Journal of Organometallic Chemistry, 107 (1976) C5—C10

Preliminary communication

CONFORMATIONAL EQUILIBRIA IN CYCLOHEXYLTRIMETHYLSTANNANE AND CYCLOHEXYLTRIMETHYLPLUMBANE BY LOW TEMPERATURE ^{13}C NMR SPECTROSCOPY

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(Received December 10th, 1975)

Summary

The variable temperature carbon-13 NMR spectra of cyclohexyltrimethylstannane and cyclohexyltrimethylplumbane have been recorded, and at $-69°$C, the chair—chair conformational interconversion is "frozen". A values ($A = -\Delta G° = RT \ln K$) for the $(CH_3)_3Sn$ (1.06 ± 0.14) and $(CH_3)_3Pb$ (0.67 ± 0.06) groups are derived.

The factors determining the "effective steric sizes" of metal containing groups are poorly understood [1,2], yet this understanding is crucial for detailed discussions of reactivity as well as spectroscopic and structural properties. A useful measure of steric interactions is the A value [3,4] ($A = -\Delta G° = RT \ln K$) where $\Delta G°$ is the difference in free-energy content (kcal/mol) between the *axial* and *equatorial* cyclohexane derivatives, and for the magnesium [5] and mercury [1,2] compounds, A values have been determined. Although compounds of the type $RM(CH_3)_3$ (R = organic group; M = Si, Ge, Sn, Pb) have been widely studied in a variety of connections, no direct assessment of the A values of the $M(CH_3)_3$ moieties have been reported**. In this Communication we wish to report direct observation of the *axial* conformers of the title compounds by ^{13}C NMR spectroscopy, and A values of the $(CH_3)_3Sn$ and $(CH_3)_3Pb$ groups.

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**The $(CH_3)_3Si$ group has been suggested to be similar to a t-butyl group [6a]. An estimate of the "steric bulk" of $(CH_3)_3Sn$, based on rates of epoxidation and hydroboration of certain *syn*-7-substituted norbornenes, has been made and the "steric hindrance" sequence t-Bu > CH_3 > Br > $(CH_3)_3Sn$ > Cl > H was observed [6b].

TABLE 1

CARBON-13 NMR DATA[a] FOR CYCLOHEXYLTRIMETHYLSTANNANE (A) AND CYCLOHEXYLTRIMETHYLPLUMBANE (B) UNDER VARIOUS CONDITIONS

Compound	Conditions	C(1)	C(2,6)	C(3,5)	C(4)	$J(M(CH_3)_3)$
A	67.8 MHz; 35°C (CD_2Cl_2)	25.78 (384.5) [b]	31.18 (nr) [c]	28.83 (57.7) [d]	27.16 (nr) [e]	−11.60 (286.6; 299.4)
A (*Equatorial*)	67.8 MHz; −69°C (CD_2Cl_2)	24.75 (403.8; 385.4)	30.87 (nr)	28.98 (65.0)	26.93 (nr)	−11.92 (285.6; 299.4)
A (*Axial*)		nl —	nl —	25.89 (nr)	nl —	− 9.18 (278.9; 295.5) [f]
A	25.2 MHz; 35°C ($CDCl_3$)	25.9 (nd) [g]	31.26 (15.3) [c]	28.79 (58.0) [d]	27.15 (nr) [e]	−11.66 (289.9; 303.0)
A (*Equatorial*)	25.2 MHz; −60°C ($CDCl_3$)	24.45 (nd) [g]	30.78 nd	28.79 (65.9)	26.78 (nr)	−12.00 (288.7; 302.1)
A (*Axial*)		nl —	nl —	25.76 (nr)	nl —	− 9.27 (nd)
B	22.6 MHz; 35°C ($CDCl_3$)	36.95 (417.5)	33.77 (21.36)	29.32 (97.7)	27.00 (nr)	− 4.86 (~150 Hz)
B	67.8 MHz; 35°C (CD_2Cl_2)	36.75 (413.8)	33.64 (nr) [h]	29.29 (97.0)	26.98 (nr)	− 4.83 (142.8)
B (*Equatorial*)	67.8 MHz; −70°C (CD_2Cl_2)	35.04 (415.6)	33.66 (nr) [h]	30.06 (121.8)	26.75 (nr)	− 5.31 (148.3)
B (*Axial*)		38.72 (nd) [i]	32.19 (nr)	25.88 (nr) [h]	26.75 (nr)	− 3.18 (147.1)
Bicyclohexyl	67.8 MHz; 35°C (CD_2Cl_2)	43.41	30.20	26.98	26.98	—
	Reported [18] ($CDCl_3$)	44.0	30.4	27.0	27.0	—

