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Reactions of 3-(Diethylboryl)stannoles with Isocyanates

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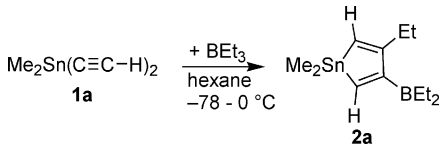
Diethynyl(diphenyl)stannane was prepared, fully characterised in solution and in the solid state, and its reaction with triethylborane, BEt_3, afforded 3-(diethylboryl)-4-ethyl-1,1-diphenyl-stannole in essentially quantitative yield. Treatment with isocyanates converted this stannole and the known analogous 1,1-dimethyl derivative into novel bicyclic compounds containing an aminoborane unit. These reactions were found to proceed diastereoselectively, again in essentially quantitative yield. The bicyclic compounds react with methanol through rearrangement and elimination of ethyl-(dimethoxy)borane to give novel 1-stannacyclopent-3-ene derivatives, one of which could be structurally characterised by X-ray analysis. All final products and intermediates were studied in solution by multinuclear NMR spectroscopy (^1H, ^{11}B, ^{13}C, ^{119}Sn NMR).

Introduction

Little is known about stannoles without alkyl or aryl substituents in the 2,5-positions[1] and the molecular structure of only a single example has been determined so far.[2] Indeed, it appears that 1,1-organoboration[3] of diethynyltin compounds provides the only convenient route to such stannoles. In contrast with numerous other (alkyn-1-yl)tin compounds,[4,5] ethynylstannanes are somewhat more difficult to prepare and less easy to handle. Therefore, they have received less attention and the synthesis and properties of some rather simple derivatives have not been described in detail. We have shown that diethynyl(dimethyl)stannane, $Me_2Sn(C{\equiv}C{-}H)_2$ **1a**, reacts with triethylborane, BEt_3, below room temperature by consecutive 1,1-ethylboration and 1,1-vinylboration[3] to give the stannole derivative **2a** (Scheme 1).[6] The stannole **2a** cannot be stored for prolonged periods of time and it decomposes by at least 50% during distillation at reduced pressure. Thus, only a few aspects of its chemistry have been so far addressed.[6–9]



Scheme 1.

In the present work, we report on the synthesis and molecular structure of diethynyl(diphenyl)stannane, $Ph_2Sn(C{\equiv}C{-}H)_2$ **1b**. This compound has been obtained previously in low yield[10] and its reaction with dicobaltoctacarbonyl $Co_2(CO)_8$ has been studied.[10,11] Here, we report that **1b** reacts with BEt_3 to afford the stannole **2b**. Reactions of the stannoles **2a** and **2b** with isocyanates were explored and some properties of the products were studied.

Results and Discussion

Diethynyl(diphenyl)stannane 1b

As reported earlier,[10] diethynyl(diphenyl)stannane **1b** can be prepared from the reaction of the diphenyltin dichloride with two equiv. of ethynylmagnesium bromide in thf (Scheme 2). One of the side products is the reported condensed compound **A**. We have found that **1b** can be purified by distillation at reduced pressure and stored for prolonged periods of time in the refrigerator at –20 °C (see Table 1 for NMR spectroscopic data of **1a** and **1b**). The condensation of **1b** by elimination of ethyne appears to occur in the reaction solutions in an unpredictable way, most likely catalysed by the magnesium salts in thf. In order to obtain more NMR spectroscopic data of the condensation products (Table 2), a concentrated solution of **1b** in [D_8]toluene was prepared, heated at 60 °C for 60 h and changes were monitored by ^{119}Sn NMR spectroscopy. Indeed, **A** was formed along with several higher condensation products (Figure 1). The ^{119}Sn NMR signals for tin atoms bearing both a terminal and a bridging C≡C unit may be observed in the typical range,[12] slightly shifted by about 7.2 ppm to higher field in comparison with the signals of **1b**, whereas the same effect is about doubled for tin atoms bearing solely bridging C≡C units in addition to the phenyl groups. The respective assignments (see expansions in Figure 1) can be accomplished by comparing the different signal intensities.

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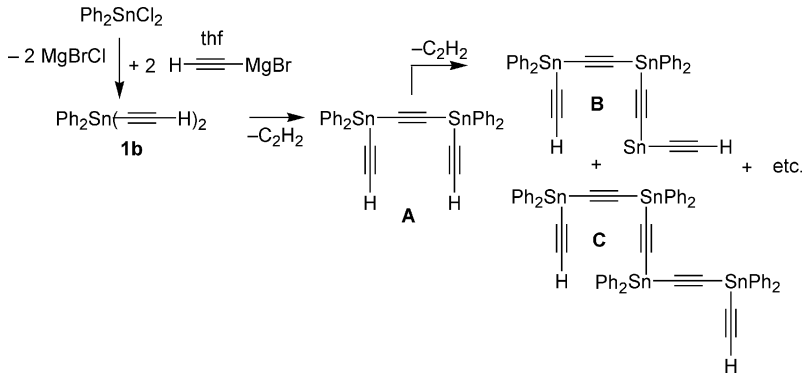


Scheme 2. Synthesis of diethynyl(diphenyl)stannane **1b** and its decomposition by elimination of ethyne.

Table 1. ^{119}Sn ^{13}C and ^{1}H NMR spectroscopic data[a] of **1a** and **1b**.

