[μ^2-,η^2-Alkynyl-hexacarbonyldicobalt]organotin complexes and the molecular structure of bis[μ^2-,η^2-ethynylhexacarbonyldicobalt]diphenyltin

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Abstract

[μ^2-,η^2-alkynyl-hexacarbonylcobalt]organotin complexes of the type (μ^2-,η^2-HC$_2$SnR$_3$)Co$_2$(CO)$_6$ (R = Et (**1b**), ^{t}Bu (**1c**)), R$_2$Sn[(μ^2-,η^2-C$_2$H)Co$_2$(CO)$_6$]$_2$ (R = Me (**2a**), Et (**2b**), ^{t}Bu (**2c**), Ph (**2d**)), Me$_{4-n}$Sn[(μ^2-,η^2-C$_2$Me)Co$_2$(CO)$_6$]$_n$ ($n = 1$ (**3**), 2 (**4**), 3 (**5**)), and MeC≡CSn[(μ^2-,η^2-C$_2$Me)Co$_2$(CO)$_8$] (**6**) were prepared and studied by ^{1}H, ^{13}C and ^{119}Sn NMR. The signs of coupling constants $^1J(^{119}$Sn,^{13}C) < 0, $^2J(^{119}$Sn,^{13}C(cluster)) > 0, $^3J(^{119}$Sn,^{1}H(cluster)) > 0 were determined for these complexes by modified 2D ^{1}H detected ^{1}H/ ^{119}Sn and ^{1}H/ ^{13}C heteronuclear shift correlations. The molecular structure of **2c** was determined by X-ray structural analysis (orthorhombic; space group *Pbca*; a = 19.46(1) Å, b = 15.992(7) Å, c = 20.10(1) Å, Z = 8). The bond angles at the substituted carbon atoms of the dicobaltetrahedrane Sn–C(1)–C(2) (151.3(3)°) and Sn–C(3)–C(4) (150.5(5)°) are significantly larger than in all other known molecular structures of dicobaltetrahedranes.

Keywords: Clusters; Cobalt; Tin; Alkynes; Dicobaltetrahedranes; X-Ray; NMR; Signs of coupling constants

1. Introduction

Alkynes react with octacarbonyldicobalt to give μ^2-,η^2-alkyne-hexacarbonyldicobalt complexes [1,2]. This reaction also works with organometallic-substituted alkynes, including various 1-alkynyltin compounds [3,4]. So far, only mono- and di-1-alkynyltin compounds have been studied [4], and, to the best of our knowledge, structural data have not been reported for the tin derivatives. The NMR data set obtained previously [4] was incomplete, in particular with respect to the signs of

coupling constants involving the nuclei $^{117/119}$Sn, ^{13}C, and ^{1}H. In this work we have prepared the known derivatives **1b**, **2a** and **2d** [4] for further NMR studies, including the new compound **2b**. Complexes **1c** and **2c**, with three and two *tert*-butyl groups respectively, linked to tin were used to study the influence of branched alkyl substituents on the coupling constants. The molecular structure of the complex **2d** was determined by single crystal X-ray diffraction. Furthermore, we report on the complexes **3–6** formed in the reaction of 1-propynyltin compounds with Co$_2$(CO)$_8$.

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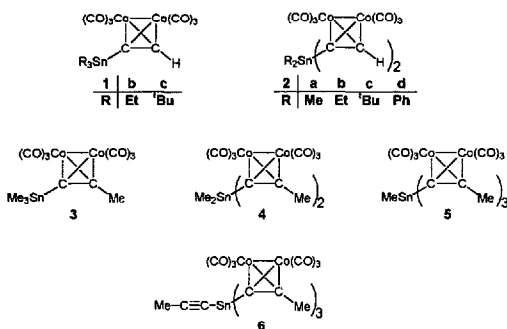
2. Results and discussion

2.1. Synthesis

The synthesis of compounds **1–6** was straightforward, following literature procedures [1–4]. In the case of **6**, the fourth 1-propynyl group did not react with $Co_2(CO)_8$, even after several days in the presence of a large excess of $Co_2(CO)_8$, presumably for steric reasons. There was no evidence for the formation of other complexes containing the $Co_2(CO)_5$ or $Co_2(CO)_4$ fragments [2,5]. The complexes **1–6** are light-sensitive, dark-red, brown or black solids, except the oily **1b**. They decompose readily above 80 °C and are moder-

ately soluble in benzene and well soluble in chlorinated hydrocarbons. Solutions in benzene can be stored for prolonged periods when kept frozen at −18 °C.

