

# Tin-carbon bond formation by simple addition of cyclic dienes to a bis(amino)stannylene: a mechanistic study

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The addition of cyclopentadiene and indene to  $\text{Bu}^t\text{NSiMe}_2\text{NBu}^t\text{Sn}$  resulted in the formation of 'adducts' (X-ray structural characterisation) through tin-carbon bonding and hydrogen migration to one of the nitrogen atoms. In the cyclopentadienyl compound  $\pi$  bonding is observed ( $\text{Sn}-\text{C}$  2.47–2.76 Å) whereas the indenyl derivative displays a  $\sigma$ -bond ( $\text{Sn}-\text{C}$  2.343 Å). In a similar reaction of  $\text{Bu}^t\text{NSiMe}_2\text{NBu}^t\text{E}$  ( $\text{E} = \text{Ge}$  or  $\text{Pb}$ ) with cyclopentadiene either the starting compounds or plumbocene along with an amine were isolated. At room temperature the reaction between indene and the cyclic stannylene is an equilibrium, the rate constants of which were raised by a factor of 3.0 for the association and slowed by a factor of 4.2 for the dissociation when deuteriated indene was used. From the kinetic data, a concerted addition mechanism of the proton and the indenyl group is favoured over an ionic two-step mechanism. If the steric hindrance of the protic cyclic diene system is raised (pentamethylcyclopentadiene) no reaction between the stannylene and diene is observed.

Examples of direct tin-carbon bond formation by the reaction of a stannylene with a nucleophilic carbon centre are rare. However, it has been unambiguously demonstrated by adding  $\text{H}_2\text{CPPH}_3$  to the cyclic bis(amino)stannylene **2** forming the Lewis acid-base complex  $\text{Me}_2\text{Si}(\text{NBu}^t)_2\text{Sn}^--\text{CH}_2\text{P}^+\text{Ph}_3$ .<sup>1</sup> Another approach to  $\text{Sn}-\text{C}$  bond formation is the addition of a  $\pi$  system (disposing of an acidic hydrogen atom) to the unsaturated  $\text{Sn}-\text{N}$  bond in the cyclic stannylene **2**.<sup>2</sup> In a preliminary report, we have described such a reaction between **2** and cyclopentadiene, but we could not get detailed information about the structure of the reaction's products nor could we draw any mechanistic conclusions.<sup>3</sup>

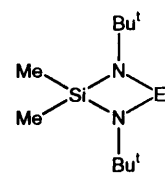
In this paper we have extended these studies to indene and pentamethylcyclopentadiene and are interested in establishing in detail the molecular structures of the addition products of cyclopentadiene and of indene to compound **2** in solution and in the solid state. From temperature-dependent NMR experiments and using deuteriated indene, we were able to obtain rate constants for the reaction of **2** and indene and propose a mechanism for the reaction pathway. The reactions of the analogous cyclic germylene **1** and plumbylene **3** with cyclopentadiene were performed for comparison.

## Experimental

All reactions were performed under a dry nitrogen atmosphere. Solvents were freshly distilled prior to use. The NMR spectra were recorded on a Bruker AC-200 spectrometer. The cyclic bis(amino)-germylene, -stannylene and -plumbylene compounds **1–3** were prepared according to the literature methods.<sup>4,5</sup> Deuteriated indene was obtained by the reaction of indene (1 mol) with  $\text{Bu}^t\text{OD}$  (10 mol) and  $\text{NaOBu}^t$  (0.05 mol) and separated by distillation.

### Compounds **4** and **5**

To cyclopentadiene or indene (0.012 mol) in pentane (10  $\text{cm}^3$ ) was slowly added compound **2** (0.012 mol) at 233 K. After stirring for 5 min the solvent was reduced in volume by condensation and crystallisation was observed. After recrystallisation from pentane, 3.70 g (80%) compound **4** and 4.28 g (82%) **5** were obtained.



