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MULTINUCLEAR NMR SPECTROSCOPY OF (METALLA)NEOPENTYL DERIVATIVES OF TIN AND MERCURY

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Summary

Proton, carbon-13, tin-119 and mercury-199 chemical shift and element–metal coupling constant data are presented for compounds of the types $Sn(CH_2MMe_3)_4$, $Hg(CH_2MMe_3)_2$, $Me_3SnCH_2MMe_3$ and $i\text{-}BuHgCH_2MMe_3$ (M = C, Si, Ge, Sn). In almost all cases the NMR parameters (shifts or coupling constants) involving corresponding organotin and organomercury species are linearly related, suggesting that tin and mercury chemical shifts, and coupling constants between protons or carbon-13 and tin or mercury, are dominated by the same terms, at least as far as the compounds studied are concerned. The electronegativity of M plays an important role in determining the magnitude of metal–carbon (and thus metal–proton) coupling constants.

Introduction

We recently synthesised the complete series of compounds $Me_nSn(CH_2MMe_3)_{4-n}$ with M = C, Si, Ge, Sn and $n = 0$–3 [1]; an NMR investigation of these compounds showed that in all cases the tin chemical shift showed a linear dependence on n. However, for M = C there was a shift to high field when n was decreased, but for M = Si, Ge and Sn a shift to low field [2]. It seemed likely that a combination of steric and electronic factors arising from the (metalla)neopentyl residues determined the tin chemical shift and also the carbon-13 spectral parameters. We considered that it should be possible to separate these factors by comparing the data for $Sn(CH_2MMe_3)_4$ with those for the corresponding mercurials $Hg(CH_2MMe_3)_2$ in which steric interactions between the residues should be very small. Since detailed studies of compounds of the type HgR_2 and i-BuHgR (R = alkyl) have recently been reported in the literature [3], we decided to extend our investigation to include the preparation and study of compounds $i\text{-}BuHgCH_2MMe_3$.

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Experimental

(a) Preparation of compounds studied

The general method of preparation involved the reaction of a Grignard reagent Me_3MCH_2MgHal in THF with the corresponding metal or organometal halide. Exceptions were: (a) $Me_3SnCH_2MMe_3$, M = Sn, from CH_2Cl_2 and Me_3SnLi, (b) $Me_3SnCH_2MMe_3$, M = Ge, from Me_3GeCl and Me_3SnCH_2MgBr, (c) $Hg(CH_2MMe_3)_2$, M = Ge, prepared in two stages via Me_3GeCH_2HgBr (from Me_3GeCH_2MgCl and $HgBr_2$) which was then treated again with Me_3GeCH_2MgCl. Boiling points and yields of new compounds (all of which gave satisfactory elemental analysis data) are as follows: $Sn(CH_2GeMe_3)_4$, b.p. 102–103 °C/0.001 mmHg, 68%; $Sn(CH_2SnMe_3)_4$, m.p. 36 °C, 50%; $Hg(CH_2SiMe_3)_2$, b.p. 92–94 °C/11 mmHg, 87%; $Hg(CH_2GeMe_3)_2$, b.p. 101–102 °C/0.01 mmHg, 34%; $Me_3SnCH_2GeMe_3$, b.p. 56–60 °C/16 mmHg, 62%; $i\text{-}BuHgCH_2CMe_3$, b.p. 102–103 °C/16 mmHg, 40%; $i\text{-}BuHgCH_2GeMe_3$, b.p. 64–66 °C/0.3 mmHg, 71%; $i\text{-}BuHgCH_2SnMe_3$, b.p. 95–98 °C/0.1 mmHg, 44%. $Hg(CH_2SnMe_3)_2$ decomposed on attempted distillation.

Compounds $i\text{-}BuHgCH_2MMe_3$ partially decomposed on standing to give $i\text{-}Bu_2Hg$ and $Hg(CH_2MMe_3)_2$, as shown by the mercury-199 NMR spectra.

(b) NMR Spectra

^1H NMR spectra were recorded using a Varian EM-360 spectrometer. Carbon-13 and tin-119 NMR data were obtained using either a Bruker HFX-90 (magnetic field 2.1 T) or a Bruker AM-300 spectrometer (magnetic field 7.05 T), the latter being used to record the mercury-199 spectra. $CDCl_3$ was used as solvent, internal lock substance and for carbon-13 measurements as internal standard. Proton noise decoupling was used for recording carbon-13 spectra, while tin-119 spectra could be recorded more advantageously using either inversed gated decoupling or the DEPT technique [4]. The latter was found to be ineffective for mercury-199, the increase in the signal to noise ratio being only ca. 2. The main reason for this is that at high field the relaxation of the mercury nucleus is rapid (T_1 for the sample of $Hg(CH_2SiMe_3)_2$ in $CDCl_3$ used for our measurements was 0.07 sec) in comparison with the length of the pulse train ($1/2J$ ca. 0.005 sec). As has been demonstrated by Gillies for diphenyl mercury [5], chemical shift anisotropy is predominantly responsible for the relaxation: this is demonstrated by the fact that the half-width of the satellite lines in the proton spectra due to the $^2J(HgCH)$ coupling increases from 1.6 Hz at 60 MHz to 4.3 Hz at 300 MHz, while that of the CH_2 resonance is constant at 1.6 Hz.