2.2. NMR spectroscopic results

Table 1 summarizes ^{13}C and ^{119}Sn NMR data; ^1H NMR data are reported in the experimental part. All data are consistent with the proposed structures (data for **1b**, **2a** and **2c** agree reasonably well with those reported previously [4]). The coupling constants $J(^{117/119}Sn,^1H)$ and $J(^{117/119}Sn,^{13}C)$ (see Fig. 1) are readily obtained from the ^1H and ^{13}C NMR spectra.

The ^{13}C and ^{119}Sn chemical shifts are in the expected

Table 1
^{13}C and ^{119}Sn NMR data [a] of the μ^2-,η^2-alkyne-hexacarbonyldicobalt complexes **1–6**

Compound	$\delta\,^{13}C$ (Sn–C)	$\delta\,^{13}C$ (CH, CMe)	$\delta\,^{13}C$ (R–Sn)	$\delta\,^{13}C$ (CO)	$\delta\,^{119}Sn$
1b	72.0 [-204.0]	86.6 [+34.0]	4.0 [−358.1], 10.7 [+25.1]	201.3	+10.6
1c	70.4 [-19.0]	90.9 [+22.9]	33.0 [−333.9], 32.1 [<3]	201.5	+58.9
2a	72.4 [-367.0]	85.5 [+22.9]	−5.2 [(−)418.0]	200.5	−4.9
2b	70.6 [-266.0]	86.0 [+20.0]	7.5 [−419.9], 10.2 [+26.8]	200.5	−20.5
2c	70.3 [-91.6]	90.9 [+22.5]	32.9 [−371.5], 32.1 [<3]	201.6	−71.3
2d (CDCl₃)	70.7 [−408.0]	85.8 [(+)12.0]	136.8 [(−)630.0] 136.6 [(−)41.7] (o) 129.0 [(−)60.0] (m) 130.2 [(±)9.0] (p)	199.9	−114.6
3	77.1 [-303.4]	107.1 [(±)10.0] 20.6 [<5] (Me)	−7.5 [(−)367.5]	201.0	+15.6
4 (CDCl₃)	75.0 [(-)342.0]	105.7 [(±)10.0] 21.5 [<5] (Me)	−4.7 [(−)405.0]	200.6	−6.0
5	74.4 [(-)389.4]	106.2 [(±)5.5] 22.1 [<5] (Me)	0.9 [(−)476.7]	200.7	−64.7
6	74.0 [(-)565.5]	105.5 [(±)23.3] 22.0 [<5] (Me)	82.8 [(−)814.1] 110.3 [(−)159.8] (≡C–) 4.2 [(−)14.4] (Me)	200.4	−172.2

[a] In C_6D_6 (ca. 5%) at 25 ± 1 °C, if not noted otherwise; coupling constants $J(^{119}Sn,^{13}C)$ ±1.5 Hz are given in brackets; proposed signs of coupling constants are given in parentheses; ± indicates that there are no reliable values available for comparison in order to propose a sign.
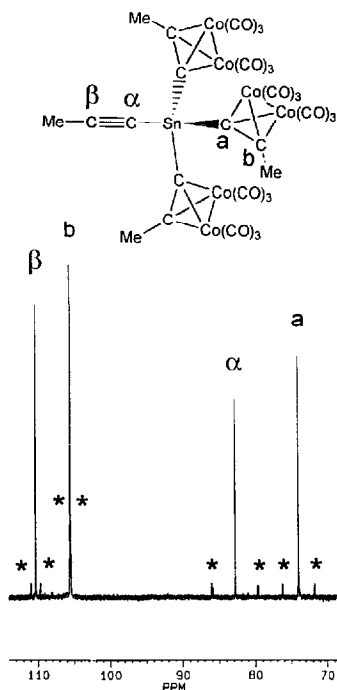
Fig. 1. 125.8 MHz ^{13}C{^{1}H} NMR spectrum of compound **6**, showing the range of ^{13}C resonances of alkynyl and cluster carbon atoms. The assignment is shown and $^{117/119}$Sn satellites are marked by asterisks.

range [4]. In the case of the complexes **1c** and **2c**, the δ ^{119}Sn values change from + 56.9 to − 71.3. This change is much larger than that observed for the pairs **1b/2b** (δ ^{119}Sn + 10.6, − 20.5) and **3/4** (δ ^{119}Sn + 15.6, − 6.0) and indicates sterical crowding in the case of the Sn–*tert*-butyl derivatives **1c** and **2c**. An increasing number of $C_2Co_2(CO)_6$ fragments attached to the tin atom leads to an increase in ^{119}Sn nuclear shielding. The δ ^{119}Sn values in the series of complexes **3–6** can be described by pairwise additive parameters [6].

