^{115}Sn NMR spectroscopy: a useful satellite pattern assignment method in gem-distannyl compounds

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^{115}Sn and ^{119}Sn NMR parameters of diastereotopic tins in model gem-distannyl compounds of the type Sn_2CHR are presented. The use of ^{115}Sn NMR INEPT experiments provides a useful simplification of spectral analysis, resulting in a complete elimination of higher-order homonuclear satellite patterns.

Owing to the known ability of tin to undergo a variety of useful transformations,[1] we recently developed a programme to prepare various organotin compounds as precursors in organic synthesis and were interested in exploring the double hydrostannation of terminal alkynes in the presence of thiol.[2] Thus, using 4-methoxybenzenethiol as catalyst, the hydrostannation of 1-alkynes promotes the formation of 1,1-distannyl adducts.

Structural assignments were based mainly on the ^{119}Sn NMR spectra.[3] Generally, while measurement of couplings is trivial because the spectra of satellite patterns arising from the ^{117}Sn–^{119}Sn and ^{119}Sn–^{119}Sn isotopomers could be analysed according to simple first-order rules, we encountered assignment difficulties when homonuclear higher-order ^{119}Sn–^{119}Sn systems were present. Such behaviour was observed for selected model compounds of the type $(Bu_3Sn)_2CHCH_2CH_2O$-THP **1**, $(Bu_3Sn)_2CHCH_2CH(CH_3)OH$ **2** and $(Bu_3Sn)_2CHCH_2CH(CH_3)OTHP$ **3**. The ^{119}Sn spectra of such compounds are characterised by the appearance of variable intensity lines between the non-coupled tin resonances which cannot be unambiguously assigned. Obviously, the large number of satellite lines due to homo- and hetero-nuclear couplings, associated with the possible presence of monostannylated species signals, renders the spectra of these gem-distannyl compounds more complicated, as shown in Fig. 1. The question is whether these lines could be ascribed to strong coupled ^{119}Sn–^{119}Sn spin systems, whose AB type central lines are superimposed in **1** and slightly separated in **2**†. In compound **3**, each pair of diastereoisomers gives rise to its own strongly coupled satellite system. No significant modification of these spectra has been observed at a higher magnetic field (9.395 T). Hence, the aim of this work is to propose a simple and versatile method for the unambiguous assignment of higher-order ^{119}Sn–^{119}Sn systems.

As a rule, while the conventional gated decoupler method allows routine assignments in monostannylated derivatives with satisfactory sensitivity, refocused INEPT spectra are required in the case of distannyl compounds for an accurate identification of ^{13}C–^{119}Sn and $^{117/119}$Sn–^{119}Sn satellite patterns. gem-Tributyldistannyl compounds, where 24 protons are coupled to the tins, are particularly suitable for producing a strong sensitivity enhancement factor.[4] In refocused INEPT experiments, homo- and hetero-nuclear spin echoes are monitored as a function of the refocusing delay time Δ and are by no means equivalent. Significant intensities and phase modulations of homonuclear satellite patterns could arise with different Δ values. In our first approach to the problem and owing to the critical choice of this time parameter, we developed a fast computer program giving rise to a graphic representation of the variations in signal intensities *versus* Δ values.[6] The prominent feature of this representation is to underscore the possibility of appearance/disappearance, as well as selective inversion, of homonuclear satellite patterns in experimental spectra for characteristic Δ values, while heteronuclear modulations remain unchanged. Unfortunately, this striking property does not apply to the strongly coupled homonuclear spin-systems encountered in compounds **1**–**3**.

To solve the assignment problem we have taken advantage of the low isotopic abundance of the ^{115}Sn magnetically active isotope (natural abundance 0.35%), for which the amount of NMR information available is still rather limited.[7] Experiments were based on the assumption that in ^{115}Sn spectra the ^{115}Sn–^{115}Sn system should be located between the non-coupled ^{115}Sn resonances, by comparison with corresponding lines in ^{119}Sn spectra. Thus, owing to the low isotopic abundance of these species, the ^{115}Sn–^{115}Sn satellite patterns should disappear. As expected, internal lines could not be detected in the ^{115}Sn spectra of compounds **1**–**3**, confirming the assignments in related ^{119}Sn spectra. An example is given for compound **1** in Fig. 1. Hence, ^{115}Sn NMR spectra exhibit only first-order coupling patterns arising from ^{13}C–^{115}Sn couplings and ^{115}Sn–^{117}Sn/^{115}Sn–^{119}Sn isotopomers. In compound **3**, connections between lines belonging to each diastereoisomer could be immediately inferred from the comparison between ^{115}Sn and ^{119}Sn spectra.

