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THERMAL [1,5] SIGMATROPIC REARRANGEMENTS IN (σ-7-CYCLOHEPTATRIENYL)TRIPHENYLTIN AND (σ-5-CYCLOHEPTA-1,3-DIENYL)TRIPHENYLTIN: A ^{1}H AND ^{13}C NMR REINVESTIGATION

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Summary

It has been confirmed by ^{1}H and ^{13}C NMR spectroscopies that $Sn(\sigma\text{-}C_7H_7)Ph_3$ undergoes either 1,4- or 1,5-shifts of the $SnPh_3$ moiety around the cycloheptatrienyl ring with $\Delta H^\ddagger = 13.8 \pm 0.4$ kcal mol^{-1}, $\Delta S^\ddagger = -5.6 \pm 1.2$ cal mol^{-1} deg^{-1}, and $\Delta G^\ddagger_{300} = 15.44 \pm 0.14$ kcal mol^{-1}. Similarly, (σ-5-cyclohepta-1,3-dienyl)triphenyltin undergoes 1,5-shifts with $\Delta H^\ddagger = 12.4 \pm 0.6$ kcal mol^{-1}, $\Delta S^\ddagger = -11.2 \pm 1.8$ cal mol^{-1} deg^{-1}, and $\Delta G^\ddagger_{300} = 15.76 \pm 0.13$ kcal mol^{-1}. It is therefore probable that $Sn(\sigma\text{-}5\text{-}C_5H_5)R_3$ and $Sn(\sigma\text{-}3\text{-indenyl})R_3$ do not undergo 1,2-shifts as previously suggested but really undergo 1,5-shifts.

Introduction

Recently Mingos [1] has suggested that many of the 1,2-shifts found for fluxional organometallic compounds [2] are really 1,5-shifts. Examination of the wealth of information available on these compounds makes this interpretation very attractive. However, a literature search has revealed only two organometallic compounds which are thought to be undergoing 1,5-shifts, viz., (σ-7-cycloheptatrienyl)triphenyltin [3] and (σ-5-cyclohepta-1,3-dienyl)trimethyltin [4]. Unfortunately, the evidence is based on rather poorly resolved 60 or 100 MHz ^{1}H NMR spectra and cannot be taken as an unambiguous proof of 1,5-shifts. It was therefore decided to repeat these measurements before looking for further evidence of 1,5-shifts among fluxional organometallic compounds.

Experimental

The NMR spectra were measured on either a Perkin-Elmer R34 (^{1}H) or JEOL PFT-100 (^{1}H, ^{13}C) NMR spectrometer. The temperatures were calibrated using either MeOH or $HOCH_2CH_2OH$ for ^1H spectra or a Comark Electronic thermometer for ^{13}C NMR spectra.

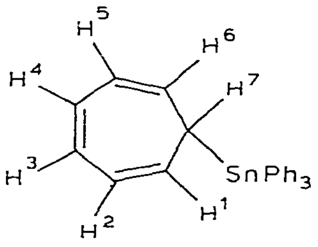
The $[C_7H_7]^+[BF_4]^-$ was prepared following the literature method [5]. The preparation of $Sn(C_7H_7)Ph_3$ follows that previously outlined [3].

Cycloheptatrienyltriphenyltin(IV)

Chlorotriphenyltin (5.78 g; 0.015 mol), dissolved in dry THF (23 ml) was added at a moderate rate to lithium metal (0.35 g; 0.05 g atoms; activated by broken glass) stirred in dry THF (15 ml) at room temperature. After 6 h, the solution was filtered under nitrogen. Solid $[C_7H_7]^+[BF_4]^-$ (2.67 g; 0.015 mol) was added under nitrogen. After stirring for 1 h, the solution was evaporated to dryness and the impure product extracted with diethyl ether. The product was purified by chromatography on silica gel, eluting with petroleum ether (boiling range 40—60° C)/diethyl ether (4/1, v/v), and was isolated as a yellow crystalline solid (3.04 g, 47.5% yield), m.p. 120° C. Anal.: Found: C, 67.84; H, 4.86%. Calc. for $C_{25}H_{22}Sn$: C, 68.07; H 5.03%. Mass spectrum primary ion 442 ($^{12}C_{25}{}^1H_{22}{}^{120}Sn$).