$\text{E} = \text{Ge}$  **1**,  $\text{Sn}$  **2**,  $\text{Pb}$  **3**

Compound **4** (Found: C, 46.90; H, 7.95; N, 7.10. Calc. for  $\text{C}_{15}\text{H}_{30}\text{N}_2\text{SiSn}$ : C, 46.75; H, 7.85; N, 7.25%). NMR (293 K,  $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ ,  $\delta$  6.41 (5 H,  $^2J = 9$ ,  $\text{C}_5\text{H}_5$ ), 1.23 (9 H,  $\text{Bu}^t$ ), 0.93 (9 H,  $\text{Bu}^t$ ) and 0.18 (6 H, Me);  $^{13}\text{C}$ ,  $\delta$  110.7 (5 H,  $^1J = 10.49$ ,  $\text{C}_5\text{H}_5$ ), 52.3 (1 C,  $^2J = 7.6$ ,  $\text{Bu}^t$ ), 52.1 (1 C,  $\text{Bu}^t$ ), 35.5 (3 C,  $^3J = 17.1$ ,  $\text{Bu}^t$ ), 31.7 (3 C,  $^3J = 27.48$ ,  $\text{Bu}^t$ ) and 7.8 (2 C, Me);  $^{29}\text{Si}$ ,  $\delta$   $-0.33$  ( $^2J = 18.7$  Hz);  $^{119}\text{Sn}$ ,  $\delta$  257.1;  $^{15}\text{N}$ ,  $\delta$   $-239.3$  and  $-303.6$ .

Compound **5** (Found: C, 52.60; H, 7.55; N, 6.25. Calc. for  $\text{C}_{19}\text{H}_{32}\text{N}_2\text{SiSn}$ : C, 52.40; H, 7.40; N, 6.45%). NMR (223 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $^1\text{H}$ ,  $\delta$  7.65–7.73 ( $\text{H}^{4,7}$ ), 7.30–7.37 ( $\text{H}^{5,6}$ ), 7.21 ( $\text{H}^2$ ), 6.68 (d,  $^4J = 13.7$ ,  $\text{H}^3$ ), 4.72 (d,  $^2J = 35.5$ ,  $\text{H}^1$ ), 1.31 (9 H,  $\text{Bu}^t$ ), 0.39 (9 H,  $\text{Bu}^t$ ), 0.21 (3 H, Me) and 0.19 (3 H, Me);  $^{13}\text{C}$ ,  $\delta$  140.6, 139.7 ( $^2J = 7$ ,  $\text{C}^{8,9}$ ), 136.8 ( $^2J = 9$ ,  $\text{C}^2$ ), 122.0, 121.5 ( $\text{C}^{4,7}$ ), 121.1, 120.1 ( $\text{C}^{5,6}$ ), 111.8 ( $^3J = 25.8$ ,  $\text{C}^3$ ), 74.8 ( $^1J = 200$ ,  $\text{C}^1$ ), 52.0 (1 C,  $\text{Bu}^t$ ), 50.9 (1 C,  $\text{Bu}^t$ ), 35.3 (3 C,  $\text{Bu}^t$ ), 30.7 (3 C,  $\text{Bu}^t$ ), 9.2 (1 C, Me) and 7.9 (1 C, Me);  $^{29}\text{Si}$ ,  $\delta$  5.20 ( $^2J = 17.4$  Hz);  $^{119}\text{Sn}$ ,  $\delta$  120.8.

### Reaction of compound **1** with cyclopentadiene

To cyclopentadiene (0.012 mol) in pentane (10  $\text{cm}^3$ ) was slowly added compound **1** (0.012 mol) and the whole solution heated to reflux. After removal of the solvent and cyclopentadiene under reduced pressure, 3.27 g (99%) of unreacted **1** (NMR spectroscopy) were recovered.

### Reaction of compound **2** with pentamethylcyclopentadiene

The reaction was performed as above (0.012 mol compound **2** and 0.012 mol pentamethylcyclopentadiene); 3.75 g (98%) of unreacted stannylene **2** (NMR spectroscopy) were recovered.

### Reaction of compound 3 with cyclopentadiene

Compound 3 (0.012 mol) in toluene (15 cm<sup>3</sup>) was added to an equimolar amount of cyclopentadiene at 210 K. The <sup>1</sup>H NMR spectrum showed the formation of adduct 6. NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.19 (6 H, Me), 0.94 (9 H, Bu<sup>t</sup>), 1.18 (9 H, Bu<sup>t</sup>) and 6.36 (5 H, C<sub>5</sub>H<sub>5</sub>). If the temperature is raised to 278 K 6 decomposes giving starting material 3, plumbocene Pb(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> and the bis(amino)silane SiMe<sub>2</sub>(NHBu<sup>t</sup>)<sub>2</sub> according to <sup>1</sup>H NMR spectroscopy in C<sub>6</sub>D<sub>6</sub>: δ 0.17 (6 H, Me) and 1.19 (18 H, Bu<sup>t</sup>).

