Stereochemically Non-rigid Silanes, Germanes, and Stannanes. Part 5.[1] Characterization of Non-degenerate Rearrangements in Methylcyclopentadienyl Derivatives using Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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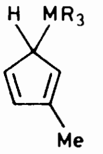
The intramolecular rearrangement behaviour of silyl(methyl)cyclopentadiene, (1), germyl(methyl)cyclopentadiene, (2), trimethylgermyl(methyl)cyclopentadiene, (3), and trimethylstannyl(methyl)cyclopentadiene, (4), has been investigated using variable-temperature ^{13}C Fourier-transform n.m.r. spectroscopy. The exchange process is discussed in terms of (*a*) vanishingly small equilibrium concentration for the geminal isomer compared with those of the two possible non-geminal isomers, (*b*) predominance of the non-geminal isomer with the substituents on non-adjacent carbon atoms of the C_5 ring over that with substituents on adjacent carbon atoms where one of these configurations is preferred. From the temperature dependence of the equilibrium constant for compound (3) the enthalpy difference between the non-geminal isomers is estimated to be *ca*. 2 kJ mol^{-1} and may be even smaller for compounds (1) and (2). The frequency separation between the ^{13}C resonances in fast-limiting spectra due to the two pairs of equivalent carbon atoms is correlated with the equilibrium ratio of the species participating in the non-degenerate exchange.

FLUXIONAL character of monohapto-metallocyclopentadienes has been thoroughly investigated using variable-temperature ^{1}H n.m.r. spectroscopy,[2] a situation perhaps most notably exemplified by studies on appropriate compounds of silicon, germanium, and tin.[1,3,4] By contrast, stereochemical non-rigidity which gives rise to equally ready non-degenerate intramolecular rearrangements in some closely related (' quasi-fluxional ') species is not understood in detail.[4-6] This paper describes the characterization of such dynamic properties for some methylcyclopentadienyl derivatives through analysis of the temperature dependence of ^{13}C n.m.r. data. Four compounds have been examined: silyl(methyl)cyclopentadiene, (1), germyl(methyl)cyclopentadiene, (2), trimethylgermyl(methyl)cyclopentadiene, (3), and trimethylstannyl(methyl)cyclopentadiene, (4). All have been synthesized previously,[3-5,7] and shown to have temperature-dependent ^{1}H n.m.r. spectra accountable for in terms of ready interconversion between the three possible isomers,† (5)—(7) where $MR_3 = SiH_3$, GeH_3, $GeMe_3$, or $SnMe_3$. Rearrangement of compound (1) is relatively slow on the n.m.r. time scale so that a ' static ' configuration for the system can be observed and in the dynamic temperature range prototropic migration to give stereochemically rigid isomers occurs at a significant rate.[3,6] For compound (4) at ambient temperature a fast-limiting spectrum is observed; on cooling to −85 °C the olefinic resonances become broader [6] but the changes provide no explicit information concerning the rearrangement between species (5)—(7). By comparison, the germanes (2) and (3) exhibit a full range of dynamic behaviour in a convenient temperature range [4,7] and accordingly it is ^{13}C n.m.r. data for these compounds which constitute the basis for much of the discussion presented here. One obvious modification of criteria which apply to the degenerate rearrangement of fluxional analogues arises because the equilibrium isomer distribution [(5)] : [(6)] : [(7)] (a thermodynamic property) must be considered as well as the rate of interconversion between them.



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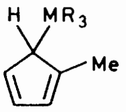

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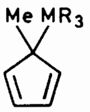

(7)

EXPERIMENTAL

The compounds were synthesized using experimental methods described previously;[1,3,7] each of the products was completely characterized by comparison of i.r., ^{1}H n.m.r., and mass spectra with literature data.[3-5,7] Variable-temperature proton noise-decoupled ^{13}C n.m.r. spectra were measured at 15.09 MHz on 50% v/v samples in dry $CDCl_3$ contained in evacuated sealed tubes using a Nicolet TT-14 Fourier-transform spectrometer.

RESULTS AND DISCUSSION

Precoalescence ^{13}C n.m.r. chemical shifts for compound (1) have been listed in Table 3 of Part 2 of this series;[3] data for compounds (2)—(4) are presented in the Table. The temperature dependence of the ^{13}C n.m.r. spectrum of compound (3) is illustrated in Figure 1 and the ^{13}C n.m.r. spectrum at ambient temperature for compound (4) is reproduced in Figure 2.

