55345-08-9; Fe(C_2-Cap)(1,2-Me_2Im), 80964-67-6; Fe(NapC_2-Cap)(1-MeIm), 80964-68-7; Fe(NapC_2-Cap)(1,2-Me_2Im), 80964-69-8; Fe(C_3-Cap)(1,5-DCIm), 80964-70-1; Fe(C_2-Cap-NO_2)(1-MeIm), 80964-71-2; Fe(C_2-Cap-NO_2)(1,2-Me_2Im), 80964-72-3; Fe(T(*p*-OCH_3)PP)-(1,2-Me_2Im), 80964-73-4; Fe(C_3-Cap)(1,2-Me_2Im), 73555-67-6; Fe-(TPP)(1,2-Me_2Im), 72186-60-8; Fe(C_2-Cap)(1,2-Me_2Im)(CO), 80964-75-6; Fe(NapC_2-Cap)(1,2-Me_2Im)(CO), 80964-76-7; Fe(C_3-Cap)(1,2-Me_2Im)(CO), 80964-77-8; Fe(TPP)(1,2-Me_2Im)(CO), 80975-58-2; Fe-(napC_2-Cap)Cl, 80964-78-9; Fe(C_2-Cap-NO_2)Cl, 80964-79-0; 1-MeIm, 616-47-7; 1,5-DCIm, 80964-44-9; 1,2-Me_2Im, 1739-84-0; *n*-$PrNH_2$, 107-10-8; *i*-$BuNH_2$, 78-81-9; *sec*-$BuNH_2$, 13952-84-6; *t*-$BuNH_2$, 75-64-9; NH_3, 7664-41-7; O_2, 7782-44-7; CO, 630-08-0.

Stereochemically Nonrigid Silanes, Germanes, and Stannanes. 10.[1] Diastereoisomerism and Metallotropic Behavior in Polyindenyl Derivatives of Germanium and Tin. Facile Stereomutation

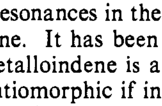
A. D. McMaster and Stephen R. Stobart*

Contribution from the Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2. Received June 29, 1981

Abstract: Variable-temperature ^1H and ^{13}C NMR data have been recorded for Ge(ind)$_4$ (I), Sn(ind)$_4$ (II), *n*-BuSn(ind)$_3$ (III), Ph_3Sn(ind) (IV), Ph_2Sn(ind)$_2$ (V), and PhSn(ind)$_3$ (VI) (ind = η^1-indenyl). For I–III and VI, slow-limiting spectra demonstrate the existence of diastereoisomerism resulting from chirality at the indenyl C^1 atom and are consistent with the presence of all possible stereoisomers. Correlation of experimental data with results of conformational analysis leads to the conclusion that for each system the diastereoisomer distribution is approximately statistical. The ground-state configuration for the meso form of II coincides with the highest symmetry molecular conformation, which belongs to the point-group S_4. Metallotropic behavior leading to temperature dependence of the NMR data results in simultaneous stereomutation having estimated $\Delta G^{\ddagger}$ near 60–70 kJ mol^{-1}.

Dynamic stereochemistry gives rise to the temperature-dependent NMR spectra which are a well-known and characteristic property of *monohapto*cyclopentadienyl (η^1-C_5H_5) metal systems.[2-4] Much of the information now available concerning this intriguing behavior has been provided by examination of appropriate derivatives of silicon, germanium, and tin. We have demonstrated recently[1,5] that the rapid degenerate intramolecular rearrangement in such compounds proceeds with retention of configuration at the migrating metal center. Thus 1,2-metallotropic migratory pathway in a fluxional η^1-C_5H_5 organometallic molecule can be closely associated with a [1,5] sigmatropic shift as defined by Woodward and Hoffmann.[6] Metallotropism is also found to occur in some related (η^1-cyclopolyenyl)metal systems, including (a) methylcyclopentadienyls (η^1-C_5H_4Me) and (b) indenyls (η^1-C_9H_7); in these compounds molecular nonrigidity may involve facile, reversible isomerization, i.e., *nondegenerate* intramolecular rearrangement.[7,8] We have shown[7] that such a description is correct for mono(η^1-C_5H_4Me) silanes, germanes, and stannanes belonging to category a, although for (η^1-C_5H_4Me)$_4$ analogues steric restrictions may reduce the complexity of the dynamic pathway to a two-site fluxional exchange.[8] Here we address the temperature-dependent NMR phenomena exhibited by polyindenyl derivatives of germanium and tin, which are representative of the second group (b) above. We find that a full analysis of ^1H and ^{13}C data introduces a new dimension into the description of these systems and also supplements our view[7,8] of the behavior of compounds of type a.

