Stereochemically Non-rigid Silanes, Germanes, and Stannanes. Part 3.[1] Intramolecular Rearrangements in Silyl-, Germyl-, and Trimethylstannyl-cyclononatetraenes

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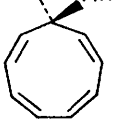
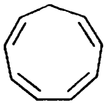
Reaction of $SnBrH_3$, $GeBrH_3$, or $SnMe_3Cl$ with the cyclononatetraenyl anion in the range −78 to −45 °C affords the 9-metallo-all-*cis*-cyclonona-1,3,5,7-tetraenes C_9H_9Y [$Y = SiH_3$(1), GeH_3(2), or $SnMe_3$(3)] characterized by ^1H and ^{13}C n.m.r. spectroscopy. On warming to ambient temperature, compounds (1)—(3) undergo electrocyclic ring closure to the isomeric 1-metallo-8,9-dihydroindenes (5)—(7), for which i.r., mass, and ^1H and ^{13}C n.m.r. spectral parameters have been recorded. N.m.r. data show that compounds (5)—(7) are formed as mixtures of *exo* and *endo* isomers, the former predominating in each case. The ^1H and ^{13}C n.m.r. spectra of *cis*-cyclononatetraene (4) and 8,9-dihydroindene (8) have also been obtained. At temperatures between −90 and 5 °C compound (3) is fluxional; comparisons with n.m.r. data for $SnMe_3(C_5H_5)$ and $SnPh_3(C_7H_7)$ indicate that successive 1,9 (' least-motion ') sigmatropic shifts rather than the alternative symmetry-allowed thermal migration (1,5; ' molecular broad-jump ') are responsible for metallotropic character. In contrast, compounds (1) and (2) are stereochemically rigid on the n.m.r. time scale at −45 °C and isomerization to compounds (5) and (6) at higher temperatures prevents observation of fluxional behaviour.

DEGENERATE metallotropic rearrangement in cyclopentadienyl derivatives of silicon, germanium, and tin, as well as of a number of other non-transition and transition elements, is by now a well known phenomenon which is qualitatively understood.[1-4] Because of synthetic limitations, however, almost without exception the data available for related systems concern non-degenerate rearrangements in, for example, methylcyclopentadienyl or indenyl compounds.[5-7] In order to examine the generality of some of the criteria which have been formulated in relation to the fluxional character of σ-metallocyclopentadienes, we have sought to isolate analogues derived from the ten-electron carbocycle cyclononatetraenide.[8] Measurement of the n.m.r. parameters for silyl-, germyl-, and trimethylstannyl-cyclononatetraenes, (1), (2), and (3) respectively, and characterization of intramolecular rearrangement to the corresponding 8,9-dihydroindenes (5)—(7) is described in this paper, together with complementary data for the unsubstituted hydrocarbons (4) and (8). At the outset of our investigation, the single example of a fluxional molecule showing comparable behaviour to the cyclopentadienes, but derived from a different parent carbocycle, was cycloheptatrienyltriphenylstannane, obtained from the tropylium cation by Larrabee.[9] Subsequently, one of the cyclononatetraenes, compound (3), has been reported[10] independently and proposed to exhibit degenerate metallotropism although no variable-temperature n.m.r. measurements were reported.



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



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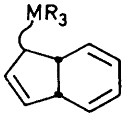
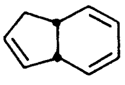


(5) M = Si, R = H
(6) M = Ge, R = H
(7) M = Sn, R = Me



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EXPERIMENTAL

General methods and details of instrumentation have been given in previous papers in this series.[1,2] Analyses of the silyl- and germyl-dihydroindenes was performed by Schwartzkopf Microanalytical Laboratories, Woodside, New York. Solvents were rigorously dried and degassed before use. The synthesis of potassium cyclo-octatetraenide,[11] *anti*-9-chlorobicyclo[6.1.0]nonatriene,[8] and lithium cyclononatetraenide[8] followed published procedures, manipulations being conducted under an atmosphere of dry dinitrogen gas using as reaction vessels double-limbed Schlenk assemblies fitted with greaseless stopcocks. Transference of air-sensitive solutions was achieved by *in situ* attachment by direct glass seals of suitable receivers using greaseless high-vacuum stopcocks where necessary. Typical syntheses of compounds (1)—(8) are described below; n.m.r. measurements were also duplicated using samples prepared *in situ*, transferred and sealed directly into n.m.r. tubes.