5-Cyclohepta-1,3-dienyltriphenyltin(IV)

Potassium metal (0.4 g, 0.01 mol) was melted in refluxing THF (1.5 ml) under nitrogen, with vigorous stirring and allowed to cool to give potassium shot. Triethylamine (0.75 ml, 0.01 mol) and cyclohepta-1,3-diene (1.2 ml, 0.011 mol) were added and the mixture was stirred for 2 h, while cycloheptadienyl potassium was formed. The solution was added to chlorotriphenyltin(IV) (1.9 g, 0.005 mol) in THF (5 ml) at −60° C and then the solution was allowed to warm to room temperature. After 1 h, the solution was evaporated and the product was chromatographed on silica gel and eluted using petroleum ether (boiling range 40—60° C)/diethyl ether (2/1, v/v). The product was crystallised from petroleum ether (boiling range 40—60° C) at −78° C, and isolated as a white solid (0.75 g, 34% yield), m.p. 52° C. Anal.: Found: C, 67.74; H, 5.42%. Calc. for $C_{25}H_{24}Sn$: C, 67.76; H, 5.46%. Mass spectrum primary ion 444 ($^{12}C_{25}{}^1H_{24}{}^{120}Sn$).



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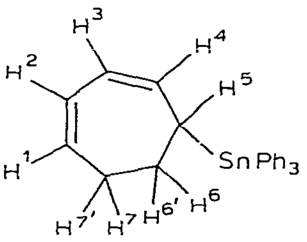

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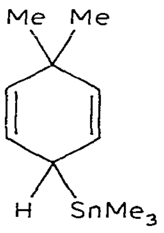

III

Results

As previously reported, $Sn(C_7H_7)Ph_3$, I, shows fluxional behaviour, giving a sharp limiting low temperature ^1H NMR spectrum below 0° C, see Fig. 1. The ^1H NMR spectrum at 100 MHz is strongly second order in the olefinic region,

