DETERMINATION OF COUPLING SIGNS IN STANNYLATED ALKYNES AND ALLENES

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Abstract

The reaction of partially lithiated propyne with trimethyltin chloride yields mixtures of alkynyltin and allenyltin compounds. The products 1,3-bis(trimethylstannyl)-1-propyne (**2**), 1,1-bis(trimethylstannyl)allene (**3**) were identified, together with tris(trimethylstannyl)allene (**4**) and tetrakis(trimethylstannyl)allene (**5**), by ^{13}C- and ^{119}Sn NMR. The reaction between 1-trimethylsilyl-1,4-pentadiyne and diethylamino-trimethylstannane affords 1-trimethylstannyl-5-trimethylsilyl-penta-1,2-diene-4-yne (**6**) as the major product. In all compounds **2** to **6** the signs of coupling constants $^nJ(^{119}Sn,^1H)$, $^nJ(^{119}Sn,^{13}C)$ and $^nJ(^{119}Sn,^{119}Sn)$ were determined by two-dimensional (2D) $^{13}C/^1H$ and $^{119}Sn/^1H$ heteronuclear shift correlations based on $^1J(^{13}C,^1H)$ or $^2J(^{119}Sn,^1H)$, respectively, and also on long range coupling constants $^nJ(^{13}C,^1H)$ $(n > 1)$ and $^nJ(^{119}Sn,^1H)$ $(n > 2)$. $\delta^{13}C$ values of the central allene carbon atom can be predicted by using pairwise additive parameters.

INTRODUCTION

Alkynes and allenes bearing stannyl substituents are attractive reagents in synthesis [1]. They are also of interest with respect to their ^{119}Sn NMR parameters because of the sensitivity of ^{119}Sn nuclear shielding and coupling constants $J(^{119}Sn,X)$ (X = ^{1}H, ^{13}C, $^{117/119}$Sn) towards changes in the electronic structure [2]. In principle, these parameters are readily available, including coupling constants between chemically equivalent tin nuclei owing to the presence of ^{117}Sn nuclei with spin I = 1/2 and an appreciable natural abundance (7.61 %). The interpretation of $\delta^{119}Sn$ values follows arguments which are well developed in particular for $\delta^{13}C$. The discussion of coupling constants, however, requires the knowledge of their signs, and this information has to be extracted by additional NMR experiments, most of which are based on schemes of one-dimensional (1D) [3] and more recently of two-dimensional (2D) heteronuclear double resonance experiments [4].

Typical examples of alkynyl- and allenyltin compounds are **1** to **5** which result from the reaction between partially or fully lithiated propyne and trimethyltin chloride [5]. With the exception of trimethyl(1-propynyl)tin (1) [6] and tetrakis(trimethylstannyl)allene (**5**) [7], signs of coupling constants have not been determined, although multinuclear NMR data were reported for **2** [8], **4** and **5** [9] and other organometallic-substituted allenes [10]. The NMR data of **3** were also given [8], however, they were incorrectly assigned to 1,3-bis(trimethylstannyl)allene. A further example is compound **6** which is formed as the major product in the reaction between 1-trimethylsilyl-1,4-pentadiyne and diethylamino-trimethyltin [eq. (2)].

$$\mathrm{Me_3Sn{-}C{\equiv}C{-}Me}$$

1

$$\mathrm{Me_3Sn{-}C{\equiv}C{-}CH_2{-}SnMe_3}$$

2

$$\mathrm{(Me_3Sn)_2C{=}C{=}CH_2}$$

3

$$\mathrm{(Me_3Sn)_2C{=}C{=}CH{-}SnMe_3}$$

4

$$\mathrm{(Me_3Sn)_2C{=}C{=}C(SnMe_3)_2}$$

5

$$\begin{array}{l} \mathrm{H{-}C{\equiv}C{-}CH_2{-}C{\equiv}C{-}SiMe_3} \\ \quad + \\ \mathrm{Me_3Sn{-}NEt_2} \end{array} \rightarrow \underset{\mathbf{6}}{\mathrm{Me_3Sn{-}CH{=}C{=}CH{-}C{\equiv}C{-}SiMe_3}} + \mathrm{HNEt_2} \quad (2)$$

We have studied the compounds **2**-**6** by ^{1}H-, ^{13}C- and ^{119}Sn NMR aiming for the determination of signs of coupling constants involving ^{119}Sn or ^{117}Sn.