Synthesis of 9-*Silyl-all*-cis-*cyclonona*-1,3,5,7-*tetraene* † (1) *and Isomerization to* 1-*Silyl*-8,9-*dihydroindene* (5).—Bromosilane (344 mg, 3.10 mmol) was condensed (−196 °C) into a reaction vessel containing a filtered, deep purple-brown solution of Li[C_9H_9] (prepared from chlorobicyclo[6.1.0]-nonatriene; 470 mg, 3.08 mmol) in tetrahydrofuran (thf) (4 cm^3). On warming to −78 °C the solution became orange-yellow within 5 min. After stirring for 0.5 h at the same temperature, fractionation of volatile materials yielded the colourless liquid *product* (130 mg, 0.88 mmol) condensed at −45 °C with thf and unchanged $SiBrH_3$ at

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† Numbered as a substituted monocyclic hydrocarbon using I.U.P.A.C. practice. The possible alternative name 1-silyl-all-*cis*-cyclonona-2,4,6,8-tetraene derived from the cyclic hydrocarbon radical would parallel that commonly used previously for cyclopentadiene analogues (see ref. 1).

-196 °C. N.m.r. data (^{1}H and ^{13}C) obtained at this stage showed signals due to both (1) and (5). After subsequent manipulation at normal laboratory temperature, all of the *product* consisted of compound (5) (Found: C, 74.3; H, 8.50. Calc. for $C_9H_{12}Si$: C, 73.0; H, 8.0%). Infrared spectrum (liquid film): 3 072w, 3 027mw, 2 990mw, 2 937m, 2 874m, 2 158vs,br, 1 608w, 1 586mw,br, 1 460w, 1 380w, 1 180w, 1 148w, 1 095m, 1 067m, 980vw, 955w(sh), 908vs,br, 873m, 810vw, 782vw, 746s(sh), 733vs,br, 680vw, 651mw, 627mw, and 550vw cm^{-1}.

*9-Germyl-all-*cis*-cyclonona-*1,3,5,7*-tetraene* (2) *and Isomerization to* 1*-Germyl-*8,9*-dihydroindene* (6).—In a similar manner to that described above, bromogermane (460 mg, 2.96 mmol) and $K[C_9H_9]$ (from C_9H_9Cl; 540 mg, 3.54 mmol) were allowed to react at -63 °C for 3 h. After fractionation of volatile material, compound (6) (234 mg, 1.22 mmol) formed *via* (2) (^{1}H and ^{13}C n.m.r.) was isolated as a colourless *liquid* (Found: C, 54.8; H, 5.95. Calc. for $C_9H_{12}Ge$: C, 56.1; H, 6.25%). Infrared spectrum (liquid film): 3 065ms, 3 042s, 3 015mw, 2 968w,br, 2 930mw, 2 915m(sh), 2 912ms, 2 860ms, 2 064vvs, 1 650w, 1 616w, 1 590mw, 1 417w, 1 373w, 1 340w, 1 315w, 1 278w, 1 243w, 1 203w, 1 165w, 1 140mw, 1 093w, 1 030w, 1 010w, 975w, 968mw, 950w, 915w, 874s, 852m, 818vvs, 794w, 782s, 761m, 731w, 719ms, 710ms, 697s, 686m, 662ms, 646ms, 576ms, 560s, and 515m cm^{-1}.

*9-Trimethylstannyl-all-*cis*-cyclonona-*1,3,5,7*-tetraene* (3) *and Isomerization to* 1*-Trimethylstannyl-*8,9*-dihydroindene* (7).—To $K[C_9H_9]$ (from C_9H_9Cl; 350 mg, 2.30 mmol) in monoglyme (3 cm^{3}) was added $SnMe_3Cl$ (460 mg, 2.31 mmol). At -46 °C reaction was accompanied by a lightening of the solution to a dark orange colour. After 6 h, all volatile material was removed at -5 °C, when extraction with diethyl ether, filtration, and removal of the solvent left a very air-sensitive, pale yellow, viscous involatile oil identified as the *product*, (7), by n.m.r. and mass spectroscopy. Because of the intractibility of this compound it was subsequently manipulated as a solution in OEt_2. The same material was obtained from solutions of compound (3), formed initially in the above reaction and identified by ^{1}H and ^{13}C n.m.r. spectroscopy, on work-up at ambient temperature. Infrared spectrum in CCl_4 solution: 3 010m(sh), 2 988s, 2 930m, 2 870m, 1 640w, 1 620w, 1 460w, 1 390w,br, 1 310w, 1 200m, 1 073s, 910vs, and 728s cm^{-1}.