There are significant changes in the magnitude of the coupling constants $^1J(^{119}Sn,^{13}C(cluster))$, depending on the other substituents at the tin atom. In order to discuss the coupling constants in more detail, it is necessary to determine their sign, in particular if there are no relevant data available for comparison, as is the case of $^2J(^{119}Sn,^{13}C(cluster))$ and $^3J(^{119}Sn,^1H(cluster))$. A posi-

tive sign of $^2J(^{13}C,^1H)$ in $C_2H_2Co_2(CO)_8$ was determined by studying the ^{13}C-labelled complex, whereas $^3J(^1H,^1H)$ is close to zero [7] in contrast with $^3J(^1H,^1H)$ = + 9.5 Hz in ethyne [8]. Since all $^2J(^{13}C(cluster),^1H)$ values are rather small (ca. + 12 to + 18 Hz), the sign of $^2J(^{119}Sn,^{13}C(cluster))$ cannot be predicted on this basis, and the same is true for $^3J(^{119}Sn,^1H(cluster))$ if the corresponding value $^3J(^1H,^1H)$ is close to zero. Most likely the sign of $^1J(^{119}Sn,^{13}C(cluster))$ is negative (reduced coupling constant $^1K(^{119}Sn,^{13}C) > 0$, since γ(^{119}Sn) < 0), as for most other coupling constants $^1J(^{119}Sn,^{13}C)$ [9]; however, in the case of **1c** and **2c**, the values |$^1J(^{119}Sn,^{13}C(cluster))$| are fairly small. Thus, the prediction of a negative sign may not be justified.

The most convenient way for comparing the signs of coupling constants is provided by 2D heteronuclear shift correlations involving two so-called active spins [10], e.g. ^{13}C, ^{1}H or ^{119}Sn, ^{1}H, and observing the tilt of cross-peaks arising from coupling with the so-called passive spin. These techniques are well established for various combinations of active and passive spins [11,12]. The sensitivity of such experiments is greatly enhanced by using ^{1}H detected (inverse) shift correlations. Since the knowledge of the absolute sign of the coupling constants is required, 'key coupling constants' such as $^1J(^{13}C,^1H)$ (which is known to be positive) must be included in the series of experiments for comparison of coupling signs. As has been shown repeatedly [13,14], there are efficient ways to pre-select a particular spin pair, such as $^{13}C/^1H$, and then to use ^{1}H detection (e.g. based on HMQC [15]) of another spin pair, such as $^1H/^{119}Sn$. This allows one to measure the coupling between two rare spin − 1/2 nuclei, and at the same time to compare the sign of $^1J(^{13}C,^1H)$ (> 0) with the unknown sign of $K(^{119}Sn,^{13}C)$. The relevant experiments carried out for the complexes **1** and **2** are shown in Scheme 1 for isotopomers of **1b** as a representative

Isotopomer [a]	Experiment	Coupling signs compared	Result
(CO)₃Co—Co(CO)₃ Et₃Sn* —C☆ (¹H)	¹H/{¹³C}¹¹⁹Sn [b]	$\frac{^2K(^{119}Sn,^{13}C)}{^1K(^{13}C,^1H)} < 0$	$^2K(^{119}Sn,^{13}C) < 0$
(CO)₃Co—Co(CO)₃ Et₃Sn* —C☆ (¹H)	¹H/{¹³C}¹¹⁹Sn [b]	$\frac{^1K(^{119}Sn,^{13}C)}{^2K(^{13}C,^1H)} > 0$	$^1K(^{119}Sn,^{13}C) > 0$
(CO)₃Co—Co(CO)₃ Et₃Sn☆ —C(¹³C) (¹H)	¹H/{¹¹⁹Sn}¹³C [b,c]	$\frac{^3K(^{119}Sn,^1H)}{^2K(^{119}Sn,^{13}C)} > 0$	$^3K(^{119}Sn,^1H) < 0$
(CO)₃Co—Co(CO)₃ Et₃Sn*(¹³C) (¹H)	¹H/{¹¹⁹Sn}¹³C [b,c]	$\frac{^3K(^{119}Sn,^1H)}{^1K(^{119}Sn,^{13}C)} < 0$	$^1K(^{119}Sn,^{13}C) > 0$

