

Propargyl Derivatives with Silicon Carbon and Tin Carbon Bonds

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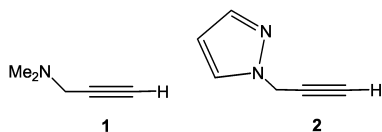
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1-Dimethylamino-propyn-2-ylsilanes **3a** [$\text{Me}_2\text{Si}(\text{C}\equiv\text{C}-\text{CH}_2\text{NMe}_2)_2$], **3b** [$\text{Me}(\text{H})\text{Si}(\text{C}\equiv\text{C}-\text{CH}_2\text{NMe}_2)_2$], **4a** [$\text{Me}_2(\text{Cl})\text{Si}-\text{C}\equiv\text{C}-\text{CH}_2\text{NMe}_2$], **4b** [$\text{Me}(\text{H})(\text{Cl})\text{Si}-\text{C}\equiv\text{C}-\text{CH}_2\text{NMe}_2$], and **5** [$\text{Me}_2\text{NCH}_2-\text{C}\equiv\text{C}-\text{SiMe}_2\text{SiMe}_2-\text{C}\equiv\text{C}-\text{CH}_2\text{NMe}_2$] were prepared. Similarly, the 1-(pyrazol-1-yl)-propin-2-ylsilanes **6** and **7** (analogous to **3a** and **5**, respectively) and the tin compounds **8** [$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{CH}_2\text{-pz}$] (pz = pyrazol-1-yl) and **9** [$\text{Me}_2\text{Sn}(\text{C}\equiv\text{C}-\text{CH}_2\text{-pz})_2$] were synthesized, using the reaction of $\text{Li}-\text{C}\equiv\text{C}-\text{CH}_2\text{-pz}$ (**2-Li**) with the respective chlorosilanes or tin chlorides. The compounds **3** to **9** were characterised in solution by a consistent set of ^1H , ^{13}C , ^{29}Si and ^{119}Sn NMR data.

Key words: Silicon, Tin, Alkynes, NMR Data

Introduction

The synthetic potential of alkynylsilicon and -tin compounds can be enhanced if additional functional groups are present, linked either to silicon and tin or to the $\text{C}\equiv\text{C}$ bond. The latter derivatives can be prepared starting from the respective terminal alkynes and using the well documented procedures [1, 2] for forming $\text{Si}-\text{C}\equiv$ or $\text{Sn}-\text{C}\equiv$ bonds. We are interested to study the 1,1-organoboration [3] of such compounds, since the presence of functional groups such as a dimethylamino group or an azine type nitrogen atom (in the pyrazolyl group, pz) may change the regio- and stereoselectivity of these reactions. Furthermore, the presence of these functions in addition to the $\text{C}\equiv\text{C}$ bond is attractive for complexation [4], in particular if two alkynyl groups are linked to a central element. In this work, we report on the synthesis and NMR spectroscopic properties of propargyl silanes and stannanes derived from the alkynes **1** and **2**.



Results and Discussion

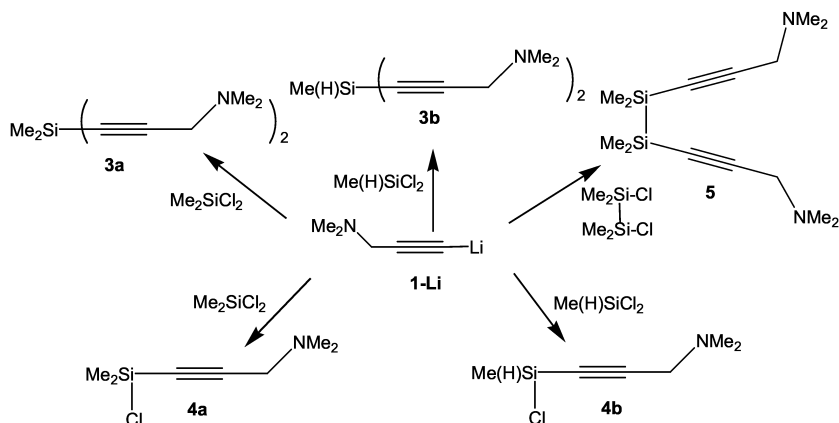
Synthesis of the alkyn-1-ylsilicon and -tin compounds