RESULTS AND DISCUSSION

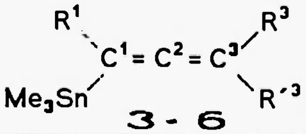
Chemical shifts $\delta^{13}C$ and $\delta^{119}Sn$ and coupling constants together with experimentally determined absolute signs for compounds **1** to **6** are given in Table 1. The assignment of ^{1}H, ^{13}C and ^{119}Sn resonances as well that of the coupling constants $^{2}J(^{119}Sn,^{1}H)$ and $^{4}J(^{119}Sn,^{1}H)$ follows conclusively from the consistent results of 2D heteronuclear shift correlations (HETCOR). The latter experiments of the type $^{13}C/^{1}H$ and $^{119}Sn/^{1}H$, based on various coupling constants $^{n}J(^{13}C,^{1}H)$ (n = 1, 2, 3) and $^{n}J(^{119}Sn,^{1}H)$ (n = 2, 3, 4, 6), served also for the determination of the coupling signs.

In the $^{13}C/^{1}H$ HETCOR experiments, the ^{119}Sn nucleus serves as a passive spin and the observation of ^{119}Sn satellites in both dimensions reveals the relative signs of coupling constants $J(^{119}Sn,^{1}H)/J(^{119}Sn,^{13}C)$ by the tilt of the cross peaks [4,6,7]. A typical example is shown in Figure 1 for compound **4**, taking advantage of the long range coupling constant $^{2}J(={}^{13}C,^{1}H)$. In the $^{119}Sn/^{1}H$ HETCOR experiment, the ^{117}Sn nucleus plays the role of the passive spin and the signs of $J(^{117}Sn,^{1}H)/J(^{119}Sn,^{117}Sn)$ are compared [7]. It is advisable to use the reduced coupling constants K $[K(A,X) = 4\pi^2 \cdot J(A,X) \cdot (\gamma_A \cdot \gamma_X \cdot h)^{-1}]$ for the comparison of

Table 1: ^{13}C- and ^{119}Sn NMR data[a] of the alkynyl compounds **1** (R^3 = H), **2** ($R^3 = SnMe_3$) and the allenes **3** ($R^1 = SnMe_3$, $R^3 = R'^3$ = H), **4** ($R^1 = Me_3Sn$, R^3 = H, $R'^3 = SnMe_3$), **5** ($R^1 = R^3 = R'^3 = SnMe_3$) and **6** ($R^1 = R^3$ = H, $R'^3 = C\equiv C-SiMe_3$)