Previously we have assigned the low-temperature limit ^{1}H n.m.r. spectrum measured at −60 °C for compound (2) to that of a mixture of the two non-geminal isomers (5) and (6), $MR_3 = GeH_3$, present in very nearly 1 : 1 ratio as estimated from relative peak heights. At 100 °C dynamic behaviour results in averaging of both ring-proton and germyl-proton resonances, coupling

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† It must be emphasized that only isomers in which the metal atom is attached to the saturated carbon atom (C^1) may participate in the exchange process: all possible isomers other than (5)—(7) involve attachment of the metal to an olefinic carbon atom and such compounds are known to be stereochemically rigid.[2,5-7]

between these ^1H sites with an averaged $J = 0.55$ Hz in the GeH signal giving rise to a quintet structure.[7] The latter observation establishes that (*a*) the dynamic process is intramolecular, (*b*) at the fast limit of exchange, equivalence is established among the four ring protons, *i.e.* assuming a sigmatropic shift, the GeH_3 group is migrating between, and is instantaneously bonded to, at least four of the five carbon atoms of the cyclopentadiene skeleton.

Although it is true that signal heights in Fourier-transform ^{13}C n.m.r. spectra may be subject to considerable variation with pulse time as a result of relaxation effects, comparisons for nuclei with very similar molecular environments should approximate to relative populations. With this assumption the ^{13}C data for compound (2) at −30 °C confirm (Table) that at the slow limit an equilibrium mixture of isomers (5) and (6) ($MR_3 = GeH_3$) exists in a 1 : 1 ratio: approximately equal peak heights are found for the methyl (15.5, 15.4 p.p.m.), the aliphatic (45.2, 41.6 p.p.m.), and the highest-frequency olefinic signals (145.6, 139.7 p.p.m.), the latter being assigned to the ring carbon atoms bearing the methyl group in the configurations (5) and (6) through diminished Overhauser enhancement. The absence of additional resonances in carbon or proton[7] spectra established that the equilibrium concentration of the geminal isomer (7; $MR_3 = GeH_3$) must be low (<1%). Similar reasoning leads us to conclude that at −30 °C the equilibrium for compound (1) lies slightly in favour of one of the isomers (5) or (6) (ratio *ca.* 1.2 : 1) while at the same temperature for compound (3) one isomer is more strongly preferred (*ca.* 3.2 : 1). The latter situation is clear in Figure 1, where at −30 °C we have labelled signals attributed to the two species as a or b, and from ^1H data illustrated in ref. 4 which at −40 °C show two aliphatic signals (τ 6.5—7.0) in *ca.* 3 : 1 ratio. No

Carbon-13 n.m.r. data [a]

Compound	T/K	Chemical shift/p.p.m.[b] C(olefinic)	C(aliphatic)	C(methyl)
(2)	243	145.6 (18) [c]	45.2 (56)	15.5 (61)
		139.7 (18)	41.6 (48)	15.4 (56)
		135.9 (56)		
		132.7 (64)		
		132.4 (78)		
		129.9 (100)		
		125.7 (69)		
(3) [d]		143.0 (13)	52.0 (36)	15.8 (25)
		138.2 (41)	49.4 (87)	14.6 (80)
		132.9 (100)		
		131.4 (92)		
		130.0 (44)		
		128.6 (42)		
		127.1 (99)		
		125.0 (34)		
(4)	298	138.5 (9)		15.3 (30)
		111.7 [e] (96)		
		105.9 [f] (100)		

[a] Data for compound (1) at 233 K are listed in Table 3 of ref. 3. Here $CDCl_3$ was used as solvent and internal reference throughout. [b] High frequency relative to δ 77.2 p.p.m. for $CDCl_3$ (central component of triplet). [c] Numbers in parentheses indicate relative peak heights; pulse interval 1.36 s, pulse width 8 μs. [d] $\delta[^{13}C(GeMe_3)]$ at −2.3 p.p.m. [e] $^1J_{av}(^{117,119}Sn-^{13}C) = 24.0$ Hz. [f] $^1J_{av}(^{117,119}Sn-^{13}C) = 25.9$ Hz.