Treatment of the alkynes **1** and **2** with butyl lithium affords the respective lithium alkynides which then can

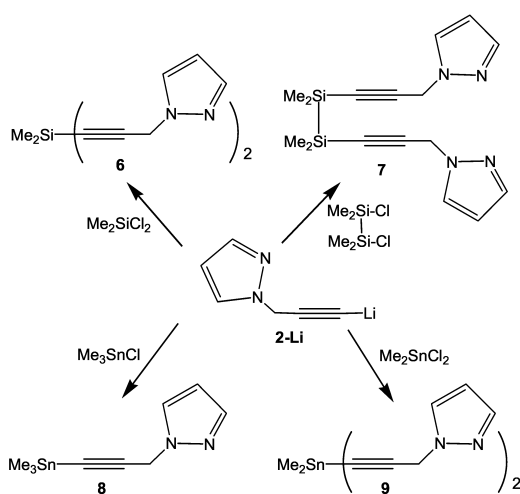
be reacted with organosilicon or -tin chlorides to give the desired products in good yield. Representative results for the reactions of **1-Li** and **2-Li** with silicon or tin chlorides are shown in the Schemes 1 and 2, respectively. With the exception of the tin compound **9** which was always obtained along with allenyl tin derivatives, all other products were pure (> 95%) even without distillation. The alkyne derivatives **3**–**9** are oily, colourless liquids which can be stored for prolonged periods without decomposition. The tin compounds **8** and **9** are sensitive towards moisture, as well as the chlorosilanes **4**. The silanes **3b** and **4b** are sensitive to both moisture and oxygen. The tin compound **3a(Sn)**, analogous to **3a**, has been prepared previously [5].

NMR spectroscopic results

Table 1 lists ^{13}C , ^{29}Si and ^{119}Sn NMR data of the compounds **3**–**9** together with some data of related compounds for comparison. The data support the proposed structures, and chemical shifts $\delta^{13}\text{C}$ as well as coupling constants $^nJ(^{29}\text{Si}, ^{13}\text{C})$ and $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ for the dimethylamino derivatives are similar when compared with the compounds without a functional group. In the cases of the N-pyrazolyl derivatives, the magnitude of $|^1J(^{29}\text{Si}, ^{13}\text{C}\equiv)|$ (**6**, **7**), and even more so of $|^1J(^{119}\text{Sn}, ^{13}\text{C}\equiv)|$ (**8**, **9**) is significantly smaller than in the corresponding propyn-1-yl or hexyn-1-yl compounds. Apparently, the polarising ability of the



Scheme 1.



Scheme 2.

$\text{C}\equiv\text{C}-\text{CH}_2\text{-pz}$ group is reduced with respect to that of the $\text{C}\equiv\text{C}-\text{C}_4\text{H}_9$ or $\text{C}\equiv\text{C}-\text{CH}_2\text{-NMe}_2$ groups, most likely the result of $\sigma-\pi$ delocalisation involving the heteroaromatic π system and the $\equiv\text{C}-\text{CH}_2\text{-N}$ σ bonds. Any significant association in solutions of **3–9**, which may be conceivable in the case of the dimethyltin derivatives, can be ruled out by the inspection of the chemical shifts $\delta^{29}\text{Si}$ and $\delta^{119}\text{Sn}$, since $\delta^{29}\text{Si}$ [6] and $\delta^{119}\text{Sn}$ values, in particular, are known to be extremely sensitive even to weak association [7]. Although ^{13}C NMR spectra are readily recorded owing to the good solubility of the compounds, the measurement of the coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ and $J(^{119}\text{Sn}, ^{13}\text{C})$ involving the alkynyl carbon atoms can be achieved in general more conveniently and faster by observing the ^{13}C satellites in the ^{29}Si (Fig. 1) or ^{119}Sn NMR spectra (Fig. 2). Isotope effects are rather small in the case

of ^{29}Si chemical shifts, but fairly large, at least for the $^{119}\text{Sn}-^{12}\text{C}\equiv/^{119}\text{Sn}-^{13}\text{C}\equiv$ isotopomers in **8** and **9**. The values observed (Table 1) correspond in magnitude and trend to those for other alkynyltin compounds [9].

