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Conformational Investigations of Ester-Functionalized *gem*-Distannyl Derivatives by $^1H-^{119}Sn$ Correlation NMR

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The conformational dependence on temperature and concentration of methyl 3,3-bis(tributylstannyl)propionate compounds of the type $(Bu_3Sn)_2CH-CHR-CO_2Me$ (R = H, **1**; R = $CH_2CH{=}CH_2$, **2**; R = CH_2Ph, **3**; R = CH_2NMe_2, **5**) was studied by means of Karplus-type dihedral angle relations for $^3J(^{119}Sn-^{13}C)$ couplings from ^{13}C NMR spectra and $^3J(^{119}Sn-^1H)$ couplings from $^1H-^{119}Sn$ correlation NMR experiments, assisted by ^{17}O and ^{119}Sn NMR spectroscopy. The results from these structural investigations point toward a dominant conformation in which a very weak tin−carbonyl oxygen $Sn \leftarrow O{=}C-O$ interaction is possible.

Introduction

The importance of tin chemicals to the synthetic chemist in basic and industrial research can hardly be overestimated.[1] Nevertheless, their real utility has been subordinated to the development of convenient and selective preparative methods. In this context, *gem*-distannyl compounds of the type $(R_3Sn)_2CHR'$ remain largely unused, despite a great potential usefulness as precursors in organic synthesis, due to the presence of two carbon−metal bonds on a prochiral center. Investigations on the chemical reactivity of these compounds, obtained through novel synthetic routes, confirmed this promising potential.[2] No detailed structural investigations on these compounds had been carried out, however. Our interest in the chemistry of these compounds, while exploring the catalyzed formation of 1,1-distannyl adducts via the double hydrostannation of terminal alkynes in the presence of thiol, prompted us to report on some conformational observations and underlying general trends evidenced through comparative investigations of closely related compounds.[3]

When the organic moiety R′ contains a chiral center, *gem*-distannyl $(R_3Sn)_2CHR'$ compounds present two diastereotopic tin atoms which raise the question of the assignment of their ^{119}Sn resonances. This should anticipate possible coordination between one or the other tin atom and a potentially intramolecularly coordinating substituent present in the moiety R′ and capable of generating five-membered rings. Nonfunctionalized tetraorganotin compounds are unable, in principle, to extend their coordination number, as a consequence of the poor acceptor properties of their tin atom.[4] By contrast, formation of Lewis acid−base complexes is favored when the tin atom bears electronegative substituents increasing its Lewis acidity and leading to coordination from electron-rich ligands.[4] However, coordination expansion at tin has been observed in the absence of electronegative residues on the metal in tetraorganotin compounds, when one (or more) organic substituent(s) bears a functional group with donor abilities.[4,5] One potential tool for observing this in solution is the ^{119}Sn chemical shift which strongly depends on the oxidation number of tin, its substitution pattern, coordination number, and geometric configuration around the tin center.[6,7]

As an answer to the question whether weak coordinations can be observed in *gem*-bis(trialkylstannyl) compounds, and if so, toward which of the two tin atoms,

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we report results of structural investigations on a series of novel chiral compounds derived from methyl 3,3-bis(tributylstannyl)propionate (**1**), methyl 3,3-bis(tributylstannyl)-2-allyl (**2**), -benzyl (**3**), -iodomethyl (**4**), and -(*N*,*N*-dimethylamino)methyl (**5**) propionates, which all have in common an ester function amenable to weak intramolecular O→Sn interactions. Accordingly, ^{17}O NMR experiments were performed, since interactions of oxygen with metals in Lewis donor−acceptor complexes shift the ^{17}O chemical shift to low or high frequency, depending on the type of orbital interactions involved.[8] Such ^{17}O NMR data, integrated with ^{119}Sn chemical shifts and $^{n}J(^{1}H-^{119}Sn)$ and $^{n}J(^{13}C-^{119}Sn)$ coupling constants, are anticipated to enable a discussion of self-consistent trends in structure, conformation, and bonding in *gem*-distannyl compounds.

Results and Discussion

In recent reports, applications of the refocused-decoupled INEPT pulse sequence were proposed for the determination of $^{n}J(^{119/117}Sn-^{119}Sn)$ coupling constants.[9] Hence, in an initial approach to the problem, the sequence was used to compare the magnitude of homonuclear $^{2}J(^{119}Sn-^{119}Sn)$ couplings in compounds **2**−**5** in order to find out some dependence of the coupling values on possible intramolecular coordinations. The measured $^{2}J(^{119}Sn-^{119}Sn)$ coupling values do not differ significantly in the series, ranging from 142 (compound **5**) to 144−146 Hz (compounds **2**−**4**). As a consequence, there is obviously no exploitable relationship between these coupling constants and the Sn−C−Sn bond angles. Conformational information needs to be gained from heteronuclear $^{3}J(^{119}Sn-^{1}H)$ and $^{3}J(^{119}Sn-^{13}C)$ coupling constants.

A 2D gradient-assisted $^{1}H-^{119}Sn$ heteronuclear multiple quantum correlation (HMQC)[10] experiment allows a straightforward correlation of the two ^{119}Sn resonances to the $^{3}J(^{119}Sn-^{1}H)$ coupling constants connecting the diastereotopic ^{119}Sn nuclei and the proton of the stereogenic carbon center. As an example, the gradient-assisted 2D $^{1}H-^{119}Sn$ HMQC spectrum obtained for methyl 3,3-bis(tributylstannyl)-2-benzylpropionate, **3**, is shown in Figure 1.