Scheme 1. [a] Four isotopomers are shown which contain the two active spins as marked (^{1}H, ^{13}C or ^{119}Sn) and the passive spin, marked by an asterisk. [b] Pseudo-BIRD experiment [10]. [c] The direct 2D ^{13}C/^{1}H heteronuclear shift correlation gives the same results, observing the tilt of the cross-peaks due to $^{117/119}$Sn satellites in the contour plot.

example, together with the results concerning the absolute sign of coupling constants.

The results shown in Scheme 1 prove that the coupling constant $^1J(^{119}Sn,^{13}C(cluster))$ possesses a negative sign ($^1K(^{119}Sn,^{13}C(cluster)) > 0$), whereas it turns out that $^2J(^{119}Sn,^{13}C(cluster)) > 0$ ($^2K(^{119}Sn,^{13}C(cluster)) < 0$). Thus, the sign of $^2K(^{119}Sn,^{13}C(cluster))$ has changed with respect to $^2K(^{119}Sn,^{13}C\equiv)$ in alkynes [14]. This is in contrast to the positive sign found for $^2K(^{13}C(cluster),^1H)$ in this and in previous [7] work. The positive sign of $^3J(^{119}Sn,^1H(cluster))$ ($^3K(^{119}Sn,^1H(cluster)) < 0$) is also noteworthy, since the sign has also changed compared with $^3J(^{119}Sn,^1H)$ across the C≡C bond in alkynes [14]. These are the first examples of organotin(IV) compounds with $^3J(^{119}Sn,^1H) > 0$. For vicinal coupling constants $^3J(^1H,^1H)$ one can find numerous examples for rather small values [7,16], pointing out that, in addition to the Karplus-type dependence on the dihedral angle, there is also a strong dependence of $^3J(^1H,^1H)$ on the valence angles. The polarity of the Sn–C(cluster) bond is a potential source of negative contributions to $^2K(^{119}Sn,^{13}C(cluster))$ and $^3K(^{119}Sn,^1H(cluster))$. Such contributions are less important for lighter and less polarizable nuclei such as ^{13}C and ^1H and, therefore, $^2K(^{13}C(cluster),^1H)$ or $^3K(^1H,^1H)$ have a positive sign or are close to zero in the dicobaltotetrahedranes.

2.3. Molecular structure of bis(μ²-,η²-ethyne-octacarbonyldicobalt)diphenyltin (2d)

The molecular structure of **2d** is shown in Fig. 2, and experimental data relevant to the X-ray structural analysis are given in Table 2. (Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405643, the name of the authors and the literature citation.) The bond lengths d_{Sn-C} and the bond angles at the tin atom fall in the usual range. By comparison with molecular structures of numerous dicoboltatetrahedranes [1,2,5,17,18] some trends can be noted when electronegative substituents X are attached to the tetrahedrane C–C bond. The C–C and the CO–C bond lengths become shorter and the bond angles X–C–C more acute, as would be predicted by extended Hückel MO calculations [19]. In the case of **2d**, the bonds $C(1)-C(2) = 132.2(9)$ and $C(3)-C(4) = 133.5(9)$ pm are rather short, whereas the Co–C bonds (194.4–199.0 pm) lie in the normal range; the same is also true for d_{Co-Co} (247.8(2) and 248.7(2) pm). However, the bond angles Sn–C(1)–C(2) (151.3(5)°) and Sn–C(3)–C(4) (150.5(5)°) are larger than any corresponding bond angle X–C–C in other dicobaltatetrahedranes. Clearly, this is not the result of steric interac-
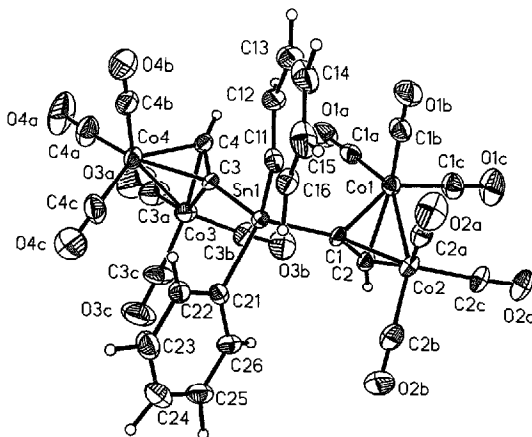