In conclusion, in compounds where the statistical distribution and mixing of first-order and higher-order satellite splitting patterns presents some assignment difficulties, the use of ^{115}Sn NMR INEPT spectroscopy leads to a useful simplification in spectral analysis, which can be analysed according to simple first-order rules. This is particularly so in compounds where several tin centres are found in combination with isotopes having similar natural abundances as $^{117/119}$Sn (such as ^{29}Si, ^{77}Se). Moreover, the use of the ^{115}Sn NMR INEPT sequence allows an unambiguous assignment of tin–carbon couplings in the case of interference between $^{2/3}J(^{13}C–^{119}Sn)$ and ^{119}Sn–^{119}Sn satellite patterns, demonstrating that the external lines of the strongly homonuclear ^{119}Sn–^{119}Sn systems do not occur in experimental spectra.

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† Examination of the ^{119}Sn NMR spectrum reveals some discrepancies with the literature data[5] with respect to the reported signs of chemical shifts, which should be positive.

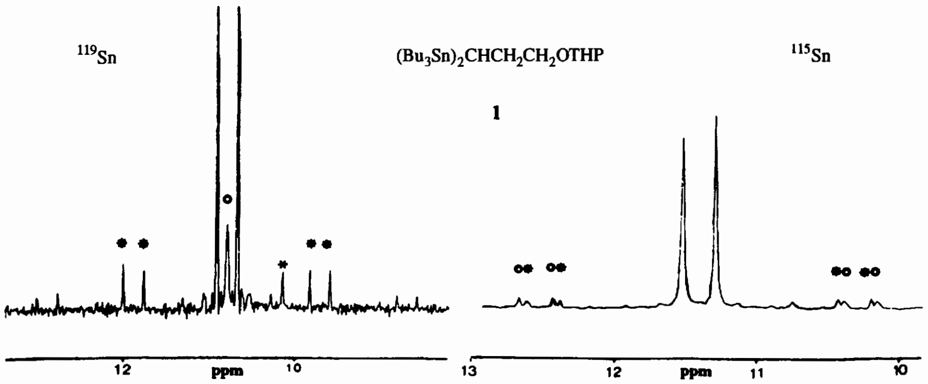

Fig. 1 ^{115}Sn and ^{119}Sn NMR spectra of gem-distannyl compound **1**: the resonances arising from the ^{117}Sn–^{119}Sn and from the ^{119}Sn–^{119}Sn isotopomers are labelled with asterisks and with circles, respectively. The resonances arising from the ^{115}Sn–^{117}Sn and from the ^{115}Sn–^{119}Sn isotopomers are labelled with asterisks and with circles, respectively (*: accompanying impurity).

Experimental

Tin NMR experiments were performed on a Bruker AC-200 spectrometer (^{115}Sn, 65.485 MHz; ^{119}Sn, 74.630 MHz) fitted with an Aspect 3000 data system using a 10 mm broad-band probe. ^{115}Sn and ^{119}Sn spectra were recorded at 22 °C in a 30% (w/v) solution in C_6D_6 for compounds **1**–**3**. ^{119}Sn spectra of compound **2** were recorded in C_6D_6 and $CDCl_3$. Chemical shifts were referenced with respect to Me_4Sn (internal standard) and are expressed as δ_{ppm}. J Values are given in Hz. ^{115}Sn/^{119}Sn chemical shifts and $^2J(^{115}Sn–^{119}Sn)$, $^2J(^{115}Sn–^{117}Sn)$, $^2J(^{117}Sn–^{119}Sn)$ values were determined using INEPT decoupled experiments.[8] Optimization of experimental polarization and refocusing parameters (τ, Δ) were obtained from a previously reported computer program.[6] The following parameters were used: ^{115}Sn 90° pulse: 19 µs, recycle delay: 1 s, H_1 90° pulse: 35 µs, polarization transfer delay: 0.005 s, refocusing delay: 0.002 s; number of scans: 3000 and 128 for ^{115}Sn and ^{119}Sn, respectively. Mass spectral data refer to the ^{120}Sn isotope. New compounds **1**–**3** were prepared according to a preceding report.[2]