	δ ^{1}H		δ ^{13}C			δ ^{119}Sn
	R^1	≡C–H	R^1	SnC≡	≡C	
1a	0.51 [70.5]	2.29 [36.0]	–6.5 [503.0][b]	85.4 [576.2][b]	97.6 [122.0]	–153.8[b] {16.0} (Me) {–27.0} (C≡)
1b	7.39–7.50 (m) 7.63–7.70 [67.0] (m)	2.45 [39.1] (s)	134.3 [757.2] (*i*) 136.1 [51.1] (*o*) 129.0 [70.7] (*m*) 130.2 [14.4] (*p*)	83.8 [675.0]	99.0 [134.5]	–229.6 {16.9} (C-*i*) {–17.3} (C≡)

[a] In CH_2Cl_2 at 299 K (**1a**)[6] and in $CDCl_3$ at 296 K (**1b**); $^{n}J_{119Sn,13C}$ in Hz in brackets; isotope-induced chemical shifts $^{1}\Delta^{12/13}C(^{119}Sn)$ in ppb in braces with a negative sign for the shift of the more heavy isotopomer to lower frequency.[24] [b] Taken from ref.[24] (in $CDCl_3$).

The complementary information is gained from the ^{13}C NMR signals for the alkynyl carbon atoms (Figure 2). As expected, there are three different regions for alkynyl carbons, two of which are located near those which give rise to the relevant ^{13}C NMR signals of **1b**. The third region is typical of Sn−C≡C−Sn moieties.[13] The magnitude of the coupling constants $^{1,2}J_{119Sn,13C\equiv}$ of the terminal alkynyl carbon atoms are similar to **1b** and the coupling constants $^{1}J_{119Sn,13C\equiv}$ of the bridging C≡C units are somewhat smaller than for terminal ethynyl groups.[13b] Severely overlapping ^{13}C NMR signals prevented the complete assignment and also some $^{117/119}$Sn satellites for $^{2}J_{119Sn,13C}$ could not be observed.

Table 2. ^{119}Sn and ^{13}C (alkyne) NMR spectroscopic data[a] of **1b** and the condensation products **A**, **B**, **C** and **D**.

	δ ^{13}C			δ ^{119}Sn	
	SnC≡	≡C	C≡C Bridging	inner	outer
1b	83.8 [681.3]	99.5 [135.6]	–	–	–228.2
A	84.1 [672.2]	99.5 [134.3]	113.6 [599.0]	–	–235.5
B	84.2 [669.8]	n.o.	113.6 [600.1] 114.0 [586.8]	–242.7	–235.3
C	84.2 [671.4]	n.o.	113.5, 114.0, 114.1	–242.4	–235.2
D	n.o.	n.o.	113.5, 113.9, 114.1, 114.2	–242.4, –242.3	–235.2

[a] In [D_8]toluene at 296 K; $^{n}J_{119Sn,13C}$ in Hz in brackets.

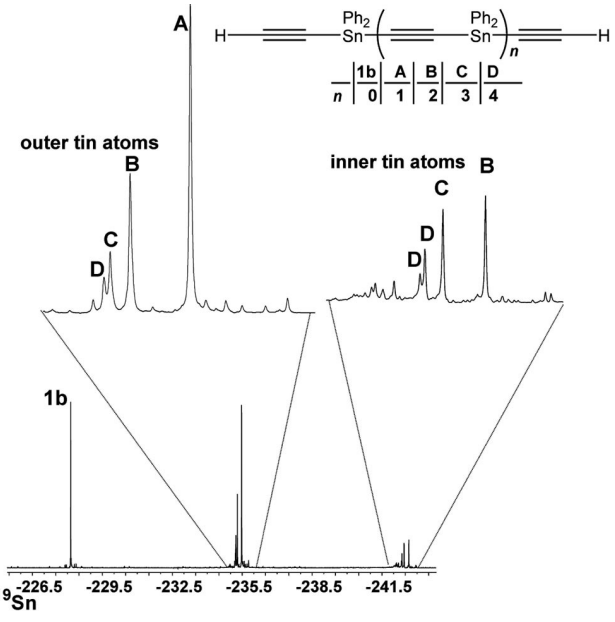


Figure 1. 149.2 MHz ^{119}Sn{^{1}H} NMR spectrum (INEPT, refocused) of **1b** in toluene after 60 h at 60 °C. Prominent signals in the expanded sections belong to the condensation products **A**, **B**, **C** and **D**, assigned by their relative intensities and on the basis of information from ^{13}C NMR spectra (see Figure 2).

The molecular structure of **1b** is shown in Figure 3. To the best of our knowledge this is the first structurally characterised ethynyltin compound. Intermolecular interactions

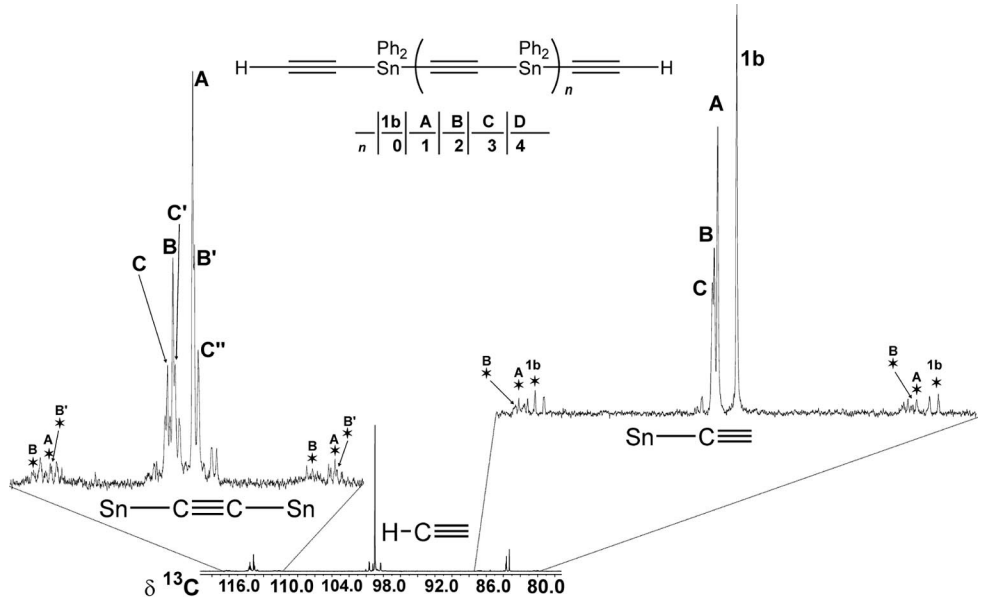


Figure 2. 100.5 MHz $^{13}C\{^1H\}$ NMR spectrum of **1b** in toluene after 60 h at 60 °C. Prominent signals in the expanded regions belong to the condensation products **A**, **B**, and **C**, as marked. Some $^{117/119}Sn$ satellites belonging to $^1J_{117/119Sn,13C}$ are also marked.