Fig. 2. ORTEP plot of the molecular structure of **2d**. Thermal ellipsoids are presented on a 25% probability scale. Selected bond lengths (pm): Sn(1)–C(1) 212.2(7), Sn(1)–C(3) 212.3(7), Sn(1)–C(11) 213.0(7), Sn(1)–C(21) 213.0(7), C(1)–C(2) 132.2(9), C(3)–C(4) 133.5(9), Co(1)–Co(2) 247.8(2), Co(3)–Co(4) 248.7(2), Co(1)–C(1) 198.8(7), Co(1)–C(2) 196.7(7), Co(2)–C(1) 199.0(7), Co(2)–C(2) 194.4(7). Selected bond angles (deg): C(1)–Sn(1)–C(3) 108.1(2), C(1)–Sn(1)–C(11) 107.3(3), C(3)–Sn(1)–C(3) 110.3(3), C(1)–Sn(1)–C(21) 111.1(3), C(3)–Sn(1)–C(21) 108.2(3), C(11)–Sn(1)–C(21) 111.9(2), Sn(1)–C(1)–C(2) 151.3(5), Sn(1)–C(3)–C(4) 150.5(5).

Table 2
Data relevant to the X-ray structure analysis of bis(μ^2-,η^2-ethynyl-hexacarbonyldicobalt)diphenyltin (**2d**) [16]

Empirical formula	$C_{28}H_{12}Co_4O_{12}Sn$
Formula weight	894.8
Crystal size (mm^3)	$0.12 \times 0.45 \times 0.63$
Crystal system; space group; Z	Orthorhombic; *Pbca*; 8
Lattice parameters (Å)	$a = 19.46(1)$, $b = 15.922(7)$, $c = 20.10(1)$
Volume (Å^3); ρ(calc) (Mg m^{-3})	6506(9); 1.827
Diffractometer	Siemens R 3m/VP4; graphite monochromator
Radiation, wavelength λ (Å)	Mo Kα, 0.71073
Temperature (K)	291
2Θ range (deg)	3.84–50.02 in *hkl*
Scan speed (deg min^{-1})	Variable; 2.6 to 29.3 in ω
Reflections collected	10814
Independent reflections	5708 ($R_{int} = 3.77\%$)
Observed reflections	3855 ($F > 4.0\sigma(F)$)
System used; solution	SHELXTL-PLUS (PC version); direct methods
Refinement method	Full matrix least squares on F^2
Final R indices (observed data) (%)	$R1 = 4.52$; $wR2 = 10.17$
Number of parameters refined	401
Max./min. residual electron density (e Å^{-3})	$0.77/-0.72$

tions in **2c**. The large bond angles result from the influence of the electropositive substituent which weakens the bonding in the C_2Co_2 cluster. The bond angle Si–C–C (144.8(3)°) in (μ^2-,η^2-PhC$_2$SiPh$_3$)Co$_2$(CO)$_6$ [18] is also rather large compared with other dicobaltatetrahedranes [17,18], but is still significantly smaller than the corresponding bond angles in **2d**.

3. Conclusions

Increasingly negative contributions to $^2K(^{119}Sn,^{13}C(cluster))$ and $^3K(^{119}Sn,^1H(cluster))$ in C–stannyl-substituted dicobaltatetrahedranes, as a result of the polar Sn–C bond, lead to negative signs of these reduced coupling constants, in contrast to corresponding values $^2K(^{13}C,^1H)$ (>0) and $^3K(^1H,^1H)$ (close to zero). The molecular structure of the complex **2c** with the unusually large bond angles Sn–C(1)–C(2) and Sn–C(3)–C(4) shows that the original geometry of the alkyne is much less distorted than in other known dicobaltatetrahedranes.

