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A compound with a tin-carbon double bond, bis(2,4,6-triisopropylphenyl)(fluorenylidene)stannane: aspects of its reactivity and X-ray structure of its dimer

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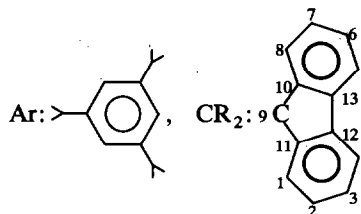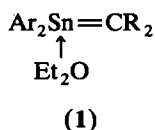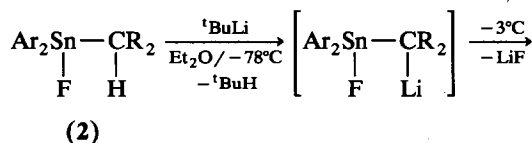
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Abstract

Bis(2,4,6-triisopropylphenyl)(fluorenylidene)stannane (**1**) reacts nearly quantitatively with compounds having active hydrogen atoms (alcohols, amines, mineral acids, phenylacetylene) and with lithium aluminium hydride to give the corresponding stannanes. Methyl iodide also adds easily to the tin–carbon double bond. Compound **1** slowly dimerizes at room temperature in solution. The head-to-tail dimer **10** has been structurally characterized by X-ray analysis which reveals long intracyclic Sn–C bonds (2.288(4) to 2.293(5) Å) and a planar four-membered ring.

1. Introduction

We have recently described the synthesis of a new stable compound with a tin–carbon double bond, bis(2,4,6-triisopropylphenyl)(fluorenylidene)stannane (**1**) [1] by dehydrofluorination of the corresponding fluorostannane **2** with tert-butyllithium:

$$Ar_2Sn\underset{F}{-}CR_2\underset{H} \xrightarrow[\substack{Et_2O/-78°C \\ -^tBuH}]{^tBuLi} \left[Ar_2Sn\underset{F}{-}CR_2\underset{Li} \right] \xrightarrow[-LiF]{-3°C}$$

(2)

$$Ar_2Sn=CR_2$$
$$\uparrow$$
$$Et_2O$$

(1)

We now report our first studies of the reactivity of **1** toward reagents with active hydrogen atoms, hydrides, and methyl iodide. The X-ray structure of its head-to-tail dimer is also described.
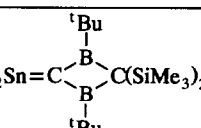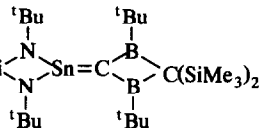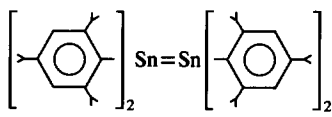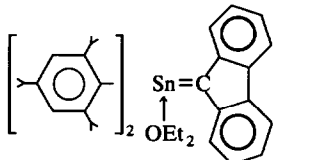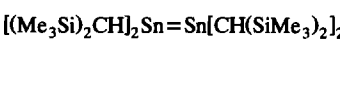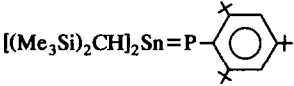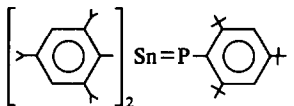
2. Results and discussion

As previously reported [1], **1** was characterized by a low-field chemical shift (+288 ppm) in the ^{119}Sn NMR spectrum, which is, however, at higher field than for other doubly-bonded tin compounds (see Table 1).

The high chemical shift observed for **1** is probably due to complexation of tin by Et_2O. However, as in some silenes [8], germenes [9] and silaimines [10] which are also complexed by bases, complexation is probably very weak and does not modify the reactivity of **1** which

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TABLE 1. Chemical shifts of some doubly-bonded tin compounds

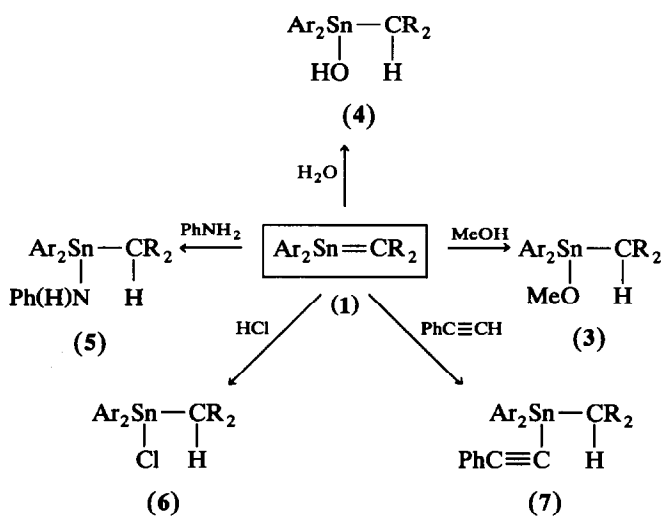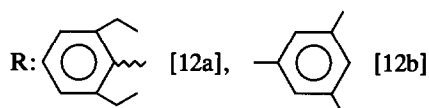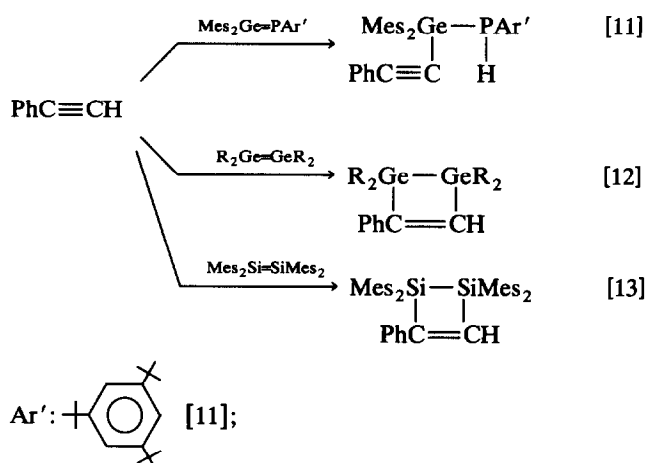| Compounds	δ^{119}Sn	Ref.
[(Me$_3$Si)$_2$CH]$_2$Sn=C$\begin{smallmatrix}^tBu\\\B\\\B\\\^tBu\end{smallmatrix}$C(SiMe$_3$)$_2$	835	[2]
Me$_2$Si$\begin{smallmatrix}^tBu\\\N\\\N\\\^tBu\end{smallmatrix}$Sn=C$\begin{smallmatrix}^tBu\\\B\\\B\\\^tBu\end{smallmatrix}$C(SiMe$_3$)$_2$	647	[2]
[Ar]$_2$Sn=Sn[Ar]$_2$	427.3	[3]
[Ar]$_2$Sn=C(fluorenylidene) OEt$_2$	288	[1]
[(Me$_3$Si)$_2$CH]$_2$Sn=Sn[CH(SiMe$_3$)$_2$]$_2$	725 740	[4,5]
[(Me$_3$Si)$_2$CH]$_2$Sn=P—Ar	658.3	[6]
[Ar]$_2$Sn=P—Ar	499.5	[7]

