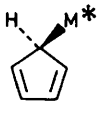
Stereochemically Non-rigid Silanes, Germanes, and Stannanes. Part 11.[1] Mechanistic Implications of Diastereotopic Effects induced in Methylcyclopentadienyl, Indenyl, and Pentamethylcyclopentadienyl Ring Systems by Chiral Tin Substituents

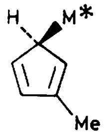
A. D. (' Lex ') McMaster and Stephen R. Stobart *
Department of Chemistry, University of Victoria, British Columbia, Canada V8W 2Y2

The synthesis and characterization by ^1H and ^{13}C n.m.r. spectroscopy of the racemic, chiral cyclopentadienyl-related compounds $Sn^*MePr^iPh(R)$ [R = C_5H_4Me (2); R = C_9H_7 (3); R = C_5Me_5 (4)] is reported. For (2) and (4) the n.m.r. data are exclusively fast-limiting; compound (3) exhibits temperature-dependent behaviour. Diastereotopic effects in the isopropyl substituent identified by ^1H [(2) and (3)] or ^{13}C n.m.r. [compound (4)] establish that for each compound metallotropic rearrangement occurs with retention of configuration at tin. The dynamic process in (2) is discussed in terms of facile epimerization; slow-limiting data for (3) show the presence of two diastereoisomers which stereomutate at elevated temperature; the degenerate rearrangement of (4) is related to the behaviour of unsubstituted analogues and the Woodward–Hoffmann [1,5] sigmatropic shift.

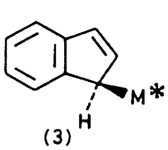
Earlier papers [2–4] have established the effect of *degenerate* metallotropic rearrangement on stereochemistry at the migrating metal centre in cyclopentadienyl-silanes, -germanes, and -stannanes, leading to a generalized mechanistic definition [4] of fluxional behaviour in σ-cyclopentadienyl derivatives such as (1) (M^* = $SnMePr^iPh$). We have also shown that in corresponding σ-methylcyclopentadienyl [5,6] and σ-indenyl [1] compounds this is paralleled by *non-degenerate* metallotropic rearrangement which may occur simultaneously with other stereochemical effects identifiable by variable-temperature n.m.r. spectroscopy, including [1] stereomutation among diastereoisomers. In the present discussion we consider the mechanistic implications presented by incorporation of a chiral metal-containing group as the migratory entity in such modified [1,5] cyclopentadienyl systems, specifically (2) and (3).



(1)

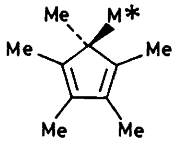


(2)



(3)

Attachment of the isopropyl group at a migrating centre (here Sn) provides a means for establishing whether rearrangement occurs with retention of configuration at this centre, or otherwise; [3,4] additionally we have extended this approach to a definitive characterization of *degenerate* metallotropism in σ-pentamethylcyclopentadienyl compounds, as typified by the tin(IV) derivative (4). While dynamic stereochemistry in molecules belonging to this category has been assumed to relate directly with corresponding properties of the σ-cyclopentadienyls, *e.g.* (1), very few substantive temperature-dependent n.m.r. data have appeared.[7]



(4)

Experimental

Synthetic and spectroscopic methods have been detailed in previous papers in this series.[1–6] The precursor isopropylmethyl(phenyl)tin bromide (5) was prepared as described by Gielen *et al.*[8] Compounds (2)—(4) were isolated as volatile liquids by identical procedures, the following providing a further example. To a suspension of KC_5H_4Me (0.5 g, 6.3 mmol) in dry toluene (30 cm^3), stirred and maintained at −78 °C, was added dropwise a solution of compound (5) (2.00 g, 5.99 mmol) in toluene (20 cm^3). Slow warming to ambient temperature was followed after 12 h by filtration and concentration to afford a yellow oil. Evaporation *in vacuo* with condensation onto a cooled probe (−78 °C, solid CO_2–acetone) yielded the pure product (2) (1.10 g, 3.31 mmol) as a yellow, air-sensitive liquid. Satisfactory microanalytical data for the three new compounds were obtained (Canadian Microanalytical Service). Further characterization was provided by mass spectral data for each which included appropriate molecular ions and contained no prominent peaks attributable to fragmentation of the C_5 ring system; this is consistent [9] with σ bonding in all three species.