Compound 1 $(Bu_3Sn)_2CHCH_2CH_2OTHP$

^{1}H NMR, δ_{ppm} 0.58–1.78 (m, 61 H), 1.96–2.14 (m, CH_2CH_2O), 3.12–3.32 (m, 1 H, OCH_2 ring), 3.36–3.5 (m, 1 H, OCH CH_2OTHP), 3.52–3.66 (m, 1 H, OCH_2 ring), 3.74–3.88 (m, 1 H, CH_2OTHP), 4.48–4.58 (m, OC*H* ring); ^{13}C NMR, δ_{ppm} −0.7 [$Sn_2CH\alpha$, $^1J(^{119}Sn–^{13}C) = 237$, $^1J(^{117}Sn–^{13}C) = 226.5$], 10.1/10.2 [$CH_2\alpha$, $^1J(^{119}Sn–^{13}C) = 307.1$, $^1J(^{117}Sn–^{13}C) = 292.8$], 13.7 ($CH_3$), 19.7 [$O(CH_2)_2CH_2$ ring], 25.6 (OCH_2CH_2 ring), 27.5 [$CH_{2\gamma}$, $^3J(^{117/119}Sn–^{13}C) = 57.2$], 29.4 [$CH_2\beta$, $^2J(^{117/119}Sn–^{13}C) = 19.1$], 30 [$O(CH_2)_3CH_2$ ring], 31.2 [Sn_2CHCH_2, $^2J(^{117/119}Sn–^{13}C) = 21$], 62.3 ($OCH_2$ ring), 71.3 [CH_2OTHP, $^3J(^{117/119}Sn–^{13}C) = 43.9$], 98.8 ($C_q$, *C*H ring). ^{119}Sn NM, δ_{ppm} +11.3 [$^2J(^{117}Sn–C^{119}Sn) = 158.7$, $^2J(^{119}SnC^{119}Sn) = 165.9$], +11.5 [$^2J(^{117}SnC^{119}Sn) = 158.9$, $^2J(^{119}SnC^{119}Sn) = 166.0$]; ^{115}Sn NMR, δ_{ppm} +11.3/+11.5 [$^2J(^{115}SnC^{117}Sn) = 139.3$, $^2J(^{115}SnC^{119}Sn) = 145.4$]; m/z 579/581/583 [$M - C_5H_9O_2 - C_4H_8$]$^+$ (80/100/79), 291/289/287 [Bu_3Sn]$^+$ (31/37/22), 235/233/231 [Bu_2SnH]$^+$ (29/30/18), 179/177/175/173 [$BuSnH_2$]$^+$ and [BuSn]$^+$ (49/61/38/9), 85 [$C_5H_9O_2$]$^+$ (21), 57 [C_4H_9]$^+$ (11) (Calc. for $C_{32}H_{68}O_2Sn_2$: C, 53.21; H, 9.49; O, 4.43; Sn, 32.87. Found: C, 53.25; H, 9.74; O, 4.59; Sn, 33.18%.)

Compound 2 $(Bu_3Sn)_2CHCH_2CH(CH_3)OH$

^{1}H NMR, δ_{ppm} 0.58–1.6 (m, 55 H), 1.16 [d, 3 H, CH_3CH, $^3J(H–H) = 6$], 1.76–1.94 (m, 2 H, CH_2CHOH), 3.42–3.6 (m, 1 H, C*H*OH); ^{13}C NMR, δ_{ppm} 0.18 [$Sn_2CH\alpha$, $^1J(^{119}Sn–^{13}C) = 236.8$, $^1J(^{117}Sn–^{13}C) = 226.6$], 10.11 [$CH_2\alpha$, $^1J(^{119}Sn–^{13}C) = 307.7$, $^1J(^{117}Sn–^{13}C) = 295.4$, $^3J(^{117/119}Sn–CH–Sn-^{13}C) = 6.06$], 10.2 [$CH_2\alpha$, $^1J(^{119}Sn–^{13}C) = 307.8$, $^1J(^{117}Sn–^{13}C) = 295.3$, $^3J(^{117/119}Sn–CH–Sn–^{13}C) = 6.23$], 13.55 ($CH_3$ butyl group), 23.04 (CH_3CHOH), 27.52 [$CH_{2\gamma}$, $^3J(^{117/119}Sn–^{13}C) = 57.2$], 29.26 [$CH_2\beta$, $^2J(^{117/119}Sn–^{13}C) = 19.07$], 40.9 [$CH_2CHOH$, $^2J(^{117/119}Sn–^{13}C) = 20.9$], 71.32 [*C*HOH, $^3J(^{117/119}Sn–^{13}C) = 41.9$]; ^{119}Sn NMR ($C_6D_6$), δ_{ppm} +9.2 [$^2J(^{117}SnC^{119}Sn) = 160.8$, $^2J(^{119}SnC^{119}Sn) = 168.3$], +10.2 [$^2J(^{117}SnC^{119}Sn) = 161.0$, $^2J(^{119}SnC^{119}Sn) = 168.5$]; ^{119}Sn NMR ($CDCl_3$; literature data:[5] −7.35/−8.85), δ_{ppm} +7.4 [$^2J(^{117}SnC^{119}Sn) = 167.4$, $^2J(^{119}SnC^{119}Sn) = 175.1$], +8.7 [$^2J(^{117}SnC^{119}Sn) = 167.4$, $^2J(^{119}SnC^{119}Sn) = 175.1$]; ^{115}Sn NMR, δ_{ppm} +9.3 [$^2J(^{115}SnC^{117}Sn) = 141.2$, $^2J(^{115}SnC^{119}Sn) = 148.0$], +10.3 [$^2J(^{115}SnC^{117}Sn) = 141.4$, $^2J(^{115}SnC^{119}Sn) = 148.5$]; m/z 593/595/597 [$M - C_4H_9$]$^+$ (90/100/79), 287/289/291 [Bu_3Sn]$^+$ (7/12/11), 231/33/235 [Bu_2SnH]$^+$ (11/16/15), 173/175/177/179 [$BuSnH_2$]$^+$ and [BuSn]$^+$ (10/29/41/37), 117/119/121 [SnH]$^+$ (11/8/11), 57 [C_4H_9]$^+$ (11) (Calc. for $C_{28}H_{62}OSn_2$: C, 51.56; H, 9.58; O, 2.45; Sn, 36.40. Found: C, 51.54; H, 9.56; O, 2.68; Sn, 36.16%.)