[a] Chemical shifts in ppm (± 0.05) relative to internal TMS. Values in parentheses are coupling constants to ^{117,119}Sn (in A) and ^{207}Pb (in B). For smaller couplings, not separately resolved to ^{117}Sn, ^{119}Sn, nr = not resolved; nl = not located; nd = not determined. [b] Based on observation of one satellite pattern only. A value of 407.4 Hz for ^{119}Sn has been reported [8]. [c] Reported [8] as 14.4 Hz. [d] Reported [8] 57.5 Hz. [e] Reported [8] ca. 5 Hz. [f] These values from a −69°C spectrum at 22.63 MHz. From our expanded spectrum (at 67.8 MHz) the satellites are clear (but broad) and not resolved separately to ^{117,119}Sn. [g] Obvious in spectrum but not registered in computer printout. [h] Broadening at base of peak due to ^{207}Pb coupling. [i] Satellites obvious in Fig. 2 but not registered in printout.

The 67.8 MHz proton-noise-decoupled ^{13}C NMR spectrum of cyclohexyltrimethylstannane [7,8] * at 35°C (CD_2Cl_2 solvent) exhibits signals at −11.66 (CH_3), 25.78 (C(1)), 31.8 (C(2,6)), 28.83 (C(3,5)) and 27.16 ppm (C(4)), together with satellite patterns due to ^{117,119}Sn—^{13}C coupling [8,9] (Table 1). Assignments were made by considerations of signal intensities, multiplicities in off-resonance decoupled spectra, chemical shifts and ^{117,119}Sn—^{13}C couplings. As the temperature is lowered**, the C(1), C(3,5) and CH_3 signals broaden (−30°C). At −60°C, the C(4) signal also exhibits broadening, but the C(2,6) signal remains sharp. At −69°C (67.8 MHz)*** (Fig. 1), two signals are resolved in the region to high field of TMS, at −9.18 and −11.92 ppm, with the latter signal far more intense. Both signals § are attended by ^{117,119}Sn satellites, identifying them as $(CH_3)_3Sn$ resonances. A new signal appears at 25.89 ppm also. These spectral changes are reversible with temperature, and are