is extremely high. Deep violet solutions of **1** immediately turn colourless or light yellow upon addition of protic reagents such as water, methanol, hydrochloric acid, aniline and phenylacetylene.

$$\begin{array}{c} Ar_2Sn-CR_2 \\ |\quad\quad| \\ HO\quad H \end{array}$$

(4)

$$H_2O \uparrow$$

$$\begin{array}{c} Ar_2Sn-CR_2 \\ |\quad\quad| \\ Ph(H)N\quad H \end{array} \xleftarrow{PhNH_2} \boxed{Ar_2Sn=CR_2} \xrightarrow{MeOH} \begin{array}{c} Ar_2Sn-CR_2 \\ |\quad\quad| \\ MeO\quad H \end{array}$$

(5)   HCl / **(1)** \ PhC≡CH   **(3)**

$$\begin{array}{c} Ar_2Sn-CR_2 \\ |\quad\quad| \\ Cl\quad H \end{array} \qquad \begin{array}{c} Ar_2Sn-CR_2 \\ |\quad\quad| \\ PhC\equiv C\quad H \end{array}$$

(6)   **(7)**

Each reaction is regiospecific with the negative moiety of the protic reagent bonded to tin, consistent with

the postulated polarity of the tin–carbon double bond Sn$^{\delta+}$=C$^{\delta-}$. Adducts **3–7**, obtained in good yields, have been characterized by ^{1}H, ^{13}C, ^{119}Sn NMR, and mass spectroscopy. In the ^{1}H and ^{13}C NMR spectra, the two methyls of an isopropyl group are theoretically inequivalent, as confirmed by the presence in all adducts of two doublets for the methyls of *ortho*-isopropyl groups. By contrast, the methyls of *para*-isopropyl groups give only one doublet, probably due to the large separations from the prochiral tin.

With phenylacetylene, only **7** was obtained, as in the reaction of protic phenylacetylene with a germaphosphene 〉Ge=P– [11], whereas only [2 + 2] cycloaddition was observed with two digermenes [12] and a disilene [13].

$$PhC\equiv CH \nearrow \xrightarrow{Mes_2Ge=PAr'} \begin{array}{c} Mes_2Ge-PAr' \\ |\quad\quad| \\ PhC\equiv C\quad H \end{array} \quad [11]$$

$$\searrow \xrightarrow{R_2Ge=GeR_2} \begin{array}{c} R_2Ge-GeR_2 \\ |\quad\quad| \\ PhC==CH \end{array} \quad [12]$$

$$\xrightarrow{Mes_2Si=SiMes_2} \begin{array}{c} Mes_2Si-SiMes_2 \\ |\quad\quad| \\ PhC==CH \end{array} \quad [13]$$

Ar′: —Ar [11];

R: [12a], [12b]

Reduction of **1** by lithium aluminium hydride, carried out at 0°C to avoid cleavage of the tin–carbon single bond, gave stannane **8** in nearly quantitative yield.

$$\mathbf{1} \xrightarrow{LiAlH_4} \begin{array}{c} Ar_2Sn-CR_2 \\ |\quad\quad| \\ H\quad H \end{array}$$

(8)
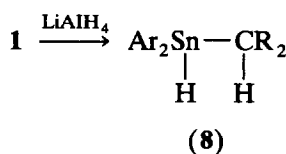
Methyl iodide also reacts almost quantitatively with **1** to form the corresponding adduct, **9**.

$$\mathbf{1} \xrightarrow{MeI} \begin{array}{c} Ar_2Sn-CR_2 \\ |\quad\quad| \\ I\quad Me \end{array}$$

(9)
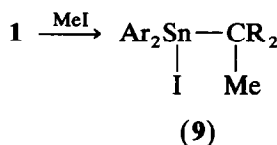
This reaction confirms the high reactivity of **1**, as additions of alkyl halides to doubly-bonded Main Group element compounds are very rare. So far, only

addition of methyl iodide to the germanium–nitrogen double bond of a germaimine has been reported [14]. In the ^{1}H NMR spectra, the methyls of the ortho-iso-propyl groups give very broad signals due to hindered rotation caused by the increased bulkiness around the tin atom, whereas sharp signals were observed for adducts 3–7, which have less sterically demanding substituents.

At room temperature, 1 dimerizes slowly to give the head-to-tail dimer 10, as expected due to the significant polarization $Sn^{\delta+}=C^{\delta-}$, as the sole product.

$$1 \xrightarrow{\times 2} \begin{array}{c} Ar_2Sn-CR_2 \\ | \quad\quad | \\ R_2C-SnAr_2 \end{array}$$

(10)
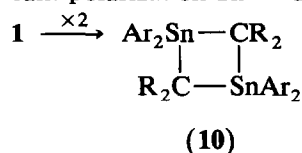
Dimerization of this type is usually observed with silenes [15,16], germenes [16,17] and the transient stannene $Me_2Sn=C(SiMe_3)_2$ [18]. Among the doubly-bonded Group 14 elements, head-to-head dimerization leading to 1,2-disilacyclobutanes [15,19] or disilanes [20] is obtained only in a few cases such as $(Me_3Si)_2Si=C(OSiMe_3)R$ where the Si=C double bond is not significantly polarized.
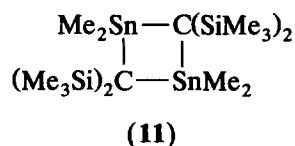
Interestingly, 10 is only the second 1,3-distannacyclobutane yet obtained. Whereas trimeric or tetrameric derivatives $(Sn-C)_n$ ($n = 3$ or 4) are well known [21], only one other 1,3-distannacyclobutane, 11, has been reported so far [18,22].