In situ *Synthesis of Compounds* (1)—(3).—These compounds were also prepared *in situ* in tubes suitable for n.m.r. experiments, maintaining temperatures low enough to avoid isomerization [to compounds (5)—(7)] and to minimize the risk of contamination, in the following way. A solution of $K[C_9H_9]$ in monoglyme was poured *in vacuo* into a ^{13}C n.m.r. tube, frozen to -196 °C, and an equimolar quantity of Group 4 halogeno-derivative condensed ($SiBrH_3$ or $GeBrH_3$) or poured ($SnMe_3Cl$) in before sealing off. Reaction at -50 °C for 6 h with the tube in an inverted position, during which time the purple-brown colour of the $[C_9H_9]^-$ anion was discharged leaving a characteristically orange solution, was followed by careful decanting of the solution from any insoluble material at the base of the tube. For ^{1}H n.m.r. measurements, similar syntheses were possible by replacing the monoglyme with $SiMe_4$ as solvent for the reaction.

*Synthesis of all-*cis*-Cyclonona-*1,3,5,7*-tetraene* (4) [8] *and its Isomerization to* cis-8,9*-Dihydroindene* (8).[8]—In a similar reaction to those described above, treatment of $K[C_9H_9]$ with glacial acetic acid gave initially a solution of compound (4) from which the pale yellow liquid *product* (8), ^{1}H n.m.r. spectrum identical to that depicted by Radlick and Alford,[12] was collected by vacuum condensation at -45 °C. Infrared spectrum (gas phase): 2 980s, 2 910vs(sh), 2 890vs, 2 870vs, 2 810s, 1 455m, 1 360m, 1 192vs, 1 120vvs,br, 1 025m, 970w, 852m, 825w(sh), and 535w cm^{-1}.

RESULTS AND DISCUSSION

Following preliminary reports in 1963 of the synthesis of the aromatic, ten-electron, carbomonocyclic system cyclononatetraenide, independently[13] by Katz and Garratt and by LaLancette and Benson, it was shown that hydrolysis of this anion yielded[8,14] 8,9-dihydroindene (8). Subsequently, the latter compound was shown to be formed in this way exclusively as the *cis* isomer, consistent with a thermal $(6\pi\rightarrow4\pi2\sigma)$ electrocyclic ring closure of all-*cis*-cyclonona-1,3,5,7-tetraene, and the monocyclic C_9H_{10} olefin (4) was ultimately characterized in 1969 in no less than four different laboratories.[12,15] Although a number of substituted cyclononatetraenes C_9H_9R are known, including R = Cl,[16] CH_2O_2CMe,[17] C_7H_7,[18] C_9H_9,[19] and $Fe(CO)_3$,[20] in all but the last case, thermal collapse readily occurs to give the appropriate dihydroindene. The exception is tricarbonyl(η^4-*cis*-cyclononatetraene)iron, which at 100 °C rearranges to a η^4-dihydroindene complex; this is the single example of a metallocyclononatetraene to have been reported previously, although since it results from a metal–olefin π interaction it is not directly comparable with compounds (1)—(3).