Rearrangement of a 1-silyl-, 1-germyl-, or 1-stannylindene results[9] in the metal-containing group M relocating to C^3 of the indene skeleton (**1** → **2**). The higher activation energies (about 60 kJ mol^{-1} for M = Sn, 90 for Ge, and 105 for Si) for these processes compared with those occurring in η^1-C_5H_5 analogues (30 kJ mol^{-1} for Sn, 50 for Ge; and 60 for Si) are consistent[4] with the intermediacy of the energetically less favorable isoindenyl structure (**3**) in a consecutive 1,2 pathway. This is further suggested (though not proven) by[10] coalescence of the silylmethyl ^1H resonances in the NMR spectrum of 1,2-bis(trimethylsilyl)indene. It has been pointed out that the C^1 carbon atom in a 1-metalloindene is asymmetric;[10] hence structures **1** and **2** are enantiomorphic if interconverted by metallotropic shifts which are confined to one face of the C_5 ring (i.e., are suprafacial). Existence of stereoisomerism in bis(η^1-indenyl)mercury has also been briefly mentioned,[11] but no evidence for its incidence was



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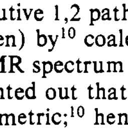

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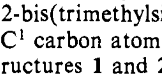

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Table I. Slow-Limiting Hydrogen-1 NMR Data[a]

compound	chemical shifts, τ			
	H^1	H^2	H^3	H^{4-7}
$Ge(C_9H_7)_4$ (I)	6.21, 6.31[b]	4.07–4.96	3.08–3.43	2.38–3.02
$Sn(C_9H_7)_4$ (II)	6.21, 6.29, 6.39, 6.54[c]	4.03–4.42	3.07–3.31	2.29–2.97
n-$BuSn(C_9H_7)_3$ (III)[d]	6.03, 6.28, 6.38, 6.49[e]	3.68–4.22	3.09–3.48	2.10–3.09
$Ph_3Sn(C_9H_7)$ (IV)	5.38[f]	2.91–3.11	*g*	2.10–2.88[h]
$Ph_2Sn(C_9H_7)_2$ (V)	5.71[i]	3.52–3.62	3.05–3.33	2.35–3.08[h]
$PhSn(C_9H_7)_3$ (VI)	5.84, 5.92, 6.11[j]	3.64–3.96	2.98–3.57	2.20–3.18[h]

[a] At −60 °C, $CDCl_3$ solvent, Me_4Si internal reference. Where a chemical shift range is indicated, signals are broad, complex multiplets that have not been analyzed in detail; for compounds IV–VI distinction between indenyl and phenyl ^1H resonances in the aromatic region was not attempted. [b] Signals in approximately 1:1 ratio. [c] Signals in approximately 1:1:3:3 ratio. [d] Signals at τ 8.65–9.69, attributable to n-Bu protons. [e] Signals in approximately 1:1:1:1 ratio. [f] $^2J(^{117,119}Sn\text{–}H^1) = 102.6$ Hz. [g] Overlapped by phenyl resonances. [h] With phenyl resonances. [i] $^2J(^{117,119}Sn\text{–}H^1) = 101.7$ Hz. [j] Signals in approximately 1:2:1 ratio.