Conclusions

Both alkynylsilicon and alkynyltin compounds containing a functional group such as a dimethylamino or a 1-pyrazolyl group in β -position with respect to the $\text{C}\equiv\text{C}$ bond can be prepared, and their monomeric structure follows from the consistent set of NMR data. Rearrangement of the propargyl into an allenyl group does not play a role under non-forcing conditions. The compounds reported here are attractive for further transformation, and work in this direction is in progress.

Experimental Section

Preparative work and handling of samples for NMR measurements were routinely carried out in an inert atmosphere, using dry solvents and oven-dried glass ware. Starting materials such as N,N-dimethylpropargylamine, *n*-butyl lithium (1.6 M in hexane), the chlorosilanes and tin chlorides were commercial products. 1-(Propyn-2-yl)pyrazole **1** was prepared following a literature procedure [10] with slight modifications (stirring of the reaction mixture after warming to room temperature for 72 h instead of 24 h gives a better yield). **1**: ^{13}C NMR (62.3 MHz): $\delta^{13}\text{C} = 74.1$ ($\equiv\text{C}-\text{H}$), 76.4 ($\equiv\text{C}$), 40.6 (CH_2), 139.2 (pz-C-3), 105.5 (pz-C-4), 128.3 (pz-C-5).

IR spectra were measured by using a Perkin Elmer, Spectrum 2000 FTIR instrument. NMR spectra were recorded by using a Bruker ARX 250 instrument, equipped with a multinuclear unit. If not mentioned otherwise, samples dissolved in C_6D_6 or CDCl_3 (ca. 10%) in 5 mm (o. d.) tubes were mea-

No / M = Si or Sn	$\delta^{13}\text{C}$				$\delta^{29}\text{Si}$ or $\delta^{119}\text{Sn}$
	M-C \equiv	$\equiv\text{C-R}$	M-Me	R	
3a	86.9 (98.3)	103.0 (19.5)	0.9 (61.9)	48.9 (CH ₂), 43.9 (NMe ₂)	-41.0
Me ₂ Si(C \equiv C-Bu) ₂	82.1 (100.3)	107.8 (20.2)	1.1 (61.0)	19.8, 30.9, 22.2, 13.8	-41.9
3b	83.8 (102.5)	104.1 (19.4)	-1.9 (62.1)	49.1 (CH ₂), 44.6 (NMe ₂)	-62.7 {221.7}
Me(H)Si(C \equiv C-Bu) ₂	79.0 (102.2)	110.0 (20.2)	-1.9 (61.6)	19.8, 30.6, 22.1, 13.7	-62.9 {217.6}
4a	85.8 (102.8)	103.4 (19.4)	3.5 (65.8)	48.3 (CH ₂), 43.8 (NMe ₂)	-0.4
Me ₂ Si(Cl)C \equiv C-Bu	81.2 (105.7)	110.3 (21.8)	4.0 (65.4)	19.6, 30.5, 22.6, 13.7	-1.3
4b	83.8 (105.4)	106.5 (21.2)	1.5 (64.6)	48.5 (CH ₂), 48.5 (NMe ₂)	-22.6 {249.3}
Me(H)Si(Cl)C \equiv C-Bu	78.9 (108.2)	112.4 (22.4)	1.8 (64.6)	19.6, 30.3, 22.0, 13.6	-22.3 {247.2}
5	87.3 (76.6)	104.4 (13.7)	-2.6 (49.4)	49.0 (CH ₂), 43.9 (NMe ₂)	-37.8
Me ₄ Si ₂ (C \equiv C-Me) ₂ [b]	81.6 (79.0)	105.3 (15.2)	-2.6 (44.4)	4.8	-38.4
6	87.9 (95.5)	100.9 (20.1)	-0.2 (62.6)	42.7 (CH ₂), 139.9 (C-3), 106.3 (C-4), 128.6 (C-5)	-38.8
7	88.8 (74.0)	101.9 (13.7)	-3.3 (50.5)	42.4 (CH ₂) 139.8 (C-3), 106.1 (C-4), 128.4 (C-5)	-36.6
8 [c]	89.9 [411.0]	102.5 [84.0]	-8.2 [405.4]	42.6 (CH ₂), 139.7 (C-3), 106.4 (C-4), 128.3 (C-5)	-67.4
Me ₃ Sn-C \equiv C-Bu	81.7 [506.6]	110.7 [105.3]	-8.1 [404.3]	20.1, 31.5, 22.2, 13.8	-73.0
3a (Sn) (in CDCl ₃)	84.9 [612.9]	105.1 [123.4]	-6.3 [499.2]	48.9 (CH ₂), 44.0 (NMe ₂)	-156.8
9 [d]	86.4 [581.5]	102.6 [120.3]	-6.9 [500.8]	42.3 (CH ₂), 140.7(C-3), 107.4 (C-4), 127.1 (C-5)	-151.6
Me ₂ Sn(C \equiv C-Bu) ₂ (in CDCl ₃)	79.1 [639.8]	110.9 [133.0]	-6.6 [497.0]	19.5, 30.6, 21.6, 13.3	-156.7