Results and Discussion

Using methods which are by now well established,[1–6] compounds (2)—(4) were isolated as pale yellow, rather air-sensitive oils through reaction of the appropriate cyclopolyenyl anion with racemic isopropylmethyl(phenyl)tin bromide.[8] The products so formed are therefore likewise racemic with respect to configuration at the metal centre and they exhibit no chiro-optical properties; however, magnetic non-equivalence induced by chirality at the tin atom was observed

Table 1. Hydrogen-1 n.m.r. data [a] for the Me, Pr^i, and Ph substituents in compounds (2)—(4)

		δ/p.p.m.[b]			
Compound	T/K	CH_3	$CH(CH_3)_2$	$CH(CH_3)_2$	C_6H_5
(2)	300	−0.16 [c]	1.4—1.9 [d]	1.20, 1.23, 1.26, 1.30	7.2—7.8 [d]
(3)	243	−0.01,[e] 0.05 [f]	1.4—1.9 [d]	1.0—1.4	7.7 [d]
	333	0.04 [f]	1.4—1.9 [d]	1.20, 1.23, 1.28, 1.31	7.7 [d]
(4)	300	0.20 [g]	1.4—1.9 [d]	1.22, 1.30	7.7 [d]

[a] At 90 MHz, 10% $CDCl_3$ solution. [b] Positive downfield from $SiMe_4$. [c] $^2J(^{117,119}Sn-H)$ = 50.4 Hz. [d] Broad multiplet. [e] $^2J(^{117,119}Sn-H)$ = 48.7 Hz. [f] $^2J(^{117,119}Sn-H)$ = 49.1 Hz. [g] $^2J(^{117,119}Sn-H)$ = 45.0 Hz.

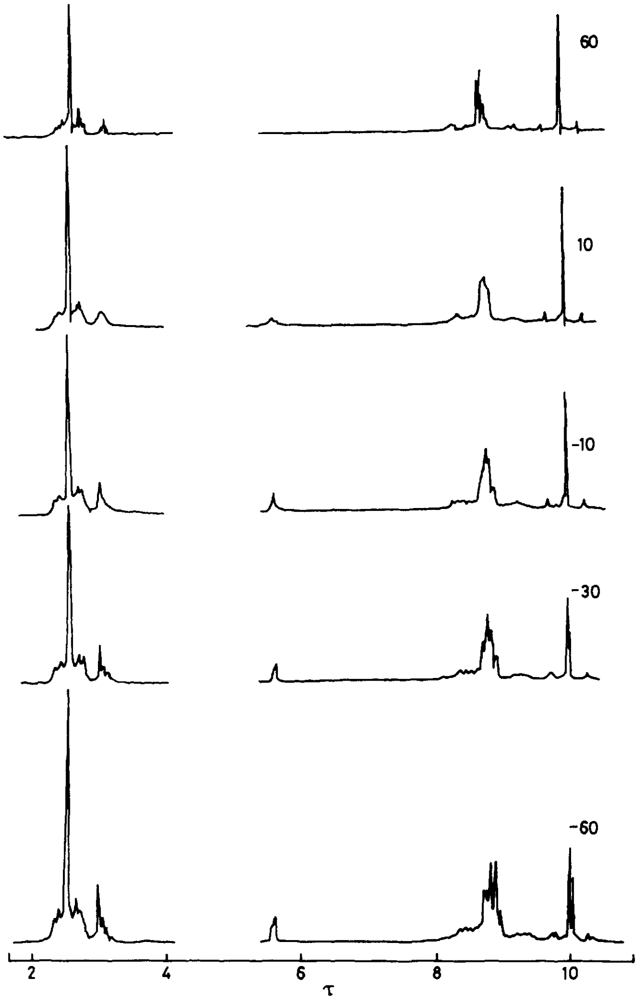
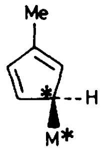


Figure 1. Hydrogen-1 n.m.r. spectrum of compound (3) at various temperatures (°C)