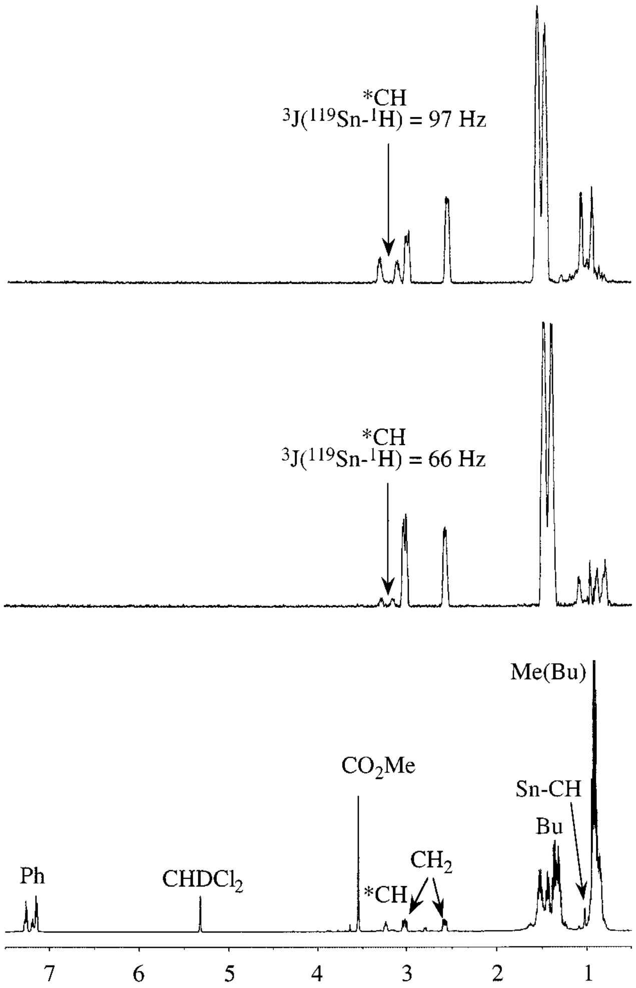

Figure 1. Gradient-assisted 2D $^{1}H-^{119}Sn$ HMQC spectra of compound **3**, $[(Bu_3Sn)_2CHCH(CH_2Ph)CO_2Me]$, recorded at 500.13 MHz for protons and 186.5 MHz for ^{119}Sn nuclei, enabling the determination of the $^{3}J(^{1}H-^{119}Sn)$ coupling constant values between the two diastereotopic ^{119}Sn nuclei and the proton of the stereogenic carbon atom. Bottom: standard ^{1}H spectrum with ^{1}H resonance assignment. Middle: correlation cross-section of the 2D $^{1}H-^{119}Sn$ HMQC spectrum for the ^{119}Sn nucleus resonating at high frequency [$\delta^{119}Sn = 4.6$ ppm; $^{3}J(^{1}H-^{119}Sn) = 66$ Hz]. Top: correlation cross-section of the 2D $^{1}H-^{119}Sn$ HMQC spectrum for the ^{119}Sn nucleus resonating at low frequency [$\delta^{119}Sn = 0.6$ ppm; $^{3}J(^{1}H-^{119}Sn) = 97$ Hz].

Figure 1 and Table 1 unambiguously show that these $^{3}J(^{119}Sn-^{1}H)$ couplings are strongly different, the larger value of 97 Hz being correlated with the ^{119}Sn resonance at low frequency (0.6 ppm), the smaller of 66 Hz with that at high frequency (4.6 ppm). For all compounds, all $^{n}J(^{119}Sn-^{1}H)$ coupling constants are readily deduced from such cross-sections of the 2D $^{1}H-^{119}Sn$ HMQC spectrum—Fourier transformed in the magnitude mode—at each of the ^{119}Sn resonance frequencies. The resulting NMR data are listed in Table 1. The $^{3}J(^{119}Sn-^{1}H)$ couplings associated with the proton of the chiral center could be assigned on a firm basis from neither INEPT

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Table 1. ^{119}Sn, ^{13}C NMR, and Dihedral Angle Data of Compounds 1−3 and 5

compounds $(Bu_3Sn)_2CHCH(CH_2X)CO_2Me$	T (K)	$^3J(^{119}Sn-^{13}C{=}O)$ [Hz]	$\theta(Sn_1)$ $\theta(Sn_2)$ [deg][b,c,g]	$^3J(^{119}Sn-^{13}CH_2)$ [Hz]	$\phi(Sn_1)$ $\phi(Sn_2)$ [deg][b,c,g]	$^3J(^{119}Sn-^1H)$[d] [Hz]	$^3J(^{119}Sn-^2H)$[e] [Hz] [calculated]	$\psi(Sn_1)$ $\psi(Sn_2)$ [deg][b,f,g]	δ^{119}Sn (ppm) Sn$_1$ Sn$_2$ (CD_2Cl_2)
X = H, **1**	303	35	30/135			65	10.0	30/135	10.1
X = $CH_2CH{=}CH_2$, **2**	303	12	65/**105**	45	15/**145**	69	10.6	**30**/135	4.3
		33	**35**/130	16	55/**110**	94	14.4	5/**145**	0.9
X = CH_2Ph, **3**	303	11	65/**105**	47	10/**145**	66	10.1	**30**/135	4.6
		31	**35**/130	15	60/**110**	97	14.9	−/**150**	0.6
X = CH_2NMe_2, **5**	303	15	60/**110**	46	10/**145**	68	10.4	**30**/135	5.0
		34	**35**/135	19	60/**110**	88	13.5	15/**145**	1.8
	253	15	60/**110**	43	20/**140**	72	11.1	**25**/135	5.4
		37	**30**/135	19	55/**115**	82	12.6	20/**140**	3.7
	233	16	55/**115**	38	30/**135**				
		40	**25**/140	21	50/**120**				
	203	*a*		*a*		80	12.3	**20**/140	5.4
		44	**15**/145	*a*		70	10.7	30/**135**	6.8

[a] Nonmeasurable, too broad. [b] Torsional angles of favored conformations in bold (see text). [c] Dihedral angle values calculated from the Karplus-type relation: $^3J(^{119}Sn-^{13}C) = 25.2\cos(2\phi) - 7.6\cos\phi + 30.4$. [d] $^3J(^{119}Sn-^1H)$ coupling constant values determined from gradient assisted 2D $^1H-^{119}Sn$ HMQC spectra. [e] $^3J(^{119}Sn-^2H)$ coupling constant values deduced from measured $^3J(^{119}Sn-^1H)$ coupling constants, taking $\gamma(^1H)/\gamma(^2H) = 6.514$. [f] Dihedral angle values calculated from the Karplus-type relation: $^3J(^{119}Sn-^2H) = 9\cos(2\psi) - 3\cos\psi + 8.5$. [g] Angles have to be taken with an uncertainty margin of 10°. Values are rounded off to the nearest fives or tens.

nor $^1H-^{119}Sn$ HMQC 1D experiments, mainly because of overlapping homonuclear proton coupling patterns and/or phase distortions. The above gradient-assisted 2D HMQC experiments[8e,f,10] made this possible, the use of gradients enabling perfect suppression of undesired ^1H resonances from protons not coupled to ^{119}Sn nuclei.