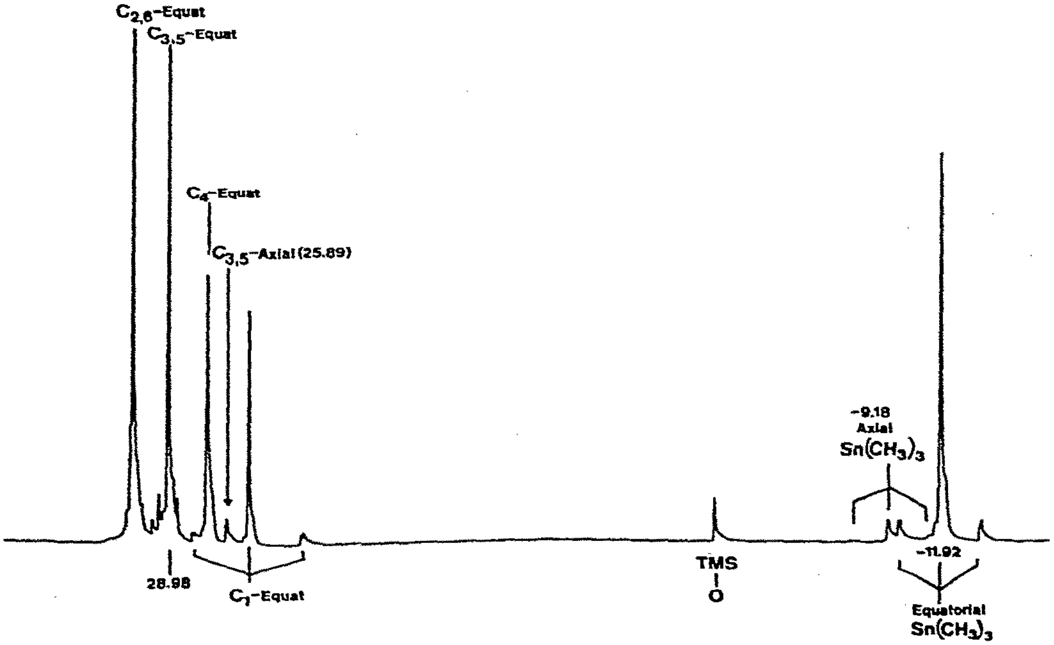

Fig. 1. Proton decoupled (270 MHz) carbon-13 (67.8 MHz) NMR spectrum of cyclohexyltrimethylstannane (ca. 20% by volume in CD_2Cl_2) at −70°C. The signals associated with the *axial* and *equatorial* conformers are indicated and listed in Table 1. An expanded and amplified trace of the $(CH_3)_3Sn$ region clearly shows the ^{117,119}Sn satellites about the *axial* $Sn(CH_3)_3$ resonance.

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*Satisfactory ^{1}H NMR spectrum was obtained. Sample 20% by volume. Chemical shifts relative to internal TMS.

**On the Varian XL-100 at Purdue University.

***On the 67.8 MHz Bruker NMR Spectrometer at National NMR Center, Canberra, Australia. Similar observations were made at −61°C (dial) on the Varian XL-100 and −69°C on the (22.62 MHz) Bruker HX-90 of the University of Adelaide. We thank Mr Evan Williams for obtaining this latter set of spectra.

§The satellites are obvious about the major $(CH_3)_3Sn$ resonance in Fig. 1, and clearly about the minor $(CH_3)_3Sn$ signal in an expanded and amplified spectrum. (4400 scans). These results were duplicated on the Bruker HX-90 of the University of Adelaide. (See Table 1).

consistent with the "freezing" of chair—chair conformational interconversion*. The signals at −9.18** and 25.89 ppm*** are assigned to $(CH_3)_3Sn$ and C(3,5) in the *axial* conformer, with the signal at −11.92 ppm representing the *equatorial* $Sn(CH_3)_3$. As anticipated, *vicinal* $^{117,119}Sn—^{13}C$ coupling (i.e. to C(3,5)) in the "frozen" equatorial conformer is larger (65.0 Hz) than *vicinal* coupling in the "averaged" 35°C spectrum (J_{av} = 57.7 Hz). The dihedral angle (θ) in the former case is 180° [9], whereas it must be smaller in the latter circumstance ($\theta_{av} < 180°$) when the *axial* population is significant. Careful measurements