TABLE 2. Crystallographic and experimental data for 10

Formula	$C_{86}H_{108}Sn_2$
MW	1378.634
Crystal dimensions (mm^3)	0.7×0.5×0.4
Colour	Light yellow
Crystal group	Monoclinic
Space group	$P2_1/c$
a (Å)	19.972(3)
b (Å)	12.366(3)
c (Å)	32.163(5)
β (°)	99.07(1)
V (Å^3)	7844(2)
Z	4
$d_{calcd.}$ (g cm^{-3})	1.17
$F(000)$	2896
μ(Mo Kα) (mm^{-1})	0.73
hkl range	$-23/+23, 0/+14, 0/+38$
No. of unique reflections	
Measured	13804
Observed ($I > 2.5\,\sigma(I)$)	9106
s (goodness of fit)	0.89
Δ/σ_{max}	<1
R	0.046
R_w	0.051
W (weighting scheme)	$0.90/(\sigma^2(F)+0.0030\,F^2)$
$\Delta\rho$ final (max/min) (e Å^{-3})	0.78/-0.67

TABLE 3. Selected interatomic distances (Å), angles (°) and torsion angles (°) with estimated standard deviations in parentheses for 10

Bond distances		Bond angles	
Sn(1)–C(1)	2.293(5)	C(1)–Sn(1)–C(2)	88.0(2)
Sn(1)–C(2)	2.292(4)	C(1)–Sn(2)–C(2)	88.1(2)
Sn(2)–C(2)	2.288(4)	Sn(1)–C(1)–Sn(2)	91.9(2)
Sn(2)–C(2)	2.289(5)	Sn(1)–C(2)–Sn(2)	92.0(2)
Sn(1)–C(3)	2.206(5)	C(1)–Sn(1)–C(3)	110.3(2)
Sn(1)–C(18)	2.205(6)	C(2)–Sn(1)–C(3)	127.5(2)
Sn(2)–C(45)	2.210(6)	C(1)–Sn(1)–C(18)	126.9(2)
Sn(2)–C(60)	2.220(5)	C(2)–Sn(1)–C(18)	110.3(2)
C(1)–C(33)	1.502(7)	C(3)–Sn(1)–C(18)	97.2(2)
C(1)–C(44)	1.508(7)	C(1)–Sn(2)–C(45)	127.0(2)
C(33)–C(38)	1.398(8)	C(2)–Sn(2)–C(45)	109.6(2)
C(39)–C(44)	1.402(8)	C(1)–Sn(2)–C(60)	110.9(2)
C(38)–C(39)	1.429(8)	C(2)–Sn(2)–C(60)	127.1(2)
C(2)–C(75)	1.485(7)	C(45)–Sn(2)–C(60)	97.4(2)
C(2)–C(86)	1.510(7)	Sn(1)–C(1)–C(33)	107.0(3)
C(75)–C(80)	1.415(7)	Sn(2)–C(1)–C(33)	126.0(3)
C(80)–C(81)	1.443(8)	Sn(1)–C(1)–C(44)	126.1(4)
C(81)–C(86)	1.404(8)	Sn(2)–C(1)–C(44)	106.7(3)
		C(33)–C(1)–C(44)	101.6(4)
		Sn(1)–C(2)–C(75)	126.0(3)
		Sn(2)–C(2)–C(75)	107.7(3)
		Sn(1)–C(2)–C(86)	105.4(3)
		Sn(2)–C(2)–C(86)	125.1(3)
		C(75)–C(2)–C(86)	102.8(4)

Torsion angles (°)
C(2)–Sn(1)–C(1)–Sn(2)   0

Angles between planes (°)	
Fluorenyl 1–plane 1	107
Fluorenyl 2–plane 1	72
Plane 1	C(1)–C(2)–Sn(1)–Sn(2)
Fluorenyl 1	C(33)···C(44)
Fluorenyl 2	C(75)···C(86)

Distances to the mean plane 1 (Å)	
C(3)	-1.61
C(18)	1.59
C(45)	-1.64
C(60)	1.59
C(33)	-1.11
C(44)	1.14
C(75)	-1.09
C(86)	1.17

$$\begin{array}{c} Me_2Sn-C(SiMe_3)_2 \\ | \quad\quad | \\ (Me_3Si)_2C-SnMe_2 \end{array}$$

(11)

3. X-Ray structure of the 1,3-distannacyclobutane (10)

Selected bond lengths, angles, torsion angles are listed in Table 3. The four-membered ring of the distannacyclobutane is planar (torsion angle C(2)–Sn(1)–C(1)–Sn(2) 0°) with four nearly identical Sn–C bonds (2.288(4)–2.293(5) Å). These Sn–C distances are

significantly longer than the standard Sn–C bond
lengths, generally 2.14–2.18 Å [23] and correspond to
single bonds in sterically encumbered tin compounds,
for example, 2.306 and 2.314 Å for the distance be-
tween tin and the *ipso* carbon of the 2,4,6-tris(trifluo-
romethyl)phenyl group [24], 2.269(5) and 2.275(4) Å for
the distance between tin and the carbon of a tert-butyl
group [25]. Shorter tin–carbon bonds are observed in
less crowded four-membered rings of tin, 2.18–2.20 Å
in a stannacyclobutane [26] and 2.17–2.20 in a 1,2-dis-
tannacyclobutane [27]. All these results demonstrate
the steric crowding in 10.

The distance between tin and the *ipso* carbon of the
2,4,6-triisopropylphenyl group (2.205(6)–2.220(5) Å) lies
in the normal range for such a bond [27,28], slightly
increased due to the bulkiness of the aromatic group.