Dimetallation of cyclo-octatetraene followed by treatment with chloroform afforded *anti*-9-chlorobicyclo[6.1.0]nonatriene, whence further metallation gave[8] a solution in thf or monoglyme of the cyclononatetraenyl anion. Treatment of this deeply coloured solution with bromosilane, bromogermane, or trimethyltin chloride at temperatures between -78 and -46 °C was accompanied by an immediate change in the colour of the reaction mixture to dark orange. The compounds isolated from these experiments using manipulations conducted at ambient temperature were characterized by analysis and i.r. and mass spectroscopy as the *cis*-8,9-dihydroindene derivatives (5)—(7). That these products were formed by intramolecular rearrangement of the corresponding *cis*-cyclononatetraenes (1)—(3) was confirmed by n.m.r. spectroscopy. In both ^{1}H and ^{13}C spectra non-reversible changes occurred between -45 °C and ambient temperature, during which the relatively simple patterns attributable to compounds (1)—(3) became transformed into the much more complex sets of resonances due to the isomeric dihydroindenes (5)—(7). This is illustrated for the germyl compounds (2) and (6) in Figures 1 (^{1}H data) and 2 (^{13}C data); a full discussion of these and other variable-temperature n.m.r. measurements appears below. In a similar fashion, acetic acid with $[C_9H_9]^-$ gave successively cyclononatetraene (4) and *cis*-8,9-dihydroindene (8). Synthesis of, and experiments using, the potassium salt (rather than Li[C_9H_9]) appeared to necessitate the presence of monoglyme rather than *thf* as solvent in order for reaction to proceed at an appreciable rate.

The silyl and germyl compounds (5) and (6) are thermally stable colourless liquids, possessing vapour pressures just high enough to permit routine manipulation under a mercury-diffusion-pump vacuum; like cyclopentadienyl analogues,[1,2] they appeared to be unaffected by brief exposure to the atmosphere. In contrast, the pale yellow, viscous, trimethyltin derivative (7) is involatile and very air-sensitive, resembling trimethylstannylcyclopentadiene which is very readily hydrolyzed.[21]

The very strong absorptions at 2 158 and 908 cm^{-1} in the i.r. spectrum of compound (5) are characteristic of the silyl group, and arise from $\nu(SiH)$ and $\delta_{sym}(SiH_3)$ modes respectively. Corresponding $\nu(GeH)$ and $\delta_{sym}(GeH_3)$ vibrations are found at 2 064 and 818 cm^{-1} for the germane (6). The strong i.r. bands at 733, 719/710, and 728 cm^{-1} for compounds (5)—(7) respectively are in the region associated with the presence of a *cis* double bond.

The mass spectrum of the hydrocarbon (8) showed a molecular ion and a group of peaks due to $[C_9H_x]^+$ ($x = 6$—10), most prominently at *m/e* 116 ($x = 8$). Conspicuous polyisotopic parent-ion families for compounds (5) and (6) accounted for 10.4 and 8.6% of the ion current respectively, and $[C_9H_x]^+$ fragments were very prominent (46.0 and 64.4%). Other important ions were $[MH_x]^+$ (M = Si or Ge) and $[C_7H_x]^+$. These data suggest fragmentation similar to the related compounds examined earlier.[1,2] Considerable difficulty was encountered in sampling compound (7) and spectra were always heavily contaminated by ions attributable to $O(SnMe_3)_2$, but the molecular-ion family $[Sn(C_{12}H_x)]^+$, and $[C_9H_x]^+$ fragments were identified.

Variable-temperature ¹H *and* ¹³C *N.M.R. Studies*.—(A) *Intramolecular rearrangement of the cyclononatetraenes* (1)—(4) *to the corresponding dihydroindenes* (5)—(8). N.m.r. data are collected in Tables 1—4. The appearance of the spectra is typified by those for the germanium compounds, reproduced in Figures 1 and 2.

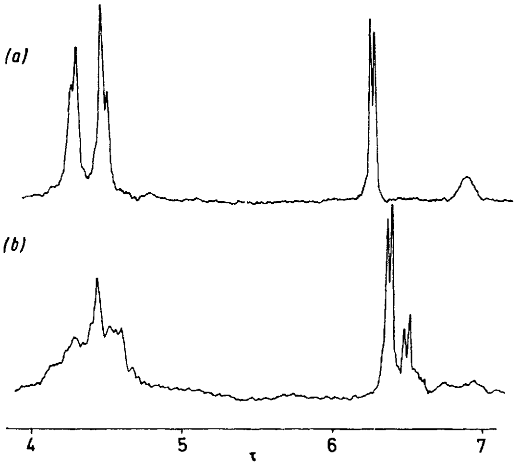


FIGURE 1 Hydrogen-1 n.m.r. spectra of (*a*) germylcyclononatetraene (2) at −45 °C, (*b*) germyl-8,9-dihydroindene (6) at 28 °C

