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ORGANOMETALLIC COMPOUNDS

XLI*. NMR SPECTRA OF STANNACYCLOALKANES

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Summary

The NMR-spectra of stannacycloalkanes are described. The validity of the additivity relationships for chemical shift and coupling constant is discussed.

The NMR data for some stannacyclo-pentanes, -hexanes and -heptanes are given in Tables 1 to 3.

TABLE 1

NMR SPECTRA OF STANNACYCLOHEXANES $MeRSn(CH_2)_5$ IN CCl_4 (TMS = 0)

R	δ(Me) (ppm)	δ(R) (ppm)	$J(^{117/119}Sn—Me)$ (Hz)		Additional data
Me	0.096		51.4	53.7	$\delta(CH_2)_\alpha$ 0.93 ppm; $J_{\alpha\beta}$ 7.0 Hz
Et	0.058		49.4	51.5	
n-Pr	0.060		48.9	51.1	
i-Pr	0.019		47.3	49.5	
n-Bu	0.057		49.1	51.4	
i-Bu	0.080		48.8	51.0	
s-Bu	0.032		47.3	49.4	
t-Bu	0.005	1.14	46.6	48.6	$J(^{117/119}Sn—t\text{-}Bu)$ 61.8/64.6 Hz
i-Pent	0.055		48.8	51.3	
neo-Pent	0.102		48.6	50.9	δ(t-Bu) 0.995 ppm; $\delta(CH_2)$ 1.0 ppm
cyclo-Pent	0.027		48.1	50.3	
cyclo-Hex	0.010		47.4	49.6	
Ph	0.300		52.0	54.4	$\delta(CH_2)_\alpha$ 1.165 ppm; $J_{\alpha\beta}$ 5.5 Hz
Cl	0.780		55.2	57.6	$\delta(CH_2)_\alpha$ 1.182 ppm; $J_{\alpha\beta}$ 6.5 Hz
Br	0.790		54.8	57.4	$\delta(CH_2)_\alpha$ 1.455 ppm; $J_{\alpha\beta}$ 6.0 Hz

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* The synthesis and the mass spectra of these compounds have been described in part XL [1].

TABLE 2

NMR SPECTRA OF STANNACYCLOPENTANES $MeRSn(CH_2)_4$ IN CCl_4 (TMS = 0)

R	δ(Me) (ppm)	δ(R) (ppm)	$J(^{117/119}Sn—Me)$ (Hz)		$\delta(CH_2)_\alpha$ (ppm)	$\delta(CH_2)_\beta$ (ppm)	$J(Sn—CH_2)\beta$ (Hz)
Me	0.195		52.7	54.9	0.71	1.6 (q)	~75
neo-Pent	0.162	t-Bu 1.0 CH_2 1.17	49.8	52.0	0.76	1.65 (q)	
Cl	0.87		56.8	59.1	1.125	1.79	
Ph	0.435	7.1	53.0	55.4	0.983	1.76 (q)	~75

TABLE 3

NMR SPECTRA OF STANNACYCLOHEPTANES $MeRSn(CH_2)_6$ IN CCl_4 (TMS = 0)

R	δ(Me) (ppm)	δ(R) (ppm)	$J(^{117/119}Sn—Me)$ (Hz)		$\delta(CH_2)_\alpha$ (ppm)	$J_{\alpha\beta}$ (Hz)
Me	0.060		49.0	51.3	0.91 (t)	6.0
Ph	0.268	7.25	49.4	51.8	1.185	

The chemical shift and the additivity relationship

Sisido has described an additivity relationship [2] which can be rewritten as follows:

$$\delta(RR'R''Sn—CH_3)(ppm) = 0.057 + \lambda(R) + \lambda(R') + \lambda(R'').$$

This relationship can be applied to mixed tetraorganotin compounds [3] to yield λ-values for a variety of organic ligands. Results are shown in Table 4.

In many cases, there is a reasonable agreement between calculated and experimental chemical shifts. However, for some compounds, a quite marked deviation (up to 2.2 Hz at 60 MHz) is observed (see Table 5). Therefore, this additivity rule must be used with caution.