Table II. Slow-Limiting Carbon-13 NMR Data[a]

compound	C^1	C^2	C^3	$C^{8,9}$	C^{4-7}			
$Ph_3SnC_9H_7$ (IV)[b]	44.6	134.4	126.9	142.8, 144.3	121.5	122.4	123.6	124.5
$Ph_2Sn(C_9H_7)_2$ (V)[c]	43.8	134.0	127.0	142.5, 143.8, 144.0	121.3	122.3	123.5	124.5
n-$BuSn(C_9H_7)_3$ (III)[d]	44.0, 44.6, 44.9, 45.5	133.4, 133.8, 134.2	126.2, 126.7	142.4, 143.9, 144.3	121.7	122.1	123.8	124.6
$PhSn(C_9H_7)_3$ (VI)[e]	43.5, 44.6, 45.1	133.4, 133.7, 134.0	127.3	142.7, 143.6, 143.9	121.7	122.5	123.9	124.9
$Ge(C_9H_7)_4$ (I)	42.5, 43.2, 44.5, 44.7	134.8	129.1, 129.4, 130.0	144.2, 144.6, 144.8	121.9	123.7	124.4	126.0
$Sn(C_9H_7)_4$ (II)	44.2, 44.6, 45.7	133.2	127.1, 127.5	143.1, 143.4, 143.7	121.9	122.6	124.0	125.2

[a] $CDCl_3$ used as solvent and reference throughout; measured positive downfield from $SiMe_4$ taking δ $CDCl_3$ 77.2 (central component of triplet). No specific assignment within $C^{8,9}$ or C^{4-7} is implied. Multiple entries correspond to diastereotopically shifted resonances; it is not certain which components are related in this way for the $C^{8,9}$ pair. Data listed are at −60 °C. [b] δ C_{phenyl} at 128.7, 129.5, 137.0. [c] δ C_{phenyl} at 128.3, 129.3, 136.4. [d] $\delta_{n\text{-butyl}}$ at 12.3, 13.5, 27.1, 28.0. [e] δ C_{phenyl} at 128.2, 129.4, 136.2.

detected. We find that the existence of diastereoisomerism is demonstrable in polyindenylgermanes and -stannanes by using both ^1H and ^{13}C NMR spectroscopy, the results being readily interpretable through conformational analysis, and that metallotropism in these molecules is synonymous with facile stereomutation (stereoisomerization). Compounds examined in this study include tetraindenylgermane (I), tetraindenylstannane (II), n-butyltri(indenyl)stannane (III), triphenyl(indenyl)stannane (IV), diphenyldi(indenyl)stannane (V), and phenyltri(indenyl)stannane (VI). Most of these materials have been synthesized before,[12-14] but no NMR data have been reported. However, the ^1H NMR spectra for a number of monoindenyl group 4 derivatives have appeared elsewhere,[3,9,10,15,16] and the ^{13}C NMR spectrum of (trimethylstannyl)indene has been assigned and its temperature dependence discussed.[17]

Experimental Section

Preparations were conducted under an atmosphere of dry dinitrogen gas by using standard bench-top techniques, following the published[12,14] procedures or as described below. Spectroscopic measurements were recorded by use of instrumentation that has been detailed previously.[1]

Synthesis of n-Butyltris(η^1-indenyl)tin (III) and Phenyltris(η^1-indenyl)tin (VI). Into a suspension of indenyllithium (3.0 g, 25 mmol) in dry hexane (50 cm^3) was introduced dropwise (ca. 30 min) $RSnCl_3$ (R = n-Bn or Ph, 7.5 mmol) in 20 cm^3 of the same solvent, with the reaction temperature maintained at 0 °C. Subsequent stirring of the reaction mixture at ambient temperature (24 h) was followed by filtration, removal of hexane, and recrystallization from $Et_2O/CHCl_3$ to give the white *products* (ca. 50%). Anal. Calcd for $C_{31}H_{30}Sn$: C, 71.43; H, 5.80. Found: C, 71.06; H, 5.79. Mp, 58 °C. Anal. Calcd for $C_{33}H_{26}Sn$: C, 73.23; H, 4.84. Found: C, 73.91; H, 4.98. Mp., 153–155 °C.