This preliminary assignment of the two diastereotopic tin atoms enables us now to tackle the problem of the preferred conformation in the *gem*-distannyl compounds **2**−**5**, one goal being to find out whether one or the other of the tin atoms can undergo coordination from the ester group. This requires the determination not only of the $^3J(^{119}Sn-^1H)$ couplings from the above 2D $^1H-^{119}Sn$ HMQC spectrum but also of $^3J(^{119}Sn-^{13}C)$ coupling constants, directly from the ^{13}C NMR spectrum. Indeed, Karplus-type relationships have been reported for the dihedral angle dependences of both $^3J(^{119}Sn-^2H)$[11] and $^3J(^{119}Sn-^{13}C)$[7a,12] coupling constants.

The dependence of the $^3J(^{119}Sn-CH-C^*H-^{13}CH_2)$ coupling constant on the dihedral angles $\phi(Sn_1)$ and $\phi(Sn_2)$ (see Figure 2) between the ^{119}Sn nuclei and the ^{13}C nucleus of the methylene group bound to the stereogenic carbon atom was assessed from equation I[7a,12,13]

$$^3J(^{119}Sn-^{13}C) = 25.2\cos(2\phi) - 7.6\cos\phi + 30.4 \quad (I)$$

The same equation was used for the estimation of the dihedral angles $\theta(Sn_1)$ and $\theta(Sn_2)$ between the ^{119}Sn nuclei and the ^{13}C nucleus of the carbonyl group of the ester function. It is indeed recognized that $^3J(^{119}Sn-CH-C^*H-^{13}CO)$ couplings likewise fit into this equation.[13]

The dependence of the $^3J(^{119}Sn-CH-C^*-^1H)$ coupling constant on the dihedral angles $\psi(Sn_1)$ and $\psi(Sn_2)$ between the ^{119}Sn nuclei and the proton of the chiral center was calculated from eq II established for deuterated compounds.[11]

$$^3J(^{119}Sn-^2H) = 9\cos(2\psi) - 3\cos\psi + 8.5 \quad (II)$$

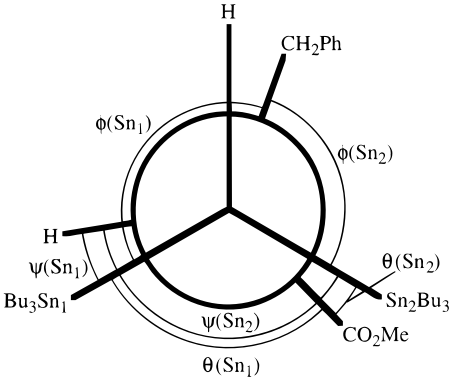

Figure 2. Approximate Newman projection of the dominant conformation of compound **3**, $[(Bu_3Sn)_2CHCH(CH_2Ph)CO_2Me]$, at 303 K (see also Figure 3). Bold lines represent the Newman projection itself; thin lines represent the arcs spanned by the different torsional angles as defined in Table 1.

The $^3J(^{119}Sn-^2H)$ coupling constants are deduced from the measured $^3J(^{119}Sn-^1H)$ ones, taking $\gamma(^1H)/\gamma(^2H) = 6.514$. It is of course assumed that torsional angles do not undergo any isotopic effect. The measured $^3J(^{119}Sn-^1H)$ and $^3J(^{119}Sn-^{13}C)$ coupling constants are measured experimentally to within ±1 Hz, which would theoretically result in an absolute error on $^3J(^{119}Sn-^2H)$ values of 0.2 Hz. However, this does not mean that the calculated torsional angle uncertainty of ca. 2° is relevant. Indeed, the empirical nature of eqs I and II must incite one to the necessary caution. Inspection of the deviation of the experimental points from the calculated curve presented in a review of Wrackmeyer[7a] indicates that the torsional angles have to be considered with an uncertainty interval of 10°.

Usually, two mathematical solutions of the above Karplus-type equations I and II, both potentially representative of different dihedral angles values, can correspond to each single $^3J(^{119}Sn-^{13}C)$ or $^3J(^{119}Sn-^2H)$ coupling constant value. Three independent coupling

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constant determinations ($^3J(^{119}Sn-CH-C^*-^1H)$, $^3J(^{119}Sn-CH-C^*H-^{13}CH_2)$, $^3J(^{119}Sn-CH-C^*H-^{13}CO)$) involving the two tin atoms lead to three times two pairs of torsional angles for a given compound (one pair for $\psi(Sn_1)$ and $\psi(Sn_2)$, one for $\phi(Sn_1)$ and $\phi(Sn_2)$, and one for $\theta(Sn_1)$ and $\theta(Sn_2)$, respectively; see Table 1). Among all the a priori possible combinations, when keeping in mind the geometric constraints relating mutually ψ, θ, and ϕ, we found only one single self-consistent set of torsional angles for compound **3** (only one solution for ψ), while two sets are potentially self-consistent for compounds **2** and **5**. Because of the globally rather similar coupling constants for all compounds (Table 1), and given the temperature dependence of the coupling data for **5** as explained below, only one single set of torsional angles can be retained as corresponding to the same dominant conformation valid for all the compounds. The corresponding torsional angles are given in bold in Table 1 for each of the compounds investigated. The resulting dominant conformation is given in Figure 2.

In this way, for instance, compound **3**, $(Bu_3Sn)_2CHCH(CH_2Ph)CO_2Me$, exhibits torsional angle values $\psi(Sn_1) = 30°$ and $\psi(Sn_2) = 150°$, and $\phi(Sn_1) = 150°$ and $\phi(Sn_2) = 110°$. This conformational preference places the ester function close to the tin atom Sn_2 with the low-frequency resonance ($\delta^{119}Sn = 0.6$ ppm). Because of the obvious homogeneity, within a few hertz, in the coupling data at room temperature of all the *gem*-distannyl compounds investigated, the favored dominant conformation obtained for compound **3** can be considered as representative of all of them.

The homogeneity in the coupling constants at room temperature demonstrates that the electronegativity of the substituent X in these $(Bu_3Sn)_2CHCH(CH_2X)CO_2Me$ compounds has no significant influence on the torsional angles and, hence, on their overall conformation. Mitchell et al. already pointed out for other organotin compounds of the type $XMe_2SnCHRCHR'CO_2Me$ (X = Me, Cl; R, R′ = Me, Ph) that such Karplus relationships are usable, even in the presence of substituents with different electronegativities.[13]

At first glance, the ester function is favorably oriented in the conformation of Figure 2 to enable a donor−acceptor chelating interaction toward tin atom Sn_2, which would therefore be five-coordinate. However, neither the ^{119}Sn chemical shifts nor the values of the $^1J(^{13}C-^{119}Sn)$ coupling constants indicate any clear coordination expansion or, at least, a marked geometry change at tin resulting therefrom. In an effort to find evidence for the suggested interaction between the tin atom Sn_2 and the ester function and to determine, if any, its nature, i.e. to find out whether the trend to weak coordination suggested by the coupling data results from the carbonyl oxygen or the alkoxy one, we recorded ^{17}O NMR spectra at 333 K on compounds **1**−**3** and **5**. Both carbonyl and alkoxy ^{17}O chemical shifts were compared with those of $Me_2CHCH_2CO_2Me$, taken as nonstannylated reference with a reasonably similar molecular skeleton as compared to methyl 3,3-bis(tributylstannyl)propionate, **1** (Table 2).