### Thermodynamic and kinetic NMR studies

To calculate the equilibrium and rate constants an equimolar concentration of compound 2 and indene (0.18 mol) in [<sup>2</sup>H<sub>8</sub>]toluene was frozen in a NMR tube and the concentration of 2 and 5 determined at different time intervals and temperatures by integration of the proton NMR spectra. Rate constants were obtained at constant temperatures by plotting the function in (6) *versus* time. The rate constants, *k<sub>d</sub>*, for the decomposition (dissociation) of adduct 5 were calculated by use of (7) (see below).

### Crystallography

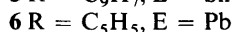
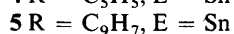
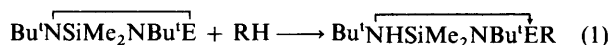
The data collection parameters and selected interatomic distances and angles for compounds 4 and 5 are presented in Tables 1 and 2. The structures were solved by direct methods and empirical absorption corrections were made. Hydrogen atoms have been fixed at idealised positions.

Full details of the data collection, structure refinement, atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen, D-76344 Eggenstein-Leopoldshafen, Germany, CSD 404037 (4) and 404038 (5).

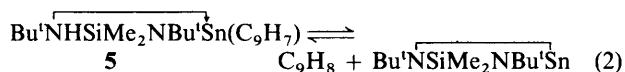
## Results and Discussion

### Synthesis and crystal structure

While the addition compounds 4 and 6 are formed instantly when equimolar amounts of cyclopentadiene and the bis(amino)element(II) compounds are brought together in a toluene solution, no similar reaction is observed in the case of 1 which is recovered quantitatively [equation (1)]. If the steric



bulk of the cyclic diene system is raised by replacing cyclopentadiene by indene, an adduct 5 is obtained from 2. However, it can only be isolated at low temperature as it decomposes to the starting materials when the temperature is raised [equation (2)].



The more sterically hindered pentamethylcyclopentadiene does not react with the stannylene 2, even under refluxing pentane. Similar to compound 5, 6 is metastable and can only be detected in the <sup>1</sup>H and <sup>13</sup>C NMR spectra at lower temperatures. Depending on time and temperature, it decomposes irreversibly to plumbocene Pb(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> the corresponding bis(amino)silane and 3 [equation (3)].

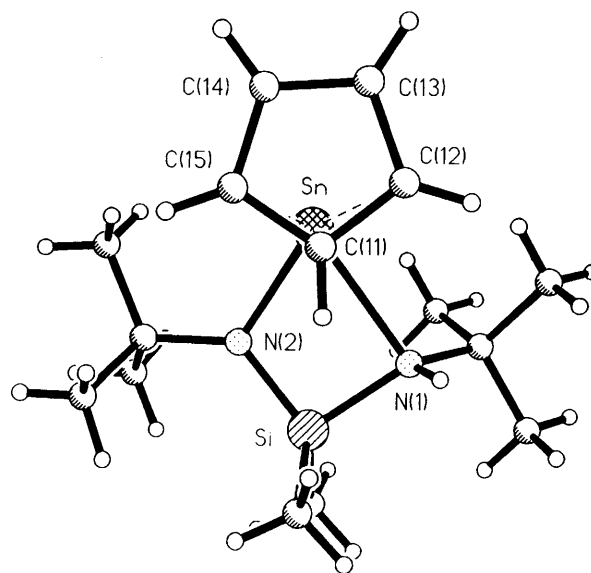


Fig. 1 Molecular structure of Bu<sup>t</sup>NHSiMe<sub>2</sub>NBu<sup>t</sup>Sn(C<sub>5</sub>H<sub>5</sub>) 4