appear to be negligible. The surroundings of the tin atom correspond to a distorted tetrahedron. All bond lengths and angles are close to the expected values when compared with those of other alkynes or phenyl tin compounds. The Sn−C(Ph) bond lengths are 211.9 pm (Sn–C5) and 211.8 pm for (Sn–C11), slightly shorter than in tetraphenyltin (214.3 pm)[14a] and close to the value for dichloro(diphenyl)tin (211.4 pm)[14b] and several other chloro(phenyl)tin compounds.[14c,14d] As expected, the Sn−C(ethynyl) bond lengths [209.4(3) (Sn–C1) and 212.3(3) (Sn–C3)] are somewhat shorter. According to other alkyn-1-yl group 14 compounds,[15] the C≡C bonds (114.0 and 115.4 pm) appear to be rather short. The bond angle C11–Sn–C5 [115.55(11)°] is smaller than the respective one in dichloro(diphenyl)tin (123.9° and 127.0°) but larger than that in tetraphenyltin (108.9° and 110.5°). The other bond angles at the tin atom in **1b** are close to the tetrahedral bond angle. The deviations of the Sn−C≡C units from a linear geometry are small [174.8°(C2–C1–Sn1) and 172.0(3)° (C4–C3–Sn1)].

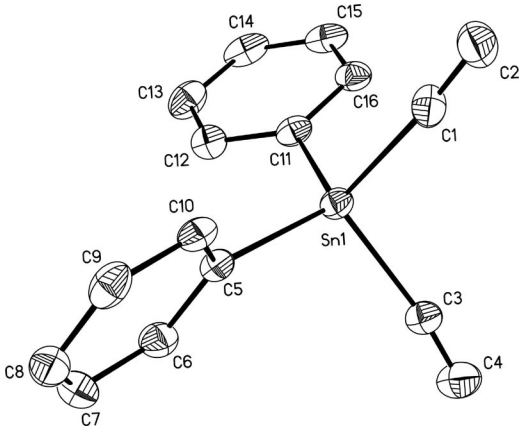
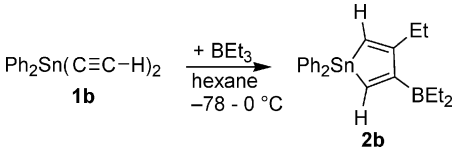


Figure 3. Molecular structure of **1b** (ORTEP, 40% probability; hydogen atoms have been omitted). Selected bond lengths [pm] and angles [°]: Sn1–C1 209.4(3), Sn1–C3 212.3(3), Sn1–C5 211.9(2), Sn1–C11 211.8(3), C1–C2 115.4(5), C3–C4 114.0(5), C1–Sn1–C11 108.84(13), C1–Sn1–C5 109.17(11), C11–Sn1–C5 115.55(11), C1–Sn1–C3 107.59(12), C11–Sn1–C3 107.01(11), C5–Sn1–C3 108.39(11), C2–C1–Sn1 174.8(3), C4–C3–Sn1 172.0(3).

3-(Diethylboryl)-4-ethyl-1,1-diphenylstannole 2b

The reaction of **1b** with BEt_3 selectively affords the stannole **2b** in essentially quantitative yield (Scheme 3). The stannole **2b** is a yellowish air- and moisture-sensitive oil which can be kept under argon in the refrigerator for prolonged periods of time. All relevant NMR spectroscopic data (Table 3) of **2a** and **2b** are, as expected, analogous.



Scheme 3. Synthesis of the stannole **2b**.

Reactions of the Stannoles 2 with Isocyanates

In addition to the well known reactivity of the cyclic diene system of metalloles[1,16] the presence of the diethylboryl group in the 3-position of the stannoles **2** opens the way to further attractive transformations. Thus, any reagent containing a nucleophilic centre will be attracted by the electrophilic boron atom. If this reagent also contains an electrophilic centre, further intramolecular reactions, e.g. at

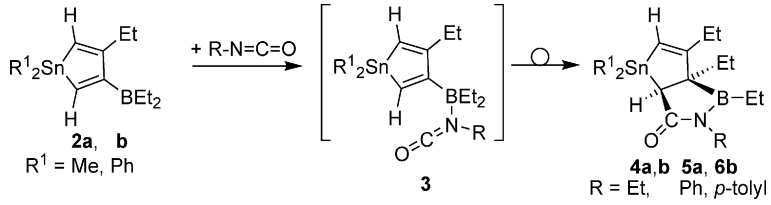
Table 3. ^{119}Sn, ^{13}C and ^{11}B NMR spectroscopic data[a] of the stannoles **2a** and **2b**.

