NMR).

Various impurities present in all the distilled samples stem from BuLi which was not fully consumed in the lithiation process, and which reacts primarily with Me_2SnCl_2 to give butyltin compounds.

NMR spectra (Table 2,3)

The assignment of the ^{13}C resonances in the aromatic region is based on the complete assignment of the corresponding ^{1}H NMR spectra (NOE-difference experiments [8], ^{1}H-{^{1}H} double resonance studies and comparison of experimental with calculated spectra) and the two-dimensional (2D) ^{13}C,^{1}H shift correlated spectra [9]. ^{15}N, ^{29}Si and ^{119}Sn NMR spectra were recorded by the refocused INEPT technique [10] with ^{1}H decoupling. In order to obtain quantitative information on the product distribution (of **3**, **4**, and other products containing tin) the ^{119}Sn NMR spectra were also recorded by inverse gated decoupling (for suppressing the negative NOE [11]). For the compounds studied there were only small differences between the integrals of ^{119}Sn resonances recorded by the two techniques. The measurement of ^{15}N NMR spectra was optimized by determination of a long range ^{15}N–^{1}H spin–spin coupling suitable for developing the *J*-ordered state required for the INEPT pulse sequence. It turned out that $^3J(^{15}N^1H)$ coupling to the MeSi or MeSn protons has a value of 0.8 to 1.5 Hz. When the best $^3J(^{15}N^1H)$ value had been found (usually the comparison of the results was possible after 8 scans for each value) it took between 3 to 6 h to observe the $^{117/119}$Sn, and ^{29}Si satellites corresponding to the coupling constants $^1J(^{117/119}\mathrm{Sn}^{15}\mathrm{N})$ and the $^1J(^{29}\mathrm{Si}^{15}\mathrm{N})$, respectively [12].

Chemical shifts $\delta(^{13}C)$, $\delta(^{15}N)$, $\delta(^{29}Si)$, $\delta(^{119}Sn)$

The $\delta(^{13}\mathrm{C})$ values for the aromatic carbon atoms serve as a measure of mesomeric interactions [13]. The decreased shielding of the ^{13}C(2,6)- and ^{13}C(4) nuclei in **1b**,**1d** with respect to these in **1a**,**1c** is typical of conformations in which the preferred orientation of the nitrogen lone electron pair is perpendicular to the plane of the benzene ring. In the ring systems of 2-stanna- (**3**) or 2-sila indoline (**4**) the coplanarity is enforced and, consequently, the shielding of the $^{13}\mathrm{C}^{4a,7}$ and $^{13}\mathrm{C}^5$ nuclei is increased with respect to that in **1b**.

Mesomeric interactions are known to affect the ^{15}N nuclear shielding [14]. In **3** and **4** π-interactions between the nitrogen atom and the aromatic system will cause reduced shielding of the ^{15}N nuclei ($\delta(^{15}\mathrm{N})$ -310.0 and -313.5, respectively) with respect to that in **1b** ($\delta(^{15}\mathrm{N})$ -332.4), although part of the $\delta(^{15}\mathrm{N})$ value has to be ascribed to the changes in the bond angles at the nitrogen atom.

The experiments A–E suggest that the nature of **2** in solution depends on the solvent. The $\delta(^{29}\mathrm{Si})$ values in Table 3 confirm when account is taken of the low ^{29}Si nuclear shielding of **2** in benzene solution as compared to that in ether or toluene/TMEDA as solvent. The reduced shielding of **2** in benzene solution can be accounted for if the neighbouring nitrogen atom serves as donor for more than one lithium ion [15*]. In donor solvents these interactions are less likely, and the coordination number of the silicon may increase as a result of carbanion formation at the CH_2 group. Although a fast equilibrium between **2**, **5** and MeLi complexes together with a cyclic species containing the Me_2Si unit cannot be ruled out, the well shielded ^{29}Si nuclei in donor solvents are more consistent with a penta-coordinate silicon atom.

The $\delta(^{29}\mathrm{Si})$ value for **3** ($\delta(^{29}\mathrm{Si})$ 1.9) is very similar to those for **1** and other *N*-trimethylsilylamines [16]. If the ^{29}Si nucleus becomes part of a five-membered ring system its nuclear shielding is considerably reduced with respect to that for non-cyclic systems or six-membered rings, as has been observed for silacyclopentanes [17], silacyclopentenes [18], and other five-membered rings containing silicon, carbon and other heteroatoms [19]. This effect is usually attributed to changes in the inter-bond angles at the silicon atom [20*], and is also observed in the case of **4** ($\delta(^{29}\mathrm{Si})$ 24.2). The large difference in the $\delta(^{29}\mathrm{Si})$ values for the structural units in **4** and **3** or **1** helps in assessment of the composition of the reaction solutions of **2** with Me_2SnCl_2 or even of the residues from distillations (as in experiment B). The changes in the $\delta(^{119}\mathrm{Sn})$ values parallel those of $\delta(^{29}\mathrm{Si})$ values in comparable compounds [21], but the effects are much more pronounced. Therefore, the shielding of the ^{119}Sn nucleus in **3** ($\delta(^{119}\mathrm{Sn})$ + 136.8) is much reduced with respect to that for **1** (+64.0) or **4** (+43.8). We note that ^{29}Si and ^{119}Sn NMR data provide complementary information on the product distribution.