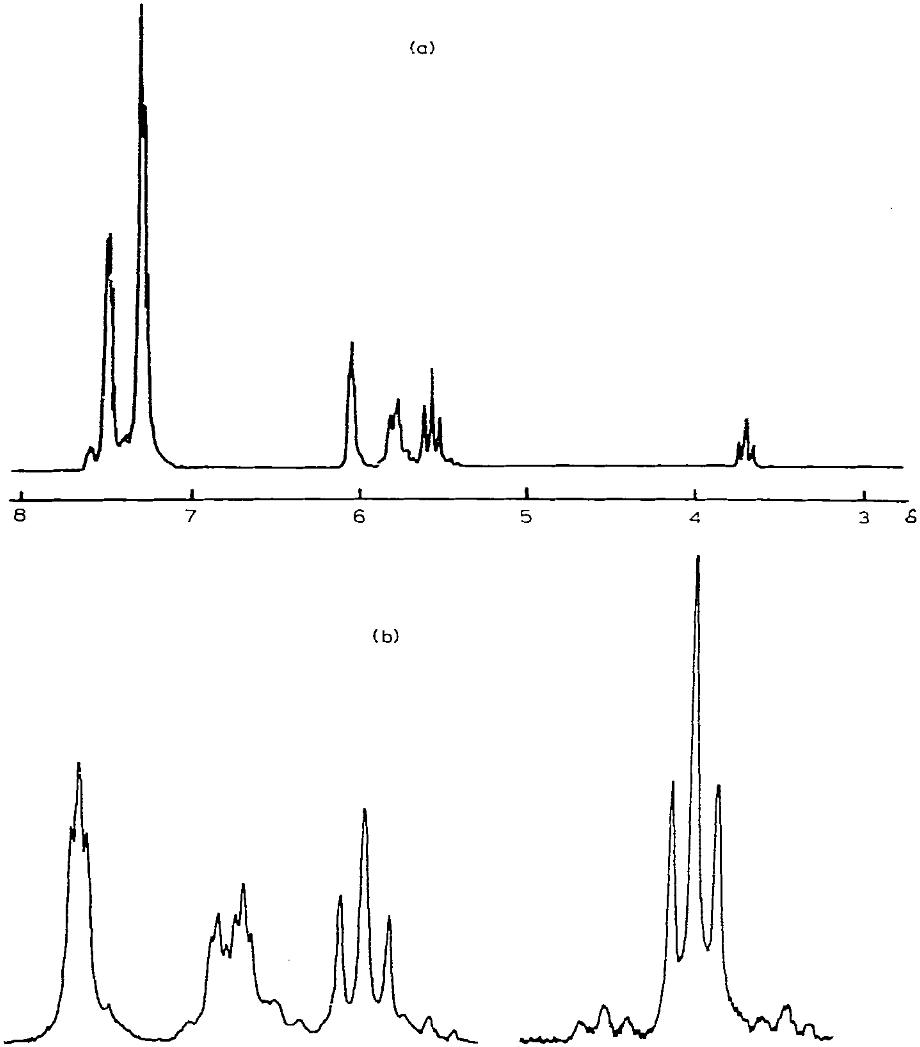

Fig. 1. The 220 MHz ^{1}H NMR spectrum of (σ-7-cycloheptatrienyl)triphenyltin in $CDCl_3$ at −20°C. (a) Complete spectrum, (b) an expansion showing, at different gains, the olefinic and H^7 protons of the cycloheptatrienyl ring.

but becomes approximately first order at 220 MHz. Although the spectrum can be assigned by inspection, the assignments were confirmed by double resonance. In $CDCl_3$, the signal at δ 3.70, $^2J(^{117,119}Sn, {}^1H^7) = 68$ Hz, $^3J(^1H^7, {}^1H^1) = 8$ Hz, intensity 1, may be assigned unambiguously to H^7. Irradiation at δ 3.70, causes the signal at δ 5.57 to collapse to a doublet, enabling the assignment of this signal to H^1 and H^6, $^3J(^1H^7, {}^1H^1) = 8$ Hz, $^3J(^1H^2, {}^1H^1) = 9$ Hz, $^3J(^{117,119}Sn, {}^1H^1) = 49$ Hz, intensity 2. Examination of the remaining two olefinic signals, shows that one is a multiplet and the other consists of a doublet of the same multiplets. The multiplet structure is characteristic of that found for an $[AX]_2$ spin system. The doublet splitting of the signal at δ 5.79 must arise from H^2 and H^5

with $^3J(^1H^2, {}^1H^1)$ = 9 Hz and $^4J(^{117,119}Sn, {}^1H^2)$ = 32 Hz, leaving the signal at δ 6.05 to be assigned to H^3 and H^4, with $|^3J(^1H^3, {}^1H^2) + {}^4J(^1H^5, {}^1H^3)|$ = 6 Hz. These chemical shifts are in marked disagreement with the published values of $\delta(H^1)$ = 4.5, $\delta(H^2)$ = 4.7, and $\delta(H^3)$ = 5.1, and the reported value of $^3J(^1H^7, {}^1H^1)$ is only 4 Hz. These discrepancies would appear to arise from an error in the previous analysis of the spectrum as the aromatic protons were also quoted as occurring at δ 6.5 rather than δ 7.3 (*meta* and *para*) and δ 7.5 (*ortho*) which are observed for this compound and are consistent with other compounds [6].