	δ ^{13}C							δ ^{119}Sn	δ ^{11}B
	R^1	C-2	C-3	C-4	C-5	BEt_2	Et	(*h*1/2 in Hz)	(*h*1/2 in Hz)
2a	–9.3 [329.7]	127.8 [410.4]	175.3 (br)	162.7 [89.9]	121.0 [484.4]	21.4 (br), 9.2	30.9 [62.6], 13.2	19.5	85.0
2b	138.5 [506.5] (*i*) 137.1 [40.0] (*o*) 128.6 [51.8] (*m*) 129.0 [11.4] (*p*)	124.8 [441.1]	176.5 (br)	164.7 [99.6]	118.4 [517.7]	21.1 (br), 8.9	30.5 [67.6], 12.7	–46.9 (23.4)	84.5 (1340)

[a] In CD_2Cl_2 (**2a**) at 299 K[19] and in $CDCl_3$ (**2b**) at 296 K. ^{13}C NMR signals for carbon atoms linked to boron are broad (br) owing to partially relaxed ^{13}C-^{11}B spin-spin coupling;[25] $^nJ_{119Sn,13C}$ in Hz in brackets.

the adjacent C=C bond, may be readily induced. This behaviour has already been observed for alkenes bearing stannyl and boryl groups in vicinal positions at the C=C bond[17a,17b] and is explored here for the stannoles of type **2** using isocyanates as reagents. In isocyanates, nitrogen and the carbonyl carbon atoms serve as nucleophilic and electrophilic centres, respectively (Scheme 4).

The intermediates **3** were not observed. In the case of ethylisocyanate, the reaction was complete after 30–60 min at room temperature, whereas in the case of arylisocynates, the reaction times were about 12 h at room temperature or 4 h at 60 °C. It should be noted that BEt_3 does not react with isocyanates under these conditions. The stereochemistry of **4**–**6** follows conclusively from ^{1}H/^{1}H NOE difference spectra[20] and the consistent NMR spectroscopic data set (Table 4) supports the proposed structure. The δ^{11}B data are typical of amino(dialkyl)boranes, in which the nitrogen atoms bear a substituent competing for the nitrogen π electron density.[21] An inspection of the ^{119}Sn-^{13}C coupling constants reveals the rather small magnitude of the coup-



Scheme 4. Reactions of the stannoles **2** with isocyanates.

Table 4. ^{119}Sn, ^{13}C and ^{11}B NMR spectroscopic data[a] of **4a**, **4b**, **5a**, **5b** and **6b**.

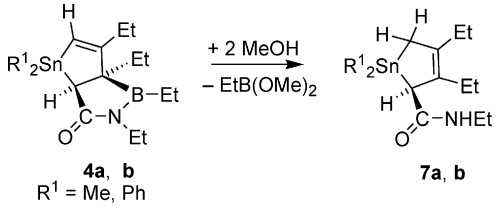
	δ ^{13}C										δ ^{119}Sn	δ ^{11}B
	R^1	C-2	C-3	C-4	C-5	C=O	BEt	Et(3)	Et(4)	NR		(*h*1/2 in Hz)
4a	–6.9 [350.4] –9.3 [344.0]	118.5 [464.9]	167.8 [51.6]	54.0 (br)	42.4 [209.6]	188.9 [15.0]	7.3 (br) 7.9	27.3 [16.0] 12.9	27.1 [78.8] 9.6	35.0 16.2	77.7	56.5 (907)
4b[b]	137.1 [524.9] 138.5 [540.6]	116.0 [499.8]	171.6 [59.2]	53.9 (br) [26.7]	43.6 [230.1]	187.8 [15.3]	7.3 (br) 8.0	27.5 [20.1] 13.1	27.7 [84.4] 9.8	35.1 15.3	–8.2	57.0 (1330)
5a	–6.5 [353.8] –8.7 [341.5]	119.1 [466.3]	168.0 [50.8]	54.6 (br)	42.8 [199.9]	188.0 [14.8]	7.8 (br) 7.7	27.7 [15.7] 13.1	27.4 [79.3] 9.9	126.8 127.4 128.8 138.7	83.5	56.5 (1020)
5b[c]	137.1 [520.1] 138.1 [548.2]	116.0 [501.8]	171.8 [57.1]	54.3 (br) [29.4]	44.0 [218.1]	186.7 [15.6]	7.5 (br) 7.7	27.8 [21.2] 13.1	27.9 [84.6] 9.9	127.1 128.5 129.4 138.3	–6.5	60.0 (1600)
6b[d]	136.9 [519.5] 138.0 [549.9]	115.8 [501.0]	171.7 [56.8]	54.1 (br) [28.3]	43.9 [219.0]	186.7 [15.4]	7.4 (br) 7.6	27.6 [21.4] 13.0	27.7 [83.3] 9.8	20.7 125.6 126.5 136.0 141.4	–6.7	58.0 (1619)

[a] In $CDCl_3$ at 296 K. ^{13}C NMR signals for carbon atoms linked to boron are broad (br) owing to partially relaxed ^{13}C-^{11}B spin-spin coupling;[25] $^nJ_{119Sn,13C}$ in Hz in brackets. [b] Other δ^{13}C(Ph) data: 128.3 [54.0], 128.7 [55.8], 129.1 [12.1], 129.2 [12.6], 136.5 [41.2], 136.9 [39.1]. [c] Other δ^{13}C(Ph) data: 128.6 [57.0], 128.7 [53.0], 129.3 [12.1], 129.4 [13.9], 136.5 [42.6], 137.1 [39.4]. [d] Other δ^{13}C values: 128.0 [52.3], 128.2 [55.4], 129.3 [n.o.], 129.4 [n.o.], 136.3 [42.0], 137.0 [39.2] ppm.

ling constant $^1J_{119Sn,13C(5)}$ when compared with other values for $^1J_{119Sn,13C}$ found here and elsewhere.[12] The reduced magnitude of $^1J_{119Sn,13C(5)}$ is in agreement with σ-π hyperconjugative effects[18] between the Sn–C(5) bond and the carbonyl carbon.