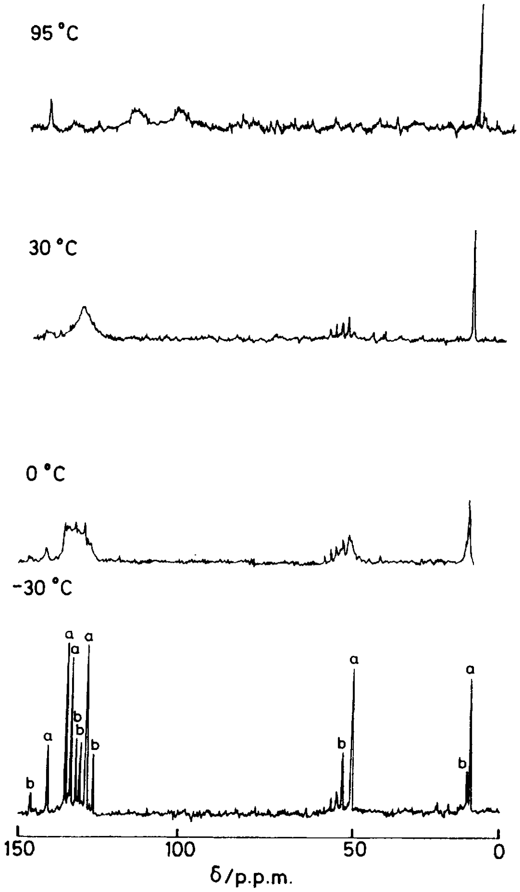


FIGURE 1 Proton noise-decoupled ^{13}C n.m.r. spectrum of trimethylgermyl(methyl)cyclopentadiene at various temperatures. For chemical-shift data see the Table and for significance of a and b labels see text. Small peaks near 55 p.p.m. are due to $CH_2Cl_2-CD_2Cl_2$ reference and lock signals in this series of spectra

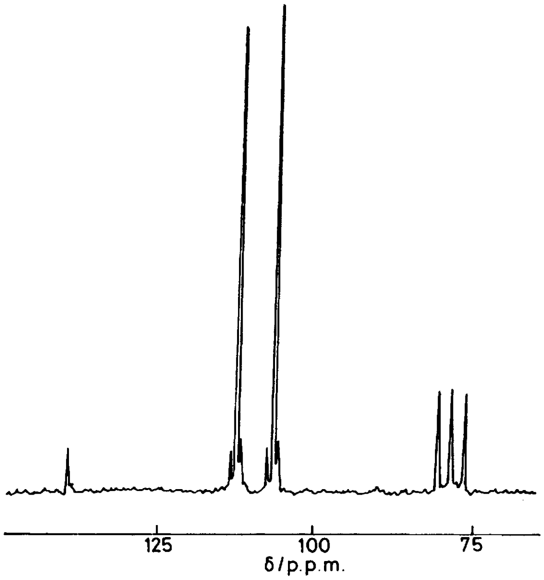
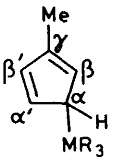


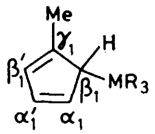
FIGURE 2 Proton noise-decoupled ^{13}C n.m.r. spectrum of trimethylstannyl(methyl)cyclopentadiene at 30 °C

comparison is possible for compound (4) since the slow limit of exchange is inaccessible. It is now necessary to decide on the identity of the isomer having higher equilibrium concentration for compounds (1) and (3), and arguing from the steric effect of increasing the size of M [compounds (1) and (2)] and of R [compounds (2) and (3)] we propose that for compounds (1)—(4) where a preferred configuration exists it will be (5) rather than (6). This becomes a crucial assumption although currently we are unable to provide direct proof.

In kinetic terms the dynamic properties of these systems depend on k_1, the rate of interconversion between two degenerate configurations (5), k_2, the rate of interconversion between the two doubly degenerate configurations (5) and (6), k_3, the rate of interconversion of configurations (6) with the non-degenerate state (7), and the rates k_1^{-1}, k_2^{-1}, and k_3^{-1} of the corresponding reverse interconversions, provided exchange occurs *via* a 1, 2 (and not random) shift.[3,7] While no attempt has been made to evaluate these rates, they result in temperature-dependent n.m.r. spectra of the kind illustrated in Figure 1, where it can be seen that the two highest-frequency ^{13}C resonances for compound (3) coalesce then sharpen much more rapidly than do the other C_5-ring carbon signals: such behaviour is consistent with averaging between isomers (5) and (6), during which the carbon atom bearing the methyl group retains its olefinic character, with only insignificant participation of isomer (7) in which the same carbon is aliphatic. Thus, we can identify isomerization between compounds (5) and (6) as the dominant process leading to stereochemical non-rigidity, redefined as exchange of (A) and (B) distinguishing ring nuclei (^1H or ^{13}C) as three types, α, β, or γ. It should be noted that by so doing magnetic inequivalence is related to the position of the methyl group, a scheme tacitly adopted by Campbell and Green[8] in discussing the ^1H n.m.r. properties of $Sn(C_5H_4Me)_4$ and $Hg(C_5H_4Me)_2$.