When the temperature is raised, all the cycloheptatrienyl signals broaden, with the signals due to H^2 and H^5 broadening at half the rate of the signals due to the other cycloheptatrienyl protons. Analysis of the consequences of 1,2-, 1,3-, and 1,4-shifts shows that this behaviour corresponds to a 1,4- or a 1,5-shift, in agreement with previous work. Variable temperature ^1H NMR spectra were measured at 100 MHz in nitrobenzene-d_5, see Fig. 2. Lineshape analysis proved to be successful above 50° C when exchange had removed the effect of coupling, but below 50° C, the analysis of the data as a simple four site exchange problem was too crude to give reliable rates. Above 90° C, the decomposition to give Sn_2Ph_6 and $(C_7H_7)_2$ became significant [3] and limited the measurements to an upper temperature of 120° C.

The ^{13}C NMR spectrum at —30° C showed the expected phenyl signals at δ 140.4, $^1J(^{117}Sn, {}^{13}C)$ = 438 Hz, $^1J(^{119}Sn, {}^{13}C)$ = 459 Hz due to the carbon atom directly bonded to tin; δ 136.8, $^2J(^{117,119}Sn, {}^{13}C)$ = 36 Hz, *o*-carbon; δ 128.0, $^3J(^{117,119}Sn, {}^{13}C)$ = 43 Hz, *m*-carbon; and δ 128.4, $^4J(^{117,119}Sn, {}^{13}C)$ =

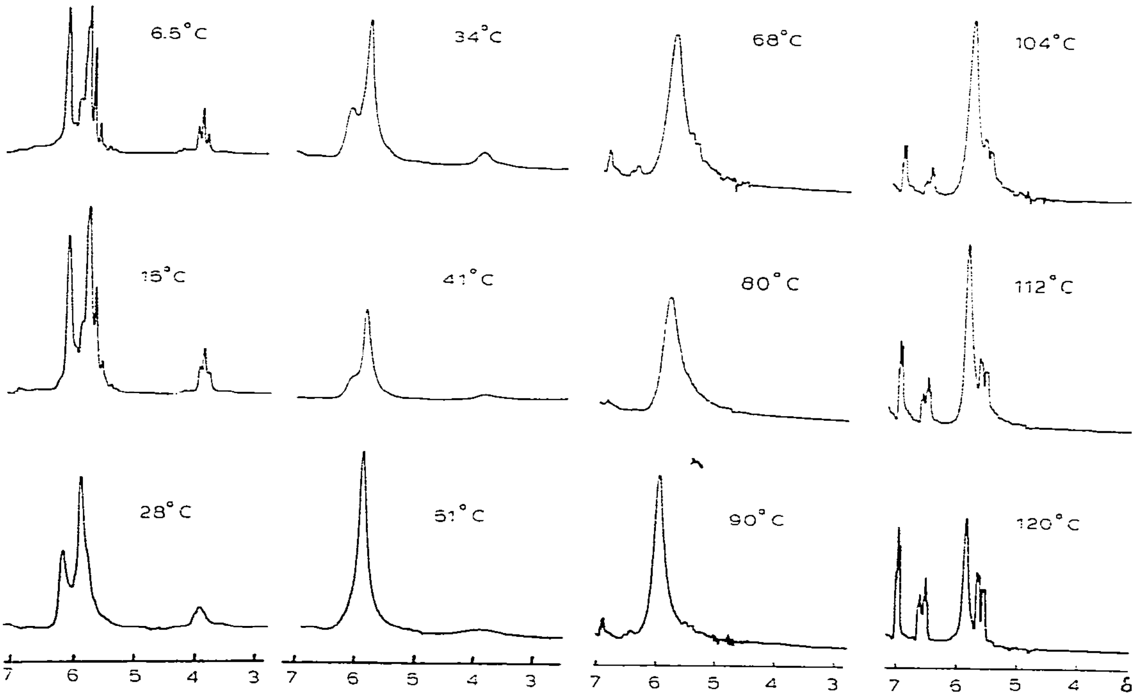

Fig. 2. The partial 100 MHz variable temperature ^1H NMR spectra of (σ-7-cycloheptatrienyl)triphenyltin in nitrobenzene-d_5.