The angles in the four-membered ring are close to
90°: 91.9(2) and 92.0(2)° for carbon, and 88.0(2) and
88.1(2)° for tin. Smaller angles on tin are found in
stannacyclobutane (67.5(2)°) [26] and in 1,2-distanna-
cyclobutane (69.7(2) and 70.3(2)°) [27]. The geometry
around the tin with angles between 88.0(2) and 127.5(2)°
is noticeably distorted from the tetrahedral because of
the four-membered ring. The fluorenyl groups (the
planarity of these groups is particularly well displayed
in Fig. 1(b)) and the aromatic groups are placed nearly
symmetrically in relation to the four-membered-ring
plane (see Table 3).

4. Experimental details

As the compounds are usually highly air- and mois-
ture-sensitive, their synthesis and handling require
high-vacuum techniques and carefully deoxygenated
solvents (generally Et_2O, THF, pentane) which must
be freshly distilled from sodium benzophenone.

^1H NMR spectra were recorded on Bruker AC 80,
AC 200 and AC 250 instruments at 80.1, 200.1 and
250.1 MHz, respectively. ^{13}C NMR spectra were
recorded on Bruker AC 200 and AC 250 instruments at
50.3 and 62.9 MHz (ref. TMS), respectively. ^{119}Sn
NMR spectra were recorded on a Bruker AC 200 at
74.6 MHz (ref. Me_4Sn) and ^{19}F NMR spectra on a
Bruker AC 80 at 75.4 MHz (ref. CF_3COOH).

IR spectra were recorded on a Perkin-Elmer 1600
FT instrument. Mass spectra were measured on a
Hewlett Packard 5989 A spectrometer by EI at 70 eV
and on a Nermag R 10010 spectrometer by DCI with
CH_4. Melting points were determined on a Reichert
apparatus. Elemental analyses were performed by the
Service de microanalyse de l'Ecole de Chimie de
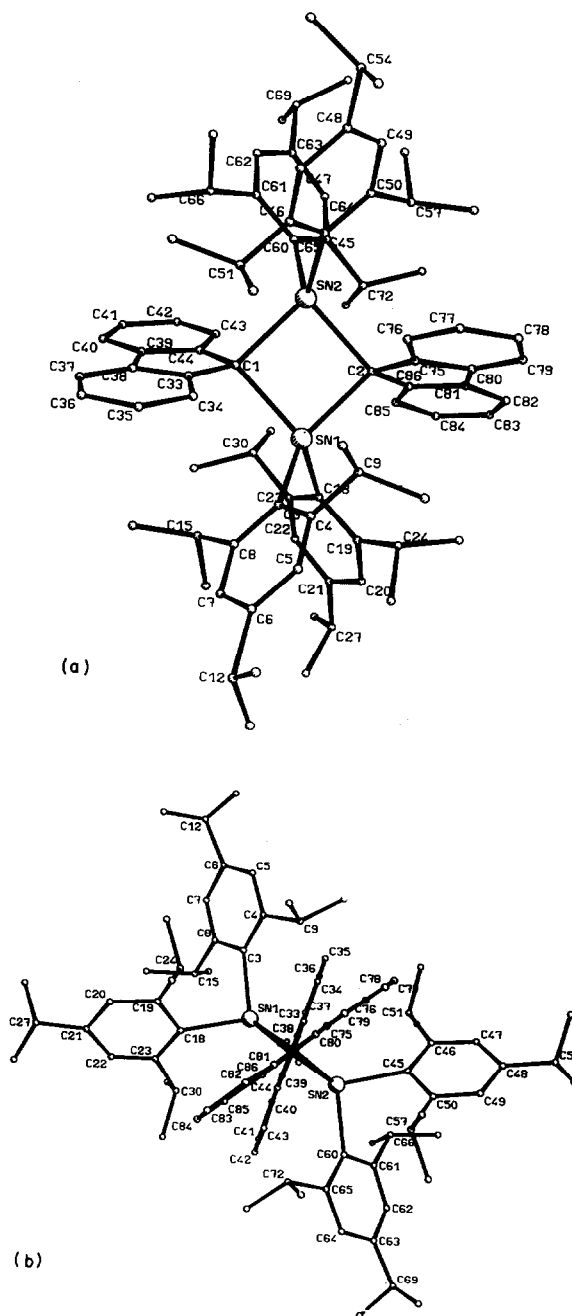Toulouse (France).

Fig. 1. Molecular structure of 10. (a) The four-membered ring and
(b) the planar four-membered ring and the planar fluorenyl groups.

4.1. X-Ray structure determination

Single crystals of 10 were obtained by direct dimer-
ization of stannene 1 in Et_2O at room temperature.
Data were collected on a Huber diffractometer. Accu-
rate cell dimensions were obtained from the centring
of reflections $(6 < 2\theta < 35°)$. A standard reflection
$(1,3, - 11)$ measured every 50 reflections showed no
significant variation. The structure was determined by
using the MULTAN 80 program. The least-squares re-

TABLE 4. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å) with e.s.d.s in parentheses

