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Review

FLUXIONAL MAIN GROUP IV ORGANOMETALLIC COMPOUNDS

The Implications for Orbital Symmetry Rules

by

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ABSTRACT: In the mid 60's, R. B. Woodward and Roald Hoffmann, among others, advanced a set of rules based on molecular orbital symmetry, to predict the direction of molecular rearrangements. The difficulty in providing strong support for these rules arises from the difficulty in proving, or even adequately defining the prerequisite condition of concertedness. This review offers the chemical behavior of main group IV substituted cyclic polyenes as evidence for the operation of symmetry predictions, with a regard for concertedness. In particular, the author's observations with triphenyl cycloheptatrienyl stannane are offered to reject the previous use of "Least Motion" predictions in favor of symmetry arguments.

OUTLINE

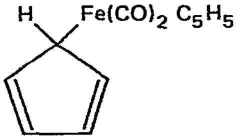
1. INTRODUCTION

Much of the twenty-year fascination of chemists with organometallic cyclopentadienyls (1, n=5) and the more general group to which they belong

$$\mathrm{c}-(\mathrm{CH})_n-\mathrm{M} \tag{1}$$

arose from their bonding capabilities. As is now well known, two classes of bonding occur. One contains those molecules in which the substituent

M is σ-bonded to a monohapto $(\underline{h}^1)$ ring.[16] The other contains those molecules in which the substituent is π-bonded to a polyhapto $(\underline{h}^n)$ ring.[16] The two classes are represented by $\underline{2}(\underline{h}^1)$[8] and $\underline{3}(\underline{h}^5)$[19] respectively. Despite the attention devoted to this chemistry, it is not yet possible to predict the type of bonding a new structure will exhibit. It may ultimately be possible to make such predictions from large-scale numerical computations. Such bonding descriptions are to be considered



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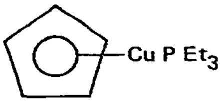

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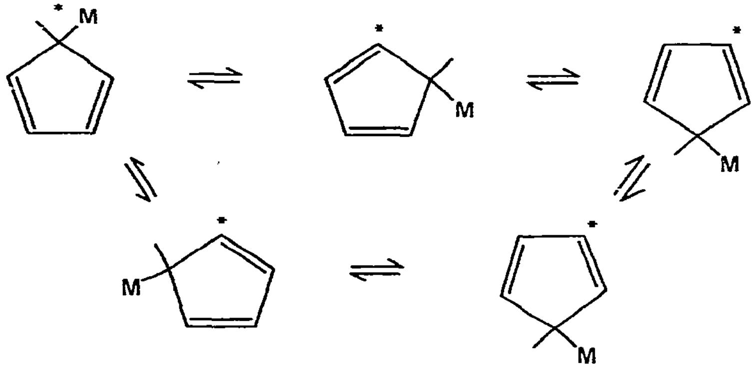
incomplete if they do not include a description of the remarkable property found in many σ-bonded organometallic compounds: their fluxional behavior.

In contrast to the usual sorts of molecules, in fluxional molecules certain of the chemical bonds do not remain fixed. In the kinds of molecules which are described here, the ring substituent M can exchange sites on the ring with a characteristic time of 10 seconds or less in a manner similar to that shown:



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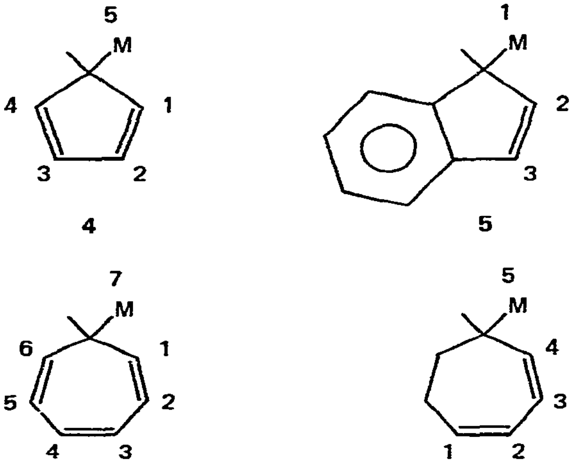
Although chemical bonds are made and broken, the bulk material is unchanged because the instantaneous structures are identical. Such rearrangements are called degenerate.[32] Most of the work described here has appeared subsequent to the excellent general review of fluxional organometallic chemistry by Cotton.[18]



4 5 6a 6b (4)

Among fluxional organometallic molecules, those containing main group IV elements warrant special attention. They are comprised chiefly of the cyclopentadienyls (4), indenyls (5) and two 7-carbon ring derivatives (6). The nonfluxional chemistry accessible in these systems has allowed the molecular source of fluxional behavior to be secured in a way not possible previously. Secondly, tetravalency of the migrating atom allows elaboration of the stereochemical fate of the migrating group. Finally, three tests of recent predicitions of Woodward, Hoffmann and others have used this chemistry.[104]

2. CYCLOPENTADIENES

2.1 Synthesis

Preparation of main group IV derivatives of cyclopentadiene have followed naturally from the stability of the cyclopentadienyl anion, a Huckel 4n+2 π-electron system. Two methods mainly have been used. Lithium or sodium salts of the cyclopentadiene, or cyclopentadienyl Grignard react with the required organometallic halide to give the expected compound, with few reported exceptions (scheme 5)

$$C_5H_5^-Li^+ + R_3M{-}X \rightarrow R_3M - C_5H_5 + LiX \;. \qquad (5)$$

A second method, somewhat milder, apparently, is the reaction of a cyclopentadiene with an N,N-(dimethylamino) organometallic compound, as in scheme 6.[53] Reported preparations are summarized in Table I-IV.

$$(CH_3)_2N - MR_3 + C_5H_6 \rightarrow C_5H_5 - MR_3 \;. \qquad (6)$$

TABLE I

Preparation of Cyclopentadienyl Silanes

Compound	bp/(m.p.) (°C)	Yield (%)	Method	Ref.
$H_3SiC_5H_5$	59-61/(-94 to -96)	89	K^+Cp^-,RBr	45
$H_3SiC_5H_4CH_3$	108-9/(-145 to 147)	99	$K^+C_5H_3CH_3^-$,RBr	45
$(CH_3)_3SiC_5H_5$	32°(12 torr)/(-19°)	71	RCl,Na/NH_3/C_6H_6;C_5H_6	38,3,97
	43°(19 torr)	40		
$(CH_3)_2SiClC_5H_5$	54-56 (14 torr)	60	NaC_5H_5,$PhCH_3$,$(CH_3)_2SiCl_2$	90
$(CH_3)SiCl_2C_5H_5$	51°(10 torr)	73		90
$Cl_3SiC_5H_5$	46-48 (4 torr)	58		90
$(CH_3)_3SiC_5H_4CH_3$	52°(20 torr)	n.a.	$SiCl_4$+NaC_5H_5,$PhCH_3$	29
$((CH_3)_3Si)_2C_5H_4$	45°(3 torr)		$Li(CH_3C_5H_4)$,$(CH_3)_3SiCl$	29,96
	80°(10 torr)	60		

TABLE II

Preparation of Cyclopentadienyl Germanes

Compound	bp/(m.p.) (°C)	Yield (%)	Method	Ref.
$H_3GeC_5H_5$	n.a.		n.a.	92
$H_3GeC_5H_4CH_3$	n.a.		n.a.	92
$(CH_3)_3GeC_5H_5$	47°, 14 torr		C_5H_5Li,RCl	29,69
$(CH_3)_3GeC_5H_4CH_3$	8-59°, 10 torr	n.a.	$CH_3C_5H_5Li$,RCl	29
$Ph_3GeC_5H_5$	/(176-77)		$C_5H_5Na+Ph_3GeBr$ $(C_5H_5)_2Mg+Ph_3GeBr$	66,85
$(CH_3)_2Ge(C_5H_4)_2$		61	NaC_5H_5	38
$((CH_3)_3Ge(C_5(CH_3)_5)$	74°, 2.1 torr		$(CH_3)_5C_5^-Li^++(CH_3)_3GeCl$	29
$(C_2H_5)_3GeC_5H_5$	105°, 16 torr		$(C_5H_5)_2Mg,(C_2H_5)_3GeBr$	29
$n(C_4H_9)_3GeC_5H_5$	109°, 0.4 torr		---	29
$\{(CH_3)_3Ge\}_2C_5H_4$	31, 1 mm	67	2 steps, n-bu Li	75