Methanolysis of the 1-Stannacyclopent-2-ene Derivatives

The new bicyclic compounds possess numerous reactive bonds, inviting further reactions. Here we report the reaction with methanol (Scheme 5). Two equiv. of methanol are necessary for the complete conversion of the bicyclic compounds. Elimination of ethyl(dimethoxy)borane was found and a rearrangement takes place into the new 1-stannacy-



4a, **b**
R^1 = Me, Ph

7a, **b**

Scheme 5. Methanolysis of the bicyclic compounds **4**.

Table 5. ^{119}Sn and ^{13}C NMR spectroscopic data[a] of **7a** and **7b**.

	δ ^{13}C									δ ^{119}Sn
	R^1	C-2	C-3	C-4	C-5	C=O	Et(3)	Et(4)	NR	
7a	–8.8 [328.4]	44.1	144.1	136.1	18.4 [323.9]	174.9	28.0 [57.5]	25.8 [38.8]	34.0, 15.5	72.6
	–10.1 [335.4]	[211.3]	[10.7]	[20.7]		[15.5]	13.4	13.3		
7b[b]	137.2 [543.5]	44.5	143.6	170.1	17.7	173.6	28.0 [61.3]	25.6 [43.2]	34.0	–25.9
	137.9 [500.5]	[236.4]	[13.9]	[12.4]	[348.1]	[15.1]	13.4	13.2	15.3	

[a] In $CDCl_3$ at 296 K; $^nJ_{119Sn,13C}$ in Hz in brackets. [b] Other δ^{13}C(Ph) data: 128.4 [53.3], 128.6 [53.1], 129.1 [11.4], 129.3 [12.3], 136.3 [37.5], 136.8 [38.8] ppm.

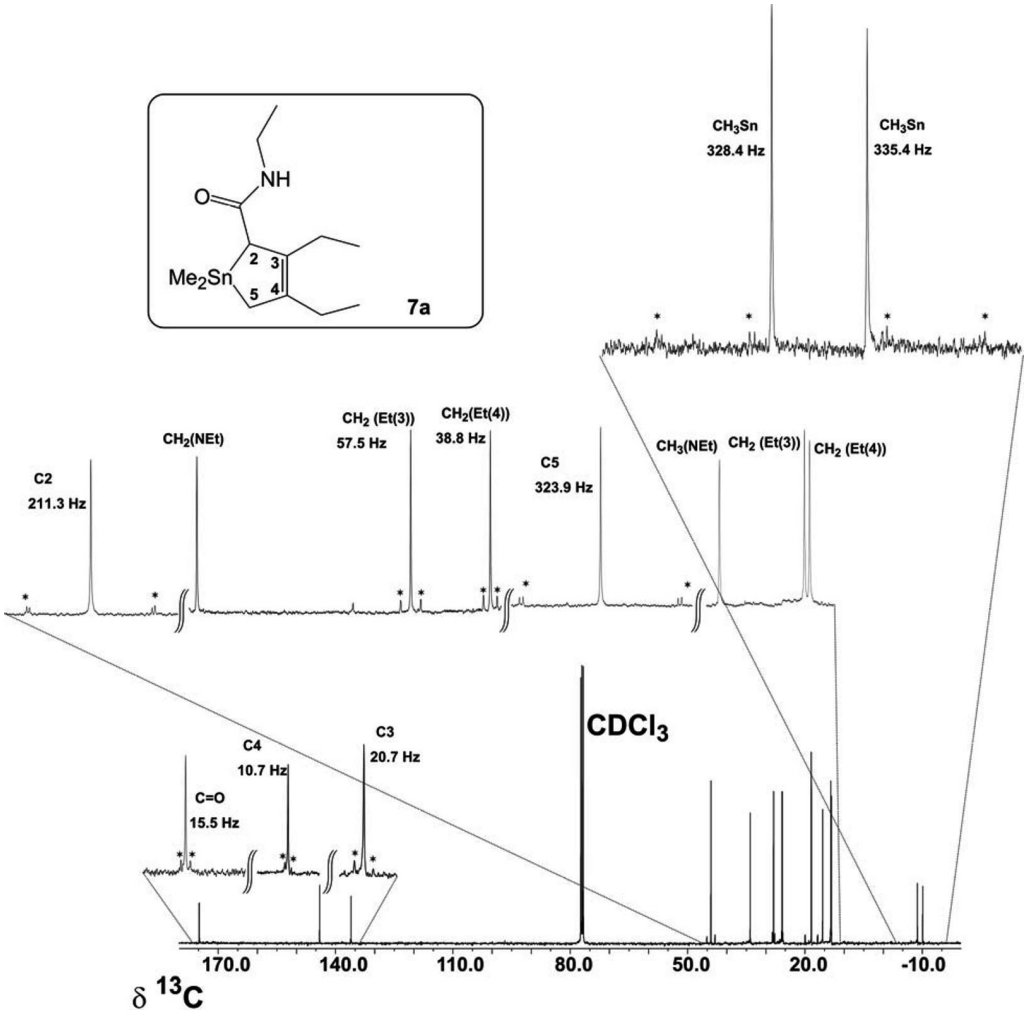


Figure 4. 100.5 MHz ^{13}C{^{1}H} NMR spectrum of the stannol-3-ene **7a**. $^{117/119}$Sn satellites in the expanded regions are marked by asterisks.

clopent-3-ene derivatives **7a**,**b** containing an acylamide group in the 2-position.

The solution state structures of **7a**,**b** were deduced from the diagnostic ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopic data (Table 5) and single crystals of compound **7a** were studied by X-ray diffraction. An example of a representative ^{13}C NMR spectrum is shown in Figure 4 and the straightforward assignment is indicated.