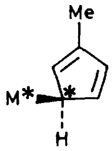
experimentally as diastereotopic effects in n.m.r. spectra for each molecule. Data are divided up as follows, for convenience of presentation: Tables 1 and 2 respectively list ^1H and ^{13}C shifts and coupling constants attributable to the methyl, isopropyl, and phenyl substituents at Sn in the three compounds. Table 3 summarizes ^1H and ^{13}C n.m.r. parameters assigned to nuclei in the appropriate C_5 framework bonded to the tin atom. Compounds (2) and (4) resemble achiral analogues in that intramolecular rearrangement occurs rapidly enough to result in fully averaged (fast-limiting) n.m.r. spectra (^1H or ^{13}C) at all accessible temperatures, *i.e.* spectra which are temperature invariant. By contrast, the rearrangement rate for the indenyl compound (3) is substantially slower and characteristic temperature dependence is found in the n.m.r. spectra, as shown in Figure 1.

For compound (2), the four C_5 ring protons give rise to signals at 5.52, 5.72, and 5.96 p.p.m. (ratio 2 : 1 : 1) in the ^1H n.m.r. spectrum (Figure 2) with those of the ring-methyl group appearing at 2.06 p.p.m. The remaining features of this spectrum are readily attributable to Ph, Me, and Pr^i substituents at tin, the multiplet assigned to the six β-protons of the third of these groups being similar to the structure anticipated [4] (pair of doublets) for two inequivalent methyl groups each coupled to the single α-proton (A_3B_3 of A_3B_3X). By contrast, in the ^{13}C spectrum no diastereotopic splitting of the $-CH(CH_3)_2$ resonance at 21.7 p.p.m. is discernible; other assignments given in Table 2 are substantiated by data given elsewhere.[4—6,10] The ^{13}C resonances of the C_5H_4Me ring system (labelled αα′,ββ′,γ as in ref. 5) occur at 100.6, 101.1, 115.4, 118.8, and *ca.* 138 p.p.m., the first two (*i.e.* those having least olefinic character) being assigned [5] to $C^{\alpha,\alpha'}$ with the conspicuously weak line attributed [5] to C^{γ} (diminished Overhauser effect).

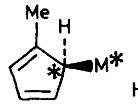
Fabian and Labinger,[11] referring to the complexes [Fe(CO)L(η^5-C_5H_5)(σ-C_5H_4Me)] [L = $P(OPh)_3$ or $PF_2(NMe_2)$], have asserted (correctly) that the AA′BB′ array observed [6,12] for the ring protons of a σ-methylcyclopentadienyl metal derivative at the fast limit of (non-degenerate) metallotropic rearrangement will transform into an ABCD multiplet in such a compound in which the metal centre is chiral. We formalize this argument here in extending it to analysis of the corresponding fast-limit ^{13}C spectrum: we begin by noting that in (2) the carbon atom at the ring position to which Sn is attached is a chiral centre. The dynamic behaviour of the



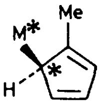
(5)



(6)



(7)



(8)

methylcyclopentadienyl (2) can therefore be represented as facile interconversion between the set of epimers (5)—(8) (M* = $SnMePr^iPh$). This single set adequately describes the data since the analogues corresponding to reversal of con-

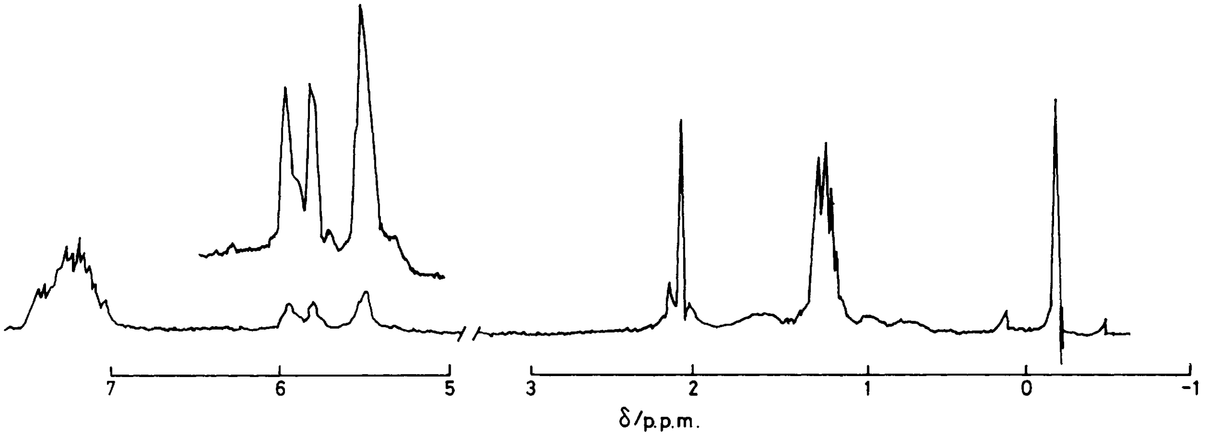
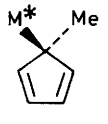