$Me_3Sn-C^1\equiv C^2-C^3H_2-R^3$

1, 2



3 - 6

	$\delta^{13}C$					$\delta^{119}Sn$	
	C^1	C^2	C^3	R^1	R^3	Sn^1	Sn^2
1 [b]	81.1	105.7	4.8	-8.2	-	-73.8	-
Sn^1	[-502.8]	[-107.4]	[-11.0]	[-404.1]			
2 [c]	79.5	110.5	0.4	-7.5	-9.5	-75.6	0.8
Sn^1	[-532.2]	[-113.5]	[-11.4]	[-404.4]	[-339.5]		[-98.0]
Sn^3	[-37.2]	[+53.4]	[-276.6]			[-98.0]	
3 [c]	75.4	206.1	53.4	-8.1	-	-10.5	-
Sn^1	[-261.9]	[+30.5]	[-61.0]	[-326.8]		[+165.5]	
4 [c]	61.8	201.3	50.6	-8.0	-8.6	-4.3	-9.7
Sn^1	[-275.6]	[+25.8]	[-59.1]	[-331.9]	[-352.9]	[+209.1]	[-260.6]
Sn^3	[-46.7]	[+6.7]	[-426.3]			[-260.6]	
5 [c]	47.5	195.7	47.5	-7.9	-7.9	2.6	2.6
Sn^1	[-292.8]	[+21.9]	[-53.9]	[-345.4]	[-345.4]	[+245.3]	[-265.7]
Sn^3	[-53.9]		[-292.8]			[-265.7]	[+245.3]
6 [d]	79.3	212.0	66.2	-8.7	100.1 [d]	-9.7	-
Sn^1	[-327.0]	[+18.0]	[-46.0]	[-360.8]	[+35.0]		

[a] In C_6D_6 (50%; v/v) at 298K. $^{n}J(^{119}Sn,X)$ ($X = {}^{13}C, {}^{119}Sn$) in Hz are given in square brackets [ ], and coupling either to Sn^1 or Sn^3 is indicated in the first column. Values $^{n}J(^{119}Sn,^{119}Sn)$, if not obtained directly from the ^{119}Sn NMR spectra, were calculated by multiplication of $^{n}J(^{119}Sn,^{117}Sn)$ with the factor 1.0465 ($= \gamma(^{119}Sn)/\gamma(^{117}Sn)$). - [b] Ref. [6]. - [c] **2**: $\delta^{1}H$ $[J(^{119}Sn,^{1}H)]$ = 0.10 [59.8] s ($\equiv C-SnMe_3$), 0.07 [54.6] s ($C-SnMe_3$), 1.53 [+60.5] $^{2}J(^{119}Sn,^{1}H)$, [+12.9] $^{4}J(^{119}Sn,^{1}H)$, s (CH_2); **3**: 0.12 [54.0] s ($SnMe_3$), 3.64 [+45.6] $^{4}J(^{119}Sn,^{1}H)$, s ($=CH_2$); **4**: 0.13 [54.0] ($=C(SnMe_3)_2$, 0.15 [55.0] s ($SnMe_3$), 3.77 [-17.9] $^{2}J(^{119}Sn,^{1}H)$, [+45.0] $^{4}J(^{119}Sn,^{1}H)$, s (=CH); **5**: 0.11 [+53.5] $^{2}J(^{119}Sn,^{1}H)$, [+1.0] $^{4}J(^{119}Sn,^{1}H)$, s ($SnMe_3$) (see also Ref. [7]); **6**: 0.04 s ($SiMe_3$), 0.10 [54.0] s ($SnMe_3$), 4.95 [37.6] d, $^{4}J(^{1}H,^{1}H)$ = -6.8 Hz ($\equiv C-C(H)=$), 5.16 [1.7] $^{2}J(^{119}Sn,^{1}H)$, d, $^{4}J(^{1}H,^{1}H)$ = -6.8 Hz ($Sn-C(H)=$). - [d] $\delta^{13}C$ ($C\equiv CSiMe_3$) = 100.1 [35.0], $^{2}J(^{29}Si,\equiv{}^{13}C)$ = 17.1 Hz; 95.3 [11.7], $^{1}J(^{29}Si,^{13}C\equiv)$ = 87.1 Hz; -0.03, $^{1}J(^{29}Si,^{13}C)$ = 54.0 Hz; - $\delta^{29}Si$ = -18.9.

signs because $\gamma^{119}\text{Sn}$ and $\gamma^{117}\text{Sn}$ are both negative, whereas $\gamma^{13}\text{C}$ and $\gamma^{1}\text{H}$ are positive.