TABLE III

Preparation of Cyclopentadienyl Stannanes and Plumbanes

Compound	bp/(m.p.) (°C)	Yield (%)	Method	Ref.
$C_5H_5Sn(CH_3)_3$	38° (10 torr)	92	$C_5H_6+(CH_3)_2N$-$Sn(CH_3)_3$	75
$(CH_3)_3SnC_5H_4CH_3$	50° (2.3 torr)			29
$(CH_3)_3SnC_5(CH_3)_5$	92° (2 torr)			
$Sn(C_5H_5)_4$	/(81-82°)	53%	$LiC_5H_5,C_6H_6;SnCl_4$	21
$Sn(C_5H_4CH_3)_4$		83%	$NaCH_3C_5H_4,C_6H_6;SnCl_4$	21
$((CH_3)_3Sn)_2C_5H_4$	102°, 4 torr		$C_5H_6+(CH_3)_3SnNEt_2$	96
	38° (3 torr)	90	"	75
$(C_5H_5)_4Pb$				38

TABLE IV

Preparation of Some (poly)-organometallic Cyclopentadienes[75]

Compound	bp/(m.p.) (°C)	Yield (%)	Method
$((CH_3)_3Si)((CH_3)_3Ge)C_5H_4$	31(1 torr)	86	
$((CH_3)_3Si)((CH_3)_3Sn)C_5H_4$	42(1 torr)	22	
$((CH_3)_3Ge)(Sn(CH_3)_3)C_5H_4$	82°(3 torr)	84	$C_5H_5(Ge(CH_3)_3)+Et_2NSn(CH_3)_3$
$\{Si(CH_3)_3\}_2(Sn(CH_3)_3C_5H_3$	102(4 torr)	64	
$C_5H_3(Si(CH_3)_3)(Ge(CH_3)_3)(Sn(CH_3)_3)$	68°(1 torr)	77%	
$C_5H_3(Si(CH_3)_3)(Ge(CH_3)_3)(Sn(CH_3)_3)$	84°(3 torr)	80%	$C_5H_5Si(CH_3)_3+Et_2N\text{-}Sn(CH_3)_3$
$C_5H_3(Si(CH_3)_3)(Sn(CH_3)_3)_2$	116°(3 torr)	86%	$C_5H_5Sn(CH_3)_3+Et_2NSn(CH_3)_3$
$C_5H_3(Sn(CH_3)_3)_3$	/(60-61°)		
$C_5H_2(Sn(CH_3)_3)_4$			

2.2 Structure

Chiefly the structural problem is one of assignment of the bonding of the cyclopentadiene to a $\underline{h}^1$ or $\underline{h}^5$ bonding type. In principle, observation of separate resonances for the olefinic and methyne protons of the ring in the low temperature limiting structure of the proton magnetic resonance spectrum allows assignment to the $\underline{h}^1$-structure. In those cases where only a single resonance is observable, other data are necessary.

Tetracyclopentadienyl stannane is assigned the $\underline{h}^1$ structure on the basis of observation of an infrared spectral band assigned to a conjugated double bond.[38] A more certain approach utilizes group theory, which predicts a definite upper limit to the complexity of the infrared absorption spectra of $\underline{h}^5$ cyclopentadienyl rings.[17] There are never more than two infrared active bands above 3000 cm^{-1} due to ring C-H modes[17,37,95] with the $\underline{h}^5$ compounds. Presence of 3 or more bands is positive evidence for symmetry lower than 5-fold about the ring, and thus an assignment on this basis to the h^1 class is secure.

Spectra of trimethyl 5-cyclopentadienyl silane and trimethyl 5-cyclopentadienyl germane exhibit at least three strong bands assigned to C-H stretching modes above 3000 cm^{-1}. On this basis Davison assigned the compounds to the h^1 structure.[29] Structures suggested previously[72,81] are not correct.

Another criterion, somewhat more empirical, is based on the magnitude of the one-bond ^{13}C-H coupling constant observed by nmr. This quantity is known to vary with hybridization; typical values, if there are no hetero-atoms present, are 125 Hz for an sp^3 and 165 Hz for an sp^2 carbon atom.[70,89] The average of the values from the model h^1-compounds (4 x 165 + 125) is 159 Hz (Table V).[42] π-cyclopentadienyls have values near 175

TABLE V

One-Bond J(^{13}CH) for Various Cyclopentadienes (Hz)[70,89]

	C_1-C_4 (Hz)	C_5 (Hz)
C_5H_6	165±2 167±5	125±5
$C_5H_5Si(CH_3)_3$	167±5	n.a.
$C_5H_5Ge(CH_3)_3$	167±5	n.a.
$C_5H_5Sn(CH_3)_3$	ave, 163±2	

Hz.[65] Observed for the trimethyl cyclopentadienyl stannane is 163 Hz at a temperature above coalescence (q.v.), in agreement with the $\underline{h}^1$ designation.

More complete structural data require diffraction or rotational studies. Several electron diffraction studies have been reported for 5-cyclopentadienyl silanes, a germane and a stannane (Table VI). All structures contain $\underline{h}^1$-cyclopentadienyl rings, which have been interpreted to contain unusual non-planar rings.[98,99,100] The methylenic carbon is placed above the ring defined by C(1) and C(4) as in

TABLE VI

Molecular Parameters for 5-Cyclopentadienylsilane and Related Compounds

Compound	$C_5H_5SiH_3$ [10]	C_5H_6 [67,80]		$(C_5H_5)_3MoNo$ [15]
Bonded Distances	(Å)			
C(5)-C(1)	1.500±0.013	1.509±0.002	1.49	1.468
C(1)-C(2)	1.389±0.013	1.342±0.003	1.32	1.344
C(2)-C(3)	1.436(fixed)	1.469±0.002	1.44	1.442
C(5)-M	1.881±0.010	n.a.	n.a.	2.29
C-H	1.109	n.a.	n.a.	1.0
Angles				
α	0° (fixed)	0°	0°	0°
C(4)C(5)C(1)	100.3±1.5	102°46'	102°	103.2°
C(5)C(1)C(2)	112.0±1.0	109°16'	110°	109.7
C(1)C(2)C(3)	107.9±0.6	109°21'	112°	108.5
β	116.5°	n.a.	n.a.	n.a.
Method	e diffr.	microwave	X-ray	X-ray

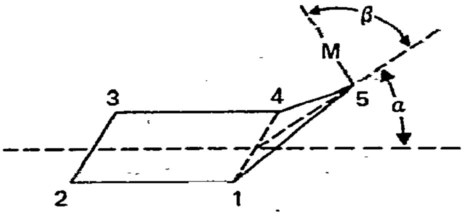


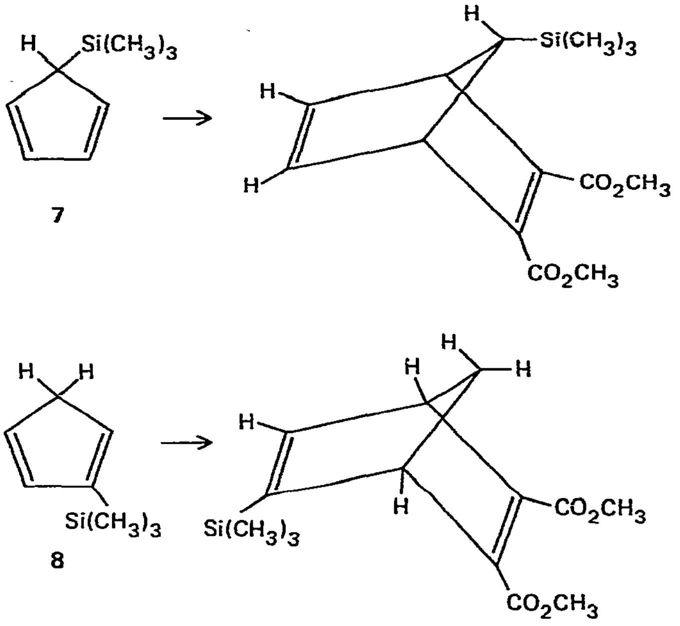
Figure 1. Cyclopentadienyl geometry.

Figure 1. The angle α for the trimethyl silane, germane and stannane are 22°±4, 24±4 and 19.5±4, respectively.

Bentham and Rankin have solved the gas-phase molecular structure of 5-cyclopentadienyl silane.[10] The molecular parameters are listed in Table VI. The silane ring is *monohapto* and planar. The parameters for cyclopentadiene[67,80] and for tris (cyclopentadienyl) nitrosyl molybdenum[15] are also tabulated. One of the rings in the molybdenum compound is *monohapto* and planar. The bond lengths and angles of the silane correspond closely to those observed in the molybdenum compound, which is fluxional, and to the cyclopentadiene. As it is puzzling that presence of methyl groups on silicon should lead to the large deviation from planarity for the cyclopentadiene ring observed by the Russian workers, their result is considered controversial.