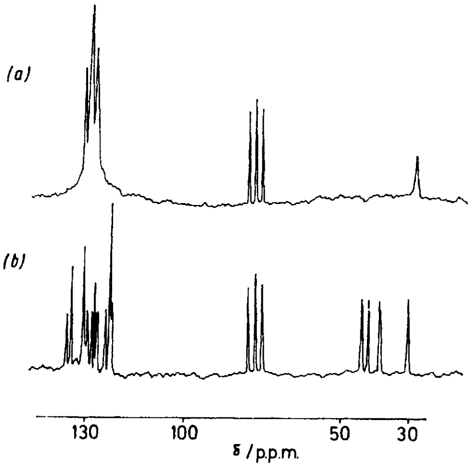


FIGURE 2 Carbon-13 n.m.r. spectra. Details as in Figure 1

The resemblance of the ¹H spectrum of compound (2) at −45 °C [Figure 1(*a*)] to the slow-limiting spectrum for germylcyclopentadiene illustrated in an earlier paper [2]

TABLE 1

Proton n.m.r. data [a] for compounds (1)—(3)

		Chemical shifts [b] (τ)			
T/K	Compound	$H_{aa'bb'cc'dd'}$	H_x	H_y	H_z
228	(1)	4.28—4.43	6.98	6.38 [c]	
	(2)	4.25—4.52	6.80	6.27 [d]	
183	(3)	4.06—4.22	n.o.		9.86
243	(3)	4.45	n.o.		9.87

[a] In $SiMe_4$ for compounds (1) and (2) or OEt_2 for (3). [b] Proton environments are distinguished as follows: aa′bb′cc′dd′, olefinic C_9 hydrogen atoms; *x*, aliphatic C_9 hydrogens; *y*, substituent Si or Ge hydrogens; and *z*, substituent methyl hydrogens. [c] Doublet, $^3J(H_x–H_y)$ 3.2, $^2J(^{29}Si–H)$ 206 Hz. [d] Doublet, $^3J(H_x–H_y)$ 2.5 Hz.

TABLE 2

Carbon-13 n.m.r. spectra [a] of cyclononatetraene and derivatives C_9H_8R (R = H, SiH_3, GeH_3, or $SnMe_3$)

	Chemical shifts/p.p.m.		
Compound	C(olefinic)	C(aliphatic)	*T*/K (solvent)
R = H	128.0	27.0	248 ($MeCO_2H$–monoglyme)
	125.6		
SiH_3	128.4	26.5	253 ($CDCl_3$) [b]
	128.0		
	127.6		
	126.5		
GeH_3	128.9	28.0	228 (monoglyme)
	127.3		
	127.1		
	125.5		
$SnMe_3$ [c]	117.0 (br)	n.o.	278 (CH_2Cl_2–CD_2Cl_2) [d]
	126.4 126.2	28.0(?)	183 (CH_2Cl_2–CD_2Cl_2)

[a] Block-averaging was used to enhance sample spectra relative to solvent resonances where required. Chemical shifts ±0.3 p.p.m., relative to $SiMe_4$ (0 p.p.m.) or $CDCl_3$ (77.2 p.p.m.). n.o. = Not observed. [b] Compare with 127.2, 125.9 (and partly resolved signals at 127.6, 127.0) and 25.9 p.p.m. in monoglyme solution at 232 K. [c] $\delta[^{13}C(Me)]$ observed at 0.0 p.p.m. with $^1J(C–H)$ 131.6, $^1J(^{117}Sn–C)$ 427.0, and $^1J(^{119}Sn–C)$ 446.4 Hz. [d] Compare with 116.5 (br) and −0.7 p.p.m. (Me) in monoglyme solution at 268 K.