	x	y	z	B_{eq}
Sn(1)	7525(1)	1542(1)	2540(1)	2.2
Sn(2)	7753(1)	1340(1)	3574(1)	2.3
C(1)	6946(2)	2068(4)	3067(1)	2.4
C(2)	8339(2)	831(4)	3049(1)	2.4
C(3)	6847(3)	656(5)	2047(2)	3.3
C(4)	6876(3)	−471(5)	1974(2)	3.9
C(5)	6498(4)	−931(6)	1619(2)	5.7
C(6)	6063(4)	−333(8)	1332(3)	7.3
C(7)	6028(4)	773(7)	1409(2)	6.2
C(8)	6407(3)	1270(5)	1754(2)	4.0
C(9)	7290(3)	−1216(5)	2284(2)	4.0
C(10)	6844(3)	−2090(5)	2444(2)	5.2
C(11)	7870(3)	−1786(6)	2119(2)	5.3
C(12)	5635(11)	−730(11)	881(6)	21.7
C(13)	5605(7)	−1790(22)	961(5)	24.8
C(14)	5870(16)	−323(19)	539(4)	27.6
C(15)	6298(3)	2473(5)	1799(2)	4.5
C(16)	5576(3)	2729(7)	1862(2)	5.7
C(17)	6494(4)	3127(7)	1420(2)	6.6
C(18)	7995(3)	2606(4)	2117(2)	2.9
C(19)	8282(3)	2093(5)	1791(2)	3.4
C(20)	8477(3)	2739(6)	1468(2)	4.4
C(21)	8380(3)	3836(6)	1445(2)	4.5
C(22)	8117(3)	4305(5)	1775(2)	4.0
C(23)	7940(3)	3734(4)	2103(2)	2.9
C(24)	8416(3)	898(5)	1768(2)	3.8
C(25)	9180(3)	663(6)	1818(2)	5.5
C(26)	8040(4)	378(6)	1368(2)	5.4
C(27)	8526(4)	4443(7)	1056(2)	6.2
C(28)	7998(6)	4214(9)	692(3)	9.9
C(29)	8646(6)	5576(9)	1110(3)	10.5
C(30)	7699(3)	4356(4)	2453(2)	3.6
C(31)	8233(4)	5170(5)	2654(2)	4.9
C(32)	7029(4)	4952(5)	2318(2)	5.2
C(33)	6230(2)	1672(4)	2949(2)	2.6
C(34)	5984(3)	681(5)	2778(2)	3.3
C(35)	5287(3)	505(6)	2681(2)	4.5
C(36)	4839(3)	1323(6)	2757(2)	5.2
C(37)	5069(3)	2316(6)	2910(2)	4.5
C(38)	5767(3)	2486(5)	3006(2)	3.1
C(39)	6138(3)	3427(4)	3162(2)	3.2
C(40)	5911(4)	4455(5)	3274(2)	4.5
C(41)	6380(4)	5229(5)	3427(2)	5.7
C(42)	7066(4)	4999(5)	3474(2)	5.0
C(43)	7294(3)	4008(5)	3363(2)	3.6
C(44)	6835(3)	3216(4)	3200(2)	2.8
C(45)	7635(3)	−65(4)	3980(2)	3.0
C(46)	7029(3)	−637(5)	3989(2)	3.8
C(47)	6992(4)	−1393(5)	4299(2)	5.2
C(48)	7533(4)	−1669(6)	4595(2)	5.7
C(49)	8133(3)	−1140(5)	4581(2)	4.6
C(50)	8204(3)	−356(5)	4284(2)	3.4
C(51)	6408(3)	−479(5)	3659(2)	4.2
C(52)	6201(3)	−1547(5)	3435(2)	5.2
C(53)	5798(3)	23(7)	3821(2)	6.0
C(54)	7475(5)	−2552(8)	4925(3)	8.8
C(55)	7266(7)	−3614(7)	4722(4)	11.2
C(56)	7073(8)	−2207(11)	5246(4)	16.1
C(57)	8911(3)	147(5)	4298(2)	3.7
C(58)	9423(3)	−714(6)	4230(2)	5.3

TABLE 4. (Continued)

	x	y	z	B_{eq}
C(59)	9136(3)	733(6)	4722(2)	5.0
C(60)	8078(3)	2526(4)	4084(2)	2.8
C(61)	7665(3)	2609(5)	4399(2)	3.4
C(62)	7915(3)	3150(6)	4772(2)	4.4
C(63)	8546(3)	3581(6)	4853(2)	4.6
C(64)	8934(3)	3559(5)	4532(2)	4.0
C(65)	8711(3)	3045(5)	4150(2)	3.5
C(66)	6942(3)	2184(5)	4350(2)	3.6
C(67)	6841(4)	1407(6)	4706(2)	5.0
C(68)	6443(3)	3134(6)	4320(2)	5.2
C(69)	8845(4)	4033(8)	5289(2)	6.8
C(70)	9437(5)	3400(8)	5498(2)	7.9
C(71)	8997(5)	5213(8)	5263(3)	10.3
C(72)	9168(3)	3091(5)	3814(2)	3.8
C(73)	9847(3)	2507(6)	3943(2)	5.3
C(74)	9287(3)	4285(6)	3701(2)	5.2
C(75)	8511(3)	−332(4)	3109(2)	2.8
C(76)	8127(3)	−1203(5)	3215(2)	3.6
C(77)	8419(4)	−2226(5)	3274(2)	4.7
C(78)	9096(4)	−2400(5)	3237(2)	4.7
C(79)	9482(3)	−1553(5)	3130(2)	4.3
C(80)	9199(3)	−517(5)	3074(2)	2.9
C(81)	9490(3)	506(5)	2981(2)	3.3
C(82)	10147(3)	750(6)	2898(2)	3.8
C(83)	10301(3)	1772(6)	2809(2)	4.8
C(84)	9813(3)	2593(6)	2794(2)	4.3
C(85)	9166(3)	2364(5)	2874(2)	3.1
C(86)	8999(2)	1323(4)	2970(2)	2.5

finement was performed (using F) by SHELX-76 (carbon and tin atoms anisotropic). Hydrogens are in calculated positions.

There is a strong thermal agitation of C(12), C(13) and C(14) atoms; therefore bond distances and angles involving these atoms show large standard deviations. There is also some thermal agitation (but smaller) of C(27), C(28), C(29), C(54), C(55), C(56), C(69), C(70) and C(71).

4.2. Synthesis of 1

To a solution of $Ar_2Sn(F)C(H)R_2$ (600 mg, 0.84 mmol) in Et_2O (10 ml) cooled to $-78°C$ was added 1 equiv. of tert-butyllithium (1.7 M in pentane). The solution immediately became orange-red, due to the formation of $Ar_2Sn(F)C(Li)R_2$ (^{119}Sn NMR +9.8 ppm, $^1J(SnF) = 1999$ Hz) [1]. The reaction mixture was allowed to warm and at 0°C it turned deep violet. ^{119}Sn NMR analysis showed the nearly quantitative formation of 1 (δ +288 ppm). Due to its extreme sensitivity to air and moisture, and to its poor thermal stability, 1 could not be isolated pure. Crude solutions of 1 containing LiF were used to study its chemical reactivity.

4.3. Synthesis of 4

To a violet solution of 1 (0.70 mmol) in 5 ml of Et_2O was added a large excess of oxygen-free water. The

reaction mixture immediately became light yellow. The organic layer was dried over Na_2SO_4. Recrystallization in Et_2O afforded 317 mg (yield 64%) of pure white crystalline **4**.