2.3 Non-fluxional Chemical Properties

Chemical properties expected for *monohapto*-cyclopentadienides are observed in the fluxional main group IV compounds. These are chiefly prototropic rearrangements and Diels-Alder reactions. For example, mixtures of dimethyl acetylene dicarboxylate and 5-trimethylsilylcyclopentadiene(*7*) react on heating to form mixtures corresponding to the adducts of *7* and *8*.[56]



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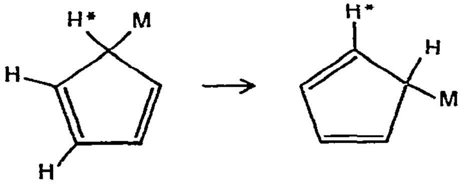
(7)

These observations correspond to a conversion of 7 to 8 via a prototropic shift followed by a Diels-Alder reaction. Kraihanzel and Losee, on the basis of this evidence, indicated the possibility that the proton migration, if sufficiently fast, could explain the temperature effects on the nuclear magnetic resonance spectrum.[56] Apparently this possibility had not previously been considered.

Ashe measured the first-order rate constants for the prototropic rearrangement of 5-trimethylsilylcyclopentadiene to the 1-isomer(9).[56]



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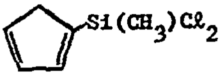
The rate, at 55°; is 1.1 times that for cyclopentadiene-^{5}d-1,2,3,4,5. The temperature dependence of the rate constant is described by $k_1 = 2\text{x}10^{13}$ exp{-26,200/RT}. The nmr spectra of 9 and the subsequent thermal product 2-trimethylsilylcyclopentadiene(8) have been analyzed.[86] The rate constant for the analogous rearrangement of 5-cyclopentadienyl-methyl dichlorosilane is $10^{11.9}$ x exp{-23,700±1,000/RT}.[6] The structural assignment of the product, 1-cyclopentadienyl methyl dichloro silane was secured on the basis of nmr double resonance experiments.[83] Activation parameters for the reverse reaction from the 1-isomer to the 5-isomer are A, $10^{14.5}$ and E_a, 26.8 kcal. The thermodynamic parameters reported for the 5-1 equilibrium are in agreement with the rate data.[35]

The trimethyl 5-cyclopentadienyl silane, germane and stannane do not dimerize in the Diels-Alder fashion[6] as does cyclopentadiene itself. Nor does proton rearrangement occur in the germane or stannane below 100°.[6] The rate of dimerization of methyldichloro-5-cyclopentadienyl silane has been measured.[6] The rate parameters are similar to those for cyclopentadiene (see Table VII).[58] 1-, 2- and 5-cyclopentadienyl trimethyl silane all react with activated dienophiles such as dimethyl acetylene dicarboxylate.

TABLE VII

Activation Parameters for Dimerizations of Cyclopentadienes

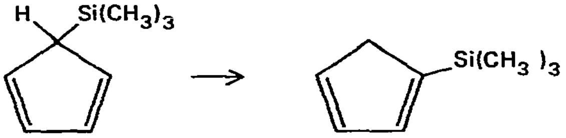
Compound	E_a	log A	Ref.
	17.3	6.5	79
	16.6	7.7	82

The prototropic rearrangements always occur slowly compared to the nmr time scale. Thus, in these cases, it will be seen that the observed fluxional behavior is not due to migration of protons.

2.4 Fluxional Chemical Properties

2.4.1 General

Fluxional behavior is found in characteristic changes of nmr spectral lineshapes with temperature. Successive rearrangement of an $\underline{h}^1$-organometallic group about a carbocyclic ring would cause the ring carbons and protons to exchange their local magnetic environments. Computational synthesis of nmr spectral lineshapes have been reviewed several times.[13,51] The formalism will not be repeated here. It is well-known by this time that chemical exchange of nuclei at rates fast compared to their separation in chemical shift causes broadening of their nmr absorption lines. More specific expectations are best summarized in a hypothetical example of a typical fluxional monohapto cyclopentadienide. At low temperature, the nmr spectrum will show one methyne proton absorption (τ7-9, 1H) due to H(5) and two olefinic proton absorptions (τ5-6) due to H(1), H(4) and H(2), H(3). (This is termed the low-temperature limiting spectrum.)



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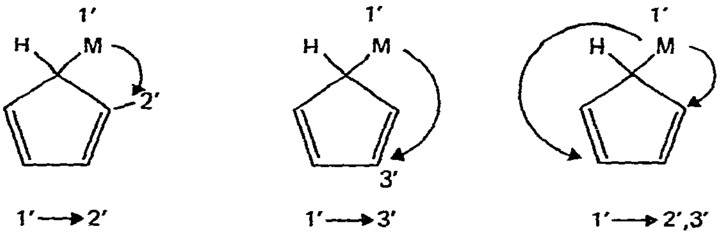
(9)

All ring-proton resonances will broaden as the temperature is raised. One of the two olefinic resonances broadens to a lesser extent than the other resonances. At higher temperatures the resonances disappear, due to further broadening. Still higher temperatures cause a single line to appear at the number-weighted average of the chemical shift of the exchanging protons, and cause the line to narrow. Couplings between exchanging and non-exchanging nuclei will be averaged in the high-temperature limiting spectrum.

There are three pathways for exchange of the cyclopentadienyl nuclei (scheme 10). One pathway involves migration of the organometallic group from C(5) to C(1) or C(4). The second pathway involves exchange from C(5) to C(2). The third pathway is a random one in which rearrangement occurs to C(1) or C(2) with equal facility. The exchange behavior of the nuclei is compactly described by a matrix of exchange probabilities. For this purpose the sites are re-designated 1' C(5); 2' C(1) and C(4) and 3' C(2) and C(3).



(10)

5,1 pathway (1' → 2')

$$\begin{array}{c} \\ 1' \\ 2' \\ 3' \end{array}\begin{array}{c}\begin{array}{ccc} 1' & 2' & 3' \end{array}\\ \left[\begin{array}{ccc} 0 & 1 & 0 \\ 1/2 & 0 & 1/2 \\ 0 & 1/2 & 1/2 \end{array}\right]\end{array}$$

5,2 pathway (1' → 3")

$$\begin{bmatrix} 0 & 0 & 1 \\ 0 & 1/2 & 1/2 \\ 1/2 & 1/2 & 0 \end{bmatrix}$$

random pathway (1' → 2',3')

$$\begin{bmatrix} 0 & 1/2 & 1/2 \\ 1/4 & 1/4 & 1/2 \\ 1/4 & 1/2 & 1/4 \end{bmatrix}$$

Row indices of matrix elements correspond to migration origins and column indices to migration termini. The matrix elements are the transition probabilities between those sites. In the non-coalesced spectra, line-broadening depends on the chemical shift differences between the exchanging nuclei and on the exchange rate which in turn is related to the exchange probability. The migration pathway can be determined, in principle, by use of these facts.

In the matrix for the 1' → 2' pathway, note row 3'. This row indicates 50% of 1' → 2' metal shifts result in 3' → 2' exchange for a particular site, and 50% result in no exchange of magnetic environments. As the 3',3' element is the only diagonal element of this matrix, only 3' sites self-exchange; every other site moves to a new site with each metal migration. Thus rates of net exchanges of sites 1' and 2' exceed the rates for 3' exchange.

This has the interesting consequence that at slow or intermediate rates of exchange the nuclear magnetic resonances due to site 3' nuclei broaden less rapidly than those at the other sites. This was first pointed out by Davidson, Faller and Cotton.[8]

Likewise in the 1' → 3' pathway, the 2' resonance will broaden less rapidly. In the random pathway, the relative broadening is about the same. Assignment of the nmr spectral resonances in principle allows designation of the predominant migration pathway. Designation of the migration pathway does not allow inferences regarding subtleties of mechanism. The mechanism may in principle be uni- or bi-molecular, or inter- or intra-molecular. Intermediates are not excludable on the basis of pathway. The pathway simply designates the termini for the migration of nuclei.

In well-designed experiments, the phenomena are repeatable on several temperature runs with the same sample, and also allow exclusion of reaction with solvent as an important occurrence. Absence of a concentration effect on the nmr lineshape is evidence for first-order reaction.