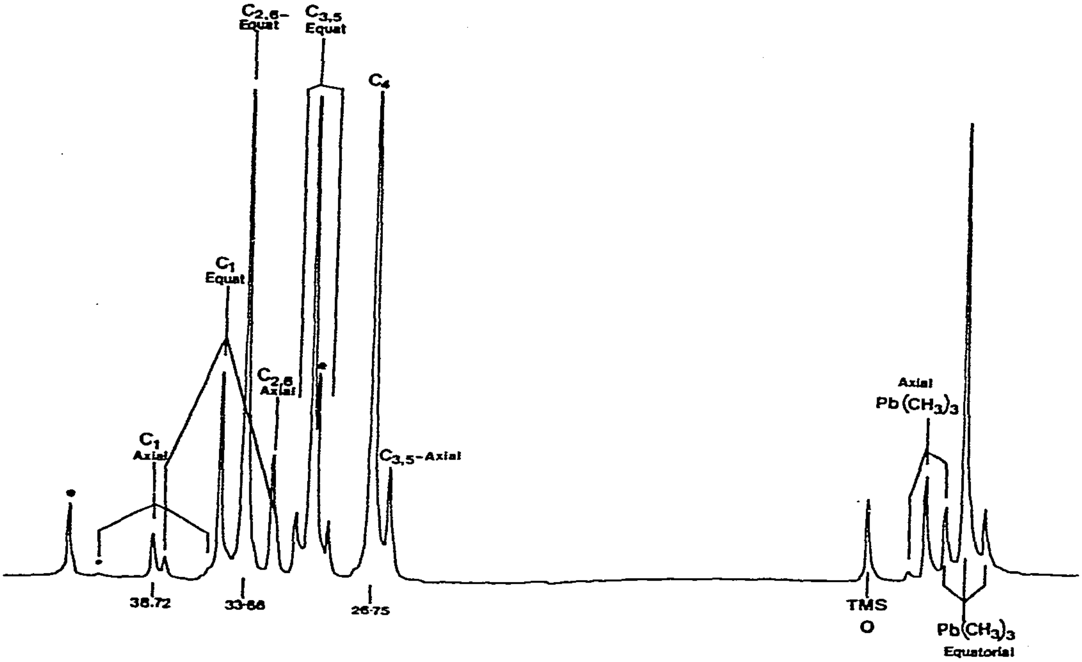

Fig. 2. Proton decoupled (270 MHz) carbon-13 (67.8 MHz) NMR spectrum of cyclohexyltrimethylplumbane (Ca. 20% by volume in CD_2Cl_2) at −70°C. The signals assoicated with the *axial* and *equatorial* conformers are indicated and listed in Table 1. The resonance marked with asterisk are due to ca. 10% of bicyclohexyl. The C(3,5) and C(4) resonances of this contaminant are coincident with C(4) of the lead compound.

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[*] In principle, duplication of all signals should occur, but significant chemical shift differences between conformers are required for detection. It would be anticipated that $(CH_3)_3Sn$, C(1) and C(3,5) would show the largest differences. Lack of duplication of the C(4) signals, is not surprising, considering the relative remoteness from the substituent. C(1) in the *axial* conformer was not identified but in all likelihood is hidden beneath one of the intense signals of the *equatorial* conformer at lower field.

[**] In the only other analogous situation known to us involving steric compression of $(CH_3)_3Sn$, i.e. in *exo*- and *endo*-2-norbornyltrimethylstannanes [9], the $(CH_3)_3Sn$ resonance in the *endo* isomer is 0.6 ppm to lower field than that in *exo*. Stereochemically more rigid cyclohexyl systems are being examined, and data obtained for 4-alkylcyclohexyltrimethylstannanes (*cis* and *trans*) fully support the above assignments [10].

[***] γ-effects of $(CH_3)_3Sn$ are negative in situations of compressional interaction, e.g. C(6) in *endo*-2-norbornyltrimethylstannane exhibits a γ-effect of −0.4 ppm, but positive otherwise, e.g. C(6) in *exo*-2-norbornylisomer exhibits a γ-effect of +3.3 ppm [9]. These γ-effects will be discussed more fully elsewhere. The intensity of the 25.89 ppm signal and its chemical shift are consistent with C(3,5) in the *axial* conformer.

of the areas of the CH_3 signals show 7.0 ± 2% of *axial* conformer present at -69°C, providing an *A* value of 1.06 ± 0.14.