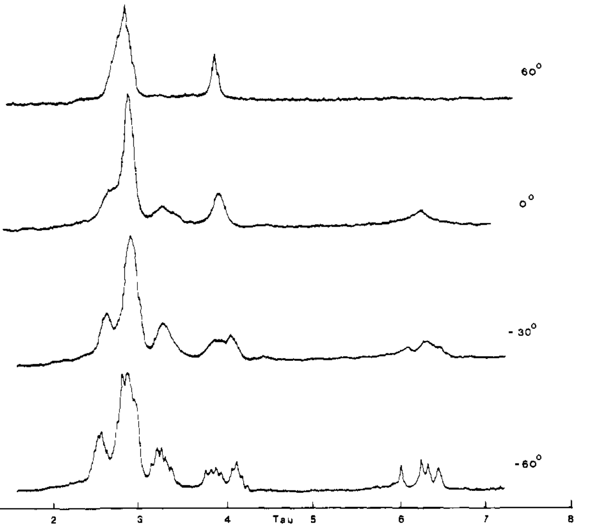

Figure 1. Hydrogen-1 NMR spectrum of n-$BuSn(C_9H_7)_3$ (III) at various temperatures.

Results

The ^1H NMR spectrum of n-$BuSn(C_9H_7)_3$ (III) is shown in Figure 1. At −60 °C this consists of a complex multiplet at low field arising from the strongly coupled aromatic/olefinic H^2–H^7 nuclei together with four distinct diastereotopic H^1 shifts in the range τ 6.21–6.54. These latter collapse as the temperature is raised, and this is accompanied by coalescence in the downfield contour, which consolidates into a single broad feature at 60 °C; at the same time, a signal at τ 3.84 progressively resolves into an apparent triplet. Very similar changes were observed for the other compounds: disappearance on warming of the upfield signal(s) attributable to H^1 protons and development of a triplet structure separated to high field of the major olefinic envelope. Slow-limit

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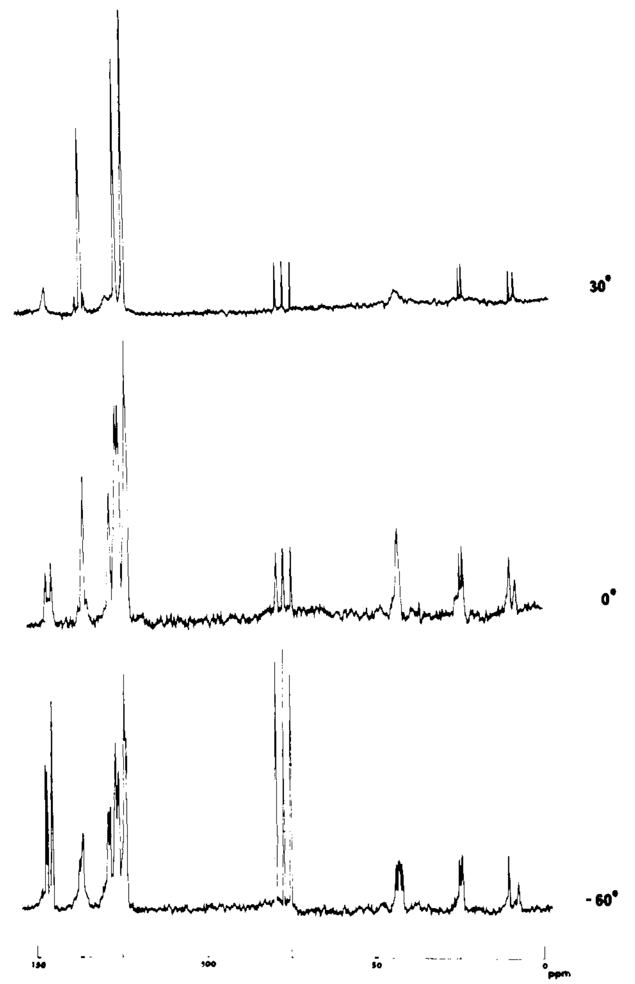
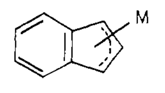