(A)



(B)

Considered in this way the exchange process should result in a fast limiting ^{13}C n.m.r. spectrum at temperature T consisting of three resonances with frequencies ν_1, ν_2, and ν_3 [equations (1)—(3)] in which ν_α, $\nu_{\alpha'}$, ν_β, $\nu_{\beta'}$,

$$\nu_1 = \tfrac{1}{2}[a(\nu_\alpha + \nu_{\alpha'}) + b(\nu_{\alpha_1} + \nu_{\alpha_1'})] \qquad (1)$$

$$\nu_2 = \tfrac{1}{2}[a(\nu_\beta + \nu_{\beta'}) + b(\nu_{\beta_1} + \nu_{\beta_1'})] \qquad (2)$$

$$\nu_3 = a\nu_\gamma + b\nu_{\gamma_1} \qquad (3)$$

and ν_γ are the resonant frequencies at the slow-limit for isomer (A) and a is its equilibrium mol fraction at T K; ν_{α_1}, $\nu_{\alpha_1'}$, ν_{β_1}, $\nu_{\beta_1'}$, and ν_{γ_1} are the corresponding frequencies for, and b the mol fraction of, isomer (B). To neglect the participation in the exchange of the geminal species (7) is a reasonable approximation as discussed above.

The ^{13}C n.m.r. spectrum of trimethylgermyl(methyl)-cyclopentadiene (3) at −30 °C has appeared elsewhere.[9] This was obtained by a proton-decoupled continuous-wave experiment with a much lower signal-to-noise ratio than for the present data but is essentially identical with that shown in Figure 1. While the temperature dependence of the spectrum was not investigated, comparison of the data at −30 °C with those for cyclopentadiene and methylcyclopentadiene isomers (spectra analyzed by selective proton decoupling) allowed an assignment to be deduced[9] which identified resonances attributable to each of the carbon atoms in isomers (A) and (B). Substituting these data appropriately into expressions (1) and (2) gives ν_1 = 101.6 p.p.m. and ν_2 = 120.9 p.p.m. as values for the frequencies of these lines in the coalesced spectrum resulting from fast-limiting exchange, assuming a ratio $a : b$ of 3.2 : 1 as measured at −30 °C. At 95 °C (Figure 1) these signals are becoming discernable experimentally, centred at 105.9 and 118.1 p.p.m. On the assumption that the experimental fast-limiting frequencies will not be shifted markedly from these values, their proximity to ν_1 and ν_2 calculated from (1) and (2) is consistent with a relatively minor temperature dependence of the $a : b$ ratio between −30 and 95 °C. Indeed, back-substitution in (1) and (2) of 105.9 and 118.1 for ν_1 and ν_2 leads to $a : b$ near 2 : 1, whence we estimate that the enthalpy difference between isomers (A) and (B) is *ca.* 2 kJ mol^{-1}, if their exchange can be regarded as a unimolecular reaction which involves only a small change in entropy. For compounds (1) and (2) where the equilibrium ratio of (A) and (B) at −30 °C is close to unity the enthalpy difference may be even smaller. The third expression (3) represents the averaging of the two γ resonances to give the signal well separated to high frequency, a coalescence which because of the small difference between ν_γ and ν_{γ_1} will be more rapid on the n.m.r. time scale than those giving rise to ν_1 and ν_2.

Further manipulation of equations (1) and (2) is revealing: when $a = b$, $\nu_1 \simeq \nu_2$ while for $a \gg b$, $\nu_1 \ll \nu_2$ and the two averaged signals reach their maximum separation, all the aliphatic character being concentrated in ν_1, with ν_2 composed almost entirely of olefinic character. Thus for the trimethyltin compound (4) the narrow separation of the two main peaks in the coalesced spectrum (111.7 and 105.9 p.p.m.; Figure 2) suggests that although the rearrangement cannot be slowed sufficiently by reducing the temperature to distinguish the individual isomers (A) and (B), their equilibrium concentrations must be fairly close to each other. By contrast, the fast-limiting ^{13}C n.m.r. spectrum of $Sn(C_5H_4Me)_4$ (ambient temperature) contains[10] ν_1, ν_2, and ν_3 at 96.5, 123.6, and 139.5 p.p.m., the much larger shift between ν_1 and ν_2 being consistent with preference for a ring configuration corresponding to (A), in accordance with the suggestions of Campbell and Green.[8]

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