The molecular structure of **7a** is shown in Figure 5. The molecules are associated by hydrogen bridges, indicated by the distance between N and O (288 pm).[22] The two enantiomers are present in an alternative way in the crystal structure. The Sn−C(Me) bond lengths [211.8(10) and 212.9(12) pm] are in the normal range for methyltin compounds[23a,23b,23c] and the Sn1–C3 [216.1(11) pm] and Sn1–C6 [217.9(9) pm] bonds are slightly elongated compared with many other Sn–C bonds. The endocyclic C–C bond lengths correspond to the literature values of single bonds [151.1(15) pm (C3–C4) and 151.0(13) pm (C6–C5)] or double bonds, respectively [133.8(15) pm (C5–C4)]. All angles at the tin atom are enlarged with respect to the tetrahedral angle, except for the endocyclic angle C6–Sn1–C3 [85.6(4)°] which is acute as expected. The angles at the C=C bond are close to the expected 120° [C6–C5–C4 121.9(9)° and C5–C4–C3 122.5(9)°].

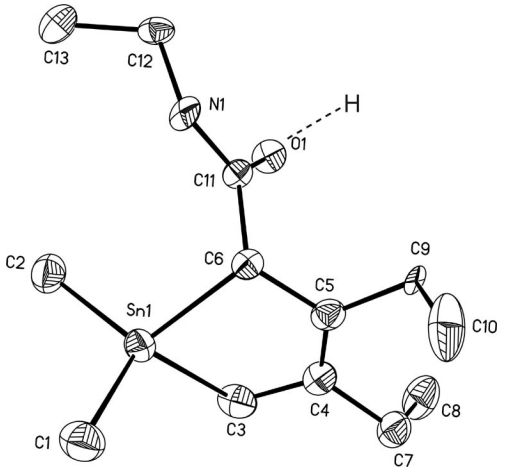


Figure 5. Molecular structure of **7a** (ORTEP, 40% probability; hydrogen atoms have been omitted; the O·H·N hydrogen bond to the next molecule is indicated). Selected bond lengths [pm] and angles [°]: Sn1–C1 211.8(12), Sn1–C2 212.9(10), Sn1–C3 216.1(11), Sn1–C6 217.9(9), C3–C4 151.1(15), C5–C4 133.8(15), C6–C5 151.0(13), N–H–O 288.0, C2–Sn1–C1 113.8(5), C6–Sn1–C2 113.8(4), C6–Sn1–C1 111.8(4), C3–Sn1–C2 116.7(5), C3–Sn1–C1 112.1(4), C6–Sn1–C3 85.6(4), Sn1–C6–C5 103.1(6), C6–C5–C4 121.9(9), C5–C4–C3 122.5(9), C4–C3–Sn1 102. 9(7).

Conclusions

The straightforward synthesis of stannoles by 1,1-organoboration can be extended to diphenyltin derivatives, using diethynyl(diphenyl)stannane which is available in a highly pure state in reasonable yield. The diethylboryl group in the 3-position at the stannole ring serves to attract nucleophilic reagents such as isocyanates which also contain an electrophilic centre for further intramolecular rearrangements. The novel bicyclic products, thus obtained, react readily with methanol to give stannole-3-enes which possess an unprecedented pattern of substituents.

Experimental Section

General: All preparative work as well as handling of the samples was carried out observing strict precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. Diphenyltin dichloride, dimethyltin dichloride, triethylborane, ethynylmagnesium bromide and the isocyanates were commercial products. Diethynyl(dimethyl)stannane was prepared as described.[6] NMR measurements in $CDCl_3$ or [D_8]-toluene (concentration ca. 5–10%) were carried out for samples in 5 mm tubes at 23 ± 1 °C using Varian Inova 300 and 400 MHz spectrometers for ^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR. Chemical shifts are given relative to Me_4Si, $\delta^{1}H$ ($CHCl_3$) = 7.24; $\delta^{1}H$ ($C_6D_5CD_2H$) = 2.03; $\delta^{13}C$ ($CDCl_3$) = 77.0; $\delta^{13}C$ ($C_6D_5CD_3$) = 20.4; external Me_4Sn [$\delta^{119}Sn$ = 0 for $\Xi(^{119}Sn)$ = 37.290665 MHz]; external BF_3–OEt_2 [$\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.083971 MHz]. Chemical shifts are given to ± 0.1 for ^{13}C and ^{119}Sn, spectra and ± 0.4 ppm for ^{11}B. Coupling constants are given to ± 0.4 Hz for $J_{119Sn,13C}$. ^{119}Sn NMR spectra were measured by using the refocused INEPT pulse sequence[26] based on $^{2}J_{119Sn,1H}$ (50 –100 Hz) after optimising the delay times in the pulse sequence. IR spectra were recorded with a Perkin–Elmer Spectrum 100 FTR spectrophotometer equipped with an ATR sampling unit. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

Synthesis of Diethynyl(diphenyl)stannane 1b: A two-necked Schlenk flask equipped with magnetic stirring bar and dropping funnel was charged with thf (230 mL) and diphenyltin dichloride (16.556 g, 48.15 mmol), and cooled whilst stirring to –78 °C. With vigorous stirring, ethynylmagnesium bromide (101 mmol) in thf (202.2 mL) was then added drop wise from the dropping funnel. The reaction mixture was allowed to reach room temperature and stirring was maintained for 12 h. Most of the thf was removed in vacuo and the residue was suspended in hexane (100 mL). Insoluble materials were filtered off, washed four times with hexane (4× 50 mL) and the combined hexane solutions were evaporated. This left a colourless oil which could be distilled under reduced pressure (113 °C/7.5 10^{-3} Torr) to give pure **1b** (6.9 g, 44%) as an oil. After storage in the refrigerator, **1b** solidified and remained solid (m.p. 52–55 °C). Repeated crystallisation from its melt finally gave single crystals suitable for X-ray structural analysis. Compound **1b** can be stored at –20 °C for prolonged periods of time (> 1 year) without decomposition.