From our results on stannacyclohexanes $MeRSn(CH_2)_5$ (Table 1), one can calculate $\lambda[(CH_2)_5]$ = 0.037 ppm. Table 6 reveals that, surprisingly enough,

TABLE 4

λ-VALUES OF ORGANIC LIGANDS

R	λ(R)(ppm)	Ref.
Me	0	2
Et	−0.035	2
n-Pr	−0.024	
i-Pr	−0.063	
n-Bu	−0.030	2
s-Bu	−0.046	
t-Bu	−0.055	
cyclo-Pent	−0.063	
cyclo-Hex	−0.057	
Ph	0.207	2
Benz	−0.073	2

TABLE 5

COMPARISON OF CALCULATED AND EXPERIMENTAL $\delta(CH_3)$-VALUES OF MIXED TETRAORGANOTIN COMPOUNDS

RR'R"SnMe	$\delta_{calc}(CH_3)$ = 0.057 ppm + λ(R) + λ(R') + λ(R")	$\delta_{exp}(CH_3)$ (ppm)	$\Delta\delta$(Hz) at 60 MHz
PhSnMe$_3$	0.264	0.267	0.2
Ph$_2$SnMe$_2$	0.471	0.475	0.2
Ph$_3$SnMe	0.678	0.676	−0.1
Benz-t-BuSnMe$_2$	−0.071	−0.041	1.8
Benz$_2$-t-BuSnMe	−0.144	−0.176	−1.9
Benz-t-Bu$_2$SnMe	−0.126	−0.163	−2.2
t-BuSnMe$_3$	0.002	0.000	−0.1
t-Bu$_2$SnMe$_2$	−0.053	−0.053	0
t-Bu$_3$SnMe	−0.108	−0.11	−0.1
t-Bu-cyclo-HexSnMe$_2$	−0.055	−0.080	−1.5
t-Bu-cyclo-PentSnMe$_2$	−0.061	−0.068	−0.4
s-BuEtSnMe$_2$	−0.024	−0.018	0.4
s-BuPrSnMe$_2$	−0.013	−0.013	0 [a]
s-Bu-i-PrSnMe$_2$	−0.052	−0.052	0 [a]
s-Bu-t-BuSnMe$_2$	−0.044	−0.050-0.057	−0.4-0.8
s-BuPhSnMe$_2$	0.218	0.237	1.1
s-Bu-n-BuSnMe$_2$	−0.019	−0.018	0.1
s-BuBenzSnMe$_2$	−0.062	−0.068	−0.4
s-Bu-cyclo-PentSnMe$_2$	−0.052	−0.048	0.2
s-Bu-cyclo-HexSnMe$_2$	−0.046	−0.058	−0.7
Ph-cyclo-HexSnMe$_2$	0.207	0.215	0.5
Ph-cyclo-Hex$_2$SnMe	0.150	0.153	0.2
Ph$_2$-cyclo-HexSnMe	0.414	0.420	0.4
PhBu$_2$SnMe	0.204	0.204	0
PhEt$_2$SnMe	0.194	0.194	0

[a] These products have been used to determine λ(n-Pr), λ(i-Bu) and λ(i-Pr) given in Table 4.

the agreement between calculated and experimental values is reasonable except for R = t-Bu and cyclo-Hex.

The $\delta(CH_3)$-values for the two stannacycloheptanes (Table 3) give $\lambda[(CH_2)_6]$ = 0.003, and the agreement is excellent. For the stannacyclopentanes,

TABLE 6

COMPARISON OF CALCULATED AND EXPERIMENTAL $\delta(CH_3)$-VALUES OF 1-ALKYL- AND 1-PHENYL-1-METHYL-STANNACYCLOHEXANES $RCH_3Sn(CH_2)_5$

R	$\delta_{calc}(CH_3) = 0.057 + \sum_i \lambda_i$ (ppm)	$\delta_{exp}(CH_3)$ (ppm)	$\Delta\delta$(Hz) at 60 MHz
Me	0.094	0.096	0.1
Et	0.059	0.058	−0.1
n-Pr	0.070	0.060	−0.6
i-Pr	0.031	0.019	−0.7
n-Bu	0.064	0.057	−0.4
i-Bu	0.083	0.080	−0.2
s-Bu	0.048	0.032	−1.0
t-Bu	0.039	0.005	−2.0
cyclo-Pent	0.037	0.027	−0.6
cyclo-Hex	0.037	0.010	−1.6
Ph	0.301	0.300	−0.1