Results and discussion

The NMR parameters of the organotin and organomercury compounds are presented in Tables 1–3.

(a) Tin-119 and mercury-199 chemical shifts

Table 1 contains the relevant data. Regression analysis shows that the chemical shifts for $El(CH_2MMe_3)_n$ are linearly related by equation 1.

$$\delta(Hg) = 1.747\,\delta(Sn) - 70.0\ (r = 0.981) \tag{1}$$

TABLE 1

^{119}Sn AND ^{199}Hg CHEMICAL SHIFTS OF COMPOUNDS $Sn(CH_2MMe_3)_4$, $Hg(CH_2MMe_3)_2$, $Me_3SnCH_2MMe_3$ AND i-$BuHgCH_2MMe_3$ (M = C, Si, Ge, Sn)

(^{119}Sn chemical shifts vs. Me_4Sn, ^{199}Hg chemical shifts with respect to Me_2Hg but measured vs. $Hg(NO_3)_2$ (0.84 *M* in 2*M* HNO_3), the literature value for which is −2361 ppm [12].)

	M			
	C	Si	Ge	Sn
$\delta(^{119}Sn(CH_2MMe_3)_4)$	−53.3	23.0	40.6	87.4[a]
$\delta(^{199}Hg(CH_2MMe_3)_2)$	−149.4[b]	−55.4[c]	−5.2	100.6[d]
$\delta(Me_3{}^{119}SnCH_2MMe_3)$[e]	−14.4	7.6	11.6	23.3[f]
δ(i-$Bu^{199}HgCH_2MMe_3$)	−132.4	−90.9	−65.8	−16.3[g]

[a] $^2J(^{119}Sn-^{119}Sn)$ 281 Hz. [b] Lit. [13] −153 ppm. [c] Lit. [14] −58 ppm. [d] $^2J(^{119}Sn-^{199}Hg)$ 454 Hz. [e] Lit. [15] −14.4, 7.6, 11.4, 23.0 ppm. [f] $^2J(^{119}Sn-^{119}Sn)$ 287 Hz, cf. Lit. [15] 286.1 Hz. [g] $^2J(^{119}Sn-^{199}Hg)$ 508 Hz.

However, while this suggests that the same factors are involved in determining tin and mercury chemical shifts in these compounds, their behaviour is by no means typical for compounds R_4Sn and R_2Hg in general. Thus a regression analysis for six compounds R_4Sn and R_2Hg (R = Me, Et, Pr, i-Pr, Bu, $PhCH_2$) gives equation 2.

$$\delta(Hg) = 14.2\delta(Sn) - 87.8 \ (r = 0.936) \qquad (2)$$

TABLE 2

^{1}H CHEMICAL SHIFTS AND METAL–PROTON COUPLING CONSTANTS FOR COMPOUNDS $Sn(CH_2MMe_3)_4$, $Hg(CH_2MMe_3)_2$, $Me_3SnCH_2MMe_3$ AND i-$BuHgCH_2MMe_3$ (M = C, Si, Ge, Sn) (in ppm vs. TMS and in Hz)

(Chemical shifts and coupling constants agree well with literature data for $Hg(CH_2CMe_3)_2$ [16], $Hg(CH_2SiMe_3)_2$ [17], and $Me_3SnCH_2MMe_3$ [15].)

	M			
	C	Si	Ge	Sn
$Sn(C\mathit{H}_2MMe_3)_4$	1.18	0.15	0.15	−0.25
	(48)	(72)	(64)	(62)
$Hg(C\mathit{H}_2MMe_3)_2$	1.10	0.03	0.25	0.25
	(94)	(128)	(114)	(108)
$Sn(CH_2M\mathit{Me}_3)_4$	1.00	0.05	0.07	0.10
$Hg(CH_2M\mathit{Me}_3)_2$	1.00	0.00	0.15	0.08
$\mathit{Me}_3SnCH_2MMe_3$	0.08	0.08	0.08	0.07
	(56)	(54)	(54)	(54)
$Me_2CHC\mathit{H}_2HgCH_2MMe_3$	1.13	1.15	1.17	1.18
	(96)	(136)	(108)	(104)
$Me_3SnC\mathit{H}_2MMe_3$	0.93	−0.27	−0.13	−0.24
	(56)	(72)	(64)	(62)
$Me_2CHCH_2HgC\mathit{H}_2MMe_3$	0.90	0.00	0.20	0.21
	(78)	(120)	(102)	(98)
$Me_3SnCH_2M\mathit{Me}_3$	0.98	0.00	0.15	0.08
$Me_2CHCH_2HgCH_2M\mathit{Me}_3$	1.00	0.00	0.15	0.08
$Me_2C\mathit{H}CH_2HgCH_2MMe_3$	2.73	2.65	2.73	2.73
	(120)	(106)	(132)	(132)
$\mathit{Me}_2CHCH_2HgCH_2MMe_3$	1.03	0.95	0.97	0.95