Figure 2. Hydrogen-1 n.m.r. spectrum (90 MHz) of compound (2)

figuration at (racemic) tin constitute an enantiomeric set with identical n.m.r. properties. We have previously proposed[5,13,14] that the equilibrium concentration of *gem* isomers is negligible so that participation in the rearrangement of configuration (9) will be ignored. Defining the equilibrium mol fractions at temperature T(K) of (5)—(8) as a, b, c, and d respectively, and the resonant frequencies for the individual configurations (5)—(8) according to the labelling scheme used earlier[5] as (α^{A}, $\alpha^{A'}$, β^{A}, $\beta^{A'}$, γ^{A}), (α^{B}, $\alpha^{B'}$, β^{B}, $\beta^{B'}$, γ^{B}), (α^{C}, $\alpha^{C'}$, β^{C}, $\beta^{C'}$, γ^{C}), and (α^{D}, $\alpha^{D'}$, β^{D}, $\beta^{D'}$, γ^{D}) we obtained expressions (1)—(5) for the five non-degenerate carbon frequencies in the fast-limiting exchange situation.



(9)

$$\nu_1 = \tfrac{1}{4}[a\alpha^{A} + b\alpha^{B} + c\alpha^{C} + d\alpha^{D}] \quad (1)$$

$$\nu_2 = \tfrac{1}{4}[a\alpha^{A'} + b\alpha^{B'} + c\alpha^{C'} + d\alpha^{D'}] \quad (2)$$

$$\nu_3 = \tfrac{1}{4}[a\beta^{A} + b\beta^{B} + c\beta^{C} + d\beta^{D}] \quad (3)$$

$$\nu_4 = \tfrac{1}{4}[a\beta^{A'} + b\beta^{B'} + c\beta^{C'} + d\beta^{D'}] \quad (4)$$

$$\nu_5 = \tfrac{1}{4}[a\gamma^{A} + b\gamma^{B} + c\gamma^{C} + d\gamma^{D}] \quad (5)$$

Since the large chemical shift difference observed experimentally between signals attributed to the $C^{\alpha,\alpha'}$ and $C^{\beta,\beta'}$ pairs suggests[5] that a and $b \gg c$ or d, neglecting these simplifies

$$\nu_1 = \tfrac{1}{2}[a\alpha^{A} + b\alpha^{B}] \quad (6)$$

$$\nu_2 = \tfrac{1}{2}[a\alpha^{A'} + b\alpha^{B'}] \quad (7)$$

$$\nu_3 = \tfrac{1}{2}[a\beta^{A} + b\beta^{B}] \quad (8)$$

$$\nu_4 = \tfrac{1}{2}[a\beta^{A'} + b\beta^{B'}] \quad (9)$$

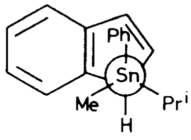
$$\nu_5 = \tfrac{1}{2}[a\gamma^{A} + b\gamma^{B}] \quad (10)$$

$$\nu_1 - \nu_2 = \tfrac{1}{2}[a(\alpha^{A} - \alpha^{A'}) + b(\alpha^{B} - \alpha^{B'})] \quad (11)$$

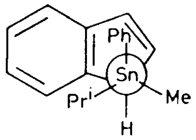
$$\nu_3 - \nu_4 = \tfrac{1}{2}[a(\beta^{A} - \beta^{A'}) + b(\beta^{B} - \beta^{B'})] \quad (12)$$

equations (1)—(5) to equations (6)—(10), which lead to equations (11) and (12). Equations (11) and (12) relate the observed ($\nu_1 - \nu_2$) and ($\nu_3 - \nu_4$) (here, 0.5 and 3.4 p.p.m. respectively; Table 3) to parameters for the contributing epimeric configurations (5) and (6). While these latter cannot be characterized individually because of the low barrier to metallotropic exchange in (2), the analysis is a general one applicable to systems in which rearrangement occurs at slower rates.