Table 1. ^{13}C , ^{29}Si and ^{119}Sn NMR data^[a] of **3–9** and some related alkyn-1-ylsilicon and -tin compounds for comparison.

^[a] Measured in C₆D₆ (ca. 10%), if not noted otherwise; coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ are given in parentheses (± 0.2 Hz), $J(^{29}\text{Si}, ^1\text{H})$ in braces (± 0.2 Hz), and $J(^{119}\text{Sn}, ^{13}\text{C})$ in brackets (± 0.3 Hz); ^[b] data taken from Ref. [11]; $J(^{29}\text{Si}, ^{13}\text{C}(\text{Me})) = 49.4$ corrects a misprint in [11]. ^[c] $J(^{119}\text{Sn}, ^{13}\text{C})$ data measured from ^{119}Sn NMR spectra; isotope-induced chemical shifts $^1\Delta^{12/13}\text{C}_{\text{Me}}(^{119}\text{Sn}) = -4 \pm 2$ ppb, and $^1\Delta^{12/13}\text{C}_{\text{C}\equiv}(^{119}\text{Sn}) = -58 \pm 2$ ppb. ^[d] $J(^{119}\text{Sn}, ^{13}\text{C})$ data measured from ^{119}Sn NMR spectra; isotope-induced chemical shifts $^1\Delta^{12/13}\text{C}_{\text{Me}}(^{119}\text{Sn}) = -1 \pm 2$ ppb, and $^1\Delta^{12/13}\text{C}_{\text{C}\equiv}(^{119}\text{Sn}) = -53 \pm 2$ ppb.

sured at 23 ± 1 °C. Chemical shifts are given with respect to Me₄Si using the solvent signals [$\delta^1\text{H}$ (C₆D₅H) = 7.15, (CHCl₃/CDCl₃) = 7.24; $\delta^{13}\text{C}$ (C₆D₆) = 128.0, (CDCl₃) = 77.0], and the absolute frequencies for $\delta^{29}\text{Si}(\text{Me}_4\text{Si}) = 0$ [$\Xi(^{29}\text{Si}) = 19.867184$ MHz], and for $\delta^{119}\text{Sn}(\text{Me}_4\text{Sn}) = 0$ [$\Xi(^{119}\text{Sn}) = 37.290665$ MHz]. Mass spectra: (EI MS; 70 eV): Finnigan MAT 8500 with direct inlet; the m/z data refer to the isotopes ^1H , ^{12}C , ^{14}N , ^{28}Si , ^{120}Sn .