The ^{17}O alkoxy resonances of compounds **1**, **2**, **3**, and **5** are hardly shifted with respect to the reference compound, the maximum shift, observed for **1**, not exceeding 4 ppm to low frequency. This situation is somewhat different for their carbonyl ^{17}O chemical shifts, which are shifted to low frequency by −4, −12, −11, and −13 ppm, respectively. This low-frequency shift for compounds **2**, **3**, and **5** of slightly over 10 ppm with respect to the reference compound should not be overstated as to its significance, given the line width of ca. 600 Hz and the low signal-to-noise ratio of ^{17}O resonances. Nevertheless, these carbonyl low-frequency shifts, combined with the torsional angle data from the three series of coupling constants ($^3J(^{119}Sn-CH-C^*-^1H)$, $^3J(^{119}Sn-CH-C^*H-^{13}CH_2)$, $^3J(^{119}Sn-CH-C^*H-^{13}CO)$), suggest a possible existence of a specific intramolecular coordinative interaction to the tin atom from the carbonyl oxygen, any interaction from the alkoxy oxygen being unsupported by the above data.[8e,g] By contrast, the data observed for compound **1** do not allow any conclusion. Globally, the data for compounds **2**, **3**, and **5** do not point toward a real five-coordinate tin atom, but are at most consistent with the presence of a very weak donor−acceptor contact of van der Waals nature associated with a very shallow potential well.

Table 2. ^{17}O NMR Chemical Shifts (ppm) at 333 K, obtained from C_6D_6 Solutions of Compounds 1, 2, 3, and 5, As Compared with Those of $Me_2CHCH_2CO_2Me$ Taken as a Nonstannylated Reference with Similar Molecular Skeleton[a]

compound	$\delta(C{=}^{17}O)$	$\delta(^{17}O-CH_3)$
$Me_2CHCH_2CO_2Me$ (reference)	361	138
$(Bu_3Sn)_2CHCH_2CO_2Me$ (**1**)	357 (−4)	134 (−4)
$(Bu_3Sn)_2CHCH(CH_2CH{=}CH_2)CO_2Me$ (**2**)	349 (−12)	136 (−2)
$(Bu_3Sn)_2CHCH(CH_2Ph)CO_2Me$ (**3**)	350 (−11)	137 (−1)
$(Bu_3Sn)_2CHCH(CH_2NMe_2)CO_2Me$ (**5**)	348 (−13)	136 (−2)

[a] Chemical shift differences with respect to reference are given in parentheses.

To provide further support to this interpretation, variable-temperature NMR data were determined from 303 to 193 K for compounds **2**, **3**, and **5**. The ^{119}Sn chemical shifts and coupling constants appear essentially temperature independent for compounds **2** and **3**, with no significant modification in the line shape of the resonances. Consequently, as no evidence for conformational equilibria between rotamers is found, compounds **2** and **3** can be regarded as conformationally stable in the considered temperature range, with the conformation of Figure 2 being dominant.

Compound **5**, however, showed a slight temperature dependence, both at 74.63 MHz (in $CDCl_3$) and 186.50 MHz (in CD_2Cl_2) and at two concentrations (ca. 50 and 200 mg of sample in 0.5 mL of solvent). Table 3 reports the ^{119}Sn chemical shifts measured at various temperatures in diluted and concentrated solution at 186.50 MHz. The absence of any significant ^{119}Sn chemical shift change upon concentration modification rules out, as expected, the existence of even weak aggregation phenomena through *inter*molecular coordinative interactions.

The same ^{119}Sn chemical shift dependence on the temperature is observed at both resonance frequencies. The chemical shift $\delta(^{119}Sn_1)$ displays a temperature dependence between 303 and 193 K within the very narrow chemical shift range of 5.0−5.6 ppm. The $\delta(^{119}Sn_2)$ resonance displays a temperature dependence in the slightly broader range 1.6−7.0 ppm, showing, whatever the concentration, a high-frequency shift

Table 3. ^{119}**Sn Chemical Shifts (ppm) of Compound 5, [(Bu$_3$Sn)$_2$CHCH(CH$_2$NMe$_2$)CO$_2$Me], at Two Concentrations in CD$_2$Cl$_2$, as a Function of Temperature**

temperature (K)	diluted solution (ca. 50 mg/0.5 mL)		concentrated solution (ca. 200 mg/0.5 mL)	
	$\delta^{119}Sn_1$	$\delta^{119}Sn_2$	$\delta^{119}Sn_1$	$\delta^{119}Sn_2$
303	5.0	1.9	5.0	1.7
283	5.2	2.6	5.2	2.3
263	5.4	3.4	5.4	3.1
253			5.5	3.6
243	5.4	4.4	5.5	4.1
233	5.5	4.7	5.6	4.7
223	5.5	5.5	5.6	5.3
213	5.4	6.1	5.5	5.8
203	5.4	6.4	5.5	6.4
193			5.4	6.9

with respect to its value at 303 K. At 223 K, the two resonances cross over, giving rise to a reversal of the $\delta(^{119}Sn_1)$ and $\delta(^{119}Sn_2)$ values, with, at 193 K, the ^{119}Sn resonance initially at low frequency being now at high frequency. This behavior is confirmed at 74.63 MHz, with the resonance crossover occurring at the same temperature and without any coalescence broadening at both resonance frequencies.