Rate-temperature correlations can be made by comparison of spectra calculated for various exchange rates with those observed at various temperatures. The range of utility is for rates between about 10 and 10^6 sec^{-1}.

Spin-saturation with chemical exchange is a second technique for identification of the migration pathway. This method, discovered by Forsen and Hoffmann[48] is useful for rates below the region of line broadening. If a nucleus is saturated, and it moves to a new site at a rate slow compared to relaxation, a decrease in signal intensity due to this second site is observed.

2.4.2 Silanes-Arrhenius Parameters

Fritz and Kreiter reported the first fluxional main group IV molecules, a group including trimethyl 5-cyclopentadienyl silane.[38] Each compound listed in Table I is fluxional. This includes trimethyl methylcyclopentadienyl silane[27] which had been previously reported to be a non-fluxional molecule.[38] Trimethyl cyclopentadienyl silane has an activation energy for migration of 13.0 ± 1.0 kcal $mole^{-1}deg^{-1}$. Successive substitutions of chlorine for methyl on silicon monotonically increase the relative rates of silane migration. This is summarized in Table VIII.

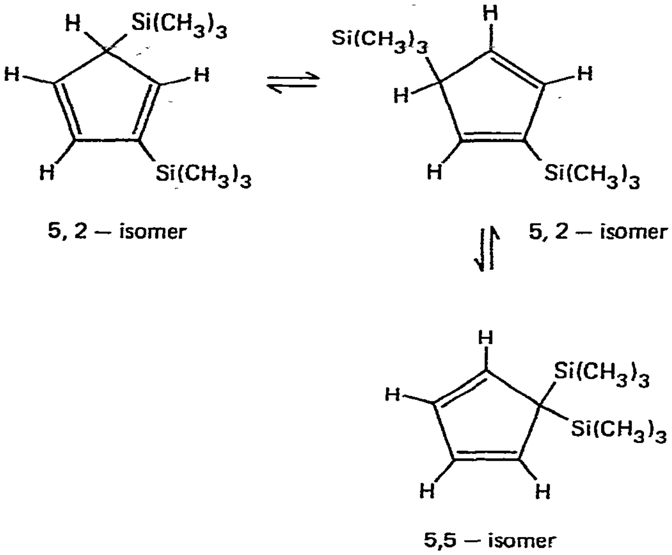
TABLE VIII

Activation Parameters for Silicon Migration in Certain 5-cyclopentadienyl Silanes

	log A	E_A	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$	Rel Rates	Ref.
$C_5H_5Si(CH_3)_3$	11.3±1.0	13.0±1.0	15.2±0.2	-9.2±4		82
$C_5H_5Si(CH_3)_2Cl$			15.5			82
$C_5H_5Si(CH_3)Cl_2$			15.9			82
$C_5H_5SiCl_3$			16.3			82
$C_5H_4(Si(CH_3)_3)_2$	14.5±1.8					96
5,2→5,2-		14.5±1.8		1.5±4		96
5,5→5,2-		15.8±1.0		-4.7±4		96
5,2→5,5-		18.6±1.0		0.3±4		96

Most of the effect on the rates is due to changes in the entropy of activation. Because of the uncertainties in these values no interpretation was offered for the trends noted.[82] The activation parameters for the fluxional rearrangements (both degenerate and non-degenerate) in <u>bis</u>-

(trimethylsilyl)cyclopentadiene are also tabulated. These values are similar to those for the mono silanes. The observed migration pathways observed in this molecule are illustrated in scheme (11).[96]



(11)

The activation energies observed for fluxional exchange in trimethylsilyl 5-cyclopentadiene, and in dichloromethylsilylcyclopentadiene are significantly lower than those for proton migration. Also, stable proton shifted isomers are isolable in each case. These data indicate that proton migration is too slow to explain the fluxional behavior. In every case it is then concluded that migration of the organometallic group explains the observed nmr temperature effects. Note the small or highly negative entropy parameters. This is evidence for intra-molecularity of the reaction (q.v.).

2.4.3 Germanes, Stannanes and Plumbanes

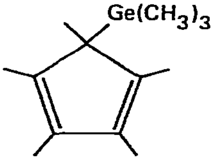
The cyclopentadienyl germanes in Table II and the stannanes and plumbanes in Table III are fluxional. The only possible exception is

TABLE IX

Activation Parameters for Some 5-cyclopentadienides

Compound	log A	E_A	$\Delta S^{\ddagger}_{300}$	ΔG_{300}	Nuclei	Ref.
$(CH_3)_3SiC_5H_5$	11.3	13.0±1	-9.2±4	15.2±0.2	H	55
$(CH_3)_3GeC_5H_5$	9.9±1	9.2±1	-15.8±4	13.3±1	H	55
		10.7±0.9		13.4±0.9	C	42
$(CH_3)_3SnC_5H_5$	13.8±1	7.8±1	+2±4	6.6±1	H	55
		6.4±1.0		7.2±1.0	C	42

triphenyl cyclopentadienyl germane, which apparently has not been investigated. Reported activation parameters for the fluxional exchange are recorded in Table IX. The observed activation energies, and the fluxional behavior of pentamethylcyclopentadienes[29] 10 and 11 lead to the conclusion that the fluxional behavior is due to metal migration.[29]



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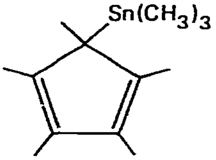


11

(12)

Rates of proton site-exchange in trimethylstannylcyclopentadiene was correlated in Arrhenius fashion together with ring carbon site exchange from ^{13}C nmr lineshape analysis. The correlation coefficient, 0.992, between each set of data indicates that exchange of both types of sites occurs by the same mechanism, "ring-whizzing" of the trimethyl tin.[42]

The nmr spectrum of germylmethylcyclopentadiene shows the presence of satellites due to H-Ge to ring proton couplings of 0.55 Hz at 35°, which is above the coalescence point.[29] Presence of $^{117,119}Sn$ couplings with ring protons in the proton magnetic resonance[55] spectrum and $^{117,119}Sn$ couplings with ring carbons in the ^{13}C nmr spectrum[42] above coalescence have also been reported.

2.4.4 NMR Spectral Assignments—The Migratory Pathway

NMR lineshape analysis together with assignment of nmr spectral resonances gives the migratory pathway. The first clearly correct assignment of a migratory pathway in these compounds was made by Cotton and Marks,[20] from a series of nmr spin-tickling experiments.[73] The assignment was made after determination of the absolute magnitudes of certain H,H coupling constants, specifically J(1,5) and J(2,5). The argument can be made that J(1,5), a 3-bond coupling is greater than 0 and

TABLE X

Proton Magnetic Resonance Parameters for Some Cyclopentadienes

5-isomers of $C_5H_5Si(CH_3)_nCl_{3-n}$

n	Chemical Shift			Coupling Constants (Hz)					Ref.
	H(1)	H(2) (δ)	H(5)	J_{12}	J_{23}	J_{24}	J_{15}	J_{25}	
0	6.44	6.74	3.65	-			0.9	-0.9	87
1	6.53	6.75	3.65	5.2	2.0	1.2	1.1	-0.9	87
2	6.48	6.64	3.50	5.4	2.0	1.2	1.0	-1.0	9,87
3	6.42	6.53	3.31	5.0	2.2	1.4	1.2	-0.95	87
<u>Compound</u>									
Cyclopentadiene	-	-	-	5.06	1.90	-	+1.36	-1.52	68
Indene				2.02	5.58		J_{13} =	-1.98	36

that J(2,5), a 4-bond coupling, is less than 0.[14,44,54] The signs of the two couplings to H(5) were determined relative to J(2,3), a three-bond cis coupling, therefore positive.[14,44,54] The determination of the signs allows the resonances to be assigned to H(1) and H(2), respectively. The coupling constants and chemical shifts are tabulated in Table X. For comparison, cyclopentadiene[68] and indene[36] are included. The temperature effect on the linewidth of H(2) and H(3) allows a secure assignment of the migratory pathway to 1 → 5 or 1' → 2'.