TABLE 3

CARBON-13 CHEMICAL SHIFTS AND CARBON–METAL COUPLING CONSTANTS FOR COMPOUNDS $Sn(CH_2MMe_3)_4$, $Hg(CH_2MMe_3)_2$, $Me_3SnCH_2MMe_3$, AND i-$BuHgCH_2MMe_3$ (M = C, Si, Ge, Sn) (in ppm vs. TMS and in Hz)

(Chemical shift and coupling constant data agree within ±0.2 ppm and ±2 Hz with literature data for $Sn(CH_2CMe_3)_4$ [18], $Hg(CH_2CMe_3)_2$ [19], $Me_3SnCH_2MMe_3$ [15] and i-$BuHgCH_2SiMe_3$ [3].)

	M			
	C	Si	Ge	Sn
$Sn(\mathit{C}H_2MMe_3)_4$	33.5	−0.5	−1.6	−10.6
	(301)	(239)	(258)	(268)
$Hg(\mathit{C}H_2MMe_3)_2$	63.2	28.4	30.3	22.4
	(689)	(545)	(601)	(596)
$Sn(CH_2M\mathit{Me}_3)_4$	33.9	2.2	1.7	−8.2
	(31)	(15)	(15)	(9)
$Hg(CH_2M\mathit{Me}_3)_2$	35.8	2.7	2.2	−6.9
	(72)	(42)	(40)	(31)
$\mathit{Me}_3SnCH_2MMe_3$	−8.4	−7.8	−8.1	−7.1
	(317)	(331)	(330)	(320)
$Me_2CH\mathit{C}H_2HgCH_2MMe_3$	56.5	55.2	55.3	55.4
	(676)	(784)	(771)	(779)
$Me_3Sn\mathit{C}H_2MMe_3$	31.3	−3.6	−4.7	−14.8
	(368)	(250)	(258)	(272)
$Me_2CHCH_2Hg\mathit{C}H_2MMe_3$	63.3	29.9	31.7	24.1
	(685)	(446)	(504)	(488)
$Me_3SnCH_2M\mathit{Me}_3$	33.3	1.8	1.0	−7.9
	(35)	(15)	(15)	(-)
$Me_2CHCH_2HgCH_2M\mathit{Me}_3$	35.9	2.9	2.1	−7.0
	(72)	(39)	(38)	(29)
$Me_2\mathit{C}HCH_2HgCH_2MMe_3$	29.9	29.2	29.1	29.2
	(31)	(30)	(34)	(29)
$\mathit{Me}_2CHCH_2HgCH_2MMe_3$	28.4	28.2	28.1	28.3
	(82)	(87)	(85)	(87)

The slope of 1.747 for the (metalla)neopentyl derivatives compares quite well with the ratio of the $\langle r^{-3}\rangle_{np}$ values (1.36) quoted by Webb [6], suggesting that at least in these compounds the paramagnetic term is dominant, while ΔE_{av} in the Karplus–Pople equation [7] for this term plays only a minor role. It should be noted that the chemical shifts for the symmetrical stannaneopentyl derivatives are very extreme for what are formally alkylmetal compounds.

(b) Carbon-13 and proton chemical shifts; metal-element coupling constants

The data are collected in Tables 2 and 3: it can be seen that the trends in both chemical shifts and coupling constants for the analogous tin and mercury compounds are often very similar, particularly in the case of parameters involving carbon-13. Thus in R_4Sn and R_2Hg the following r values are obtained for correlation of: $\delta(\mathit{C}H_2)$ 0.996, ^1J(El–C) 0.997, $\delta(M\mathit{Me}_3)$ (^{13}C) 1.000, ^3J(El–C) 0.998, $\delta(C\mathit{H}_2)$ 0.894, ^2J(El–C–H) 0.998. Though a comparison of $Me_3SnCH_2MMe_3$ and i-$BuHgCH_2MMe_3$ is not strictly valid, the correlation coefficients for corresponding parameters in these series are also of similar magnitudes. Thus again similar factors are involved in determining carbon and proton chemical shifts of the mercury and tin derivatives and the relevant coupling constants.