Synthesis of the bis(1-dimethylamino-propyn-2-yl)silanes 3a, 3b and 5 (general procedure): The freshly prepared suspension of **1-Li** (10 mmol) in hexane (30 ml) was kept stirring and cooled to -78 °C, and the respective chlorosilane or dichlorodisilane (5 mmol) was added dropwise within 15 min as a solution in hexane (5 ml). Then the mixture was warmed to room temperature, heated at reflux for 1 h, and kept stirring for further 12 h at room temperature. Insoluble materials were filtered off, volatile materials were removed *in vacuo* and the fractional distillation of the residue under reduced pressure gave **3a** (b.p. $86-88$ °C/1 Torr) and **3b** (b.p. $70-$

80 °C/1 Torr) in $70-78\%$ yield. Compound **5** was obtained in 85% yield in high purity (see Fig. 1) and distillation was not carried out. **3a**: C₁₂H₂₂N₂Si (222.4): calcd. C 64.8, H 10.0, N 12.6; found C 64.3, H 9.8, N 12.4; ^1H NMR (250.1 MHz; CDCl₃): δ = 0.37 (s, 6H, SiMe₂), 2.21 (s, 12H, NMe₂), 3.20 (s, 4H, NCH₂); IR: $\nu(\text{C}\equiv\text{C}) = 2184, 2166$ cm⁻¹; EI MS: m/z (%) = 221 (5) (M⁺-H), 207 (10), 179 (100), 164 (20), 82 (25), 58 (45), 44 (15). **3b**: ^1H NMR (250.1 MHz; CDCl₃): δ = 0.22 (d, 3H, SiMe; $^3J(^1\text{H}, \text{Si}, ^1\text{H}) = 3.8$ Hz), 2.12 (s, 12H, NMe₂), 3.11 (s, 4H, NCH₂), 4.10 (q, 1H, SiH; $^3J(^1\text{H}, \text{Si}, ^1\text{H}) = 3.8$ Hz); IR: $\nu(\text{C}\equiv\text{C}), \nu(\text{Si-H}) = 2185, 2167, 2170$ (sh) cm⁻¹. **5**: ^1H NMR (250.1 MHz; C₆D₆): δ = 0.42 (s, 12H, Me₂SiSiMe₂), 2.25 (s, 12H, NMe₂), 3.25 (s, 4H, NCH₂).

Synthesis of the 1-dimethylamino-propyn-2-yl(chloro)methylsilanes 4a, 4b (general procedure): The lithium alkynide **1-Li** (10 mmol) was freshly prepared from a solution of **1** in THF (10 ml) and *n*-butyl lithium in hexane (1.6 M; 6.25 ml) at -78 °C. After warming to room temperature a clear so-

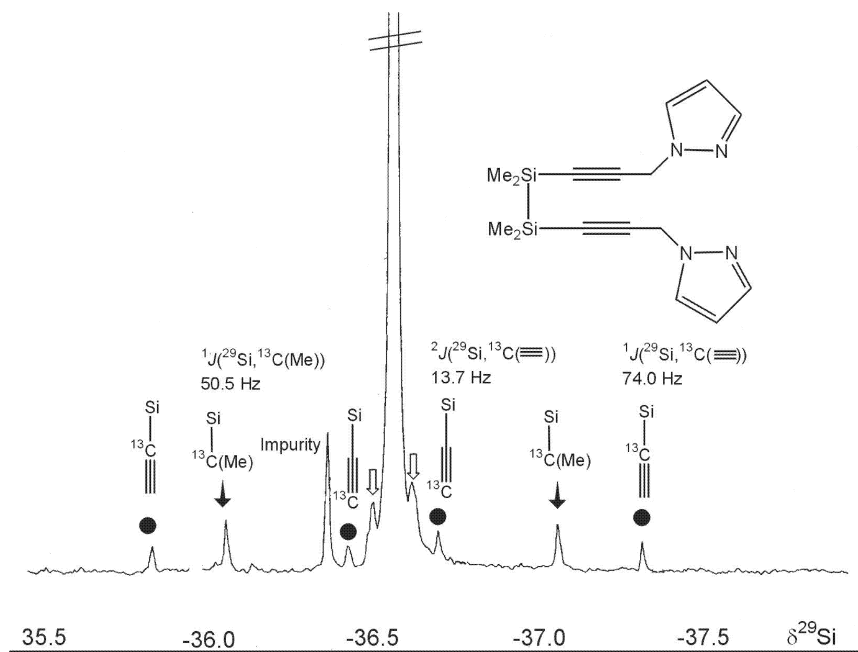


Fig. 1. 49.9 MHz $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the 1,2-di(alkyn-1-yl)disilane **7** (in C_6D_6 , 10%), showing the ^{13}C satellites as marked [open arrows mark overlapping ^{13}C satellites corresponding to the coupling constants $^2J(^{29}\text{Si}, \text{Si}, ^{13}\text{C}(\text{Me}))$ and $^2J(^{29}\text{Si}, \text{Si}, ^{13}\text{C}\equiv)$]. The spectrum was measured by using the refocused INEPT pulse sequence [9] based on $^2J(^{29}\text{Si}, ^1\text{H}(\text{Me})) = 7$ Hz (result of 160 transients; repetition delay 4 s, acquisition time 5 s).