Each silane in Table X follows a non-random migratory pathway. From the resonance assignments and observed line broadenings, 5-trimethylsilyl and 5-dimethylchlorosilylcyclopentadiene metal migrations were assigned to the 1' → 2' pathway.[42]

TABLE XI

Carbon Chemical Shifts of 5-cyclopentadienides (δ, relative to TMS)[42]

Compound	C_1	C_2	C_5	τ°C
$C_5H_5Si(CH_3)_3$	134.0	131.3	52.5	-20°
$C_5H_5Si(CH_3)_2Cl$	133.0	133.7	54.0	-10°
$C_5H_5Si(CH_3)Cl_2$	131.9	135.6	53.3	-10°
$C_5H_5Ge(CH_3)_3$	133.9	129.8	52.1	-20°
	117.7	117.7	117.7	125°
$C_5H_5Sn(CH_3)_3$	114.3	114.3	114.3	-30°
C_5H_6	133.0	133.4	42.2	n.a.

^{13}C nmr spectroscopy of these materials[78] is summarized in Table XI. Olefinic carbons C(1) and C(2) have resolved resonances. The resonances show a temperature dependence which mimics that of the proton magnetic resonance lineshape. A higher rate difference is required to cause the same change in the ^{13}C-nmr spectrum, relative to the H-nmr spectrum due to the greater span in chemical shift. ^{13}C spectra of model compounds are summarized in Table XII. The silylpropene resonances were assigned using off-resonance decoupling.[78] Assignments of the cyclopentadienyl ring carbon resonances were made on the basis of the propene shift data. On the basis of relative broadenings, the metal migrations in each of the silanes belongs to the 1' → 2' pathway.

TABLE XII[78]

^{13}C NMR Spectral Shifts of 3-silyl-1-propenes

	C_1	C_2	C_3
$C_3H_5Si(CH_3)_3$	113.5	135.3	25.4
$C_3H_5Si(CH_3)_2Cl$	116.3	133.0	28.3
$C_3H_5Si(CH_3)Cl_2$	118.9	130.6	29.6
$C_3H_5SiCl_3$	120.6	128.1	31.6

The ^{13}C assignments in 5-trimethylgermylcyclopentadiene were made assuming that the trimethylgermyl group has the same effect on the ring resonances as the trimethylsilyl group.[78] The migratory pathway for the carbon nuclei is 1' → 2'.

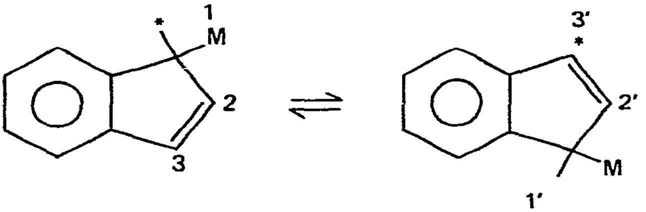
Proton magnetic resonance spectral assignments (Table XIII) also allow designation of the fluxional migration in 5-trimethylgermylcyclopentadiene to the 1' → 2' pathway. As the signs of J(1,5) and J(2,5) are assumed, having been assigned on the basis of absolute magnitude only,[55] these assignments are not considered fully secured. 5-cyclopentadienyl stannane follows a non-random pathway, but overlap of resonances prevented spectral, and therefore, pathway, assignments to be made.[55] At 20° the ^{13}C spectrum of the stannane is fully coalesced. Also as noted above, there is a 1' → 2' rearrangement for 2,5-bis-trimethylsilylcyclopentadiene.[96]

An apparent 1' → 3' pathway between 5,5-bis-trimethylsilylcyclopentadiene and the 2,5-isomer could as well occur by way of an undetectable quantity of the 1,5-isomer, on the 1',2'-pathway.[96]

3. INDENES

3.1 General

1-substituted indenes (12) represent a second class of fluxional main group IV organometallics.



12 11

(13)

Indenes are benzologues of cyclopentadienes. This feature markedly reduces degeneracy in the indene system relative to the cyclopentadiene. While 5-cyclopentadienides have 5 potentially equivalent ring sites, indene has one unique position, C(2), and 2 degenerate sites C(1) and C(3). The product of rearrangement from C(1) to C(2) is a different isomer (13) no longer iso-energetic with starting material. This isoindene,

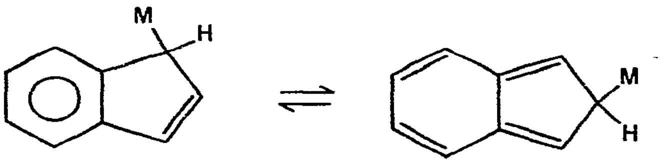
TABLE XIII

NMR Spectral Assignments of Some 5-substituted Cyclopentadienes[55]

			Shifts (PPM)						
			H(1)		H(2)		H(5)		
Compound	H(1)	H(2)	H(5)	J(1,2)	J(1,3)	J(1,4)	J(1,5)	J(2,5)	
		δ				Hz			
$C_5H_5Si(CH_3)_3$	6.50	6.65	3.30	5.0	1.4	2.2	1.20	-0.95	reat.
$C_5H_5Ge(CH_3)_3$	6.33	6.44	3.45	5.0	1.45	2.2	1.1	0.60	From -60°
$C_5H_5Sn(CH_3)_3$	6.51	6.51	4.25	5.0	1.2	2.1	1.2	+0.25[a]	From -140°

[a] Signs not known; assignments based in magnitude. See footnote to Table 8, ref. 55.

[b] Some of these values are assumed only; see notes to Table 8, ref. 55.



(14)

13

or 2H-indene (13) is expected to be less stable due to loss of aromatic resonance energy.[79] The destabilization has been predicted to be 11.5,[21] 8.6-9.4[24] or 13 kcal.[42] Thus rates of metallotropic rearrangement would be expected to be slower in the indenyl systems relative to cyclopentadienyl systems as a result of this destabilization.

The first confirmation of this expectation was found in the 1,2-deuteriotropic rearrangement of indene-d[1], [21] and subsequently in metallotropic properties of bis-(1-indenyl)mercury.[24]

3.2 Synthesis

Syntheses are conceptually and, in practice, quite similar to those reported for the cyclopentadienes. Reports of syntheses are summarized in Table XIV.

3.3 NMR Spectra and Structure

Low temperature limiting spectra of trimethylsilyl- (at 29°),[66] trimethylgermyl- (at 29°) and trimethylstannylindenes (below -37°) are in accord with the monohapto-structure assigned to the respective molecules.[30,77] NMR data are summarized in Table XV. Assignment of the olefinic resonances of indene[25] and 1-trimethylsilylindene[76] on the basis of a small coupling between the H(3) resonance and an aromatic-H resonance is conclusive.

TABLE XIV

Synthesis of Some Substituted Indenes

	bp/(m.p.) (°C)	Yield (%)	Method	Ref.
Indene 1-trimethylsilyl-	87°(4 torr)	55	Li-indene	21,91
2-trimethylsilyl-	8°(4 torr)	n.a.	Grignard	21
1-trimethylgermyl-	72°(0.8 torr)	n.a.	Li-indene	21
1-trimethylstannyl-	64(0.15 torr)	n.a.	Li-indene	21
1-triethylgermyl-	161°(4 torr)	↓		66
1-triphenylgermyl-	/(126°)	↓		30
1-diphenylgermyl-	/(144°)	↓		↓
Tetraindenyl germane	/(196-98°)	↓		↓
Dimethyl phenyl 1-indenyl stannane	107°(0.06 torr)	↓	Li-indene	↓
Dimethyl phenyl 1-indenyl stannane	112°(0.22 torr)	78%	Li-indene	↓
1,2-*bis*-Trimethylsilylindene	73°(0.05 torr)/68–69	73%		↓
1,2 and 1,3-*bis*-Trimethylsilylindene	116°(3.5 torr)			↓
1-Trimethylsilyl-3-methylindene	76°(1.05 torr)	53%	Li-salt	↓
1-Trimethylstannyl-3-methylindene	76°(0.12 torr	73%		↓
1-Trimethylstannyl-1,3-dimethylindene	69°(0.17 torr)	34%		↓
1-Triphenylstannylindene	/(128°)	75%	Li-salt	25

3.4 Non-fluxional Chemical Properties

Thermolysis of 1-trimethylsilylindene gives rise to 2 products only, 2- and 3-trimethylsilylindene[76] (16 and 17). Formation of the 2-isomer represents the first chemical evidence for migration of organosilicon groups from one carbon to another, reported by Larrabee and Dowden.