Radeglia et al. [8] were able to show that a comparison of coupling constant data for compounds R_4Sn, Me_4Sn and R_nSnMe_{4-n} ($n = 1$–3) yields the following relation between the ^1J(Sn–C) values:

$$J^1/J^3 = (-nJ^2/J^4 + 4)/4 - n \qquad (3)$$

where J^1 and J^2 are $^1J(\text{Sn–C}_{\text{Me}})$ and $^1J(\text{Sn–C}_{\text{R}})$ in the mixed compounds, J^3 the value for Me_4Sn and J^4 that for R_4Sn. We found this relation to apply to derivatives with M = C, Si and Ge but not to stannaneopentyltin compounds, the deviation from ideality increasing with increasing n.

The same authors had previously [3] studied isobutylmercury compounds $^{i}Bu_2Hg$ and $^{i}BuHgR$ and found the following relation to apply:

$$J^1/J^3 = -J^2/J^4 + 2 \qquad (4)$$

where J^1 and J^2 are $^1J(\text{Hg–C}_{\text{i-Bu}})$ and $^1J(\text{Hg–C}_{\text{R}})$ in the mixed compounds, J^3 the value for $^{i}Bu_2Hg$ and J^4 that for R_2Hg. They could also show that the equations 5 and 6 were obeyed

$$J^1 + J^2 = J^3 + J^4 \qquad (5)$$

$$\delta^1 + \delta^2 = \delta^3 + \delta^4 \qquad (6)$$

We found that equations (4) and (5) are satisfied in all cases except that when M = Si eqn. 4 shows a slight deviation. Eqn. 6 applies in all cases.

When analysing the chemical shift and coupling constant data in these compounds one must remember that each of the four series contains the fragment $M^{\delta+}$–$CH_2{}^{\delta-}$–$El^{\delta'+}$ and that the electronegativity difference between M and El is constantly being changed when M changes, so that $\delta+$, $\delta-$, and $\delta'+$ are also changing. The Pauling electronegativities are as follows: C 2.5, Si 1.8, Ge 1.8, Sn 1.8 and Hg 1.9; while it is accepted that the electronegativities of silicon and germanium are almost equal, that of tin is subject to discussion.

In both $Me_3SnCH_2MMe_3$ and i-$BuHgCH_2MMe_3$ the CH_2 carbon shift is almost equal for M = Si and Ge but shifted somewhat for M = Sn, indicating that the tin electronegativity may in fact be lower than that of silicon and germanium. The chemical shift of the CH_2 carbon of the isobutyl group in i-$BuHgCH_2MMe_3$ is almost independent of M, as is the methyltin carbon shift in $Me_3SnCH_2MMe_3$.

We have previously [2] noted that in compounds of the type $Me_nSn(CH_2MMe_3)_{4-n}$ ($n = 1$–3) the relative magnitudes of $^1J(\text{Sn–}C\text{H}_3)$ and $^1J(\text{Sn–}C\text{H}_2)$ change on going from M = C to M = Si; the same is clearly true for ^1J(HgC) in compounds i-$BuHgCH_2MMe_3$. Our earlier suggestion that this is due to rehybridisation should perhaps be modified by including the effect of the electronegativity of M on the effective nuclear charge of the methylene carbon atom: this should decrease appreciably when M changes from carbon to silicon, germanium or tin. Thus $^1J(\text{El–}C\text{H}_2)$ decreases and rehybridisation causes an increase in $^1J(\text{Sn–}C\text{H}_3)$ or $^1J(\text{Hg–}C\text{H}_2\text{-i-Pr})$.

Because of the differing signs of ^1J(Sn–C) and ^1J(Hg–C), the foregoing discussion has only involved the magnitudes of these coupling constants. However, when the variations in ^nJ(El–C) and ^{n+1}J(El–H) are compared, signs must be taken into account. For El = Sn, we have three sets of values for $n = 1$; for El = Hg there is additionally one set for $n = 2$. We can assume that ^1J(Hg–C) is positive [9], ^1J(Sn–C) negative [10], ^2J(HgCH) negative [9], ^2J(SnCH) positive [11], ^2J(HgCC) negative and

^3J(HgCCH) positive [9]: on the basis of these assumptions, ^nJ(El–C) and ^{n+1}J(ElH) show fair ($r = 0.709$) to very good ($r = 0.997$) linear correlations, except for $n = 2$ (El = Hg), where the correlation is very poor. However, while ^1J(ElC) and ^2J(ElH) change in the same direction in $\mathrm{El(CH_2MMe_3)}_n$ and in the neopentyl fragments of $\mathrm{Me_3SnCH_2MMe_3}$ and i-$\mathrm{BuHgCH_2MMe_3}$, the opposite is true for the $\mathrm{CH_2Hg}$ fragment in $\mathrm{(Me_2CH)}\mathit{CH_2Hg}\mathrm{(CH_2MMe_3)}$: the reason for this difference in behaviour is unclear.

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