^{1}H NMR (CDCl$_3$): δ 0.81 (d, ^3J(HH) = 6.6 Hz, 12H, o-CH*Me*); 0.85 (d, ^3J(HH) = 6.6 Hz, 12H, o-CH*Me'*); 1.18 (d, ^3J(HH) = 6.7 Hz, 12H, p-CH*Me$_2$*); 2.43 (sept, ^3J(HH) = 6.6 Hz, 4H, o-C*H*MeMe'); 2.81 (sept, ^3J(HH) = 6.7 Hz, 2H p-C*H*Me$_2$); 4.79 (s, 1H, C*H*R$_2$); 6.91 (s, 4H, arom H Ar); 6.75–7.98 (m, 8H, CR$_2$).

^{13}C NMR (C$_6$D$_6$): δ 24.14 (p-CH*Me$_2$*); 25.08 (o-CH*Me* and o-CH*Me'*); 34.62 (p-CHMe$_2$); 38.21 (o-CHMeMe'); 48.95 (CHR$_2$); 120.24 (C$_4$C$_5$); 122.48 (m-C Ar); 124.96, 126.02 and 126.82 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$); 140.87, 141.57 and 145.28 (ipso-C Ar, C$_{10}$–C$_{13}$); 151.16 (p-C Ar), 155.35 (o-C Ar).

^{119}Sn NMR (C$_6$D$_6$): −54.9

IR: ν(OH): 3644 (free), 3517 (associated) cm^{-1}.

4.4. Synthesis of 5

Aniline (0.1 ml, 1.09 mmol) in Et_2O (3 ml) was added at 0°C to a deep violet solution of **1** (1.05 mmol) in Et_2O. The reaction mixture immediately turned orange. After removal of the solvents *in vacuo*, recrystallization from pentane afforded 472 mg of light yellow crystals of **5** (yield 57%), m.p. 141°C.

^{1}H NMR (CDCl$_3$): δ 0.74 (d, ^3J(HH) = 6.6 Hz, 12H, o-CH*Me*); 0.79 (d, ^3J(HH) = 6.6 Hz, 12H, o-CH*Me'*); 1.17 (d, ^3J(HH) = 6.8 Hz, 12H, p-CH*Me$_2$*); 2.43 (sept, ^3J(HH) = 6.6 Hz, 4H, o-C*H*MeMe'); 2.80 (sept, ^3J(HH) = 6.8 Hz, 2H, p-C*H*Me$_2$); 3.60 (s, 1H, NH); 4.96 (s, 1H, C*H*R$_2$); 6.89 (s, 4H, arom H Ar); 6.40–7.98 (m, 13H, Ph and CR$_2$).

^{13}C NMR (CDCl$_3$): δ 24.00, 24.48 and 24.69 (o-CH*Me*, o-CH*Me'* and p-CH*Me$_2$*); 34.22 (p-CHMe$_2$); 38.55 (o-CHMeMe', ^3J(SnC) = 33.7 Hz); 47.76 (CHR$_2$); 115.88 (p-CPh); 117.43 (o-CPh); 119.78 (C$_4$C$_5$); 122.39 (m-CAr); 125.03, 125.68 and 126.49 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$); 128.87 (m-C Ph); 140.49, 141.08 and 144.75 (C$_{10}$–C$_{13}$, ipso-C Ar); 150.60 (p-C Ar); 151.79 (ipso-C Ph); 154.30 (o-C Ar, ^2J(SnC) = 47.8 Hz).

^{119}Sn (CDCl$_3$): δ −101.2 (^2J(SnH) = 110 Hz).

IR (CDCl$_3$): ν(NH) 3373 cm^{-1}.

MS (EI, 70 eV, ^{120}Sn): m/z 691 (M − PhNH, 1); 618 (M − CHR$_2$, 45); 525 (Ar$_2$Sn-1, 19); 414 (ArSnNHPh, 1); 323 (ArSn, 22); 165 (CHR$_2$, 100).

Anal. Found: C, 74.80; H, 7.79; N, 1.62. C$_{49}$H$_{61}$NSn calcd.: C, 75.22; H, 7.80; N, 1.79%.

4.5. Synthesis of 6

To a solution of stannene **1** prepared as previously described from 500 mg of **2** (0.70 mmol) and cooled to 0°C was slowly added 0.2 ml of a solution of HCl (1 M) in Et_2O. Reaction was immediate, as shown by the complete decolouration of the reaction mixture. After

removal of the solvents *in vacuo*, recrystallization from pentane gave 312 mg of white crystals of **6** (yield 61%) m.p. 158°C.

^{1}H NMR (CDCl$_3$): δ 0.85 (d, ^3J(HH) = 6.6 Hz, 12H, o-CH*Me*); 0.88 (d, ^3J(HH) = 6.6 Hz, 12H, o-CH*Me'*); 1.23 (d, ^3J(HH) = 6.8 Hz, 12H, p-CH*Me$_2$*); 2.46 (sept, ^3J(HH) = 6.6 Hz, 4H, o-C*H*MeMe'); 2.87 (sept, ^3J(HH) = 6.8 Hz, 2H, p-C*H*Me$_2$); 4.97 (s, 1H, C*H*R$_2$); 6.97 (s, 4H, arom H Ar); 6.82–8.03 (m, 8H, CR$_2$).

^{13}C NMR (CDCl$_3$): δ 23.94, 24.19 and 24.47 (o-CH*Me*, o-CH*Me'* and p-CH*Me$_2$*); 34.22 (p-CHMe$_2$); 38.59 (o-CHMe$_2$); 50.67 (CHR$_2$); 119.90 (C$_4$C$_5$); 122.64 (m-C Ar); 124.90, 126.26, 126.81 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$); 140.56, 140.78 and 143.93 (C$_{10}$–C$_{13}$, ipso-C Ar); 151.19 (p-C Ar); 154. 37 (o-C Ar).

^{119}Sn NMR (CDCl$_3$): δ −25.06.

MS (DCI, CH$_4$, ^{120}Sn): m/z 725 (M + 1 − H$_2$, 3); 691 (M + 1 − HCl, 29); 561 (M + 1 − R$_2$CH$_2$, 78); 205 (IsH − 1, 100).