11 Hz, *p*-carbon. The remaining four signals are due to the cycloheptatrienyl ring with the signals at δ 34.6, $^1J(^{117}\mathrm{Sn}, ^{13}\mathrm{C}) = 358$ Hz, $^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C}) = 375$ Hz, readily assignable to C^1 on the basis of chemical shift and coupling constant. The remaining signals at δ 126.4, $J(^{117,119}\mathrm{Sn}, ^{13}\mathrm{C}) = 44$ Hz; δ 127.6, $J(^{117,119}\mathrm{Sn}, ^{13}\mathrm{C}) = 33$ Hz; and δ 134.2, $J(^{117,119}\mathrm{Sn}, ^{13}\mathrm{C}) < 5$ Hz are not as easily assigned, but the absence of ^{117,119}Sn coupling to the signal at δ 134.2 makes it probable that this signal is due to C^3 and C^4. Attempts at using $^{13}\mathrm{C}\{^1\mathrm{H}\}$ off resonance decoupling to assign these signals failed on account of the proximity of the intense phenyl ^{13}C resonances. Synthesis of $\mathrm{Sn(C_7H_7)Et_3}$ to avoid these problems also failed yielding only $\mathrm{Sn_2Et_6}$ and $\mathrm{(C_7H_7)_2}$. On warming, the signal at δ 127.6 broadened at half the rate of the other $\mathrm{C_7H_7}$ signals, showing that the mechanism is either a 1,3- or 1,4-shift depending on the assignment of this signal to either $C^{1,6}$ or $C^{2,5}$ respectively. When the signal at δ 34.6 is irradiated, all the signals due to the $\mathrm{C_7H_7}$ ring decrease in intensity, with the signal at δ 134.2 decreasing most, consistent with a 1,4-shift mechanism. On the basis of this and the ^{1}H NMR results it is concluded that a 1,4- or 1,5-shift mechanism is occurring, and consequently the assignments of the two ^{13}C NMR signals at δ 126.4 and δ 127.6 are to $C^{1,6}$ and $C^{2,5}$ respectively. Variable temperature ^{13}C NMR experiments were performed from 17 to 56° C. Above this temperature, the signals were either obscured by the phenyl resonances or were too broad to be observed. The ^{1}H and ^{13}C NMR data were combined to yield the activation energies $\Delta H^{\ddagger} = 13.8 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.6 \pm 1.2$ cal mol^{-1} deg^{-1}, and $G_{300} = 15.44 \pm 0.14$ kcal mol^{-1}. The errors are one standard deviation based on the best fit straight line through the Eyring plot, and consequently gives only the minimum error.