1b: ^{1}H NMR (400 MHz): δ = 2.45 (s, $J_{119Sn,H}$ = 39.1 Hz, 2 H, ≡C−H), 7.39–7.50 (m, 6 H, $SnPh_2$-*meta, para*), 7.63–7.70 (m, $J_{119Sn,H}$ = 66.8 Hz, 4 H, $SnPh_2$-*ortho*) ppm. IR (ATR): $\tilde{\nu}$ = 3262, 3251 [ν(≡C–H)], 3067, 3047, 3022, 2995 [ν(C–H_{phenyl})], 2012 [ν(C≡C)] cm^{-1}.

Observation of the Condensation Products of 1b (A, B, C, etc.): Diethynyl(diphenyl)stannane **1b** [0.25 g, (0.774 mmol)] was dissolved in [D_8]toluene (0.6 mL). The sample was kept in an oil bath at 60 °C for 60 h and changes were monitored by ^{119}Sn NMR spectroscopy. After this time, when almost all material was in solution, the reaction was stopped and the mixture was analysed by ^{13}C and ^{119}Sn NMR spectroscopy (see Figures 1 and 2).

Synthesis of 3-(Diethylboryl)-3-ethyl-1,1-diphenyl-stannole 2b: In a two-necked flask equipped with a magnetic stirring bar, the diethynylstannane **1b** (0.43 g, 1.331 mmol) was dissolved in hexane (10 mL) and cooled to –78 °C. A slight excess of BEt_3 (0.2 mL, 1.382 mmol) was added in one portion. The mixture was warmed to room temperature and stirred for 30 min. Then the solvent was removed in vacuo and the pure stannole **2b** was left as a yellowish oil (> 98% by ^{1}H NMR).

2b: ^{1}H NMR (400 MHz): δ = 1.26, 0.88 (q, t, 10 H, BEt_2), 2.21, 1.01 (q, t, 5 H, 4-Et), 6.04 (s, $J_{119Sn,H}$ = 163.5 Hz, 1 H, 5-H), 6.11 (s, $J_{119Sn,H}$ = 162.2 Hz, 1 H, 2-H), 7.15–7.27 (m, 6 H, $SnPh_2$), 7.42–7.50 (m, 4 H, $SnPh_2$) ppm.

Reactions of the Stannoles 2a and 2b with Isocyanates: General procedure: The respective isocyanate (one equiv.) was added in one portion to a solution of the freshly prepared stannole **2a** or **2b** (≈ 1.2–1.5 mmol) in hexane (10 mL) at room temperature. In the case of EtNCO, the reaction mixture was stirred for 1 h. In the case of the aromatic isocyanates, the reaction mixtures were stirred for 12 h at room temperature (or 4 h at 60 °C) in the absence of light. The solvent was removed in vacuo and the products were left in essentially quantitative yield (NMR) as yellow oils. They can be used without further purification.

4a: ^{1}H NMR (400 MHz): δ = 0.09 (s, $J_{119Sn,H}$ = 55.2 Hz, 6 H, $SnMe_2$), 0.29 (s, $J_{119Sn,H}$ = 58.2 Hz, 6 H, $SnMe_2$), 1.02–1.09/1.12–1.22, 0.84 (m, m, t, 5 H, BEt), 1.37–1.52/1.63–1.76, 1.03 (m, m, t, 5 H, 3-Et), 2.07–2.19/2.19–2.32, 0.64 (m, m, t, 5 H, 4-Et), 2.39 (s, $J_{119Sn,H}$ = 67.0 Hz, 1 H, 2-H), 3.05–3.18/3.24–3.26, 0.98 (m, m, t. 5 H, NEt), 5.86 (s, $J_{119Sn,H}$ = 140.2 Hz,1 H, 5-H) ppm.

4b: ^{1}H NMR (400 MHz): δ = 2.13–2.26/2.26–2.39, 0.43 (m, m, t, 5 H, 4-Et), 0.82–0.92/0.95–1.04, 0.64 (m, m, t. 5 H, BEt), 1.34–1.46/1.66–1.79, 1.05 (m, m, t, 5 H, 3-Et), 2.65 (s, $J_{119Sn,H}$ = 71.1 Hz, 1 H, 2-H), 2.71 –2.82/2.96–3.08, 0.76 (m, m, t, 5 H, NEt), 5.93 (s, $J_{119Sn,H}$ = 141.7 Hz, 1 H, 5-H), 7.05–7.08 (m, 10 H, $SnPh_2$).

5a: ^{1}H NMR (400 MHz): δ = 0.26 (s, $J_{119Sn,H}$ = 56.4 Hz, 6 H, $SnMe_2$), 0.39 (s, $J_{119Sn,H}$ = 58.8.4 Hz, 6 H, $SnMe_2$), 2.18–2.28/2.28–2.40, 0.65 (m, m, t, 5 H, 4-Et), 0.86–0.92/0.94–1.02, 0.81 (m, m, t, 5 H, BEt), 1.66–1.76/1.76–1.87, 1.11 (m, m, t, 5 H, 3-Et), 2.61 [s, $J_{119Sn,H}$ = 67.2 Hz, 1 H, 2-CH(2)], 5.99 (s, $J_{119Sn,H}$ = 144.8 Hz, 1 H, 5-H), 6.90–7.35 (m, 5 H, NPh).