Keeping in mind that at 303 K the resonance at low frequency, $\delta(^{119}Sn_2)$, is assigned to the tin atom close to the ester function (Sn$_2$, see Newman projection in Figure 2, with the CH$_2$Ph moiety of **3** being substituted for the CH$_2$NMe$_2$ one of **5**), the high-frequency shift is, at least at first glance, in disagreement with the expected reinforcement of five-coordination at the Sn$_2$ tin atom upon lowering the temperature from 303 to 193 K. This initiated the investigation of the coupling constants at lower temperatures, the $^3J(^1H-^{119}Sn)$ coupling constants of compound **5** again exhibiting a quite drastic change upon temperature decrease (Table 1), from respectively 66 and 88 Hz at 303 K through 72 and 82 Hz at 253 K to 80 and 70 Hz at 203 K. Use of the Karplus-type equation II reveals however that this strong change in coupling constants is perfectly explainable in terms of only a slight change in the dihedral angles, the angles $\psi(Sn_1)$ and $\psi(Sn_2)$ decreasing from respectively 30° and 145° at 303 K to 20° and 135° at 203 K, corresponding to a decrease in dihedral angle of only 10° upon temperature decrease toward a conformation that is slightly more eclipsed than the initial one at high temperature (Figure 2). Although this change in torsional angle lies within the uncertainty margin to be considered in view of the empirical character of the Karplus equations, this variation is not meaningless, as it results from calculations of coupling constants varying *within* the same product. Similar changes in the $^3J(^{13}C-^{119}Sn)$ coupling constants lead to corresponding slight changes in dihedral angles ϕ and θ, likewise compatible with a more eclipsed conformation at lower temperature. The destabilization expected from the conformation being more eclipsed is counterbalanced by the stabilization of the ester−Sn-2 interaction, which is reinforced in this way. Although this interpretation seems to be in disagreement with the observed high-frequency shift of the $^{119}Sn_2$ resonance, the latter observation should not be overstated, being small, on one hand, and being in agreement, on the other hand, with an expected deshielding resulting from the CH$_2$-NMe$_2$ rotating away from Sn$_2$ upon temperature decrease.

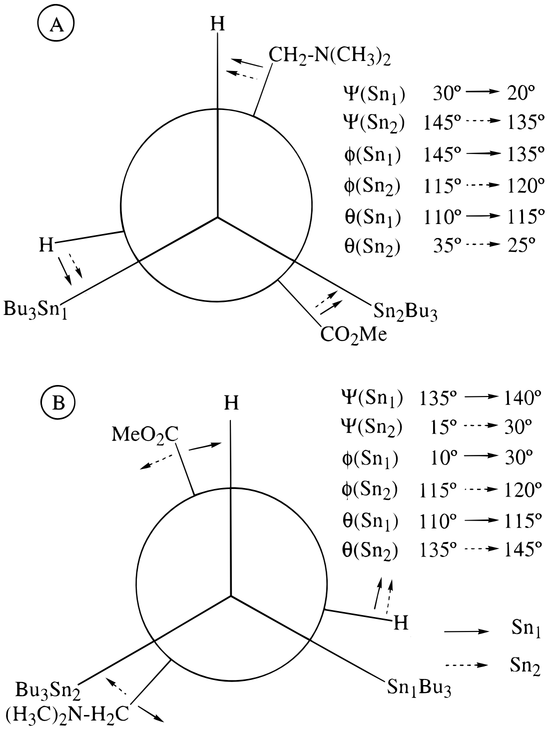

Figure 3. Two a priori possible conformations, A and B, for compound **5**, as obtained from the two possible solutions of the appropriate Karplus equation applied to the angles $\psi(Sn_1)$ and $\psi(Sn_2)$, $\phi(Sn_1)$ and $\phi(Sn_2)$, $\theta(Sn_1)$ and $\theta(Sn_2)$ (definition: see Figure 2, Table 1, and definitions in text) calculated from the experimentally determined coupling constants. The arrows in the drawings indicate the direction of the variation of the torsional angles upon temperature decrease from 303 to 203 K, according to the coupling constant temperature dependence, for the two sets of Karplus equation solutions. The full and dotted arrows refer to the tin atoms Sn$_1$ and Sn$_2$, respectively. While self-consistent, within experimental error, for conformation A, the torsional angle variations are non-self-consistent for conformation B, enabling conformation A to be considered as the only realistic dominant conformation for compound **5** and, indirectly, for compounds **1**−**3**.

The observed variation in coupling constants, and therefore of dihedral angles in compound **5**, finally also confirms the conformation assignment, illustrated in Figure 2 for compound **3**, to be the only possible *dominant* conformation in agreement with *all* NMR data. Thus the conformation proposed for compound **3** (and **2**), and illustrated again in Figure 3A for compound **5**, can perfectly well manage the changes in dihedral angles upon temperature lowering, as indicated by the arrows in the figure; by contrast, as illustrated by Figure 3B, the alternative conformation, compatible with the data at high temperature, leads to contradictious torsional angle changes upon temperature decrease, as indicated by the inconsistent set of arrows; this directly confirms the validity of the conformation A of Figure 3 rather than conformation B for compound **5**, and indirectly of the conformation of Figure 2 for compound **3** (as well as **2**), in addition to the arguments already invoked above. The driving force to the slight variation in torsional angles in compound **5** upon temperature decrease, while absent in compounds **1**−**3**, is proposed to result from a stabilization of the O→Sn interaction accompanied by a release of the steric repulsion induced by the sterically crowded $(CH_3)_2N$ group rotating away from the Sn_2 atom, while the high temperature would favor a slightly more staggered conformation in which interactions with tin should be weaker. Indeed, a self-consistent combination of torsional angles resulting from the experimental coupling constant values and compatible with a conformation in which the $(CH_3)_2N$ group would interact directly with any of the tin atoms Sn_1 and Sn_2 could not be found at any temperature. Thus, since both the latter conformation and that of Figure 3B can be rejected safely, and no self-consistent set of NMR data supports the existence of any alternative dominant conformation, an interpretation of the temperature dependence of the NMR data in terms of the changing average of two equilibrating different conformations can be ruled out. Actually, the temperature dependence of the NMR data is more dramatic than the torsional angle changes that explain them, a roughly identical conformation to within 10° torsional angle change being compatible for compound **5** with both the low and room temperature.

Conclusion

In this study we have evidenced a conformational preference in *gem*-bis(tributylstannyl) compounds. We have demonstrated that despite the negligible acceptor properties of the tin atoms in this series, the presence of an ester function in the organic moiety of $(R_3Sn)_2CHR'$ promotes a very weak tin−donor interaction of van der Waals force nature rather than a real coordination bond. ^{17}O NMR data undoubtedly indicate that the carbonyl oxygen is involved. The site of the tin−donor interaction could be determined from $^3J(^{119}Sn-^1H)$ and $^3J(^{119}Sn-^{13}C)$ couplings, using Karplus-type relations.