The ^{1}H n.m.r. spectrum of compound (3) at −60 °C at which temperature rearrangement is slow,[1] Figure 1, is complex in the low-field region because of overlapping multiplets due to substituent phenyl protons and H^{3}—H^{7} of the indenyl skeleton. The indenyl H^{2} resonance is centred at 6.9 p.p.m. while the corresponding H^{1} signal consists of two components (4.41 and 4.46 p.p.m., ratio *ca.* 60 : 40) as does the substituent CH_3 signal (0.05, −0.01), with the protons of the isopropyl group appearing as a multiplet envelope at 1.0—1.9 p.p.m. This can be interpreted in terms of a mixture in unequal ratio of the two diastereoisomers (10) and (11), exhibiting different spectra which are most obviously distinguishable for H^{1}(indenyl) and Sn$-$CH_3, in relative concentration determined[5] by the free-energy difference between the two. Similarly, the low-temperature ^{13}C n.m.r. spectrum (Tables 2 and 3) includes two lines for Sn$-$$CH_3$ (−13.9, −13.2 p.p.m.) and for C^{1}(indenyl) (43.9, 44.4).



(10)



(11)

Metallotropism in achiral analogues of (3) is well characterized[1] and leads at elevated temperature to spectral averaging between indenyl 1- and 3-positions, *i.e. via* an overall 1,3-shift.[1,15] Corresponding behaviour of (10) by a suprafacial rearrangement reverses the C^{1} configuration to give what is in fact the enantiomer of (11), and *vice versa*; this provides an exchange pathway which will result in coalescence of the distinguishable n.m.r. spectra for the two diastereoisomers, an effect which is clearly evident from the Tables and in Figure 1. At 60 °C the spectra are fast-limiting (disappearance of H^{1}, C^{1} signals; triplet structure[1] for H^{2}); however, coalescence in the isopropyl proton contour produces a multiplet structure which is recognizable as an A_3B_3X pattern, *i.e.* establishing

Table 2. Carbon-13 n.m.r. data [a] for the Me, Pr^i, and Ph substituents in compounds (2)—(4)

		δ/p.p.m.[b]			
Compound	T/K	CH_3	$CH(CH_3)_2$	$CH(CH_3)_2$	C_6H_5 [c]
(2)	300	−13.4 [d]	17.7	21.7 [e]	128.4, 128.8, 136.4, 141.4
(3)	243	−13.9, −13.2 [f]	16.5	21.6 [e]	128.4, 128.9, 136.5, 140.3
(4)	300	−12.9 [g]	16.9	21.7, 22.0	127.9, 128.4, 136.8, 141.4

[a] At 15.09 MHz, 25% $CDCl_3$ solution. [b] To high frequency relative to δ 77.2 p.p.m. for $CDCl_3$ (central component of triplet). [c] Listed as $C^{3,5}$, C^4, $C^{2,6}$, C^1 respectively as in ref. 10. [d] $^1J(^{117,119}Sn-C)$ = 129.9 Hz. [e] Broad. [f] Coalesced to single peak, δ −13.2 p.p.m. at 333 K. [g] $^1J(^{117,119}Sn-C)$ = 130.4 Hz.