Figure 2. Carbon-13 NMR spectrum of n-BuSn(C_9H_7)$_3$ (III) at various temperatures.

^{1}H parameters are listed in Table I.

As suggested previously[17] for $Me_3SnC_9H_7$, the temperature-dependent proton-decoupled ^{13}C NMR spectra are much easier to analyze fully than corresponding proton data, showing excellent resolution between individual carbon environments. Slow-limiting chemical shifts are collected in Table II, in which our assignment of observed resonances to particular carbon atoms is based on the spectral changes resulting as magnetic equivalence (averaging of magnetic environment) is established between carbon pairs $C^{1,3}$, $C^{8,9}$, $C^{4,7}$, and $C^{5,6}$ at rapid rearrangement rates of **1** $\rightleftarrows$ **2**. This approach has been validated in the case of $Me_3SnC_9H_7$ by using off-resonance and spin-saturation techniques.[17] The temperature dependence is illustrated in Figure 2, again by use of compound III as a typical example. Signals due to the four n-butyl carbon atoms are at lowest frequency and are invariant in position. Progressive coalescence occurs to higher frequency with increasing temperature, most noticeably between C^1 (centered at 44.7 ppm) and C^3 (126.4 ppm), but also results in loss of resolution in the $C^{8,9}$, $C^{4,7}$, and $C^{5,6}$ pairs. At 30 °C (Figure 2) a simple four-line array accounts for all but two of the indenyl carbons while C^1 and C^3 are broad and symmetrically disposed about an average position of 85.6 ppm. This is consistent with representation **4** for the fast-limiting situation where a plane of symmetry relates $C^{1,3}$, $C^{8,9}$, $C^{4,7}$, and $C^{5,6}$ and contains C^2; the resonant frequency for the latter is thus temperature independent, as observed (Figure 2). Analogous coalescence phenomena were encountered in each of the other systems. In addition, however, a novel feature of the slow-limit spectra for the polyindenylmetal species I–III and VI is the incidence of multiplicity due to diastereotopic effects: this is mot striking in the C^1 shift range, depicted in detail for each compound in Figure 3. Minor splittings were also detected in C^2, C^3, and $C^{8,9}$ (Table II).



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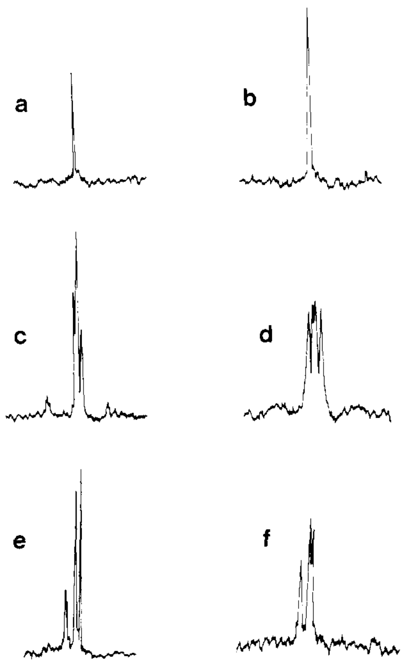

Figure 3. Appearance of C^1 region (ca. 45 ppm) in slow-limiting carbon-13 NMR spectrum of (a) $Ph_3Sn(C_9H_7)$ (IV), (b) $Ph_2Sn(C_9H_7)_2$ (V), (c) $PhSn(C_9H_7)_3$ (VI), (d) n-BuSn(C_9H_7)$_3$ (III); (e) $Ge(C_9H_7)_4$ (I), and (f) $Sn(C_9H_7)_4$ (II).