In the case of cyclohexyltrimethylplumbane*, the 35°C spectrum (67.8 MHz, CD_2Cl_2 solvent)** is easily assigned as follows: $(CH_3)_3Pb$ (-4.83 ppm, $J(^{207}Pb—^{13}C)$ 142.8 Hz), C(1) (36.75; *J* 413.8 Hz); C(2,6) (33.64; *J* 21.36 Hz), C(3,5) (29.29; *J* 97.0 Hz) and C(4) (26.98 ppm). Rich detail appears in the low temperature (-69°C) spectrum where duplication of resonances (other than for C(4) for the *axial* and *equatorial* conformers appears (Fig. 2). The full listing is located in Table 1, and $^{207}Pb—^{13}C$ coupling [12] (^{207}Pb is 21.11% naturally abundant; $I = ½$) is clearly visible. At -69°C, 16 ± 2% of *axial* conformer is present***, providing an *A* value of 0.67 ± 0.06 for the $(CH_3)_3Pb$ group. *Vicinal* $^{207}Pb—^{13}C$ coupling appears to be dihedral angle dependent also [12], as the value in the "frozen" equatorial conformer (θ 180°, *J* 121.8 Hz) is significantly larger than the "averaged" situation at 35°C (J_{vic} 97.7 Hz). Taking δ(C) of cyclohexane as 27.00 ppm, α, β and γ-effects of *axial* and *equatorial* $Pb(CH_3)_3$ groups are (+11.7, +5.19 and -1.12) and (+8.04, +6.7 and +3.0 ppm) respectively. For *equatorial* $Sn(CH_3)_3$, comparable values are -2.95, +3.87 and +1.98 ppm, while the γ-effect of *axial* $Sn(CH_3)_3$ is -1.11 ppm.

As judged by these *A* values, the steric requirements of $Sn(CH_3)_3$ and $Pb(CH_3)_3$ are certainly smaller than those of t-butyl (estimated [13] > 4.5) and methyl (1.5 - 1.9) [14], despite the larger atomic radii of tin (1.405) and lead (1.750) compared with carbon (0.772), and larger group geometric sizes [15]. However, size is not always a reliable criterion in this regard [1], and variation in the bond lengths [15] (C—C, 1.534; C—Sn, 2.18; C—Pb, 2.20 Å) with relief of energy-raising interactions may be more important [1]. Polarisability effects [1], and the relatively polar nature of the carbon—metal bonds which could conceivably engage in favorable 1,3 diaxial interactions deserve attention also. Reliable estimates of the *A* values of $(CH_3)_3Ge$ and $(CH_3)_3Si$ have not yet been obtained, but there is no doubt that the values are larger than 1.0§ [16].

Extensive studies by ^{13}C NMR of a range of metal-containing groups X in cyclo-$C_6H_{11}X$ and related compounds are being conducted, and we hope that they will define more adequately the factors regulating these conformational preferences.

Acknowledgements

This research was generously supported by the Australian Research Grants

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*From "cyclohexylmagnesium bromide" in ether, and $(CH_3)_3PbCl$ in THF. Distilled as a colorless liquid b.p. 44-46°C (2 mm Hg) with an appropriate ^1H NMR spectrum. It was contaminated with ca. 10% of bicyclohexyl (as judged from the ^{13}C spectrum) confirmed by the identity of its ^{13}C chemical shifts with those of the authentic compound. Found: C, 36.14; H, 6.67%. This corresponds to 92.75% of cyclohexyltrimethylplumbane, admixed with 7.25% of bicyclohexyl. Some decomposition during distillation apparently occurs [11].

**Sample 20% by volume. Chemical shifts relative to internal TMS.

***Several measures of relative intensities are available, e.g. $(CH_3)_3Pb$, C(1) resonances, and with more difficulty C(3,5) and C(2,6). The comparisons assume that relaxation times for similar carbons in the two conformers are essentially identical. Since concordant conclusions from all estimates were obtained, we believe the error limits cited are realistic. Attempts to observe separate $(CH_3)_3Sn$ ^1H resonances at 270 MHz at -100°C were not successful.

§In the $(CH_3)_3Si$ group, $\Delta G^\circ(Si(CH_3)_3)$ may be so large that low-temperature examination by NMR will be unrewarding, and some special technique may be required [16].

Committee which also provided access to the 67.8 MHz ^{13}C spectrometer at the National NMR Centre, Canberra. We acknowledge the cooperation of the Director, Dr Alan Jones.

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