lution was obtained which was then added dropwise within 15 min to a cooled (-78°C), stirred solution of an excess of the respective chlorosilane (40 mmol) in THF (20 ml). This mixture was warmed slowly to room temperature, kept stirring for 12 h, and then the solvents were removed *in vacuo*. The residue was extracted with hexane (40 ml), insoluble materials were filtered off, and the hexane was removed *in vacuo*. Fractional distillation under reduced pressure gave the desired products **4a** (b.p. $32-33^\circ\text{C}/0.5$ Torr) and **4b** (b.p. $32-35^\circ\text{C}/1$ Torr) in 40–50% yield. **4a** $\text{C}_7\text{H}_{14}\text{ClNSi}$ (175.7): calcd. (%) C 47.8, H 8.0, N 8.0; found (%) C 47.5, H 7.9, N 8.1. ^1H NMR (250.1 MHz; CDCl_3): $\delta = 0.44$ (s, 6H, SiMe_2), 2.17 (s, 6H, NMe_2), 3.18 (s, 2H, NCH_2); IR: $\nu(\text{C}\equiv\text{C}) = 2185, 2168\text{ cm}^{-1}$. **4b**: ^1H NMR (250.1 MHz; CDCl_3): $\delta = 0.45$ (d, 3H, SiMe ; $^3J(^1\text{H}, \text{Si}, ^1\text{H}) = 3.3$ Hz), 2.18 (s, 6H, NMe_2), 3.13 (s, 2H, NCH_2); IR: $\nu(\text{C}\equiv\text{C})$, $\nu(\text{Si-H}) = 2186, 2167\text{ cm}^{-1}$.

Synthesis of the 1-(pyrazol-1-yl)-propyn-2-yl derivatives 6, 7, 8, 9 (general procedure): A suspension of **2-Li** (10 mmol) in hexane (20 ml) was freshly prepared from **2** and *n*-butyl lithium (1.6 M in hexane; 6.25 ml) at -78°C , warmed to room temperature and cooled again at -78°C . Then the respective chlorosilane (5 mmol) or tin chloride (10 mmol Me_3SnCl or 5 mmol Me_2SnCl_2) was added either as a solution in hexane (10 ml) or as a solid in portions

(tin chlorides). The reaction mixture was kept stirring and warmed to room temperature. After 15 min of heating at reflux, all insoluble materials were filtered off, the solvent was removed *in vacuo*, and the products were obtained in 89–85% yield as oily, colourless liquids. According to ^1H NMR spectra, the compounds **6**, **7** and **8** (see Fig. 2 for the ^{119}Sn NMR spectrum) were pure (> 95%). In the case of **9**, a variable amount (about 10–30%) of an impurity was present which according to signals in the ^{13}C NMR spectra must be an allenyltin derivative. Attempts to purify **9** by crystallisation from pentane at -85°C were not successful. **6**: ^1H NMR (250.1 MHz; C_6D_6): $\delta = 0.25$ (s, 6H, SiMe_2), 4.51 (s, 4H, NCH_2), 7.24, 6.09, 7.58 (m, m, m, 1H, 1H, 1H, $\text{H}^{3,4,5}$). **7**: $\text{C}_{16}\text{H}_{22}\text{N}_4\text{Si}_2$ (326.5): calcd. (%) C 58.9, H 6.8, N 17.2; found C 58.5, H 6.7, N 17.5. ^1H NMR (250.1 MHz; C_6D_6): $\delta = 0.30$ (s, 12H, $\text{Me}_2\text{Si-SiMe}_2$), 4.76 (s, 4H, NCH_2), 7.44, 6.16, 7.54 (m, m, m, 1H, 1H, 1H, $\text{H}^{3,4,5}$). **8**: $\text{C}_9\text{H}_{14}\text{N}_2\text{Sn}$ (268.9): calcd. C 40.2, H 5.2, N 10.4; found C 39.9, H 5.0, N 10.1. ^1H NMR (250.1 MHz; C_6D_6): $\delta[J(^{119}\text{Sn}^1\text{H})] = 0.21$ [60.5] (s, 9H, SnMe_3), 4.79 [10.1] (s, 2H, NCH_2), 7.20, 6.17, 7.60 (m, m, m, 1H, 1H, 1H, $\text{H}^{3,4,5}$); EI-MS: m/z (%) = 270 (3) (M^+), 165 (100) (Me_3Sn^+), 105 (35) ($\text{M}^+ - \text{SnMe}_3$). **9**: ^1H NMR (250.1 MHz; C_6D_6): $\delta[J(^{119}\text{Sn}^1\text{H})] = 0.21$ [70.0] (s, 6H, SnMe_2), 4.7 [10.8] (s, 4H, NCH_2), 7.61, 6.15, 7.64 (m, m, m, 1H, 1H, 1H, $\text{H}^{3,4,5}$).