Experimental Section

A typical synthesis of compounds **2**−**5** was as follows: an amount of 0.50 g (4.95 mmol) of diisopropylamine in 5 mL of anhydrous THF was placed in a Schlenk tube under nitrogen atmosphere. At 0 °C, 1.89 mL of butyllithium (4.7 mmol; 2.5 M in hexane) was added. After standing at this temperature for 15 min, a solution of 3 g (4.5 mmol) of methyl 3,3-bis(tributylstannyl)propionate[2b,c,14,15] was added at −78 °C. After stirring the reaction mixture at this temperature for 1 h, 5 mmol of the appropriate halide, namely allyl bromide for **2**, benzyl bromide for **3**, diiodomethane for **4**, and *N*,*N*-dimethylaminomethyl iodide for **5**, in 3 mL of THF was added. The mixture was stirred and allowed to warm to room temperature. Water was then added at 0 °C and the mixture extracted with diethyl ether. After drying and removal of the solvent, the residue was purified at ca. 10^{-4} mmHg using a Kugelrohr apparatus followed by chromatography on silica gel (compounds **2**−**4**: eluent, petroleum ether/ethyl acetate, 99/1; **5**: eluent, petroleum ether/ether, 90/10). In the case of compound **5**, the intermediate enolate $(Bu_3Sn)_2CHCH{=}C(OLi)OMe$ is added on an excess of Eschenmoser salt (immonium salt/ester, 3/1) in 3 mL of anhydrous THF. Compound **1** was prepared as previously described.[14]

^1H and ^{13}C NMR spectra were recorded on a Bruker AC250 spectrometer (solvent $CDCl_3$, internal reference Me_4Si); ^{119}Sn NMR experiments were performed on a Bruker AC200 spectrometer (^{119}Sn, 74.630 MHz) fitted with an Aspect 3000 computer, using a 10 mm broad-band probe. Chemical shifts are referenced to Me_4Sn (internal standard) and are expressed as $\delta^{119}Sn$ chemical shifts. $^2J(^{119}Sn-^{119}Sn)$ values were determined using INEPT decoupled experiments[16] $[D_1-(90°_x{}^1H)-\tau-(180°_x{}^1H)(180°_xX)-\tau-(90°_{\pm y}{}^1H)(90°_xX)-\Delta/2-(180°_x{}^1H)\text{-}(180°_xX)-\Delta/2$-acquisition X with ^1H broad-band decoupling]. Optimization of the experimental polarization and the refocusing parameters (τ, Δ) has been obtained from a previously reported computer program.[17] The following parameters were used: ^{119}Sn 90° pulse 19 μs, recycle delay 1 s, ^1H 90° pulse 29 μs, polarization transfer delay 0.005 s, refocusing delay 0.002 s; number of scans 128. Routine ^{119}Sn experiments were performed using the “gated decoupler” method, to cancel the negative nucleus Overhauser effect.

The values of $^nJ(^1H-^{119}Sn)$ coupling constants were determined from gradient assisted 1D/2D HMQC sequences. 1D $^1H-^{119}Sn$ HMQC spectra of compound **2**, $(Bu_3Sn)_2CHCH(CH_2CH{=}CH_2)CO_2Me$, were recorded at 200.16 MHz, using the 1D sequence of Bax et al.,[10a] $[(90°_x{}^1H)-D_2-(90°_\phi{}^{119}Sn)-D_{13}-(180°_x{}^1H)-D_{13}-(90°_x{}^{119}Sn)-$acquisition $^1H]$; $D_2 = 0.01$ and 0.0071 s; $D_{13} = 3$ μs; 90° $^1H = 7.7$ μs; 90° $^{119}Sn = 5.5$ μs; relaxation delay = 1 s; acquisition delay = 2.045 s; NS = 64 (standard Bruker microprogram DPX (INV4ND1D)).

2D $^1H-^{119}Sn$ HMQC spectra were recorded on a Bruker AMX500 spectrometer equipped with a digital lock and operating at 500.13 and 186.50 MHz for ^1H and ^{119}Sn nuclei, respectively (microprogram GRINV4LRND2D). Experimental settings were reported previously.[8e,f,10b]

^{17}O NMR spectra were recorded at 333 K on a Bruker AMX500 spectrometer operating at 67.8 MHz resonance frequency. The spectra were acquired at natural abundance level in C_6D_6 (concentration of 200 mg/0.5 mL). The signals were referenced in ppm to external deionized water. Standard instrumental settings were used:[8e,f,18] a spectral width of 50 kHz, 2K data points, 90° pulse angle, 200 μs acquisition delay, and 40 ms acquisition time with a number of scans varying between 20 000 and 100 000. Zero-filling to 8K data points and an exponential line broadening of 20 Hz were applied to improve the resolution and signal-to-noise ratio. The reproducibility of the chemical shift is within ±1−2 ppm.

Mass spectral data refer to the ^{120}Sn isotope and were obtained using a VG AutoSpec Q instrument, operating at 70 eV.

Elemental analyses were performed by the “Service Central d’Analyses du CNRS”, Vernaison, France.

Compound 1, $(Bu_3Sn)_2CHCH_2CO_2Me$:[2b,c,14] Yield 92%. Anal. Found: C, 50.47; H, 9.08; O, 4.24; Sn, 35.56. Calcd for $C_{28}H_{60}O_2Sn_2$: C, 50.48; H, 9.08; O, 4.80; Sn, 35.64. ^1H NMR (250 MHz, $CDCl_3$, δ ppm): 0.50−1.69 [m, 55H, butyl, Sn_2CH, $^2J(^{119}Sn-^1H) = 62$ Hz]; 2.73 [d, 2H, CH_2CO_2, $^3J(^1H-^1H) = 7.0$ Hz, $^3J(^{119}Sn-^1H) = 65$ Hz]; 3.60 [s, 3H, CO_2CH_3]. ^{13}C NMR ($CDCl_3$, δ ppm): −2.0 [Sn_2CH, $^1J(^{119}Sn-^{13}C) = 230$ Hz, $^1J(^{117}Sn-^{13}C) = 220$ Hz]; 10.11 [$CH_2\alpha$, $^1J(^{119}Sn-^{13}C) = 314$ Hz, $^1J(^{117}Sn-^{13}C) = 300$ Hz]; 13.66 [CH_3 butyl]; 27.61 [$CH_2\gamma$, $^3J(^{119/117}Sn-^{13}C) = 57$ Hz]; 29.32 [$CH_2\beta$, $^2J(^{119/117}Sn-^{13}C) = 19$ Hz]; 35.28 [CH_2CO_2, $^2J(^{119/117}Sn-^{13}C) = 21$ Hz]; 51.58 [CO_2CH_3]; 176.10 [CO_2, $^3J(^{119/117}Sn-^{13}C) = 35$ Hz]. ^{119}Sn NMR (C_6D_6, δ ppm): +11.12 [$^2J(^{119}Sn-C-^{117}Sn) = 154$ Hz]. MS: m/z (%) = 609 (100) $[M - CO_2Me]^+$, 179/177 (14/14) $[BuSnH_2]^+$ and $[BuSn]^+$.