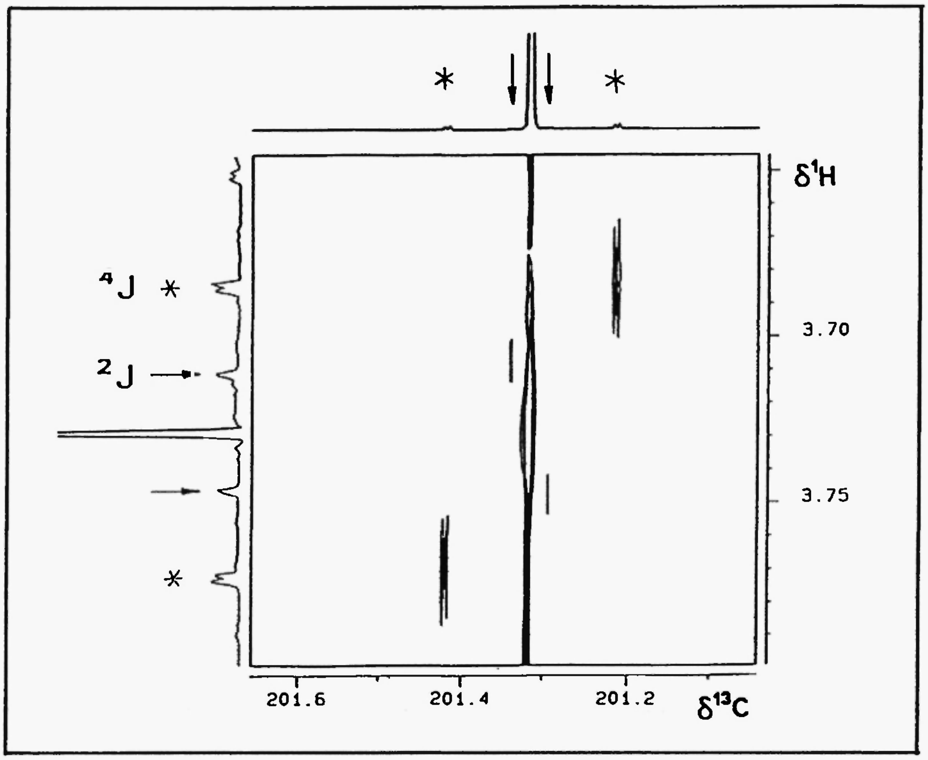
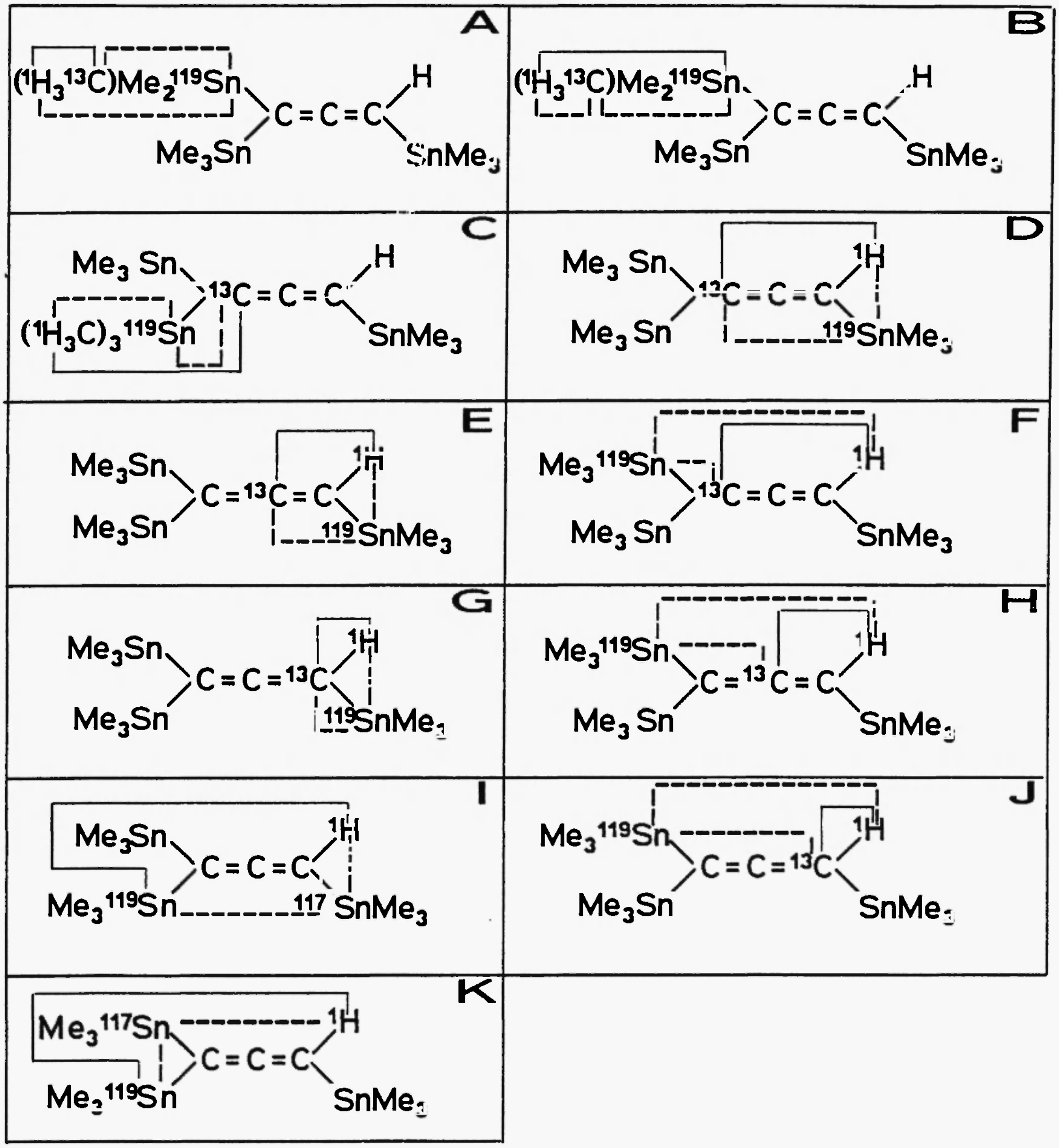