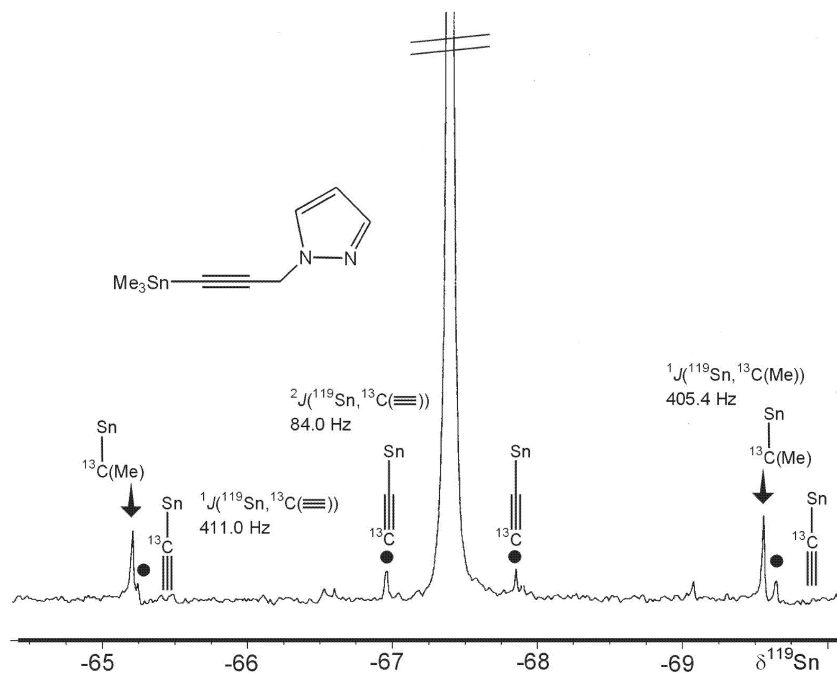


Fig. 2. 93.3 MHz $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of the alkyn-1-yl(trimethyl)stannane **8** (in C_6D_6 , 10%), showing the ^{13}C satellites as marked. The spectrum was measured by using the refocused INEPT pulse sequence [9] based on $^2J(^{119}\text{Sn}, ^1\text{H}(\text{Me})) = 60$ Hz (result of 160 transients; repetition delay 3 s, acquisition time 2.5 s). The isotope-induced chemical shifts $^1\Delta^{12/13}\text{C}_{\text{Me}}(^{119}\text{Sn})$ (-4 ± 2 ppb) and $^1\Delta^{12/13}\text{C}_{\text{C}\equiv}(^{119}\text{Sn})$ (-58 ± 2 ppb), typical of mono-alkyn-1-yl(trimethyl)stannanes [8], can be recognized by inspection, since the positions of the $^{13}\text{C}(\text{C}\equiv)$ satellites are markedly unsymmetric with respect to the central signal of the ^{12}C - ^{119}Sn isotopomer.

Acknowledgements

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