Coupling constants $^1J(^{29}Si^{13}C)$, $^nJ(^{119}Sn^{13}C)$, $^1J(^{29}Si^{15}N)$, $^1J(^{119}Sn^{15}N)$, $^2J(^{119}Sn^{29}Si)$

The $^1J(^{29}\mathrm{Si}^{13}\mathrm{C})$ [16] and $^1J(^{119}\mathrm{Sn}^{13}\mathrm{C})$ values [11] fall in the usual range. In the case of **4** the observation of a value of $^1J(^{29}\mathrm{Si}^{13}\mathrm{C})$ of 54.5 Hz for the CH_2 group is further proof for the incorporation of silicon in the five membered ring. The same holds for **3** on consideration of the values of $^1J(^{119}\mathrm{Sn}^{13}\mathrm{C})$ of 384.6 Hz for the CH_2

group. However, the coupling constants ${}^nJ({}^{119}Sn{}^{13}C)$ are even more instructive, particularly for $n = 3$, where we expect the usual Karplus-type dependence on the dihedral angle. There are numerous data for ${}^3J({}^{119}Sn{}^{13}C)$ coupling across C–C bonds for compounds with rigid structures [11,22], and for **3** the ${}^3J({}^{119}Sn{}^{13}C^4)$ value (75.7 Hz) fits into the data set with a dihedral angle close to 180°. To our knowledge, the data reported here show for the first time that this relationship for ${}^3J({}^{119}Sn{}^{13}C)$ is also valid if one of the intervening atoms is a nitrogen atom. This is shown by the ${}^3J({}^{119}Sn{}^{13}C^7)$ values for **3** (40.3 Hz), **4** (23.4 Hz) and ${}^3J({}^{119}Sn{}^{13}C^6)$ for **1b** (12.5 Hz), for which we have to assume dihedral angles in the vicinity of 180° (**3**), 0° (**4**), and between 60 to 90° (**1b**).

Many ${}^1J({}^{29}Si{}^{15}N)$ values have been reported recently [12,23,24], mostly for compounds with Si–NH groups, e.g. for $Me_3SiNHPh$ ${}^1J({}^{29}Si{}^{15}N)$ 15.7 Hz [24a]. The values for **1**, **3**, **4** are smaller, owing to the presence of the stannyl group as a second electropositive substituent [12]. The relationship between ${}^1J({}^{29}Si{}^{13}C)$ and ${}^1J({}^{29}Si{}^{15}N)$ values [24b] shows that all ${}^1J({}^{29}Si{}^{15}N)$ values in *N*-trimethylsilylamines have a positive sign. So far ${}^1J({}^{119}Sn{}^{15}N)$ values for *N*-trimethylstannylarylamines have been reported only for ${}^{15}N$-labelled derivatives, such as $Me_3SnNHPh$ (-26.7 Hz [25]) and $(Me_3Sn)_2NPh$ (-41.4 Hz [26]). Thus we assume that the sign of ${}^1J({}^{119}Sn{}^{15}N)$ is also negative in **3** and **4**. Then we observe the analogous trend for ${}^1J({}^{119}Sn{}^{15}N)$ (< 0) and ${}^1J({}^{29}Si{}^{15}N)$ (> 0), i.e. a negative contribution to the ${}^1J$-values if the ${}^{119}Sn$ or the ${}^{29}Si$ nucleus is part of the five-mebered ring. The $|{}^2J({}^{119}Sn{}^{29}Si)|$ values are identical for **3** and **4** (14.0 Hz), but they are smaller than for compounds **1** (22 ± 1 Hz). As their sign is not known and the data set for comparison is still limited, further discussion must be postponed.

Experimental

All the compounds were prepared and handled with the usual precautions for excluding moisture and oxygen. The *N*-trimethylsilylamines were prepared by published procedures [3] and checked for purity by ${}^1H$, ${}^{13}C$ and ${}^{29}Si$ NMR spectroscopy. Commercial solutions of BuLi in hexane (1.56 *M*) were used. The solution of BuLi in Et_2O was obtained by removing the hexane in vacuo and slowly adding the same volume of Et_2O.