Compound 3 $(Bu_3Sn)_2CHCH_2CH(CH_3)OTHP$

^{1}H NMR, δ_{ppm} 0.44–2.2 (66 H), 3.24–3.56 (m, 4 H, OCH_2 ring), 3.72–3.9 [m, $CH(CH_3)O$], 4.4–4.58 (m, OC*H* ring); ^{13}C NMR, δ_{ppm} −0.33 [$Sn_2CH\alpha$, $^1J(^{117/119}Sn–^{13}C) = 233.6$, $^1J(^{117/119}Sn–^{13}C) = 231.7$], 10.03/10.08/10.22 [$CH_2\alpha$, $^1J(^{119}Sn–^{13}C) = 301.3/310.9/306.1$, $^1J(^{117}Sn–^{13}C) = 288/299.4/291.8$], 14.11 ($CH_3$, butyl), 18.49/21.03 ($CH_3$–CHOTHP), 20.04/20.37 (C-4, ring), 25.53/25.62 (C-5, ring), 27.9 ($CH_{2\gamma}$), 29.7 ($CH_2\beta$), 31.28/31.38 (C-3, ring), 38.08/38.22 (Sn_2CHCH_2), 62.70/63.05 (C-6, ring), 75.32/77.58 [$CH(CH_3)O$], 96.43/98.93 (C-2, ring); ^{119}Sn NMR, δ_{ppm} diastereoisomer A: +10.6 [$^2J(^{117}SnC^{119}Sn) = 166.1$, $^2J(^{119}SnC^{119}Sn) = 173.7$], +11.5 [$^2J(^{117}SnC^{119}Sn) = 166.0$ Hz, $^2J(^{119}SnC^{119}Sn) = 173.8$]; diastereoisomer B: +10.9 [$^2J(^{117}SnC^{119}Sn) = 168.2$, $^2J(^{119}SnC^{119}Sn) = 175.9$], +11.2 [$^2J(^{117}SnC^{119}Sn) = 168.1$, $^2J(^{119}SnC^{119}Sn) = 176.0$]; ^{115}Sn NMR, δ_{ppm} diastereoisomer A: +10.6 [$^2J(^{115}SnC^{117}Sn) = 145.3$, $^2J(^{115}SnC^{119}Sn) = 152.6$], +11.5 [$^1J(^{115}SnC^{117}Sn) = 146.0$, $^2J(^{115}SnC^{119}Sn) = 152.6$], diastereoisomer B: +11.0 [$^2J(^{115}SnC^{117}Sn) = 147.8$, $^2J(^{115}SnC^{119}Sn) = 154.5$], +11.2 [$^2J(^{115}SnC^{117}Sn) = 147.8$, $^2J(^{115}SnC^{119}Sn) = 154.0$]; m/z 677/679/681 [$M - C_4H_9$]$^+$ (16/18/15), 593/595/597 [$M - C_5H_9O_2 - C_4H_8$]$^+$ (89/100/80), 287/289/291 [Bu_3Sn]$^+$ (11/17/18), 231/233/235 [Bu_2SnH]$^+$ (9/15/15), 173/175/177/179 [$BuSnH_2$]$^+$ and [BuSn]$^+$ (9/28/40/37), 85 [$C_5H_9O_2$]$^+$ (71), 57 [C_4H_9]$^+$ (18) (Calc. for $C_{33}H_{70}O_2Sn_2$: C, 53.83; H, 9.58; Sn, 32.24. Found: C, 53.99; H, 9.90; Sn, 31.97%.)

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