4. Experimental details

All compounds were handled in an inert atmosphere of Ar or N$_2$, and syntheses were carried out using carefully dried solvents. Starting materials such as Co$_2$(CO)$_8$ or ^{n}Bu–Li (1.6 M in hexane) were used as commercial products without further purification. The 1-alkynyltin compounds were prepared as described in Refs. [4,20], or by using slightly modified literature methods [20]. The new complexes **1c**, **2b**, **2c** and **3–6** were prepared and isolated in the same way as de-

scribed for **1b**, **2a** and **2d** [4]. NMR spectra were recorded using Bruker ARX 250, AC 300 and AM 500 spectrometers, equipped with multinuclear units. Chemical shifts are given with respect to Me$_4$Si (δ ^{1}H(C$_5$D$_6$H) = 7.15; δ ^{1}H (CHCl$_3$/CDCl$_3$) = 7.24; δ ^{1}H (CDHCl$_2$) 5.33; δ ^{13}C (C$_6$D$_6$) = 128.0; δ ^{13}C(CDCl$_3$) = 77.0); Me$_4$Sn (δ ^{119}Sn: Ξ(^{119}Sn) = 37.290665 MHz). Pulse angles and delays for polarization transfer were optimized in the usual way for 1D NMR spectra before 2D heteronuclear shift correlations, either X or ^{1}H detected, were carried out. Infrared spectra were measured in hexane by using a Perkin Elmer 383 G instrument; the usual five to six bands for ν(CO) stretching frequencies (see Ref. [18] for a compilation of such IR data) were resolved between 2090 and 2004 cm^{-1}. Electron impact (EI) mass spectra (70 eV): Varian MAT CH7 with a direct inlet.

4.1. C–stannyl-substituted dicobaltatetrahedranes 1–6 (general procedure)

The respective 1-alkynyltin compound (6 mmol in the case of the compounds **1** and **3**, 3 mmol for **2** and **4**, 2 mmol for **5**, and 1 mmol for **6**) was added at room temperature in one portion to a stirred solution of 1.55 g of Co$_2$(CO)$_8$ (5 mmol) in 25 ml of hexane. After 12 h, the reaction mixture was cooled to $-78\,°C$ for 6 h, and then it was decanted and most of the solvent was removed in vacuo. The residue was purified by chromatography on Al$_2$O$_3$ (neutral) with hexane–toluene (1:1).

1c: yield 50%; m.p. 70 °C; ^{1}H NMR (250 MHz; C$_6$D$_6$): δ ^{1}H (J(^{119}Sn,^{1}H)) = 5.93 (8.0) s 1H HC; 1.28 (63.4) s 27H, ^{t}Bu$_3$Sn; EI mass spectra: m/z(%) = 574 (5) [M$^+$ – CO]; 350 (20); 259 (28); 177 (30); 57 (100) [C$_4$H$_9^+$].

2b: yield 55%; m.p. 50 °C; ^{1}H NMR (250 MHz; C_6D_6): δ ^{1}H ($J(^{119}Sn,^1H)$) = 5.88 (10.0) s 2H. HC; 1.23 m 10H, Et_2Sn.

2c: yield 77%; m.p. 92 °C; ^{1}H NMR (250 MHz; C_6D_6): δ ^{1}H ($J(^{119}Sn,^1H)$) = 5.99 (8.4) s 2H, HC; 1.35 (80.8) s 18H, $^tBu_2Sn$; EI mass spectra: $m/z(\%)$ = 772 (35) [$M^+ - 3CO$]; 744 (15) [$M^+ - 4CO$]; 716 (35) [$M^+ - 5CO$]; 632 (30); 575 (44); 547 (56); 519 (54); 491 (70); 460 (80); 404 (100) [$C_{12}H_{20}Co_2Sn^+$]; 377 (40); 344 (68); 286 (45); 260 (45); 143 (60); 57 (90) [$C_4H_9^+$].

3: yield 85%; m.p. > 85 °C (decomp.); ^{1}H NMR (250 MHz; C_6D_6): δ ^{1}H ($J(^{119}Sn,^1H)$) = 2.40 s 3H, Me–C; 0.25 (56.3) s 9H, Me_3Sn.

4: yield 80%; m.p. > 80 °C (decomp.); ^{1}H NMR (250 MHz; CD_2Cl_2): δ ^{1}H ($J(^{119}Sn,^1H)$) = 2.77 s 6H, Me–C; 0.60 (57.0) s 6H, Me_2Sn.

5: yield 85%; m.p. > 85 °C (decomp); ^{1}H NMR (250 MHz; C_6D_6): δ ^{1}H ($J(^{119}Sn,^1H)$) = 2.63 s 9H, Me–C; 0.82 (57.2) s 3H, MeSn.

6: yield 90%; m.p. > 90 °C (decomp.); ^{1}H NMR (250 MHz; C_6D_6): δ ^{1}H ($J(^{119}Sn,^1H)$) = 2.66 (7.0) s 9H, Me–C; 1.57 (13.1) s 3H, Me–C≡.

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