In the case of $\mathrm{Sn(C_7H_7)Ph_3}$, it is impossible to distinguish between a 1,4- and a 1,5-shift mechanism as both produce the same atomic movements. Consequently, (σ-cyclohepta-1,3-dienyl)triphenyltin was synthesised for comparison. The previous synthesis of (σ-cyclohepta-1,3-dienyl)trimethyltin had used the deprotonation of 1,3,6-heptatriene by n-butyllithium followed by cyclisation to give cyclohepta-1,3-dienyllithium [4]. As cyclohepta-1,3-diene is more readily available, and the reaction of cycloocta-1,3-diene with potassium had been previously reported to give cyclooctadienylpotassium [7], cyclohepta-1,3-diene was treated with potassium to yield cycloheptadienylpotassium which on addition of $\mathrm{SnClPh_3}$ gave the desired product, (σ-5-cyclohepta-1,3-dienyl)triphenyltin, II. At −20° C in toluene-d^8, a static ^{1}H NMR spectrum is obtained, see Fig. 3, with H^5 at σ 3.01, $^2J(^{117,119}\mathrm{Sn}, ^1\mathrm{H}^5) = 106$ Hz. This value for $^2J(^{117,119}\mathrm{Sn}, ^1\mathrm{H})$ is much larger than that normally found in tin compounds, but is comparable with the 91 Hz observed for Sn(σ-5-indenyl)$\mathrm{Me_3}$ [8]. The olefinic protons show three resonances at δ 6.04, δ 5.78, and δ 5.52, with intensities 1 : 1 : 2. Irradiation of the signal at δ 3.01 causes the signal at δ 6.04 to collapse from two doublets to one doublet, showing this to be due to H^4, $^3J(^1\mathrm{H}^5, ^1\mathrm{H}^4) = 7$ Hz, $^3J(^1\mathrm{H}^4, ^1\mathrm{H}^3) = 12$ Hz, $^3J(^{117,119}\mathrm{Sn}, ^1\mathrm{H}^4) = 24$ Hz. On warming (Fig. 4) H^4 exchanges with H^2 at δ 5.78, $^3J(^1\mathrm{H}^3, ^1\mathrm{H}^2) = 7$ Hz, and $^3J(^1\mathrm{H}^2, ^1\mathrm{H}^1) = 11$ Hz, and a sharp triplet at δ 5.52 emerges due to H^3 with $\frac{1}{2}|^3J(^1\mathrm{H}^3, ^1\mathrm{H}^2) + {}^3J(^1\mathrm{H}^4, ^1\mathrm{H}^3)| = 9$ Hz, $^4J(^{117,119}\mathrm{Sn}, ^1\mathrm{H}^3) = 24$ Hz. The tin coupling to H^3 is retained, even at 108° C, showing that the mechanism is intramolecular. Similarly, at 108° C, the averaged $H^{2,4}$ signal shows ^{117,119}Sn coupling. The missing

Fig. 3. The partial 220 MHz ^1H NMR spectrum of (σ-5-cyclohepta-1,3-dienyl)triphenyltin at —20°C in toluene-d_8.

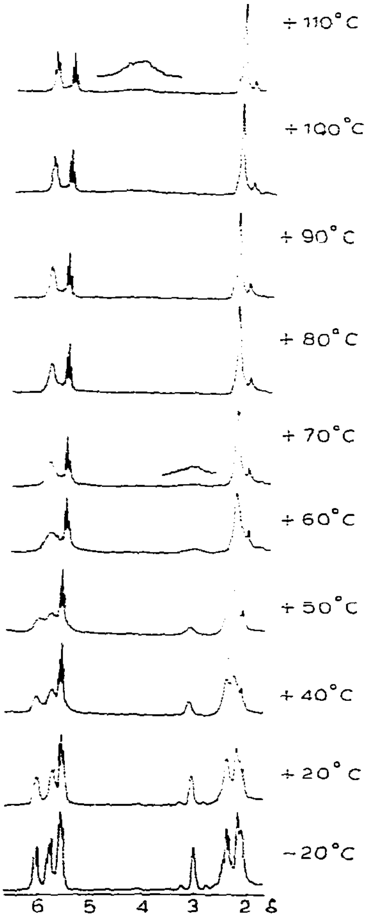

Fig. 4. The partial 220 MHz variable temperature ^1H NMR spectra of (σ-5-cyclohepta-1,3-dienyl)triphenyltin in toluene-d_8.

signal due to H^1 must be under H^3 at δ 5.52. The CH_2 protons form a complex multiplet centred at δ 2.26. The exchanges of H^2 and H^4 and of H^1 and H^5 were analysed to give rates of exchange.