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Compound 2, $(Bu_3Sn)_2CHCH(CH_2CH{=}CH_2)CO_2Me$: Yield 92%. Anal. Found: C, 52.64; H, 9.09; Sn, 34.01. Calcd for $C_{31}H_{64}O_2Sn_2$: C, 52.72; H, 9.13; Sn, 33.62. ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 0.44−1.60 [m, 55H, butyl, Sn_2CH]; 1.82−2.00 [m, 1H, $CH_2CH{=}CH_2$]; 2.30−2.48 [m, 1H, $CH_2CH{=}CH_2$]; 2.80−2.96 [m, 1H, $CHCO_2CH_3$]; 3.56 [s, 3H, CO_2CH_3]; 4.84−5.04 [m, 2H, $CH_2CH{=}CH_2$]; 5.50−5.74 [m, 1H, $CH_2CH{=}CH_2$]. ^{13}C NMR ($CDCl_3$, δ ppm): 8.57 [Sn_2CH]; 10.60 [$CH_2\alpha$, $^1J(^{119}Sn-^{13}C) = 312$ Hz, $^1J(^{117}Sn-^{13}C) = 299$ Hz, $^3J(^{119/117}Sn-CH-Sn-^{13}C) = 7$ Hz]; 11.40 [$CH_2\alpha$, $^1J(^{119}Sn-^{13}C) = 316$ Hz, $^1J(^{117}Sn-^{13}C) = 301$ Hz, $^3J(^{119/117}Sn-CH-Sn-^{13}C) = 8$ Hz]; 13.60 [CH_3 butyl]; 27.62 [$CH_2\gamma$, $^3J(^{119/117}Sn-^{13}C) = 59$ Hz]; 27.64 [$CH_2\gamma$, $^3J(^{119/117}Sn-^{13}C) = 58$ Hz]; 29.33 [$CH_2\beta$, $^2J(^{119/117}Sn-^{13}C) = 19$ Hz]; 29.41 [$CH_2\beta$, $^2J(^{119/117}Sn-^{13}C) = 18$ Hz]; 41.34 [CH_2-$CH{=}CH_2$, $^3J(^{119/117}Sn-^{13}C) = 45$ Hz, $^3J(^{119/117}Sn-^{13}C) = 16$ Hz]; 47.00 [Sn_2CHCH, $^2J(^{119/117}Sn-^{13}C) = 23$ Hz, $^2J(^{119/117}Sn-^{13}C) = 18$ Hz]; 51.50 [CO_2CH_3]; 116.50 [$CH_2CH{=}CH_2$]; 177.50 [CO_2, $^3J(^{119/117}Sn-^{13}C) = 33$ Hz, $^3J(^{119/117}Sn-^{13}C) = 12$ Hz]. ^{119}Sn NMR (C_6D_6, δ ppm): +0.76 [$^2J(^{119}Sn-C-^{119}Sn) = 147$ Hz, $^2J(^{119}Sn-C-^{117}Sn) = 140$ Hz]; +6.25 [$^2J(^{119}Sn-C-^{119}Sn) = 147$ Hz, $^2J(^{119}Sn-C-^{117}Sn) = 140$ Hz]. MS: m/z (%) = 649 (100) $[M - CO_2Me]^+$, $[BuSnH_2]^+$, and $[BuSn]^+$, 319 (20) $[M - Bu_3Sn - CO_2Me - Allyl]^+$, 179/177 (22/23).

Compound 3, $(Bu_3Sn)_2CHCH(CH_2Ph)CO_2Me$: Yield 50%. Anal. Found: C, 54.78; H, 8.69; Sn, 32.31. Calcd for $C_{35}H_{66}O_2Sn_2$: C, 55.58; H, 8.80; Sn, 31.39. ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 0.66−1.74 [m, 55H, butyl, Sn_2CH]; 2.55−2.68 [m, 1H, CH_2Ph]; 3.05−3.16 [m, 1H, CH_2Ph]; 3.21−3.33 [m, 1H, $CHCO_2CH_3$]; 3.65 [s, 3H, CO_2CH_3]; 7.14−7.36 [m, 5H, Ph]. ^{13}C NMR ($CDCl_3$, δ ppm): 8.50 [Sn_2CH]; 10.50 [$CH_2\alpha$, $^1J(^{119}Sn-^{13}C) = 312$ Hz, $^1J(^{117}Sn-^{13}C) = 297$ Hz]; 11.73 [$CH_2\alpha$, $^1J(^{119}Sn-^{13}C) = 317$ Hz, $^1J(^{117}Sn-^{13}C) = 302$ Hz, $^3J(^{119/117}Sn-CH-Sn-^{13}C) = 7$ Hz]; 13.73/14.13 [CH_3 butyl]; 27.67 [$CH_2\gamma$, $^3J(^{119/117}Sn-^{13}C) = 59$ Hz]; 27.76 [$CH_2\gamma$, $^3J(^{119/117}Sn-^{13}C) = 59$ Hz]; 29.33 [$CH_2\beta$, $^2J(^{119/117}Sn-^{13}C) = 19$ Hz]; 29.39 [$CH_2\beta$, $^2J(^{119/117}Sn-^{13}C) = 19$ Hz]; 43.37 [CH_2Ph, $^3J(^{119/117}Sn-^{13}C) = 47$ Hz, $^3J(^{119/117}Sn-^{13}C) = 15$ Hz]; 49.45 [Sn_2CHCH, $^2J(^{119/117}Sn-^{13}C) = 23$ Hz, $^2J(^{119/117}Sn-^{13}C) = 18$ Hz]; 51.52 [CO_2CH_3]; 126.33/128.34/128.94 [CH, Ph]; 139.71 [C_q, Ph]; 177.59 [CO_2, $^3J(^{119/117}Sn-^{13}C) = 31$ Hz, $^3J(^{119/117}Sn-^{13}C) = 11$ Hz]. ^{119}Sn NMR (C_6D_6, δ ppm): −0.99 [$^2J(^{119}Sn-C-^{119}Sn) = 146$ Hz, $^2J(^{119}Sn-C-^{117}Sn) = 139$ Hz]; +6.80 [$^2J(^{119}Sn-C-^{119}Sn) = 146$ Hz, $^2J(^{119}Sn-C-^{117}Sn) = 139$ Hz]. MS: m/z (%) = 699 (92) $[M - CO_2Me]^+$, 609 (53) $[M - PhCH_2]^+$, 539 (14) $[M - 2\ C_4H_9 - PhCH_2 - Me]^+$, 291 (11) $[Bu_3Sn]^+$, 235 (14) $[Bu_2SnH]^+$, 179/177 (26/27) $[BuSnH_2]^+$ and $[BuSn]^+$, 91 (100) $[PhCH_2]^+$, 57 (39) $[C_4H_9]^+$.