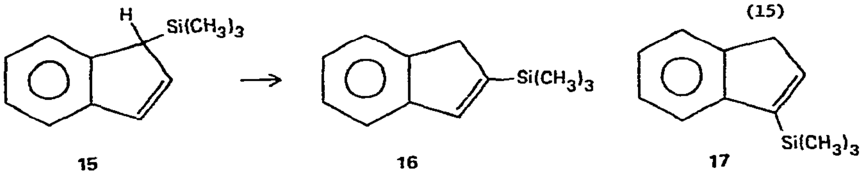
TABLE XV

NMR Spectral Parameters of Some Substituted Indenes

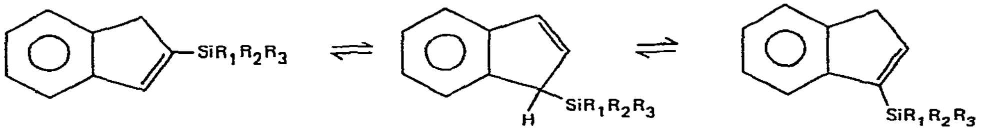
Compound	δ (PPM)			Solvent	Coupling Constants (Hz)			
	H_1	H_2	H_3		J_{12} Hz	J_{13} Hz	J_{23} Hz	Ref.
1-trimethylsilylindene	3.43	6.54	6.88	a	1.5	+1.0	5.4	76
1-trimethylgermylindene	3.50	6.50	6.80	a				
1-trimethylstannylindene	3.85	6.64	6.85	CS_2	+1.5	-1.0	5.2	
indene	2.99	6.50	6.80	a	2.02	-1.0	5.58	76

[a] neat.

(15)

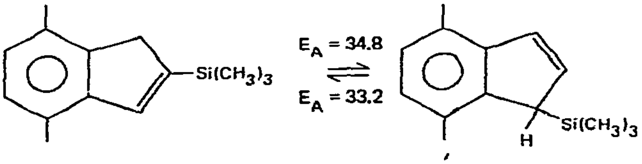


15 16 17



18 19 20

(16)



(17)

The rearrangements are unimolecular. Activation parameters have been determined, and are recorded in Tables XVI[77] and XVII.[2]

TABLE XVI

Activation Parameters for Thermolysis of 1-Trimethylsilylindene[77]

	$\Delta G^{\ddagger a}$ kcal/mole	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ eu	E_a kcal/mole	log A
15 → 16	35.4±0.2	35.8±5	-0.4±10	36.7	13.5
16 → 15	35.0±0.1	37.1±4	4.3±8	38.0	14.4
15 → 17	36.0±0.2	24.3±4	-25.0±8	25.2	8.0
17 → 15	32.6±0.3	25.5±5	-19.6±10	26.4	9.2

[a] at 200°

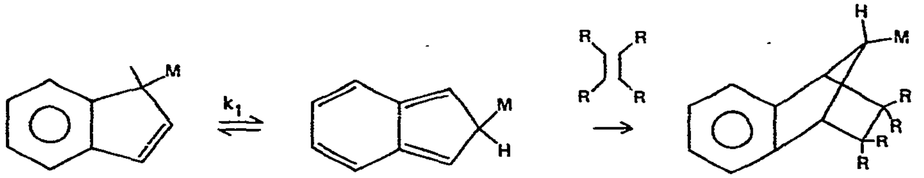
TABLE XVII

Free Energies of Activation for Substituted Indenyl Silanes[2]

	$\Delta G^{\ddagger}$ (kcal mole^{-1})(200°C)			
$R_1R_2R_3$*	18 → 19	19 → 18	19 → 20	20 → 18
$(CH_3)_3$	35.1	36.0	36.1	34.8
$(CH_3)_2Ph$	35.1	35.4	36.3	35.6
$(CH_3)Ph_2$	35.4	35.0	35.7	35.5

*Substituents on silicon.

Reaction of 1-substituted silyl and germyl indenes with effective Diels-Alder dienophiles affords products which correspond to trapping of an iso-indene in which the metalloid had migrated to the 2-position (scheme 18). 1-trimethylsilylindene adds one molecule of tetracyanoethylene (TCNE)[4] or one molecule of maleic anhydride.[61] 1-trimethylgermyiindene adds 1 molecule of TCNE.[63] The adducts have the bicycloheptene structure, in the case of the maleic anhydride adduct and the bicycloheptadiene structure in the case of the acetylene adduct. The kinetics of the reaction between 1-trimethylsilylindene and tetracyanoethylene was observed and analyzed using the Huisgen model[49] for trapping of quasi-stable intermediates. An activation energy for the first-order rate constant k_1 (scheme 18) was determined to be 22.5 kcal/mole degree with Arrhenius pre-exponential factor of 10^{12} for the solvent ethyl acetate.[4]



(18)

3.5 Fluxional Chemical Properties

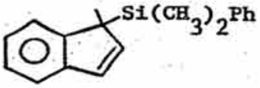
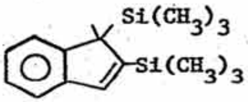
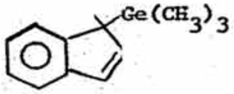
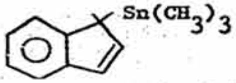
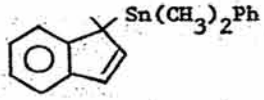
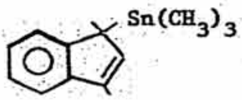
Indenes substituted by main group IV elements are fluxional due to migration of the organometallic group. Proton migrations are too slow to account for the changes observed in the nmr spectra with variation in temperature.

The changes are particularly well illustrated in the paper by Davison and Rakita.[76] For instance, 1-trimethylstannylindene exhibits a low-temperature limiting spectrum at -36°. of an ABM multiplet for the 5-ring protons. Above 139°, the 5-ring resonances appear as a doublet in the olefinic region and a triplet in the high field region with ^{117,119}Sn satellites. The trimethylgermylindene shows similar changes, although at higher temperatures.[76] The trimethylsilyl compound shows only slight changes at 180°, but the differences are quite similar to those in the first two indenes at quite lower temperatures.[61,76] Double irradiation of the 1-H resonance at 140° causes a decrease in the 3-H resonance.[61] All of the evidence is in accord with exchange between sites 1 and 3 by an intramolecular metal migration.

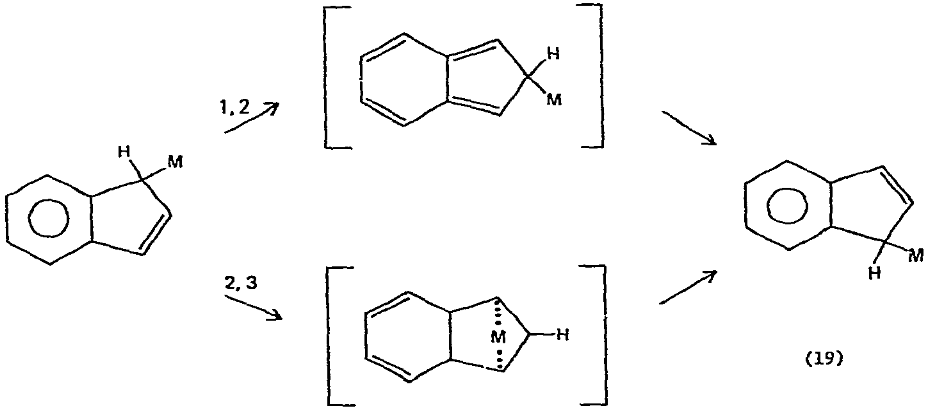
The activation parameters for fluxional metallotropic rearrangements

TABLE XVIII

Activation Parameters for Metallotropic Rearrangements

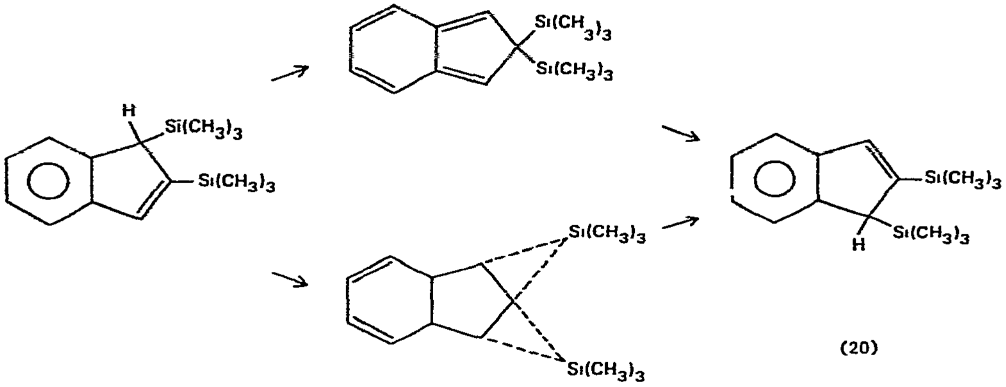
	E_a(kcal/mole)	Log A	Ref.
	23.0±1.6	11.5±0.8	30
	26.1±1.4	14.4±0.7	30
	22	12	67
	13.8±0.8	11.7±0.8	84
	14.1±0.4	11.9±0.3	84
	14.2±0.7	12.5±0.6	84

of a number of compounds are summarized in Table XVIII. The activation energies increase with increasing atomic number, as observed in the cyclopentadiene system. In every case migration in the indenyl system is harder than in the cyclopentadienyl system. From the data, with one exception, a 1,2 migratory pathway via undetectable quantities of the isoindene (scheme 19) is experimentally indistinguishable from a 1,3 migration. The exception is 1,2(bis)-trimethylsilylindene (scheme 20) which shows