The NMR spectra were recorded with a Bruker AC 300 spectrometer, (see Table 2 for further details). Mass spectra (80 eV) were obtained with a Finnigan MAT CH5 instrument.

*N-Trimethylsilyl-N-trimethylstannyl-arylamines (**1a, b, c, d**)*

At room temperature 10 ml of BuLi in hexane (15.6 mmol) were added to a stirred solution of 15 mmol of the *N*-trimethylsilylarylamine in 30 ml of hexane. The mixture was heated under reflux for 4 h, then cooled to −78°C, and a solution of 3 g (15 mmol) of Me_3SnCl in 10 ml Et_2O was added. The suspension was allowed to warm to room temperature then heated under reflux for 2 h. The unsoluble materials were filtered off and the solvents were removed in vacuo. Fractional distillation of the residue gave compounds **1** as colourless, extremely moisture-sensitive liquids. Yields and b.p.: **1a** (89.6%) 45–48°C/0.15 Torr; **1b** (82.5%) 60–61°C/0.2 Torr; **1c** (80.0%) 56–57°C/0.15 Torr; **1d** (68.5%) 61–63°C/0.03 Torr. 300 MHz ${}^1H$ NMR in C_6D_6: **1a** $\delta({}^1H)$ (${}^nJ({}^{119}Sn{}^1H)$) 0.12 Hz [55.7] s, 9H,

Me_3Sn; 0.13 s, 9H, Me_3Si; 6.85 m, 3 H, 7.05 m, 2H, Ar–H; **1b** 0.07 [55.3] s, 9H, Me_3Sn; 0.10 s, 9H, Me_3Si; 2.17 s, 2-Me; 7.10 m, 1 H, Ar-H^3; 6.88 m, 1H, Ar-H^4; 6.98 m, 1H, Ar-H^5; 6.89 m, 1H, Ar-H^6; **1c** 0.13 [55.4], 9H, Me_3Sn; 0.16 s, 9H, Me_3Si; 2.15 [5.2] s, 3H, 4-Me; 6.8 m, 3H, 6.9 m, 2H Ar-H; **1d** 0.08 [55.1] s, 9H, Me_3Sn; 0.10 s, 9H, Me_3Si; 2.20 s, 6H 2,6-Me_2; 6.81 m, 1H, Ar–H^4; 7.00 m, 2H, Ar-$H^{3,5}$.

2,2-Dimethyl-1-trimethylsilyl-2-stannaindoline (3)

The reaction conditions specified in Table 1 for experiment E were used, and 3.3 g (15mmol) of Me_2SnCl_2 were taken. After filtration the hexane was removed in vacuo and the residue fractionally distilled to give 1.2 g (25%) of **3** (b.p. 85–87 °C/0.4 Torr), which became a yellow solid at room temperature and was shown to be 90% pure by NMR spectroscopy. Molecular weight 327 (MS). 300 MHz ^1H NMR in C_6D_6; $\delta(^1H)$ $^nJ(^{119}Sn^1H)$ 0.19 Hz [57.2] s, 6H, Me_2Sn; 0.26 s, 9H, Me_3Si; 2.04 [46.1] s, 2H, CH_2; 7.22 m, 1H, Ar-H^4; 6.66 m, 1H, Ar–H^5; 6.95 m, 2H, Ar-$H^{6,7}$.

2,2-Dimethyl-trimethylstannyl-2-silaindoline (4)

Under the conditions shown in Table 1 for experiment A, reaction of **2** with 3.3 g (15 mmol) of Me_2SnCl_2 gave 1.7 g **4** (35%) as colourless liquid (b.p. 56–64 °C/0.1 Torr) which was shown in NMR spectroscopy to be 90% pure. Molecular weight 327 (MS). 300 MHz ^1H NMR in C_6D_6: $\delta(^1H)$ $^nJ(^{119}Sn^1H)$ 0.15 Hz s, 6H, Me_2Si; 0.26 [57.3] s, 9H, Me_3Sn; 1.92 s, 2H, CH_2; 7.20 m, 1H, Ar–H^4; 6.60 m, 1H, Ar–H^5; 6.93 m, 2H, Ar–$H^{6,7}$.

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28 *Note added in proof.* We have repeated the quenching of **2** with Me_3SiCl as described in ref. 4. We, however obtained the 2,2-dimethyl-1-trimethylsilyl-2-silaindoline [δ^{29}Si +24.5 ($SiMe_2$), +1.9 ($SiMe_3$)] as the main product in place of the expected product *ortho-N,N*-bis(trimethylsilyl)trimethylsilylmethyltoluidine [4].