Anal. Found: C, 70.76; H, 7.53. C$_{43}$H$_{55}$ClSn calcd.: C, 71.15; H 7.58%.

4.6. Synthesis of 7

To a solution of **1** (0.70 mmol) in 5 ml Et$_2$O was added a solution of phenylacetylene (0.1 ml, excess) in the same solvent. The reaction mixture turned yellow. After filtration and removal of solvents *in vacuo*, recrystallization from Et$_2$O gave 251 mg of white crystals of **7** (yield 45%), m.p. 78–79°C.

^{1}H NMR (CDCl$_3$): δ 0.82 (d, ^3J(HH) = 6.6 Hz, 12H, o-CH*Me*); 0.87 (d, ^3J(HH) = 6.6 Hz, 12H, o-CH*Me'*); 1.19 (d, ^3J(HH) = 6.6 Hz, 12H, p-CH*Me$_2$*); 2.63 (sept, ^3J(HH) = 6.6 Hz, 4H, o-C*H*MeMe'); 2.71 (sept, ^3J(HH) = 6.6 Hz, 2H, p-C*H*Me$_2$); 4.83 (s, 1H, C*H*R$_2$); 6.91 (s, 4H, arom H Ar); 6.95–7.95 (m, 13H, CR$_2$ and Ph).

^{13}C NMR (CDCl$_3$): δ 24.03, 24.49, 24.92 (o-CH*Me*, o-CH*Me'* and p-CH*Me$_2$*); 34.22 (p-CHMe$_2$); 38.33 (o-CHMeMe'); 45.04 (CHR$_2$); 119.85 (C$_4$C$_5$); 122.23 (m-C Ar); 124.65 (ipso-C Ph); 124.72, 125.59 and 126.44 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$); 127.93 and 128.28 m- and p-C Ph); 131.75 (o-C Ph), 138.53 (ipso-C Ar); 140.44 and 145.56 (C$_{10}$–C$_{13}$); 150.37 (p-C Ar); 154.95 (o-C Ar).

^{119}Sn NMR (CDCl$_3$); δ −192.98 (^2J(SnH) = 110 Hz).

MS (DCI, CH$_4$, ^{120}Sn): m/z 791 (M + 1 − H$_2$, 15); 777 (M + 1 − CH$_4$, 9); 691 (M + 1 − C$_6$H$_5$C=CH, 42); 627 (M + 1 − R$_2$CH$_2$, 100); 589 (M + 1 − ArH, 38); 203 (Ar, 70).

4.7. Synthesis of 8

To a solution of **1** (0.70 mmol) in Et$_2$O (5 ml) was added a suspension of LiAlH$_4$ (1.40 mmol) in Et$_2$O at 0°C. The reaction mixture immediately turned from deep violet to light yellow. After 5 min stirring, water

was added to eliminate the excess of $LiAlH_4$, and the organic layer was dried over Na_2SO_4. Crude **8** was recrystallized from Et_2O as white crystals, m.p. 171–172°C (283 mg, 58%).

^{1}H NMR (C_6D_6): δ 0.99 (d, $^3J(HH) = 6.7$ Hz, 12H, o-CH*Me*); 1.07 (d, $^3J(HH) = 6.7$ Hz, 12H, o-CH*Me'*); 1.15 (d, $^3J(HH) = 6.7$ Hz, 12H, p-CH*Me$_2$*); 2.73 (sept, $^3J(HH) = 6.7$ Hz, 4H, o-C*H*MeMe'); 2.82 (sept, $^3J(HH) = 6.7$ Hz, 2H, p-C*H*Me$_2$); 4.82 (s, 1H, C*H*R$_2$); 7.04 (s, 4H, arom H Ar); 7.13 (s, 1H, SnH, $^1J(^{117}SnH)$ = 1682 Hz, $^1J(^{119}SnH) = 1760$ Hz); 6.90–7.87 (m, 8H, CR$_2$).

^{13}C NMR (C_6D_6): δ 24.08, 24.80 and 25.06 (o-CH*Me*, o-CH*Me'* and p-CH*Me$_2$*); 34.57 (p-C*H*Me$_2$); 38.92 (o-C*H*MeMe', $^3J(SnC) = 38.1$ Hz); 51.22 (C*H*R$_2$); 120.24 (C$_4$C$_5$); 123.01 (m-C Ar); 125.33, 126.64 and 127.18 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$); 141.07, 141.51 and 144.43 (C$_{10}$–C$_{13}$, ipso-C Ar); 151.65 (p-C Ar); 155.12 (o-C Ar).

^{119}Sn(C_6D_6): δ -183.34 (dd, $^1J(SnH) = 1760$ Hz, $^2J(SnH) = 103$ Hz).

IR: ν(Sn–H) 1838 cm^{-1}.

MS (EI, 70 eV, ^{120}Sn): m/z 563 (M – 3 ^{i}Pr, 13); 561 (M – 3 ^{i}Pr – 2, 30); 323 (IsSn, 3); 202 (Ar – 1, 71); 165 (CHR$_2$, 100).

4.8. Synthesis of 9

To a solution of 0.70 mmol of **1** in Et_2O (5 ml) was added at 0°C a solution of methyl iodide (0.2 ml, excess) in the same solvent. The reaction mixture turned from deep violet to red, and finally dark brown. After filtration and removal of solvents *in vacuo*, recrystallization from Et_2O afforded 363 mg of yellow crystals of pure **9** (yield 62%), m.p. 139°C.

^{1}H NMR (CDCl$_3$): δ 0.51–0.92 (m, 24H, o-CH*Me* and o-CH*Me'*; very broad signal due to the hindered rotation of these groups); 1.12 (d, $^3J(HH) = 6.8$ Hz, 12H, p-CH*Me$_2$*); 2.22 (s, 3H, Me); 2.30–2.90 (m, 6H, o-C*H*Me, o-C*H*Me' and p-C*H*Me$_2$); 6.82 (s, 4H, arom H Ar); 6.85–7.90 (m, 8H, CR$_2$).