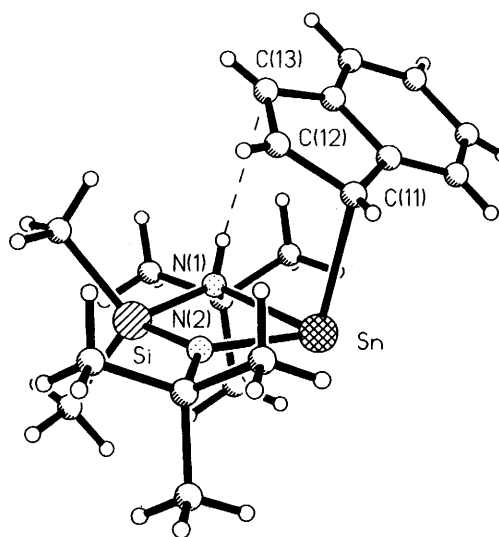
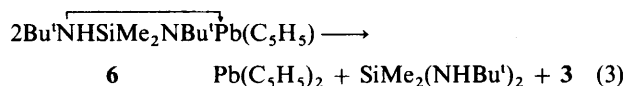


Fig. 2 Molecular structure of Bu<sup>t</sup>NHSiMe<sub>2</sub>NBu<sup>t</sup>Sn(C<sub>9</sub>H<sub>7</sub>) 5



Whereas crystals of compound 4 are stable at ordinary temperature those of 5 are metastable and the crystal structure of the latter was determined by special low-temperature techniques.<sup>8</sup> The results of the structure determinations are shown in Figs. 1 and 2. In each case the protic hydrogen atom is added to the nitrogen atom N(1) of the bis(amino)stannylene 2 [N(1) becoming four-co-ordinate] while the organic moiety is bonded to the tin atom, elongating the corresponding Sn–N bond from 2.091(8) Å in 2<sup>9</sup> to 2.468(7) Å in 4 or 2.312(5) Å in 5. The planar cyclopentadienyl ring in 4 is oriented almost parallel to the SiN<sub>2</sub>Sn four-membered ring, and the tin–cyclopentadienyl interaction can be described by η<sup>2</sup> to 3 or as an asymmetrical π bond.<sup>10,11</sup> Thus the distances between Sn and C(11), C(12) and C(15) lie in the range 2.474(9)–2.768(9) Å. The η<sup>2/3</sup> bonding is due to the fact that the *tert*-butyl and hydrogen atom at N(1) seem to push the cyclopentadienyl ring away from the SnN<sub>2</sub>Si ring system, the Sn atom maintaining a pyramidal co-ordination environment with angles of almost 90°. Compound 5 differs from 4 as the Sn atom is bonded only to a single carbon atom [C(11)] and the hydrogen atom at N(1) interacts with the indene ring, especially with C(13) in such a way that the

**Table 1** Data-collection parameters for compounds **4** and **5**\*

	<b>4</b>	<b>5</b>
Empirical formula	C <sub>15</sub> H <sub>30</sub> N <sub>2</sub> SiSn	C <sub>15</sub> H <sub>32</sub> N <sub>2</sub> SiSn
<i>M</i>	385.19	435.25
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	25.666(26)	8.744(11)
<i>b</i> /Å	9.530(11)	11.496(12)
<i>c</i> /Å	16.428(19)	21.076(24)
β/°	107.54(9)	99.10(10)
<i>U</i> /Å <sup>3</sup>	3831(7)	2092(4)
<i>Z</i>	8	4
<i>D<sub>c</sub></i> /Mg m <sup>−3</sup>	1.332	1.382
μ/mm <sup>−1</sup>	1.389	1.281
<i>F</i> (000)	1576	896
<i>T</i> /K	233(2)	173(2)
Crystal size/mm	0.30 × 0.15 × 0.10	0.60 × 0.20 × 0.16
θ range for data collection/°	1.66–20.00	1.96–20.00
<i>hkl</i> ranges	−24 to 23, 0–8, 0–11	−8 to 8, −3 to 10, −10 to 20
Reflections collected	1282	1943
Independent reflections	1282	1878
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	1193	1785
Data, restraints, parameters	1282, 0, 113	1874, 0, 196
Goodness of fit on <i>F</i> <sup>2</sup>	1.113	0.936
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0426, <i>wR</i> 2 = 0.1121	<i>R</i> 1 = 0.0354, <i>wR</i> 2 = 0.0966
<i>R</i> (all data)	<i>R</i> 1 = 0.0448, <i>wR</i> 2 = 0.1146	<i>R</i> 1 = 0.0381, <i>wR</i> 2 = 0.1140
Largest difference peak and hole/e Å <sup>−3</sup>	0.438, −0.692	0.565, −0.458

\* Details in common: monoclinic; Siemens Stoe AED 2 diffractometer; graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å); ω-θ scans; three standard reflections measured every 90 min. SHELXS 86<sup>6</sup> and SHELXL 93<sup>7</sup> programs; full-matrix least-squares refinement on *F*<sup>2</sup>.