TABLE 3

Proton n.m.r. data [a] for compounds (5)—(7)

Compound	Chemical shifts τ(CH)(olefinic)	τ(CH)(aliphatic)	τ(MH) [b]
(5)	4.2—4.7 [c]	6.7—8.4 [d]	6.45,[e] 6.59[f]
(6)	4.1—4.7 [c]	6.6—8.6 [d]	6.40,[g] 6.51 [h]
(7)	3.8—4.6 [c]	6.5—8.5 [d]	9.92, 9.99 [i]

[a] Recorded at ambient temperature in $SiMe_4$ for compounds (5) and (6) and $CDCl_3$ for (7). Integration of unresolved multiplets gave ratios consistent with assigned structures. [b] τ(Si*H*), τ(Ge*H*), or τ(SnCH_3) respectively for (5), (6), or (7). [c] Multiplets, strongest component at τ 4.42 (Si and Ge compounds) or τ 4.22 (Sn). [d] Very broad multiplet of weak resonances. [e] Doublet, *J* 3.3 Hz. [f] Doublet, *J* 3.7 Hz. [g] Doublet, *J* 3.0 Hz. [h] Doublet, *J* 3.3 Hz. [i] Unresolved $J(^{117,119}Sn–C–H)$ 51 Hz.

TABLE 4

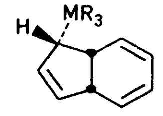
Carbon-13 n.m.r. spectra [a] of *cis*-8,9-dihydroindene and derivatives [b] C_9H_9R ($R = H, SiH_3, GeH_3$, or $SnMe_3$)

	R H	SiH_3	GeH_3	$SnMe_3$
δ(CH), olefinic	132.3	133.5	134.8	133.4
	130.6	132.1	133.4	130.7
	130.0	130.7	129.9	129.9
	126.4	130.1	129.6	129.6
	120.9	129.4	128.8	128.2
			128.4	
		128.8	126.0	128.1
		125.9	125.5	126.4
		125.8	122.9	125.8
		123.1	122.0	125.5
		123.0		121.0
			121.4	
		121.3		120.7
			121.1	
		121.2		120.6
		120.9		
δ(CH), aliphatic	44.0	44.2	44.1	44.0
	42.2	41.1	43.8	43.8
	35.9	37.7	42.1	40.5
		36.1	38.5	35.7
		35.5	38.1	31.6
		28.6	30.0	30.5
δ(CH_3)				0.96 [c]

[a] Recorded at ambient temperature, in $CDCl_3$ solution for compounds (5), (6), and (8) or monoglyme solution for (7). [b] As mixtures of *exo* and *endo* isomers: see text for discussion. [c] $J(^{117}Sn–C)$ 444.6, $J(^{119}Sn–C)$ 465.2 Hz.

is immediately obvious. The GeH_3 resonance at τ 6.27 is split into a doublet (*J* 2.5 Hz) through coupling to the tertiary (H_x) proton, the latter appearing at τ 6.80 as an unresolved multiplet. These values may be compared [2] with τ 6.67 (*J* 1.7 Hz), and τ 6.98 at —60 °C for $Ge(C_5H_5)H_3$. The eight olefinic protons (aa'bb'cc'dd') give rise to the resonances near τ 4.3 with a distinctive appearance [Figure 1(*a*)], resembling an asymmetric doublet of doublets. The ^1H spectrum at —45 °C for the silyl compound (1) is extremely similar, with ' satellite ' signals centred on the SiH_3 resonance at τ 6.38 due to $^1J(^{29}Si–H)$ 206 Hz. The ^{13}C spectra of compounds (1) and (2) recorded at the same temperature each show five resonances [Figure 2(*a*)] of which one is well removed to low frequency (26.5 or 28.0 p.p.m.) and can be assigned to C_x. The four high-frequency signals near 125 p.p.m. represent differentiation of (a,b,c,d) carbon atoms * but not of (a,a'),(b,b') and so on. Data for the parent hydrocarbon (4) are included in Table 2, and are very similar, the signal at 125.6 p.p.m. being roughly three times as intense as the other high-frequency line. These results are in complete agreement with those anticipated for the cyclononatetraenes (1), (2), and (4) existing at —45 °C as structures which are stereochemically rigid on the n.m.r. timescale. In contrast, the trimethyltin derivative (3) behaves very differently: low-temperature n.m.r. spectra are consistent with a ready fluxional rearrangement, discussed separately below.