Figure 1. Contour plot and projections (power spectrum in $F_2(^{13}C)$) of the 2D $^{13}C/^{1}H$ HETCOR of $(Me_3Sn)_2C^1=C^2=C^3H-SnMe_3$ (**4**), showing the region of the $^{13}C^2$ NMR signal of the central allenic carbon atom and the $^{1}H(=C^{1}H)$ resonance. The correlation is based on $^{2}J(^{13}C^{2}, {}^{1}H^{3}) \approx$ 3 Hz with a spectral window of 70 Hz (64 experiments) in F_1 (^{1}H) and 1500 Hz (8192 data points) in F_2; Gaussian multiplication and zero-filling was applied in both dimensions. The tilt of the cross peaks according to $^{4}J(^{119}Sn^{1}, {}^{1}H^{3})$ and $^{2}J(^{119}Sn^{1}, {}^{13}C^{2})$ is positive, whereas that for $^{2}J(^{119}Sn^{3}, {}^{1}H^{3})$ and $^{2}J(^{119}Sn^{3}, {}^{13}C^{2})$ is negative. Consistent with other experiments (see Scheme 1), it follows that the signs of $^{4}J(^{119}Sn^{1}, {}^{1}H^{3})$ and $^{2}J(^{119}Sn^{3}, {}^{1}H^{3})$ are opposite and the signs of $^{2}J(^{119}Sn^{1}, {}^{13}C^{2})$ and $^{2}J(^{119}Sn^{3}, {}^{13}C^{2})$ are alike.