Discussion

Coalescence phenomena in ^{1}H and ^{13}C NMR spectra paralleling those observed here for compounds I–VI are well-documented in the literature, in which averaging between nuclei at the 1-position in structure **1**, involving those having instantaneously olefinic character,[4,9-11,17] occurs. The significantly higher $\Delta G^\ddagger$ parameters for dynamic processes in these systems compared with η^1-C_5H_5 analogues have been tentatively ascribed[4,17] to intermediacy of configurations corresponding to **3**, in a successive 1,2-migratory pathway. The present data do not resolve uncertainties associated with the latter. They do, however, focus attention on some novel stereochemical aspects of these systems: influence of chirality at C^1 in structure **1**, leading to observable diastereotopic shifts, and the configurational reversal synonymous with metallotropic rearrangement of **1** to its enantiomer (**2**).

Conformational analysis using simple group theory is required to systematically explain the diastereotopic effects observed in the slow-limiting ^{1}H or ^{13}C NMR spectra (Figures 1 and 3). Stereoisomerism in molecules of the type MR^*_4, RMR^*_3, and $R_2MR^*_2$ must be cataloged (R = achiral substituent), where R^*_n implies attachment to M of n identical chiral carbon centers (here indenyl C^1 atoms). The related R_3MR^* exists only as an enantiomeric pair and will show only homotopic behavior.[10,17] The analysis is summarized in Table III, which takes into account as necessary the existence of enantiomers and incidence of diastereoisomerism. The meso form (+−) possesses an internal plane of symmetry; the special properties of the meso (++−−) configuration were first recognized over 20 years ago by McCasland et al.[18] The other isomers are either dissymetric, where chemically equivalent nuclei can be related by C_n or S_n operations, or asymmetric (C_1), with no symmetry elements apart from the identity operation E. These latter species [i.e., (++−)-(III), (++−)-(VI), (+++−)-(I), and (+++−)-(II)] may therefore be

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Table III. Stereoisomerism in Polyindenyl Derivatives

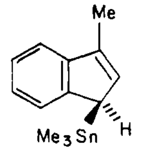
type	example	isomer[a]	S[b]	point group	mag[c]	N[d]
$R_2MR^*_2$	$Ph_2Sn(ind)_2$	(++)[e]	1	C_2	H	2
		(+−)[f]	1	C_s	H	2
RMR^*_3	*n*-$BuSn(ind)_3$	(+++)	1	C_1	H	3
		(++−)	3	C_1	D	(1,1,1)
MR^*_4	$Ge(ind)_4$	(++++)	1	D_2	H	4
		(+++−)	4	C_1	D	(3,1)[g]
		(++−−)[f,h]	3	S_4	H	4

[a] Each possible isomer for a given type is symbolized in terms of relative configuration + or − at an indenyl C^1 carbon center. [b] S represents the *statistical* distribution of the stereoisomers as listed in the preceding column. [c] Relationship between chemically equivalent nuclei in terms of magnetic properties; H = homotopic, D = diastereotopic. [d] N is the number of chemically equivalent nuclei per molecule sharing an identical magnetic environment i.e., which can be interchanged by some symmetry operation. [e] Racemic form. [f] Meso isomer. [g] Reduces from (1,1,1,1); see text. [h] At the suggestion of a referee, we note that this notation [rather than (+−+−)] implies that the first two descriptions are related by an $S_4{}^2$ $(=C_2)$ rotation.

expected to exhibit diastereotopic NMR shifts. It may be noted that although in (++−)-RMR^*_3 chemically equivalent nuclei are magnetically nonequivalent over all three R* groups, for (+++−)-MR^*_4 the unique center lies on a C_3 axis, assuming free rotation about the M–R* bond; in these circumstances the number of nonequivalent nuclei will reduce from four to two with a 3:1 distribution. From a stereochemical viewpoint, compounds III and VI are analogues of trimesitylborane which has been the subject of a detailed conformational analysis.[19] The resolution of anisochronicity in the ^{119}Sn NMR spectrum of Sn(*i*-Bu)$_4$ (where the diastereoisomers do not interconvert and could not be separated) has been discussed[20] on a similar basis to that adopted above for compounds I and II.