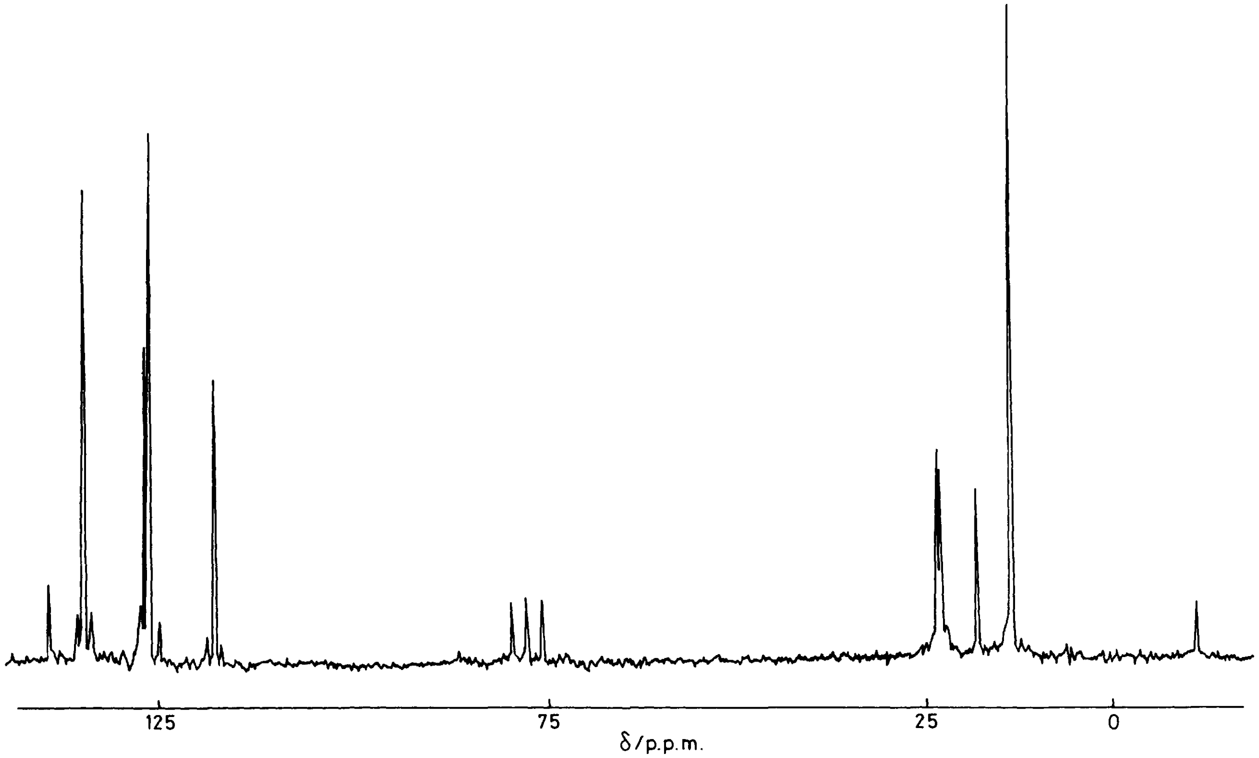


Figure 3. Carbon-13 n.m.r. spectrum (15.09 MHz) of compound (4)

Table 3. N.m.r. data [a] for C_5 ring systems of compounds (2)—(4)

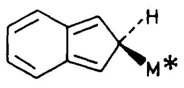
			δ(^{1}H)/p.p.m.[a]		δ(^{13}C)/p.p.m.[a]			
Compound	T/K		Me	H(ring)	Me	$C^{\alpha,\alpha'}$	$C^{\beta,\beta'}$	C^{γ}
(2)	300		2.06 [b]	5.52 5.72 5.96	15.4	100.6 101.1	115.4 118.8	138.1(?)
(4)	300		1.78 [c]		12.1		119.3	
			H^1	H^2	$H^{3,4-7}$			
(3)	243	δ(^{1}H)	4.41	6.8—7.1 (m) [d]	6.1—6.8 (m)			
			C^1	C^2	C^3	C^{4-7}	$C^{8,9}$	
(3)	243	δ(^{13}C)	43.9 44.4	134.7 135.4 } [e]	125.2	121.2 121.9 123.1 123.8 } [f]	142.2 145.2 145.5 } [g]	

[a] Measured as in Tables 1 and 2. Nuclear environments distinguished as in refs. 1, 4, and 5. [b] $^3J(^{117,119}Sn-H)$ = 11 Hz. [c] $^3J(^{117,119}Sn-H)$ = 19 Hz. [d] Triplet centred at 6.91 p.p.m., 333 K: $^3J[H^{1,3}(average)-H^2]$ = 3.6 Hz. [e] Single line at 333 K, δ 134.9 p.p.m. [f] Two lines only at 333 K, δ 121.7 and 123.7 p.p.m. [g] Single line at 333 K, δ 144.1 p.p.m.

that in the fast limit the isopropyl methyl (β) protons remain magnetically non-equivalent. A corresponding diastereotopic shift is not resolvable (at 15.09 MHz) in the carbon-13 spectrum.