All these experiments give relative signs; for determining absolute signs it is necessary to include "key coupling constants" for which the absolute signs are known. Such coupling constants are $^{1}J(^{13}C, {}^{1}H)$ (> 0 [11]) and also $^{2}J(^{119}Sn, {}^{1}H_{Me})$ (> 0, reduced coupling constant $^{2}K(^{119}Sn, {}^{1}H) < 0$ [12]) in Sn-methyl groups of this type of compounds. In the case of compound **4**, Scheme 1 shows the types of HETCOR experiments which were carried out to arrive at the absolute signs of coupling constants.

The key experiments **A** and **B** in Scheme 1 (only shown for the $(Me_3Sn)_2C^1=$ unit) prove that $^{2}K(^{119}Sn,^{1}H) < 0$. In **C** it is found that $^{1}K(^{119}Sn,^{13}C=) > 0$. This is used in **F** where it follows that $^{4}K(^{119}Sn,^{1}H) < 0$. Knowing the absolute sign of $^{4}K(^{119}SnC=C=C^{1}H)$ a number of other signs (see **H**, **J** and **K**) are accessible. The analogous procedure can be performed for the $=CH-SnMe_3$ unit as shown in **D**, **E**, **G** and **I**.



Scheme 1. Eleven isotopomers **A** to **K**, relevant for the comparison of coupling signs, are shown for compound **4**. The active spins in the 2D HETCOR are connected by a thin drawn line and the passive spin is connected with its respective coupling partner by dashed lines (see Figure 1 for experiments **E** and **H**)

The signs ($\gamma^{119}\text{Sn} < 0$!) and relative magnitudes (taking into account the greater valence s electron density of ^{119}Sn) of the coupling constants involving one or two ^{119}Sn nuclei, reported here, correspond well to trends known for analogous coupling constants $^{n}J(^{13}\text{C},^{1}\text{H})$ [13] or $^{n}J(^{1}\text{H},^{1}\text{H})$ [14] in alkynes and allenes. Thus, in accord with the changes in the magnitude of $^{2}J(^{13}\text{C},^{1}\text{H})$ or $^{2}J(^{1}\text{H},^{1}\text{H})$ in alkanes and allenes, we find that a change in the sign of $^{2}J(^{119}\text{Sn},^{1}\text{H})$ takes place in going from alkyltin compounds [$^{2}J(^{119}\text{Sn},^{1}\text{H}) > 0$, $^{2}K(^{119}\text{Sn},^{1}\text{H}) < 0$ [12]] to allenyltin compounds where the values $^{2}J(^{119}\text{Sn},^{1}\text{H})$ are either close to zero (**6**) or small (**3**, **4**) but already negative [$^{2}K(^{119}\text{Sn},^{1}\text{H}) > 0$]. In alkenyltin compounds, the values $^{2}J(^{119}\text{Sn},^{1}\text{H})$ are large and negative [2]. In agreement with the known negative sign of $^{4}J(^{1}\text{H},^{1}\text{H})$ [$^{4}K(^{1}\text{H},^{1}\text{H}) < 0$] across the C=C=C unit in allenes, $^{4}J(^{119}\text{Sn}^{1}\text{H})$ is fairly large and positive [$^{4}K(^{119}\text{Sn},^{1}\text{H}) < 0$]. This shows that the same mechanism principles are in operation for ^{119}Sn, ^{13}C and ^{1}H nuclei, meaning e.g., that the coupling information across four bonds is transferred mainly through the π-system of the alkyne or allene.

The δ^{13}C data in Table 1 for the central carbon atom (C^{2}) of the allenes and additional data from the literature [10a,d] support the proposed [9a] scheme of the six pairwise additivity terms [15] describing a tetrahedral surrounding. Thus the terms (H/H) = 35.5 (calculated for allene with $\delta^{13}\text{C}(\text{C}^{2}) = 213.0$ divided by 6), (Sn/Sn) = 32.6 and (Sn/H) = 34.6 [9a] serve for the calculation of (C≡C/H) = 37.4 and (Sn/C≡C) = 32.5, in order to predict the $\delta^{13}\text{C}^{2}$ values in allenes of the type **6**.