(19)

exchange of the trimethylsilyl groups. This could occur by a 1,2 migration, simultaneously or consecutively.[30] While the actual mechanism of migration



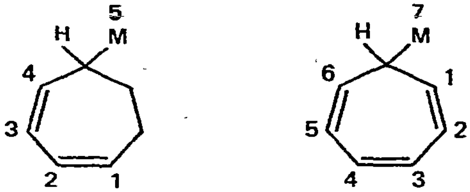
(20)

is not unambiguous at this time, it is clear from both the kinetic and the chemical evidence above that the 2-carbon site is accessible to migrating organometallic groups.

Thus the migration pathway is from C(1) to C(3); it is possible that this occurs via C(2). And in all five-membered rings, there is no definitive evidence for migration to a carbon atom more distant than the adjacent one. Such distant migrations are to be called "molecular broad jumps."[18]

4. CYCLOHEPTADIENES AND CYCLOHEPTATRIENES

In the 5-membered rings, the carbon adjacent to the migration origin and that 5 carbons from the migration origin are identical. This degeneracy is lifted in the 7-membered rings described in this section.



(21)

This separation allowed a distinction to be made between a least-motion pathway, and another mechanism, that predicted by orbital symmetry.

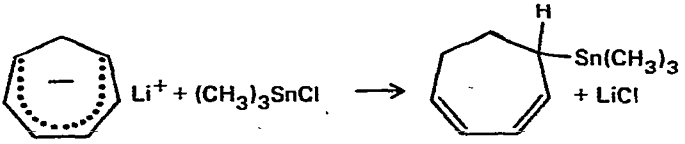
4.1 Synthesis

The stability of the 4n+2 π electron Huckel electrocycle, cycloheptatrienylium cation suggests synthesis of 7-substituted organometallics. Reaction of tetrahydrofuran solutions of triphenyl metalloidal lithiums with cycloheptatrienylium fluoroborate by Larrabee

$$RLi + C_7H_7BF_4 \rightarrow C_7H_7R + (C_7H_7)_2 + R_2 \tag{22}$$

produced the 7-substituted cycloheptatrienes along with the disproportionation products dicycloheptatrienyl and the bis-organometallic.[62] The tendency for disproportionation rather than addition increases with increasing atomic number. This tendency is also increased by presence of alkyl rather than aromatic groups on the tin atom.[64]

A cycloheptadiene[23] was synthesized by reaction of 2,4-cycloheptadienyl lithium[7] with trimethyltin chloride.



(23)

Reaction of trimethylsilyldiazomethane with benzene with copper catalysis affords 7-trimethylsilylcycloheptatriene.[5]

4.2 Structure

The organometallic cycloheptatrienes[62,64] exhibit in their static nmr spectra the characteristics generally associated with 7-substituted cycloheptatrienes.[60] Spectral assignments were made on the basis of relatively stronger couplings between H(1) and H(2), H(2) and H(3), and H(7) and H(1). One unusual feature of the spectrum for the tin compound is the rather low field absorption for the chemical shift of the 7-proton resonance. This downfield shift is possibly due to a relative preponderance of the quasi-axial conformer in solution. In cycloheptatriene-7-d the _quasi_-axial proton absorption of the relatively more stable conformer[50] is shifted downfield relative to the _quasi_-equatorial position

A crystal and molecular structure for triphenylstannyl-7-cyclohepta-1,3,5-triene[102] has appeared. The molecule consists of an approximately tetrahedral triphenyltin $\underline{h}^1$-ligand bonded to a monocyclic seven-membered ring. The seven-ring has the alternation of C-C bond distances associated with considerable double-bond character. In fact the bond distances and angles are quite similar to the only previous crystallographic study of a cycloheptatriene, that for thujic acid.[26]

The C(7)-Sn linkage of 2.21Å is considered quite normal. The triphenyl tin group occupies the quasi-axial site of the cycloheptatriene boat in the solid state. Bond distances and angles are listed in Table XIX. The distances from Sn to C(1), C(2) and C(3) are 3.07, 3.61 and 3.62Å, respectively. All these distances are non-bonding.

TABLE XIX

Some Interatomic Distances (Å) and Bond Angles (deg) in 7-triphenyl-1,3,5-cycloheptatriene[102]

Distances	
Sn-C(Ph)	2.16
Sn-C(7)	3.07
C-C(Ph)	1.38
C(1)-C(7)	1.48
C(1)-C(2)	1.29
C(2)-C(3)	1.40
C(3)-C(4)	1.32
Angles	
C(7)-C(1)-C(2)	123.0
C(1)-C(2)-C(3)	125.6
C(2)-C(3)-C(4)	128.1
C(3)-C(4)-C(5)	124.5

The structure for 5-trimethylstannyl-1,3-cycloheptadiene was assigned on the basis of its low temperature nmr spectrum.[23]

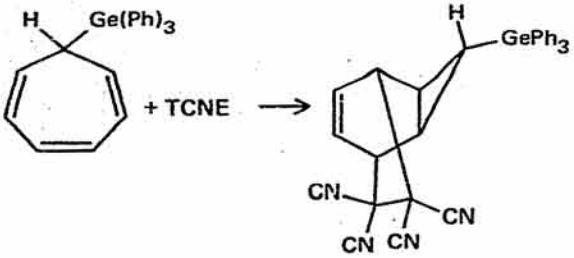
4.3 Non-fluxional Chemical Properties

The organometallic cycloheptatrienes exhibit the chemical behavior generally found among more ordinary cycloheptatrienes. The tin compound decomposes in air, even in the solid state.[63]

Prototropic rearrangements occur at moderate rates below 140° in the triphenylsilyl, germyl and tin compounds,[63] at rates qualitatively comparable to those in other substituted cycloheptatrienes.[71] In each case the products are non-fluxional.

Besides causing prototropic shifts, temperatures above 140° cleave the allylic tin-carbon bond of triphenyl cycloheptatrienyl tin, by a first-order process, to give hexaphenyl ditin and dicycloheptatrienyl. The reaction is not appreciably reversed by heating the two products at comparable temperatures.[64] The activation energy for thermolysis indicates a tin-carbon dissociation energy of at least 25 kcal mole^{-1} in tetrachloroethylene.[62]

Triphenyl 1,3,5-cycloheptatrienyl germane reacts with tetracyanoethylene to afford the expected[41] sort of tricyclic adduct (scheme 24).[64]

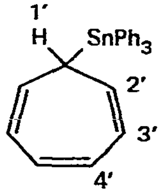


(24)

By use of deuterium labeling, prototropic rearrangement only was observed, and hence is faster than the trimethylsilyl sigmatropic rearrangement, in 7-trimethylsilyl cyclohepta-1,3,5-triene.[5]

4.4 Fluxional Chemical Properties

The first migration to a non-adjacent carbon by an organometallic group was discovered by Larrabee in triphenyl 7-cyclohepta-1,3,5-trienyl tin.[62] Of the 4 related main group IV cycloheptatrienyls the triphenyl tin compound alone shows fluxional behavior below 140°. Observations above this temperature are prevented by the prototropic rearrangements



(25)

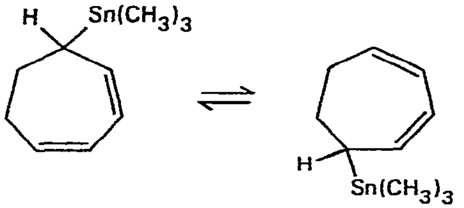
mentioned in the previous section. The fluxional behavior is noticeable in the onset of line broadening at ambient probe temperature, and the coalescence of all 7-ring proton resonances above 80°C. The activation energy in tetrachloroethylene is 10.1±0.8 kcal mole^{-1} as measured by linewidth of the 7-ring proton resonances above coalescence. The temperature effects associated with fluxional behavior are repeatable and reversible, not affected noticeably by solvent ($CHCl_3$, CH_3CN and $PhCH_3$). The spectral lineshape is independent of concentration The molecular weight observed in $CHCl_3$, 435, indicated no more than a low degree of association.[64]