**Table 2** Selected interatomic distances (Å) and angles (°) in compounds **4** and **5**

	<b>4</b>	<b>5</b>		<b>4</b>	<b>5</b>
Sn–N(2)	2.117(7)	2.115(5)	Sn–N(1)	2.468(7)	2.312(5)
Sn–C(15)	2.706(11)	—	Sn–C(12)	2.768(9)	—
Sn–C(11)	2.474(9)	2.343(7)	Si–N(2)	1.675(8)	1.687(5)
Si–N(1)	1.782(9)	1.814(6)	Si–C(10)	1.870(10)	1.860(7)
Si–C(9)	1.865(9)	1.870(7)	N(1)–C(1)	1.528(12)	1.510(8)
N(2)–C(5)	1.473(13)	1.472(8)	C(1)–C(3)	1.513(14)	1.517(9)
C(1)–C(4)	1.499(13)	1.525(9)	C(1)–C(2)	1.526(12)	1.539(9)
C(5)–C(7)	1.543(14)	1.501(10)	C(5)–C(8)	1.500(2)	1.509(11)
C(5)–C(6)	1.510(2)	1.536(10)	C(11)–C(12)	1.378(13)	1.430(11)
C(12)–C(13)	1.406(13)	1.331(10)	C(13)–C(14)	1.375(12)	1.419(10)
C(14)–C(15)	1.389(13)	1.393(10)			
N(2)–Sn–N(1)	67.6(3)	70.7(2)	N(2)–Sn–C(11)	102.2(3)	98.2(2)
N(1)–Sn–C(11)	88.7(3)	92.5(3)	N(2)–Sn–C(15)	101.2(3)	—
N(1)–Sn–C(15)	117.4(3)	—	N(1)–Sn–C(12)	90.0(3)	—
N(2)–Sn–C(12)	129.5(3)	—	N(2)–Si–C(9)	116.8(4)	115.4(3)
N(2)–Si–N(1)	95.9(4)	94.1(3)	N(2)–Si–C(10)	117.6(4)	118.1(3)
N(1)–Si–C(9)	105.5(4)	114.4(3)	C(9)–Si–C(10)	105.2(2)	106.7(3)
N(1)–Si–C(10)	115.3(5)	107.6(3)	C(1)–N(1)–Sn	112.6(5)	119.2(4)
C(1)–N(1)–Si	128.6(6)	128.8(4)	C(5)–N(2)–Si	131.4(6)	131.6(4)
Si–N(1)–Sn	89.2(3)	91.7(2)	Si–N(2)–Sn	105.2(4)	102.7(2)
C(5)–N(2)–Sn	123.1(6)	125.2(4)	C(11)–C(12)–C(13)	107.9(9)	110.9(8)
C(12)–C(11)–Sn	87.0(6)	111.6(5)	C(12)–C(13)–C(14)	106.6(9)	109.6(7)

parallelism between the inorganic and organic ring systems is destroyed. The Sn–C(11) distance of 2.343(7) Å is within the limit of a σ bond<sup>12</sup> and the N(1)⋯C(13) distance is remarkably short (3.5 Å) with an H⋯C(13) distance of about 2.8 Å which is close to the sum of the van der Waals radii of hydrogen and an aromatic carbon (2.9 Å). The tin–carbon bonding interactions described so far are paralleled by the C–C distances within the cyclopentadienyl and indenyl ligands (Figs. 1 and 2, Table 2).

### Proton and carbon NMR spectra

On recording the <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **4** and **5** in toluene, coalescence of the signals of the dimethylsilyl groups is observed at 245 or 263 K, respectively. As explained in a previous report,<sup>3</sup> we attribute this to the dynamic bond opening between N(1) and Sn, inversion of the pyramid at N(1)

accompanied by rotations around the Si–N(1) and Sn–N(2) bonds and reclosure of the Sn–N(1) bond.