Compound 4, $(Bu_3Sn)_2CHCH(CH_2I)CO_2Me$: Yield 50%. Anal. Found: C, 44.25; H, 7.69; Sn, 29.94. Calcd for $C_{29}H_{61}O_2Sn_2I$: C, 43.21; H, 7.63; Sn, 29.45. ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 0.62−1.73 [m, 55H, butyl, Sn_2CH]; 2.88−3.03 [m, 1H, CH_2I]; 3.20−3.30 [m, 1H, CH_2I]; 3.31−3.44 [m, 1H, $CHCO_2CH_3$]; 3.66 [s, 3H, CO_2CH_3]. ^{13}C NMR ($CDCl_3$, δ ppm): 9.57 [CH_2I, $^3J(^{119/117}Sn-^{13}C) = 22$ Hz]; 10.41 [Sn_2CH]; 10.73 [$CH_2\alpha$, $^1J(^{119}Sn-^{13}C) = 316$ Hz, $^1J(^{117}Sn-^{13}C) = 301$ Hz, $^3J(^{119/117}Sn-CH-Sn-^{13}C) = 6$ Hz]; 11.34 [$CH_2\alpha$, $^1J(^{119}Sn-^{13}C) = 316$ Hz, $^1J(^{117}Sn-^{13}C) = 302$ Hz, $^3J(^{119/117}Sn-CH-Sn-^{13}C) = 7$ Hz]; 13.68 [CH_3 butyl]; 27.60 [$CH_2\gamma$, $^2J(^{119/117}Sn-^{13}C) = 60$ Hz]; 27.62 [$CH_2\gamma$, $^3J(^{119/117}Sn-^{13}C) = 60$ Hz]; 29.28 [$CH_2\beta$, $^2J(^{119/117}Sn-^{13}C) = 19$ Hz]; 29.37 [$CH_2\beta$, $^2J(^{119/117}Sn-^{13}C) = 19$ Hz]; 50.97 [Sn_2CHCH, $^2J(^{119/117}Sn-^{13}C) = 22$ Hz, $^2J(^{119/117}Sn-^{13}C) = 17$ Hz]; 51.98 [CO_2CH_3]; 175.16 [CO_2, $^3J(^{119/117}Sn-^{13}C) = 27$ Hz, $^3J(^{119/117}Sn-^{13}C) = 13$ Hz]. ^{119}Sn NMR (C_6D_6, δ ppm): +0.63 [$^2J(^{119}Sn-C-^{119}Sn) = 145$ Hz, $^2J(^{119}Sn-C-^{117}Sn) = 139$ Hz]; +5.98 [$^2J(^{119}Sn-C-^{119}Sn) = 145$ Hz, $^2J(^{119}Sn-C-^{117}Sn) = 139$ Hz]. MS: m/z (%) = 749 (100) $[M - CO_2Me]^+$, 693 (11) $[M - CO_2Me - C_4H_8]^+$, 621 (35) $[M - CO_2Me - I]^+$, 333 (94) $[M - Bu_3Sn - C_4H_9 - I]^+$, 291 (18) $[Bu_3Sn]^+$, 235 (29) $[Bu_2SnH]^+$, 219 (33) $[M - Bu_3Sn - 3\ C_4H_9 - I]^+$, 179/177 (67/66) $[BuSnH_2]^+$ and $[BuSn]^+$, 121 (23) $[SnH]^+$, 57 (36) $[C_4H_9]^+$.

Compound 5, $(Bu_3Sn)_2CHCH(CH_2NMe_2)CO_2Me$: Yield 15%. Anal. Found: C, 51.36; H, 9.43; Sn, 31.59. Calcd for $C_{31}H_{67}O_2NSn_2$: C, 51.48; H, 9.34; Sn, 32.82. ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 0.52−1.56 [m, 55H, butyl, Sn_2CH]; 1.89−2.02 [m, 1H, CH_2N]; 2.13 [s, 6H, $N(CH_3)_2$]; 2.52−2.64 [m, 1H, $CHCO_2CH_3$]; 2.97−3.09 [m, 1H, $CH_2N(CH_3)_2$]; 3.58 [s, 3H, CO_2CH_3]. ^{13}C NMR ($CDCl_3$, δ ppm): 6.52 [Sn_2CH]; 10.73 [$CH_2\alpha$, $^1J(^{119}Sn-^{13}C) = 312$ Hz, $^1J(^{117}Sn-^{13}C) = 299$ Hz, $^3J(^{119/117}Sn-CH-Sn-^{13}C) = 7$ Hz]; 11.40 [$CH_2\alpha$, $^1J(^{119}Sn-^{13}C) = 316$ Hz, $^1J(^{117}Sn-^{13}C) = 301$ Hz, $^3J(^{119/117}Sn-CH-Sn-^{13}C) = 7$ Hz]; 13.61 [CH_3 butyl]; 27.61 [$CH_2\gamma$, $^3J(^{119/117}Sn-^{13}C) = 62$ Hz]; 29.36 [$CH_2\beta$, $^2J(^{119/117}Sn-^{13}C) = 17.2$ Hz]; 45.39 [Sn_2CHCH, $^2J(^{119/117}Sn-^{13}C) = 18$ Hz]; 45.78 [$N(CH_3)_2$]; 51.54 [CO_2CH_3]; 66.17 [CH_2N, $^3J(^{119/117}Sn-^{13}C) = 46$ Hz, $^3J(^{119/117}Sn-^{13}C) = 19$ Hz]; 177.37 [CO_2, $^3J(^{119/117}Sn-^{13}C) = 34$ Hz, $^3J(^{119/117}Sn-^{13}C) = 15$ Hz]. ^{119}Sn NMR (C_6D_6, δ ppm): +2.26 [$^2J(^{119}Sn-C-^{119}Sn) = 142$ Hz, $^2J(^{119}Sn-C-^{117}Sn) = 135$ Hz]; +5.31 [$^2J(^{119}Sn-C-^{119}Sn) = 141$ Hz, $^2J(^{119}Sn-C-^{117}Sn) = 135$ Hz]. MS: m/z (%) = 666 (18) $[M - CO_2Me]^+$, 58 (100) $[Me_2NCH_2]^+$.

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