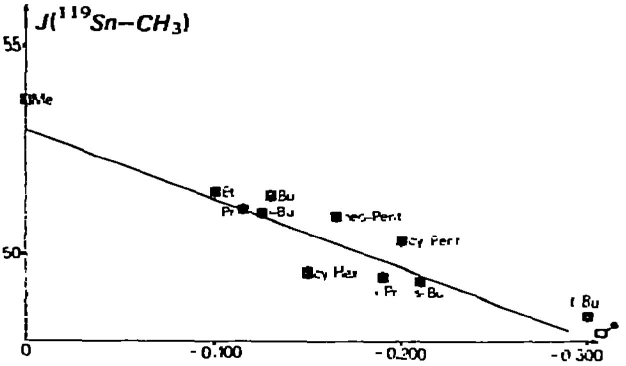

Fig. 1. Correlation between $J((^{119}Sn-CH_3)[(CH_2)_5SnMeR])$ and $\sigma^*(R)$.

the agreement is not so good (derivation of $\lambda(CH_2)_4$ from $\delta(CH_3)(Me_2Sn(CH_2)_4)$, gives 0.138; calculation of $\delta(CH_3)(MePhSn(CH_2)_4)$ gives 0.402 instead of 0.435, corresponding with an error of 2 Hz at 60 MHz).

The coupling constant and the additivity relationship

An analogous additivity relationship has been described for the Sn—CH$_3$ coupling constants [3]:

$$J((^{117}Sn-CH_3)(CH_3SnRR'R'')) = \chi(R) + \chi(R') + \chi(R'').$$

TABLE 7

COMPARISON OF CALCULATED AND EXPERIMENTAL COUPLING CONSTANTS $J(^{117}Sn-C^1H_3)$

	$\chi(R)$	$J_{calc}(^{117}Sn-C^1H_3)$ (Hz)	$\Delta J = J_{exp} - J_{calc}$ (Hz)
R in $(CH_2)_4SnMeR$			
Me	17.3 (3)	52.3	0.4
neo-Pent	15.3 (4)	50.3	—0.5
Ph	17.7 (3)	52.3	—0.1
R in $(CH_2)_5SnMeR$			
Me	17.3 (3)	51.1	0.3
Et	15.7 (3)	49.4	0
n-Pr	15.6 (5)	49.4	—0.5
i-Pr	13.9 (5)	47.7	—0.4
n-Bu	15.6 (5)	49.4	—0.3
i-Bu	15.3 (5)	49.1	—0.3
s-Bu	13.8 (7)	47.6	0.7
t-Bu	12.8 (3)	46.6	0
neo-Pent	15.3 (4)	49.1	—0.5
cyclo-Pent	14.5 (3)	48.3	—0.2
cyclo-Hex	14.0 (3)	47.8	—0.4
Ph	17.7 (3)	51	0.1
R in $(CH_2)_6SnMeR$			
Me	17.3 (3)	49.0	0
Ph	17.7 (3)	49.0	—0.4

From the data in Tables 1 to 3, one can determine $\chi(CH_2)_4$ = 35, $\chi(CH_2)_5$ = 33.8 and $\chi(CH_2)_6$ = 31.7. Table 7 gives the coupling constants calculated with this additivity relationship along with the experimental values. The agreement is quite good. The $J(Sn—CH_3)$ coupling constants have also been correlated with the inductive effects of the ligands [3]. This type of correlation is also valid for the stannacyclohexanes described in this paper, (see Fig. 1) (r = 0.879), even if it is less satisfactory than in other series [3, 4].

The $J(Sn—CH_3)$ coupling constants in dimethylstannacycloalkanes can also be used to estimate the CH_2SnCH_2 angle (β) of the heterocycle [and the CH_3-$SnCH_3$ one (α)] [4]. One finds β = 109° (α = 109.7°) for the stannacyclopentane, β = 109.7° (α = 109°) for $(CH_2)_5SnMe_2$ and β = 111° (α = 108°) for the stannacycloheptane.

The IR spectra of stannacycloalkanes

The IR spectra of stannacycloalkanes [5-7] show characteristic bands for stannacyclopentanes at 1015 cm^{-1}, associated with bands at 1020 and 1040 cm^{-1}, in the absence of a phenyl group bound to tin. For stannacyclohexanes there are two strong absorptions at 970 and 905 cm^{-1}. We do not have enough information to propose characteristic bands for stannacycloheptanes.

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