^{13}C NMR (CDCl$_3$): δ 1.07 (Me), 23.91 (p-CH*Me$_2$*); 24.63 and 25.63 (o-CH*Me* and o-CH*Me'*); 34.10 (p-C*H*Me$_2$); 38.01 (o-C*H*Me$_2$); 54.89 (CR$_2$); 119.90 (C$_4$C$_5$); 122.23 (m-CAr); 124.81, 126.65 and 127.12 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$); 139.68, 140.57 and 149.70 (C$_{10}$–C$_{13}$, ipso-C Ar); 150.64 (p-C Ar; 154.66 (o-C Ar). Due to hindered rotation, the signals of Ar groups are very weak.

^{119}Sn NMR (CDCl$_3$): δ -83.08 ($^3J(SnH) = 123$ Hz).

Anal. Found: C, 63.65; H, 6.90. C$_{44}$H$_{57}$ISn calcd.: C, 63.57; H, 6.86%.

MS (DCI, CH$_4$, ^{120}Sn): 705 (M + 1 – HI, 31); 653 (M + 1 – R$_2$CHMe, 100); 525 (653 – HI, 13); 203 (Ar, 35).

References

1 G. Anselme, H. Ranaivonjatovo, J. Escudié, C. Couret and J. Satgé, *Organometallics, 11* (1992) 2748.

2 H. Meyer, G. Baum, W. Massa, S. Berger and A. Berndt, *Angew. Chem., Int. Ed. Engl., 26* (1987) 546; A. Berndt, H. Meyer, G. Baum, W. Massa and S. Berger, *Pure Appl. Chem., 59* (1987) 1011.

3 S. Masamune and L.R. Sita, *J. Am. Chem. Soc., 107* (1985) 6390.

4 P.J. Davidson and M.F. Lappert, *J. Chem. Soc., Chem. Commun.,* (1973) 317; D.E. Goldberg, P.B. Hitchcock, M.F. Lappert, K.M. Thomas, A.J. Thorne, T. Fjeldberg, A. Haaland and B.E.R. Schilling, *J. Chem. Soc., Dalton Trans.,* (1986) 2387.

5 K.W. Zilm, G.A. Lawless, R.M. Merrill, J.M. Millar and G.G. Webb, *J. Am. Chem. Soc., 109* (1987) 7236.

6 C. Couret, J. Escudié, J. Satgé, A. Raharinirina and J.D. Andriamizaka, *J. Am. Chem. Soc., 107* (1985) 8280.

7 H. Ranaivonjatovo, J. Escudié, C. Couret and J. Satgé, *J. Chem. Soc., Chem. Commun.,* (1992) 1047.

8 N. Wiberg, G. Wagner, G. Reber, J. Riede and G. Müller, *Organometallics, 6* (1987) 35.

9 C. Couret, J. Escudié, J. Satgé and M. Lazraq, *J. Am. Chem. Soc., 109* (1987) 4411.

10 N. Wiberg, G. Wagner, G. Müller and J. Riede, *J. Organomet. Chem., 271* (1984) 381.

11 J. Escudié, C. Couret, M. Andrianarison and J. Satgé, *J. Am. Chem. Soc., 109* (1987) 386.

12 (a) S.A. Batcheller and S. Masamune, *Tetrahedron Lett., 29* (1988) 3383; (b) W. Ando and T. Tsumuraya, *J. Chem. Soc., Chem. Commun.,* (1989) 770.

13 D.J. De Young, M.J. Fink, J. Michl and R. West, *Main Group Met. Chem., 1* (1987) 19.

14 M. Veith, A. Detemple and V. Huch, *Chem. Ber., 124* (1991) 1135.

15 For a review see: G. Raabe and J. Michl, *Chem. Rev., 85* (1985) 419; A.G. Brook and K.M. Baines, *Adv. Organomet. Chem., 25* (1986) 1.

16 For a review see: N. Wiberg, *J. Organomet. Chem., 273* (1984) 141.

17 For a review see: J. Barrau, J. Escudié and J. Satgé, *Chem. Rev., 90* (1990) 283.

18 N. Wiberg and S.K. Vasisht, *Angew. Chem., Int. Ed. Engl., 30* (1991) 93.

19 A.G. Brook, J.W. Harris, J. Lennon and M. El Sheikh, *J. Am. Chem. Soc., 101* (1979) 83; A.G. Brook, S.C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. Krishna, M.R. Kallury, Y.C. Poon, Y.M. Chang and W. Wong-Ng, *J. Am. Chem. Soc., 104* (1982) 5667.

20 S. Zhang, R.T. Conlin, P.F. McGarry and J.C. Scaiano, *Organometallics, 11* (1992) 2317.

21 K.C. Molloy, *Adv. Organomet. Chem.*, *33* (1991) 171.

22 D. Seyferth and J.L. Lefferts, *J. Organomet. Chem.*, *116* (1976) 257.

23 M. Charisse, S. Roller and M. Dräger, *J. Organomet. Chem.*, *427* (1992) 23; A. Samuel-Lewis, P.J. Smith, J.H. Aupers, D. Hampson and D.C. Povey, *J. Organomet. Chem.*, *437* (1992) 131; L.N. Bochkarev, O.V. Grachev, S.F. Ziltsov, L.N. Zakharov and Y.T. Struchkov, *J. Organomet. Chem.*, *436* (1992) 299; C.J. Cardin, D.J. Cardin, M.A. Convery and M.M. Devereux, *J. Organomet. Chem.*, *411* (1991) C3.

24 H. Grützmacher, S. Freitag, R. Herbst-Irmer and G.S. Sheldrick, *Angew. Chem., Int. Ed. Engl., 31* (1992) 437.

25 M. Weidenbruch, J. Schlaefke, K. Peters and H.G. Von Schnering, *J. Organomet. Chem., 414* (1991) 319.

26 M. Weidenbruch, K. Schäfers, J. Schlaefke, K. Peters and H.G. Von Schnering, *J. Organomet. Chem., 415* (1991) 343.

27 M. Weidenbruch, A. Schäfer, H. Kilian, S. Pohl, W. Saak and H. Marsmann, *Chem. Ber., 125* (1992) 563.

28 P. Brown, M.F. Mahon and K.C. Molloy, *J. Organomet. Chem., 435* (1992) 265.