During warming to ambient temperature the n.m.r. spectra of all four compounds (1)—(4) undergo dramatic changes which are clearly shown by reference to Figures 1 and 2. That compound (4) isomerizes to *cis*-8,9-dihydroindene (8) has been reported previously,[15] and this is further confirmed by a straightforward ^{13}C spectrum (Table 4). The three aliphatic carbon atoms give well resolved signals at low frequency, of which it is tempting to assign that at 35.9 p.p.m. to C^1, the close relationship between C^8 and C^9 resulting in only a small separation between the other two shifts. Five of the six olefinic carbon atoms appear individually between 120 and 133 p.p.m. The ^{13}C data for compounds (5)—(7) however contain many more lines (Table 4); the reason for this becomes immediately apparent on inspection of the ^1H spectra, *e.g.* Figure 1(*b*) for the germane. In the latter, two GeH resonances occur in *ca.* 4 : 1 ratio, as doublets with slightly different coupling constants: τ 6.40 (*J* 3.0) and 6.51 (*J* 3.3 Hz). This situation is parallelled exactly by the silane (5) (Table 3) and two CH_3 resonances separated by 0.07 p.p.m. were detected for compound (7). Although the electrocyclic ring-closure reaction gives exclusively the *cis*-dihydroindene skeleton,[12,15] the configuration at the tertiary carbon atom C^1 is not determined by this process. The product can, therefore, be formed as two isomers (9) and (10) with the substituent *exo* or *endo* to the bicyclic skeleton. There are two different orientations for the metallo-group, resulting in distinguishable resonances in the ^1H spectra. This is confirmed by ^{13}C data, which for compounds (6) and (7) consist of 12 olefinic and six aliphatic carbon resonances (Table 4), differentiating all 18 carbon atoms in two isomeric C_9 compounds. For compound (5), an additional high-frequency line was assumed to be due to an unidentified impurity in the ^{13}C sample.



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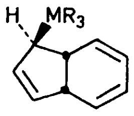

(10)

On the basis of relative intensities in ^1H spectra, the ratio of isomers (9) and (10) is close to 4 : 1 for all three compounds (5)—(7), the minor components giving rise

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* Strictly this type of labelling is appropriate only to the ^1H nuclei which constitute a spin-coupled set but it is perhaps the most convenient way of distinguishing the corresponding carbon atoms.

to a resonance *ca.* 0.1 p.p.m. upfield from the stronger signal. We attribute the latter in each case to the *exo* isomer (9), since it can be concluded from steric considerations accompanied by inspection of models that this will be the preferred configuration. This assignment is reasonable in that the upfield shift for substituent protons in the *endo* isomer can be accounted for by increased shielding due to proximity to the double bond between C^6 and C^7.

(b) *Fluxional characteristics of trimethylstannylcyclononatetraene* (3). For the silane (1) or the germane (2) we were unable to discern any firm evidence for coalescence of the H_x proton signal with the low-field region at temperatures below that at which formation of isomers (5) or (6) became rapid. Likewise, the time required to record ^{13}C spectra in the Fourier-transform mode was sufficient to result in extensive ring collapse during measurements at > -15 °C. We conclude that the activation energy $E^\ddagger$ for any metallotropic shift in these molecules similar to that occurring in cyclopentadienyl analogues[1,2] is equal to or greater than $E^\ddagger$ for the electrocyclic ring closure to give compounds (5) or (6). It has been clear for some time, however, that $E^\ddagger$ for the fluxional process in stannanes is perhaps 10—15 kJ mol^{-1} less than for that in analogous silanes or germanes,[3,22] and accordingly n.m.r. data for compound (3) are very different from those described above.

The ^1H spectrum of compound (3) at -30 °C consists of only two features, a sharp singlet at τ 9.86 and a broad resonance at τ 4.45 in *ca.* 1 : 1 ratio. This is essentially as reported by Boche and Heidenhain[10] at 20 °C, although at the same temperature our experience has been that isomerization to compound (7) prevents measurement of useful data. On cooling, the high-field signal attributable to the CH_3 protons is not affected but the other resonance is shifted successively to lower field, until at -90 °C some splitting can be seen in a broad contour in the τ 4.06—4.22 range. Corresponding ^{13}C spectra show similar temperature dependences; at 5 °C, the methyl carbon atoms of the $SnMe_3$ group resonate at 0.0 p.p.m., and the only other resonance apart from those due to solvents is a somewhat broadened one at 117.0 p.p.m. The latter broadens and moves to high frequency on cooling to -30 °C, when the linewidth begins to narrow once again to give at -90 °C (the lower experimental limit of the equipment used) a rather sharp signal centred at 126.3 p.p.m., apparently beginning to divide into two components. At this low temperature a further feature was also found, consistently near 28.0 p.p.m. in several different samples, but it was too weak for a temperature dependence to be established totally convincingly.