On a purely statistical basis and by using the products (SN) from Table III to predict the relative populations for both homotopic (H) and diastereotopic (D) species for compounds III and VI, four anisochronous shifts in 1:1:1:1 ratio are anticipated, while for compounds I and II, again four components will result, in 1:1:3:3 ratio. We suggest that just such diastereotopic effects account for the multiplicity observed in the C^1 spectral range (Figure 3) at slow rearrangement rates (slow-limit data): for the germane (I), four lines have peak heights close to 1:1:3:3, the two smaller components overlapping in the tin analogue (II). Likewise for III there are again four resonances, in ratio near 1:1:1:1 (as in the slow-limit proton spectrum, Figure 1), whereas in VI we attribute the strong central line to a combination of two unresolved components. This agreement of all experimental data with statistical predictions relating to equilibrium distribution establishes that there is a near-zero free energy difference between stereoisomers in each system. For compound IV no diasterotopic effects could be resolved, parallelling the situation described[11] for $Hg(C_9H_7)_2$.

Raising the temperature results in loss of resolution in the H^1 or C^1 region above −20 °C (Figures 1 and 2). This corresponds to scrambling of all diastereoisomers as a result of the rearrangement **1** $\rightleftarrows$ **2**. The activation energy for this stereomutation in the polyindenyltin compounds is estimated at about 60–70 kJ mol^{-1} by qualitative comparison with earlier data.[4,17] Accordingly, crystallization of compound II affords pure the meso isomer, (*R*,*R*,*S*,*S*)-tetraindenyltin, identified by single-crystal X-ray diffraction.[21] This represents only the second (first recognized as such[22]) example of a structurally characterized molecular arrangement the highest possible symmetry for which belongs to the point group S_4; all other related structures result[23] from conformational distortion of a higher symmetry configuration. By contrast with the behavior of simple 1-metalloindenes, including compounds I–VI above, Davison and Rakita[10] have reported that 1-(trimethylstannyl)-3-methylindene shows a temperature-invariant ^1H NMR spectrum consistent with the rigid structure **5**.



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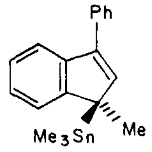

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It has since been claimed[24] that this compound is in fact separable into pure enanatiomers having some optical stability; the same paper reports that 1-methyl-1-(trimethylstannyl)-3-phenylindene (**6**) can also be resolved. An earlier very brief communication[25] describes **6** as metallotropic, $k \approx 10^2$ s^{-1}, although the rearrangement "proceeds with retention of optical activity". This confusing statement is contradictory in the sense that **6** and its rearranged product are different compounds, but details given were so sketchy as to preclude firm conclusions.

Finally, we suggest that residual broadening in low-temperature NMR spectra for some poly(methylcyclopentadienyl) derivatives[8] may in fact be due to unresolved diastereotopic splittings; these systems have instantaneous structures that also involve attachment of a metal atom to a chiral carbon center.

Acknowledgment. We are grateful to the N.S.E.R.C. (Canada), the University of Victoria, and the Research Corporation (Cottrell Foundation) for financial support and to Professor K. Mislow for his comments and continuing interest.

Registry No. I, 80865-56-1; II, 7770-22-1; III, 80865-57-2; IV, 1249-25-8; V, 80865-58-3; VI, 80865-59-4.

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