If one calculates the δ^{119}Sn values of allenyl(trimethyl)tin compounds from additive contributions of the substituents R^{1}, R^{3} and R$'^{3}$ in $\text{Me}_3\text{Sn(R}^{1})\text{C=C=C(R}^{3})\text{R}'^{3}$, using the data set available [2a, 10b-d], it is found that hydrogen atoms in 1- or 3-position provide a shielding contribution [≈-9.5 ppm (H^{1}) and ≈-6 ppm (H^{3})] whereas an additional Me$_3$Sn-group in 1-position has a deshielding effect (≈ +3 ppm), and additional Me$_3$Sn-groups in 3-position exert only a small effect (≈± 0.5 ppm). This allows to predict the hitherto unknown δ^{119}Sn values of $\text{Me}_3\text{Sn(H)C=C=CH}_2$ ($\delta \approx -21.5$) and $\text{Me}_3\text{Sn(H)C=C=C(H)SnMe}_3$ ($\delta \approx -15.5$). The replacement of a geminal hydrogen atom by a Me$_3$Sn-group always causes deshielding, irrespective of the nature of the intervening carbon atom:

	$\text{Me}_3\text{Sn-CH}_3$	$(\text{Me}_3\text{Sn})_2\text{CH}_2$	$\text{Me}_3\text{SnCH=CH}_2$	$(\text{Me}_3\text{Sn})_2\text{C=CH}_2$
δ^{119}Sn	0	+23.3 [16]	-39.0 [2b]	-19.3 [17]

EXPERIMENTAL

All preparative work and the handling of the samples was carried out under an atmosphere of dry N$_2$ or Ar, observing all precautions to exclude oxygen and moisture. Starting materials [propyne, ^{n}BuLi/hexane (1.56 M), trimethyltin chloride, 1-trimethylsilyl-1,4-pentadiyne] were commercial products, and $Me_3Sn-NEt_2$ was prepared following the literature [18]. The lithiation of propyne and the subsequent reactions with Me_3SnCl were performed as described [5]. Treatment of $Me_3Si-C\equiv C-CH_2-C\equiv CH$ with one equivalent of $Me_3Sn-NEt_2$ in ether affords after 3 h of reflux and removal of all volatile material a mixture of compounds, containing > 80 % (^1H NMR) of 1-trimethylstannyl-5-trimethylsilyl-penta-1,2-diene-4-yne (**6**). Small amounts (< 10 %) of $(Me_3Sn)_2C=C=C(H)-C\equiv C-SiMe_3$ ($\delta^{119}Sn$ +1.9) and $Me_3Sn-C\equiv C-CH_2-C\equiv C-SiMe_3$ ($\delta^{119}Sn$ -69.2) are present, and also various unidentified further products which may result from addition of Et_2NH to the unsaturated system [10d]. If the reaction is carried out without a solvent, and the mixture is left for 3h at 0°C, followed by removal of all volatile material, the amounts of $Me_3Sn-C\equiv C-CH_2-C\equiv C-SiMe_3$ and $(Me_3Sn)_2C=C=C(H)-C\equiv C-SiMe_3$ increase to ≈20%.

NMR spectra (see also Table 1 and Figure 1) were measured using Jeol FX 90 Q, Bruker ARX 250, AC 300 and AM 500 spectrometers, all equipped with multinuclear units. Chemical shifts are given with respect to Me_4Si [$\delta^1H(C_6D_5H)$ = 7.15; $\delta^{13}C(C_6D_6)$ = 128.0; $\delta^{29}Si$ with $\Xi(^{29}Si)$ = 19.867184 MHz] and Me_4Sn [$\delta^{119}Sn$ with $\Xi(^{119}Sn)$ = 37.290665 MHz]. Ξ Values stem from ref. [19].

Acknowledgements

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