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Cyclononatetraenyl(trimethyl)stannane: Proof of Fluxional Character and Proposed Mechanism for Metallotropism

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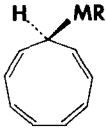
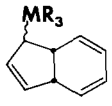
Cyclopentadienyl derivatives of silicon, germanium and tin have played a crucial role in the rationalization of the fluxional nature of *monohapto*-cyclopentadienyl compounds (Type I) formed by a wide range of metals [1, 2]. Rapid intramolecular rearrangement through consecutive sigmatropic migration of the metal-containing group has been rigorously proven and a variety of data is consistent with a 1,2 (rather than 1,3 or random) shift [3]. Larrabee has also discovered one example of a *monohapto*-cycloheptatrienyl compound, (Type II) $C_7H_7(SnPh_3)$ exhibiting nonrigidity resulting from a symmetry-dependent (rather than least-motion) shift [4]. Both Types I and II are derived from aromatic six-electron carbocycles, prompting us some time ago to explore reactions of a ten-electron analogue as a route to corresponding metallocyclononatetraene species (Type III). During the course of our work, a preliminary note by Boche and Heidenhain [5] reported synthesis of a trimethyltin derivative (1) of Type III



(1) M = Sn, R = Me
(2) M = Si, R = H
(3) M = Ge, R = H



(4) M = Si, R = H
(5) M = Ge, R = H
(6) M = Sn, R = Me

for which dynamic behaviour was inferred on the basis of its ^1H n.m.r. spectrum at 20 °C, which showed a single resonance in the olefinic region. Here we summarize results of a full investigation using variable-temperature ^1H and ^{13}C n.m.r. spectroscopy of all-*cis*-cyclonona-2,4,6,8-tetraenyl(trimethyl)stannane** (1), which unequivocally establishes its fluxional character and moreover implies a 1,2 shift⁺ (rather than successive 1,5 migrations) as the mechanism for rearrangement.

Reaction at –30 °C in dry tetrahydrofuran between potassium cyclononatetraenide [6] and chlorotrimethylstannane, bromosilane or bromogermane afforded compounds (1)–(3) respectively (30–40%), characterized by ^1H and ^{13}C n.m.r. spectroscopy at –25 °C. On warming to ambient temperature, these spectra became more complicated due to isomerization to the corresponding *cis*-dihydroindenes [4–6], evidently formed as mixtures of *endo*- and *exo*-isomers and further characterized by microanalysis, mass spectroscopy and i.r. data. For silyl- and germylcyclononatetraene [(2) and (3) respectively] resonances due to ring ^1H and ^{13}C nuclei consisted of $a_2b_2c_2d_2x$-type patterns expected for the 'static' configurations (2) or (3) below 0 °C, above which temperature isomerization to compounds (4) or (5) became predominant. By contrast, compound (1) at –25 °C showed only broadened, single signals in the olefinic region: the ^1H resonance at τ 4.45 moved downfield on cooling to give at –90 °C a partly resolved multiplet centred at τ 4.14, while the temperature-dependence of the ^{13}C resonance is depicted in Figure 1. This clearly shows the successive broadening then sharpening with increasing temperature resulting from establishment of equivalence among ring nuclei through metallotropic migration of the trimethyltin group, parallelling the behaviour of cyclopentadienyl analogues [2, 3].

If the metallotropic shifts in compounds of Types I–III are regarded as homolytic migrations, criteria put forward by Anastassiou [7] indicate from the symmetry properties of the HOMO ψ_5 for the C_9 system [8] (Figure 2) that 1,5 and 1,9 shifts should both be thermally allowed. We conclude that in compound (1) a 1,9 shift (1,2 [3]: 'least motion') is the mechanism for metallotropism, reasoning as follows. For $C_5H_5(SnMe_3)$ (Type I), an aliphatic proton [9] signal becomes discernible only below –140 °C and slow-limiting characteristics are incompletely established at –150 °C. For $C_7H_7(SnPh)_3)$ (Type II), however, a slow-limit ^1H n.m.r. spectrum is observed [4] at –19 °C with dynamic behaviour being detectable only at higher temperatures. This comparison indicates a substantially increased activation energy for a 1,5 shift occurring *via* a 'molecular broad jump' (Type II) rather than a 'least motion' migration (Type I). The qualitative analogy between the data of Figure

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**The existence of a conflict in numbering systems for compounds of the types under discussion here has been recently discussed by us in Ref. [3].

⁺Throughout this communication, 1,2 and 1,5 shifts are considered to be synonymous for C_5 systems but distinct for C_7 or C_9 systems, (1,2 and 1,9 shifts being synonymous for the latter).

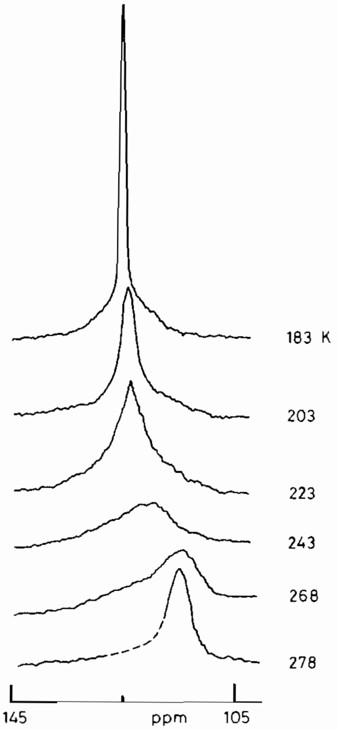

Figure 1. Carbon-13 n.m.r. spectrum (105–145 ppm downfield from TMS) for Compound (1) at various temperatures.

1, complementary ^1H results (including absence of aliphatic resonances above −90 °C) and those for [9] $C_5H_5(SnMe_3)$ leads us to believe that compound (1) (Type III) rearranges by a 'least motion' shift.

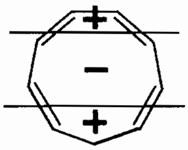

Figure 2. Symmetry properties of HOMO ψ_5 for cyclononatetraenyl radical.

Acknowledgments

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