The ^{13}C NMR spectra of Sn(5-cyclohepta-1,3-dienyl)Ph_3 were also recorded as a function of temperature. At —30° C, a limiting low temperature spectrum was obtained. The phenyl signals are very similar to those found in Sn(C_7H_7)-Ph_3: Sn—C, δ 138.8, $^1J(^{117}Sn, ^{13}C) = 449$ Hz, $^1J(^{119}Sn, ^{13}C) = 471$ Hz; *o*-carbon, δ 137.9, $^2J(^{117,119}Sn, ^{13}C) = 35$ Hz; *m*-carbon, δ 129.2, $^3J(^{117,119}Sn, ^{13}C) = 47$ Hz; and *p*-carbon, δ 129.6. Only six of the seven cycloheptadienyl resonances are clearly resolved: δ 132.3, $J(^{117,119}Sn, ^{13}C) = 20$ Hz; δ 126.2, δ 121.6, $J(^{117,119}Sn, ^{13}C) = 55$ Hz; δ 37.7, $J(^{117}Sn, ^{13}C) = 331$ Hz, $J(^{119}Sn, ^{13}C) = 346$ Hz; δ 33.9, $J(^{117,119}Sn, ^{13}C) = 35$ Hz; and δ 29.6. The missing olefinic carbon signal is obscured by the phenyl signals. From the observation of an averaged signal at ca. δ 131.6 and Forsen-Hoffman spin saturation measurements, it is concluded that the missing signal is coincident with the lower frequency $^{117,119}Sn$ satellite of the *o*-carbon atoms of the phenyl ring at δ 137.0 and exchanges with the signal at δ 126.2, i.e. these are the C^2 and C^4 signals. The signal at δ 121.6 is sharp, and shows tin coupling at all temperatures and hence is due to C^3. Consequently, the signal at δ 132.3 is due to C^1 and at δ 37.7 is due to C^5. The remaining two signals at δ 33.9 and δ 29.6, which coalesce on warming must be due to C^6 and C^7. Analysis of the variable temperature ^{13}C NMR spectrum proved to be subject to errors. Only the signals due to C^6 and C^7 could be monitored at higher temperature, but their separation is temperature dependence, being 115 Hz at —43° C and 88 Hz at 33° C. Extrapolation of the separation to high temperature was performed before carrying out lineshape analysis. However, the results will be subject to a larger error than given by the standard deviation quoted. Combination of the ^1H and ^{13}C NMR lineshape analyses yielded the activation parameters $\Delta H^{\ddagger} = 12.4 \pm 0.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -11.2 \pm 1.8$ cal deg^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{300} = 15.76 \pm 0.13$ kcal mol^{-1}.