On comparing the spectra between the coalescence point and those at lower temperatures a free enthalpy of activation for compounds **4** (51.8) and **5** (59.5 kJ mol<sup>−1</sup>) was calculated.<sup>13</sup> The higher value for **5** seems to come from the bulkier indenyl ligand. Besides this intramolecular reorientation, a second fluxional behaviour can be found in solutions of **5** which arises from flipping of the tin atom between the two carbon atoms C(11) and C(13), as may be deduced from <sup>1</sup>H [coalescence of proton signals at C(11) and C(13)] or <sup>13</sup>C NMR spectra (equivalence at > 263 or > 283 K for carbon atoms within the six-membered ring). Comparable 1,3 shifts of trimethyltin in the indenyl compound have been previously reported.<sup>14</sup> From these data, activation enthalpies can be calculated (57.8–59.6 kJ mol<sup>−1</sup>) which are within the energies estimated for the

reorientation mode described above. In view of the similarities of these energies it appears that the two processes are coupled together.

Rate and equilibrium constants and thermodynamic data have been determined from  $^1\text{H}$  NMR spectra recorded at different temperatures and concentrations of compound **2**, indene and **5** (Table 3). Initially the equilibrium constants of the reaction were measured. The dependence of the equilibrium constant  $K_d$  on reciprocal temperature  $1/T$  is depicted in Fig. 3. To a first approximation the rate constants followed second-order kinetics with respect to the association between **2** and indene and first-order kinetics with respect to the dissociation of **5** in the temperature range 250–270 K in 0.1 mol dm $^{-3}$  solutions,

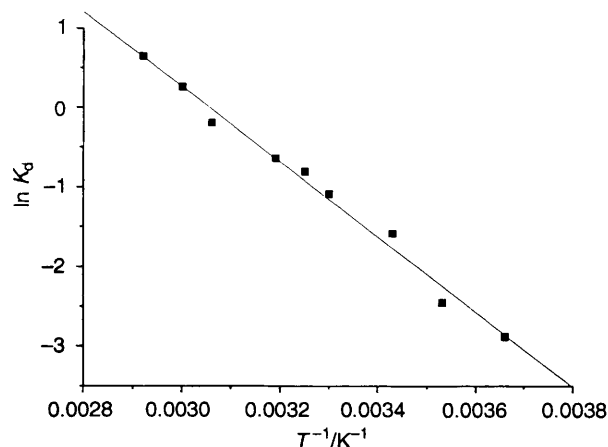


Fig. 3 Dependence of the equilibrium constant  $\ln K_d$  on the reciprocal temperature  $1/T$

Table 3 Equilibrium and rate constants for reaction (2)

$T/\text{K}$	$K_d$	$10^4 k_a$	$10^6 k_d$	$K'_d$	$10^4 k'_a$	$10^6 k'_d$
248	0.009	3.5	3.2	0.007		
253	0.014	5.4	7.6	0.010	1.8	1.8
258	0.020	8.2	16.4	0.014	2.5	3.5
263	0.029	16.2	47.0	0.019	5.7	10.8
268				0.026	8.9	23.1
273	0.056			0.037	15.1	55.9
283	0.086			0.067		
293	0.205			0.117		
303	0.338			0.178		
313	0.528			0.326		
323	0.821			0.548		
333	1.287			0.750		
343	1.906			1.315		

Primes indicate deuteriated indene;  $K_d$  is given in mol dm $^{-3}$ ,  $k_a$  in dm $^3$  mol $^{-1}$  s $^{-1}$  and  $k_d$  in s $^{-1}$ . Standard deviations: 0.001 for  $K$  and 0.028 for  $k$ .

the findings being expressed by equations (4) and (5) (a indicating association between **2** and indene, d dissociation of **5**). The

$$-dc(\mathbf{2})/dt = -dc(\text{indene})/dt = dc(\mathbf{5})/dt = k_a c(\mathbf{2})c(\text{indene}) - k_d c(\mathbf{5}) \quad (4)$$

$$-dc(\mathbf{5})/dt = dc(\mathbf{2})/dt = dc(\text{indene})/dt = k_d c(\mathbf{5}) - k_a c(\mathbf{2})c(\text{indene}) \quad (5)$$

value of  $k_a$  was determined from equation (6)<sup>15</sup> and is related to the measured equilibrium constant  $K_d$  by equation (7)

$$\ln \frac{x_e(a^2 - xx_e)}{(x_e - x)a^2} = k_a \frac{(a^2 - x_e^2)t}{x_e} \quad (6)$$

$$K_d = k_d/k_a \quad (7)$$

where  $x_e = c(\mathbf{2})_0 - c(\mathbf{2})_e$ ,  $c(\mathbf{2})_e$  is the concentration of **2** at the equilibrium,  $a = c(\mathbf{2})_0$ ,  $x = c(\mathbf{2})_0 - c(\mathbf{2})_t = c(\mathbf{5})_t$  and  $c(\mathbf{2})_t$  is the concentration of **2** at time  $t$ .