5b: ^{1}H NMR (400 MHz): δ = 2.38–2.49/2.49–2.62, 0.71 (m, m, t, 5 H, 4-Et), 0.85–0.93/1.01–1.11, 0.96 (m, m, t, 5 H, BEt), 1.75–1.86/1.93–2.06, 1.28 (m, m, t, 5 H, 3-Et), 3.02 (s, $J_{119Sn,H}$ = 69.2 Hz,1 H, 2-H), 6.21 (s, $J_{119Sn,H}$ = 142.9 Hz, 1 H, 5-H), 6.94–7.77 (m, 15 H, $SnPh_2$/NPh).

6b: ^{1}H NMR (400 MHz): δ = 2.45–2.57/2.57–2.70, 0.79 (m, m, t, 5 H, 4-Et), 0.91–1.01/1.05–1.16, 1.07 (m, m, t, 5 H, BEt), 1.83–1.93/2.01–2.12, 1.35 (m, m, t, 5 H, 3-Et), 2.31 [s, 3 H, CH_3(tol)], 3.09 (s, $J_{119Sn,1H}$ = 67.9 Hz,1 H, 2-H), 6.28 (s, $J_{119Sn,H}$ = 143.1 Hz,1 H, 5-H), 6.82–7.82 (m, 14 H, $SnPh_2$/Ntol).

Stannacyclopent-3-ene Derivatives 7a and 7b by Methanolysis: A solution of the bicyclic compound **4a** or **4b** (1.2 mmol) as obtained (vide supra) in CH_2Cl_2 (10 mL) was kept stirring at room temperature and methanol (2.5 mmol) was injected. After stirring for 3 h, all volatiles were removed in vacuo and the residues were washed several times with small amounts of hexane (2–4 mL). In the case of R^1 = Me (**7a**), a white powder precipitated at room temperature and the supernatant liquid was decanted. In the case of R^1 = Ph (**7b**), the product was purified by washing with cold hexane (–20 °C) upon which it precipitated as a colourless powder (48%) which turns into an oil at room temperature. Pure **7a** can be obtained in 61% yield as a white powder (m.p. 63–67 °C, decomp.) which was recrystallised from hexane/diethyl ether (1:1) to yield single crystals for X-ray analysis.

7a: ^{1}H NMR (400 MHz): δ = 0.29 (s, $J_{119Sn,H}$ = 56.4 Hz, 6 H, $SnMe_2$), 0.33 (s, $J_{119Sn,H}$ = 56.9 Hz , 6 H, $SnMe_2$), 1.90–2.02/2.23–2.33, 0.93 (m, m, t, 5 H, 4-Et), 2.13–2.23, 1.02 (m, t, 5 H, 3-Et), 1.55 [d, $J_{119Sn,\ H}$ = 43.4 Hz, $^2J_{H,H}$ = 16.3 Hz, 2 H, 5-H_2,], 1.83 [d, $J_{119Sn,H}$ = 33.2 Hz, $^2J_{H,H}$ = 16.3 Hz, 2 H, 5-H_2,], 3.06 (s, $J_{119Sn,H}$ = 52.8 Hz,1 H, 2-H), 3.10–3.32, 1.03 (m, t, 5 H, NEt), 5.24 (br. s, 1 H, NH).

7b: ^{1}H NMR (400 MHz): δ = 2.27–2.36, 0.83 (m, t, 5 H, 4-Et), 2.36–2.45, 1.02 (m, t, 5 H, 3-Et), 1.98 (d, $J_{119Sn,H}$ = 45.3 Hz, $^2J_{H,H}$

Table 6. Data pertinent to the crystal structure determinations[26] of **1b** and **7a**.

	1b		**7a**	
Chemical formula	$C_{16}H_{12}Sn$		$C_{13}H_{25}NOSn$	
F_w [g mol^{-1}]	322.95		330.03	
Diffractometer	STOE IPDS II, Mo-K_α, λ = 71.069 pm, graphite monochromator			
Crystal description	colourless prism		colourless plates	
Dimensions [mm]	0.28 × 0.12 × 0.10		0.18 × 0.17 × 0.06	
Crystal system	orthorhombic		orthorhombic	
Space group	$P2_12_12_1$		*Pbca*	
Lattice parameters	a = 781.80(5) Å b = 993.90(7) Å c = 1813.00(13) Å	α = 90° β = 90° γ = 90°	a = 1733.3(2) Å b = 949.60(14) Å c = 1861.5(3) Å	α = 90° β = 90° γ = 90°
Z	4		8	
density (calculated) [g cm^{-3}]	1.523		1.431	
F_{000}	632		1344	
θ measuring range [°]	1.66–26.05		2.05–26.13	
Absorption coefficient μ [mm^{-1}]	1.789		1.652	
T [K]	133(2)		133(2)	
Reflections collected	19011		8450	
Observed reflections $I > 2\sigma(I)$	2522		1708	
Absorption correction	numerical		numerical	
Refined parameters	154		145	
$R_1[I > 2\sigma(I)]$; wR_2 (all data)	0.0209; 0.0479		0.0778; 0.1367	
Max./min. residual electron density [e·m^{-3} × 10^{-6}]	0.827/–0.316		0.133/–1.302	

= 16.3 Hz, 2 H, 5-H_2), 2.28 (d, $J_{119Sn,H}$ = 33.7 Hz, $^2J_{H,H}$ = 16.3 Hz, 2 H, 5-H_2), 2.94–3.12, 1.14 (m, t, 5 H, NEt), 3.45 (s, $J_{119Sn,H}$ = 56.6 Hz,1 H, 2-H), 5.33 (br. s, 1 H, NH), 7.18–7.78 (m, 10 H, $SnPh_2$).

Crystal Structure Determinations of the 1b and 7a: Details pertinent to the crystal structure determinations are listed in Table 6.[27] Crystals of appropriate size were selected (in perfluorinated oil[28] at room temperature) and the data collections were carried out at 133 K using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit. Structure solutions and refinements were accomplished using SIR97,[29] SHELXL-97[30] and WinGX.[31]

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