Discussion

The fluxionality of carbon π-systems σ-bonded to a metal via an adjacent saturated carbon atom is at present restricted to σ-allyl, 5-σ-cyclopentadienyl, 3-σ-indenyl, 7-σ-cycloheptatrienyl, and 5-σ-cyclohepta-1,3-dienyl system [2]. The σ-allyl systems are either static on the NMR time scale or are fluxional via an ionic or intermolecular process or a η^3-allyl transition state [9]. In cases where these mechanisms are of high energy, e.g., Mn(σ-C_3H_5)$(CO)_3$ and Sn(σ-C_3H_5)Me_3, the allyl group is static on the NMR time scale giving rise to an $ABCX_2$ ^1H NMR spectrum [9]. In contrast, there have been extensive studies of the 5-σ-cyclopentadienyl ring bonded to metals, which are invariably fluxional, and it is now generally agreed that the fluxionality occurs via 1,2-(or the equivalent 1,5-) shifts. The 3-σ-indenyl systems are believed to behave similarly, but the 1,2-shift is inhibited by the required quinoid intermediate [2] with a consequential increase in energy for the overall 1,3-shift. These observations, coupled with the observation that the fluxionality of most π-systems on metals, e.g., Fe(η^4-cyclooctatetraene)$(CO)_3$, occurs via 1,2-shifts, has produced a general belief that 1,2-shifts are the rule for fluxional organometallic compounds. Exceptions arise from ionic or intermolecular processes or changes in the number of electrons in the valence shell [2,9—11]. Only two compounds fail to fit into these mechanisms, 7-σ-cycloheptatrienyltriphenyltin [3] which undergoes 1,4- or 1,5-shifts and 5-σ-cyclohepta-1,3-dienyltrimethyltin [4] which undergoes either two sequential 1,3-shifts or 1,5-shifts. These observations have been confirmed in the present work for $Sn(C_7H_7)Ph_3$ and $Sn(5\text{-}C_7H_9)Ph_3$. The absence of known examples of σ-allyltin compounds which are fluxional on the NMR time scale, even III is static [4], and the same activation parameters, within experimental error, for both $Sn(C_7H_7)Ph_3$ and $Sn(5\text{-}C_7H_9)Ph_3$ makes the occurrence of two sequential 1,3-shifts for $Sn(5\text{-}C_7H_9)Ph_3$ most unlikely. It is therefore probable that both molecules are undergoing 1,5-shifts. Further support for this suggestion comes from the observation that thermal sigmatropic rearrangements are accompanied by a negative $\Delta S^{\ddagger}$, with values in the range —5 to —10 e.u. being common. For both $Sn(C_7H_7)Ph_3$ and $Sn(5\text{-}C_7H_9)Ph_3$, $\Delta S^{\ddagger}$ is negative [12]. As it appears that in a seven-membered ring system and π-systems, 1,5-shifts are occurring, a more consistent approach for the five-membered rings would also be to describe them as 1,5-shifts rather than 1,2-shifts; the mechanism being that described earlier by Woodward and Hoffman for organic molecules [13]. The alternative, a η^5-C_7H_n intermediate, may be eliminated as the σ-allyltin system is static and the σ-cyclopentadienyl system should undergo random shifts via a η^5-C_5H_5 intermediate. In the case of transition metal σ-dienyl systems, e.g., $Fe(\sigma\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(CO)_2$, it is also probable that the shifts are better described as 1,5-shifts, but the presence of the *d*-orbitals may cause 1,2-shifts to be permitted. At present, the necessary compounds to test this mechanism for transition metals do not exist. For example, an attempt to synthesise $Fe(\sigma\text{-}C_7H_7)(\eta_5\text{-}C_5H_5)(CO)_2$ actually gave $Fe(\eta^3\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)Fe(CO)$ [14].

References

1 D.M.P. Mingos, J. Chem. Soc. Dalton, (1977) 31.
2 F.A. Cotton, in L.M. Jackman and F.A. Cotton (Eds.), Dynamic NMR Spectroscopy, Academic Press, London, 1975, p. 377.
3 R.B. Larrabee, J. Amer. Chem. Soc., 93 (1971) 1510.
4 M.D. Curtis and R. Fink, J. Organometall. Chem., 38 (1972) 299.
5 K. Conrow, Org. Synth., 43 (1963) 101.
6 See for example, V.S. Petrosyan, Progr. NMR Spectrosc. 11 (1977) 115.
7 H. Yasuda, T. Narita and H. Tani, Tetrahedron Lett., (1973) 2443.
8 Yu.N. Luzikov, N.M. Sergeyev and Yu.A. Ustynyuk, J. Organometall. Chem., 65 (1974) 303.
9 K. Vrieze, ref. 2, p. 441.
10 B.E. Mann, J. Chem. Soc. Commun., (1977) 626.
11 B.E. Mann, J. Organometall. Chem., 141 (1977) C33; K.J. Karel and M. Brookhart, J. Amer. Chem. Soc., 100 (1978) 1619.
12 C.W. Spangler, Chem. Rev., 76 (1976) 187.
13 R.B. Woodward and R. Hoffman, The Conservation of Orbital Symmetry, Verlag Chemie GmbH/-Academic Press, Weinheim/Bergstr., 1970, and references therein.
14 D. Ciappenelli and M. Rosenblum, J. Amer. Chem. Soc., 91 (1969) 3673, 6876.