With the measured equilibrium constants it was possible to determine the free enthalpy  $\Delta G$ , the enthalpy of the reaction  $\Delta H$  and by the Gibbs–Helmholtz equation the entropy  $\Delta S$ . The thermodynamic activation data were calculated by the Arrhenius and Eyring equation from the rate constants (see Tables 3, 4).<sup>16</sup> Similar experiments were performed with a deuteriated indene sample, which was obtained as a mixture of 50% [1- $^2\text{H}$ ]- and 50% [1,3- $^2\text{H}_2$ ]-indene as determined by off-resonance and inverse-gated  $^{13}\text{C}$  NMR spectroscopy. Using the deuteriated sample the association rate constant was raised by a factor of 2.98 compared with ordinary indene, while the dissociation process was slowed by a factor of 4.22 (see also Table 4).

## Conclusion

On the basis of these findings we propose the following mechanism for the reaction of compound **2** with indene. First there is a  $\pi$ -interaction between indene and an empty p orbital of tin followed by a hydrogen migration from the  $\text{CH}_2$  group of indene to one of the nitrogen atoms of the four-membered bis(amino)stannylene ring [Fig. 2, the hydrogen atom has moved from C(13) to N(1)]. The structure of **5** recorded at 175 K reveals the terminal step of this hydrogen migration. When the migrating hydrogen is replaced by deuterium the dissociation process of adduct **5** is affected more than the association process, as the deuterium migration now becomes the first step in the decomposition of the compound and  $\Delta S_a^\ddagger$  is increased by 22 J K $^{-1}$  mol $^{-1}$  (see difference in rate constants). In any case the hydrogen rearrangement is rate determining, ruling out a two-step mechanism with two comparable rate constants (separate addition or dissociation of the proton and

Table 4 Thermodynamic and kinetic data for the reactions of compound **2** with indene and deuteriated indene

	Indene	Deuteriated indene
$K_a$ (253 K)/dm $^3$ mol $^{-1}$	74.43(7)	101.8(1)
$K_d$ (253 K)/mol dm $^{-3}$	0.0134(1)	0.0098(1)
$\Delta H_a$ /kJ mol $^{-1}$	−40(1)	−38(1)
$\Delta S_a$ /JK $^{-1}$ mol $^{-1}$	−123(5)	−111(5)
$k_a$ (253 K)/dm $^3$ mol $^{-1}$ s $^{-1}$	$5.4(4) \times 10^{-4}$	$1.8(1) \times 10^{-4}$
$k_d$ (253 K)/s $^{-1}$	$7.6(5) \times 10^{-6}$	$1.8(1) \times 10^{-6}$
$E_{Aa}$ /kJ mol $^{-1}$	55(3)	62(3)
$E_{Ad}$ /kJ mol $^{-1}$	96(5)	100(5)
$\Delta H_a^\ddagger$ /kJ mol $^{-1}$	53(3)	61(3)
$\Delta H_d^\ddagger$ /kJ mol $^{-1}$	94(5)	98(5)
$\Delta S_a^\ddagger$ /JK $^{-1}$ mol $^{-1}$	−97(5)	−75(3)
$\Delta S_d^\ddagger$ /JK $^{-1}$ mol $^{-1}$	32(3)	32(3)

Symbols used:  $K_a$  = equilibrium constant for the association,  $E_A$  = activation energy.

of indenyl). This association/dissociation process leads to an equilibrium in the case of **5**, as the bonding between tin and indenyl is less effective than that between tin and cyclopentadienyl (presumably steric effects play a major role). This less effective bonding is paralleled by a shorter N(1)–Sn bond in **5** compared to that in **4**. The smaller germanium atom in the germylene **1** (compared to tin in compound **2**) seems to be effectively shielded by the ligands from attack of the cyclopentadiene as no reaction occurs between these two compounds. The less-shielded lead in **3** immediately reacts with cyclopentadiene, leading to compound **6** which is unstable with respect to decomposition to plumbocene,  $\text{SiMe}_2(\text{NHBu}^t)_2$  and **3**.

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