By contrast with compounds (2) and (3), (4) is a fluxional system (*degenerate* rearrangement) in which fast-limiting behaviour leads to only a single, averaged magnetic environment for C_5 ring nuclei: appropriately, simple singlets were observed in both ^{1}H and ^{13}C spectra (Figure 3) [1.78 p.p.m., $\delta(CH_3)$; 12.1, 119.3 p.p.m., $\delta(C_5CH_3)$, $\delta(C_5CH_3)$ respectively]. Also in compound (4), the two isopropyl β-carbon atoms resonate at different frequencies (21.7 and 22.0 p.p.m.), *i.e.* they are diastereotopically shifted, although the related effect in the ^{1}H spectrum was considerably less well resolved than for compounds (2) or (3).

Summary: Stereochemistry and Mechanism.—N.m.r. measurements clearly establish that for each of the molecules (2)—(4), diastereotopic behaviour within the isopropyl substituent at tin persists at rates of rearrangement sufficiently rapid to result in averaging of C_5 ring environments. This is consistent only with retention of configuration at the migrating metal centre in each case. For the C_5Me_5 derivative (4) the situation is directly analogous to that for the unsubstituted cyclopentadienyl systems discussed earlier, *i.e.* it is phenominologically related to a symmetry-controlled (Woodward–Hoffmann) [1,5] migration. Things are a little more complicated for (2) and (3). In the former, persistence of magnetic inequivalence among all four ring-hydrogen atoms (all five ring carbons) at fast rates of metallotropic rearrangement can only occur[11] when the latter is *suprafacial* since the configurational stability of the migrating group has been confirmed; we visualize the lowest energy rearrangement as being (5)$\rightleftarrows$(6), as suggested earlier.[5] Stereomutation[1] between (10) and (11) with retention of configuration at tin is likewise consistent only with a *suprafacial* rearrangement in the indenyl system, although our results shed no further light on the relative importance in this process of the isoindenyl form (12), *i.e.* whether or not the observed overall 1,3-shift proceeds *via* sequential 1,2-steps.[1,15,16]



(12)

Acknowledgements

We thank the N.S.E.R.C. (Canada), the University of Victoria, and the Research Corporation (Cottrell Foundation) for financial support and Drs. R. D. Holmes-Smith and J. Takats for constructive comments

References

1 Part 10, A. D. McMaster and S. R. Stobart, *J. Am. Chem. Soc.*, 1982, **104**, 2109.
2 Part 4, A. Bonny and S. R. Stobart, *J. Am. Chem. Soc.*, 1979, **101**, 2247.
3 Part 7, R. D. Holmes-Smith and S. R. Stobart, *J. Am. Chem. Soc.*, 1980, **102**, 382.
4 Part 9, A. Bonny, R. D. Holmes-Smith, G. Hunter, and S. R. Stobart, *J. Am. Chem. Soc.*, 1982, **104**, 1855.
5 Part 5, S. R. Stobart and R. D. Holmes-Smith, *J. Chem. Soc., Dalton Trans.*, 1980, 159.
6 Part 8, A. D. McMaster and S. R. Stobart, *Inorg. Chem.*, 1980, **19**, 1178.
7 A. Davison and P. E. Rakita, *Inorg. Chem.*, 1970, **9**, 289.
8 M. Gielen, J. Nasielski, and J. Topart, *Recl. Trav. Chim. Pays-Bas*, 1968, **87**, 1051.
9 Yu. A. Ustynyuk, P. J. Zakharov, A. A. Azizov, V. K. Potapov, and I. M. Pribytkova, *J. Organomet. Chem.*, 1975, **88**, 37.
10 M. J. Vaickus and D. G. Anderson, *Org. Magn. Reson.*, 1980, **14**, 278.
11 B. D. Fabian and J. A. Labinger, *J. Organomet. Chem.*, 1981, **204**, 387.
12 C. H. Campbell and M. L. H. Green, *J. Chem. Soc. A*, 1971, 3282.
13 P. C. Angus and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 1973, 2374.
14 A. Bonny, S. R. Stobart, and P. C. Angus, *J. Chem. Soc., Dalton Trans.*, 1978, 938.
15 A. Davison and P. E. Rakita, *J. Organomet. Chem.*, 1970, **23**, 407.
16 F. A. Cotton, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. Jackman and F. A. Cotton, Academic Press, New York, 1975.

Received 15*th April* 1982; *Paper* 2/637