These results establish that compound (3) is fluxional in a way entirely analogous to related cyclopentadienes.[1-4] At 5 °C the nine ring nuclei (either ^1H or ^{13}C) are equivalent and exhibit an averaged chemical shift. On cooling, migration of the metal-containing group becomes less rapid and n.m.r. spectra develop progressively towards the aa'bb'cc'dd'x characteristics identified at < -45 °C for compounds (1) and (2). Thus the averaged resonance in the olefinic region (τ 4.45, ^1H; 117 p.p.m., ^{13}C) reaches a maximum linewidth (at *ca.* -30 °C in ^{13}C spectra) then shifts downfield (high frequency, ^{13}C) and sharpens as the H_x proton becomes increasingly distinguishable as aliphatic. At -90 °C the slow-limit ^{13}C spectrum has still not been reached but the olefinic resonance is quite narrow and has shifted by nearly 10 p.p.m.* Although, due to experimental difficulties, identification of the aliphatic resonance at *ca.* 28 p.p.m. is tentative, the weighted average of the two signals, 115.4 p.p.m., is close to the observed value at 5 °C (117 p.p.m.) for the coalesced shift. This situation closely parallels that described for cyclopentadienyltrimethylstannane (11),[21] for which an almost complete range of temperature dependence has been followed in the ^1H spectrum,[22] although very low temperatures are needed for observation of slow-limiting behaviour in cyclopentadienyltin compounds.[23] Thus, for compound (11) the H_x proton resonance of an aa'bb'x spectrum is just detectable[22] at -130 °C and is reasonably well resolved only at -150 °C.

Larrabee[3] has emphasized the relationship between sigmatropic migration in Group 4 metallocyclopentadienes and related compounds and the Woodward and Hoffmann orbital-symmetry criteria, highlighted by his assignment of the fluxional character of cycloheptatrienyltriphenylstannane (12) to a 'molecular broad-jump' (m.b.j.) rather than a 'least-motion' (l.m.) shift.[9] Of these mechanisms the former is a 1,5 shift which is the (only) symmetry-allowed thermal rearrangement,[24] analogous to the 1,5 (*i.e.* 1,2) shift in metallocyclopentadienes.[1,3] This is made clear by consideration of the symmetry selection rules for sigmatropic migrations in C_nH_{n+1} monocycles discussed by Anastassiou[24] based on the assumption of a homolytic shift. If fluxional properties resulting from sigmatropic behaviour can be treated similarly, from the symmetry properties of the highest occupied molecular orbital (h.o.m.o.) ψ_5 for the cyclononatetraenyl radical (Figure 3) it can be seen that for compound (3) there are two allowed thermal migrations: 1,5 which is a m.b.j., or 1,9 (equivalent to 1,2) the l.m. shift.

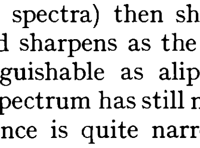

FIGURE 3 Symmetry properties of the h.o.m.o. ψ_5 for the cyclononatetraenyl radical

As reported above, the temperature dependence of the n.m.r. data for compound (3) is qualitatively rather similar to that described[22] for compound (11), implying that the $E^\ddagger$ values for metallotropism in these two systems are not dissimilar. In contrast, for compound

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* These changes have been illustrated in a preliminary communication: A. Bonny and S. R. Stobart, *Inorg. Chim. Acta*, 1978, **31**, L437.

(12) a slow-limiting ^{1}H spectrum was observed at temperatures as high as −19 °C and the $E^‡$ was estimated [9] by approximate methods to be of the order of 10 kJ mol^{-1} higher than that [22] in compound (11). If this latter increase is attributable to a migration *via* a m.j.b. rather than an l.m. shift, we then conclude that the cyclononatetraene (3) rearranges through successive 1,9 (l.m.) rather than 1,5 shifts. This represents an important modification of the predictions of the migratory pathway made by Larrabee [3] from molecular-orbital symmetry.

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