As with cyclopentadiene it is useful to examine the matrix representations for the various pathways. Illustrated is the matrix of exchange probabilities for the 1' → 5' migration pathway. H(1') is totally transferred to H(5') = H(4'). Also, the only diagonal element corresponds to non-exchange of H(3'). At moderate rates of exchange the H(3') = H(2,5) appears broadened to a

$$\begin{array}{c} 1' \\ 2' \\ 3' \\ 4' \end{array} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1/2 & 1/2 \\ 0 & 1/2 & 1/2 & 0 \\ 1/2 & 1/2 & 0 & 0 \end{bmatrix}$$

lesser extent than the other cycloheptatrienyl ring proton resonances. Double irradiation of the 7-H resonance near 0°, causes spin saturation of this site. Subsequently the intensity of the 3-proton resonance decreases selectively due to spin transfer from site 7. The predominant migratory pathway is 1' → 5', to a more distant carbon.[18] The least motion migration to C(1), a distance from the tin atom (as measured in the solid state) of 3.07Å does not occur. The actual event is a "molecular broad jump" to C(3), a distance of 3.62Å from the tin atom.[102]

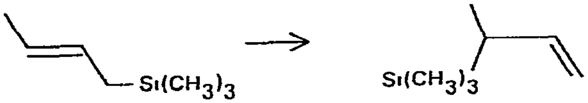
7-trimethylstannyl-1,3-cycloheptadiene exhibits fluxional behavior. The migratory pathway has been identified as 7 → 4, or a 1' → 5' pathway.



(26)

The activation energy is estimated to be near that for the cycloheptatriene, from coalescence temperature measurements [23]

5. PROPENES



(27)

No 3-substituted propenes, including 3-trimethylstannylpropene-1, have been observed to be fluxional.[29] Kwart[59] has reported a slow unimolecular thermal rearrangement for trimethylsilyl propenes (scheme 27). The highly negative $\Delta S^{\ddagger}$ (-6.2±0.3 to -7.4±0.3) indicates a non-dissociative pathway (q.v.) for the rearrangements, as does the activation energy of 47.7±0.3 kcal/mole for trimethyl-α-methylallyl silane. Recently Kwart has found evidence for the predominant inversion pathway for the process, confirming that the migration is a [1,3] sigmatropic reaction, in agreement with the prediction from orbital symmetry theory (q.v.).[57]

6. TESTS OF MOLECULAR ORBITAL SYMMETRY THEORY

The theory of least motion[47] does not predict the consistent 1' → 5' pathway for migration observed in the fluxional systems reviewed here. Rather the pathway suggested by the "Principle of Conservation of Orbital Symmetry" (q.v.) is followed. As will now be discussed, the rearrangements under review are suitable for adequate tests of the second theory.

Testing of any theory requires attention to the features depicted in Figure 2. This figure shows three alternative possible configurations of reality regarding any hypothesis. The rectangle contains all events which occur in the predicted manner. The shaded rectangle contains all events which are known to meet all criteria for the prediction to be made. Several types of events can be categorized. Events labeled E occur in the predicted manner. But it is unknown whether or not the criteria are met. Thus these events (E) are irrelevant to the question of whether or

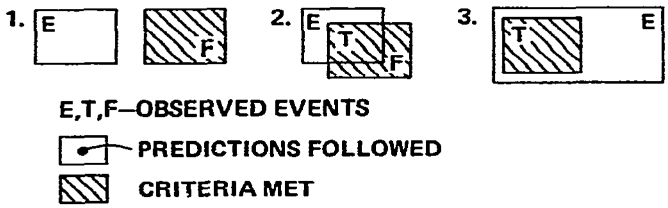


Figure 2. Possible realities.

not the theory is correct, and to the question, can predictions be made from theory. Unfortunately, many reactions cited as examples of the correctness of the rules of Woodward and Hoffmann are just such events.

A second type of event, labeled F, occurs in a manner contrary to prediction, although it is known to be in accord with the criteria for making a prediction. Observation of a single event of this sort requires that the predictions be labeled false, that the predictions be abandoned, or the criterion, or the predictions, or both, be modified.

All events labeled T are in accord with true predictions. Observation of large numbers of different types of events in accord with predictions, if also in accord with the criteria for the prediction allow the predictive hypothesis to be labeled true. Strictly speaking, existence of Reality 2 with a high degree of overlap might not be immediately distinguished from Reality 3; but this is at the heart of the methodology of Francis Bacon, the method of strong inference;[74] and this fact is acceptable.

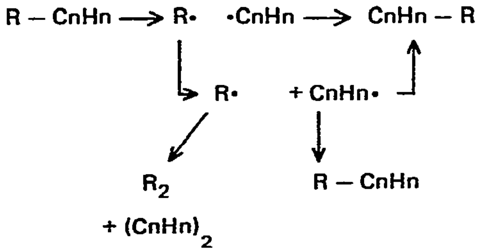
In utilizing rules of Woodward and Hoffmann, or any symmetry arguments, it is generally agreed that the criterion of concertedness is a prerequisite.[11]

7. CONCERTEDNESS

Reactions are called concerted when all relevant events within a reacting molecule occur concurrently.[31] In the fluxional reactions discussed here, bond rupture between the organometallic group and the migration origin concurrent with bond-making to the migration terminus would constitute concertedness. Experimental discrimination between concerted and non-concerted reactions has not proven easy. In fact, one previous criterion is inadequate.

A very early, and commonly accepted criterion for concertedness in sigmatropic rearrangements has been a highly negative entropy of activation for the process. Unimolecular reactions having unusually small, or negative entropy of activation occur with loss of degrees of freedom.[39] In unimolecular sigmatropic rearrangements, negative entropy, in absence of solvent effects, is generally indicative of bond formation during the rate-determining step. But there is no indication that a bond is broken concurrent with this process, or that there is no intermediate along the reaction path. Thus, the entropy criterion does not distinguish between concerted and non-concerted reactions, as was formerly held. As dissociative unimolecular reactions occur with unchanged or increased entropy,[11] the entropy criterion is a method to distinguish between dissociative and non-dissociative sigmatropic rearrangements.

In the dissociative pathway the two groups can dissociate and recombine in some new way; or they might diffuse apart and encounter suitable partners for recombination. These processes are depicted in the scheme (25).



(28)

All dissociative migration pathways are by definition non-concerted.

A new quantity can be defined for rearrangement processes. This quantity, $D_e^{\ddagger}$, is equal with the difference between the dissociation energy for bond rupture D_e and the rearrangement activation energy, $E_a^{(R)}$:

$$D_e^{\ddagger} = D_e - E_a^{(R)}$$

Consequently, a positive non-zero value of $D_e^{\ddagger}$ requires that the rearrangement be non-dissociative. All concerted reactions are included in this class of reactions. And all non-dissociative reactions are concerted only in the sense that the fragments are always bonded. All non-dissociative reactions are necessarily intra-molecular.

In principle, the two classes of rearrangements can be identified empirically. The following data are required: the activation energy for the rearrangement and the dissociation energy for cleavage at the migratory bond. Dissociation energies can be measured experimentally,[22] or can sometimes be calculated semi-empirically. This second approach seems promising, as more data become available.[9]

Bond dissociation energies in *h*^{1}-cyclopentadienyls have been predicted to be about 30 kcal mole^{-1} lower than the metal-carbon bond energy in alkyl organometallics.[33] This value is not unreasonable when compared to the resonance energy of cyclopentadienyl radical, 15-30 kcal, or cycloheptatrienyl radical, 30 kcal.[40,46,101] Bond dissociation energies (D.E.) of interest are summarized in Table XX.

Weak interactions between radicals might lower apparent dissociation energies. And dissociation energies for simple molecules are known to be lower than their bond energies.[52] These effects do not alter the

TABLE XX

Values of C_5H_5-M Dissociation Energy, D.E., and the Activation Energy for Fluxional Rearrangement, E_a, kcal/mole.

M	D.E.[a]	E_a[b]
$-Si(CH_3)_3$	50	13
$Ge(CH_3)_3$	(>30)	10
$-Sn(CH_3)_3$	(30)	7
$-Pb(CH_3)$	14	-

[a] Ref. 33.

[b] Table IX.

criterion that positive $D_e^{\ddagger}$ values identify non-dissociative rearrangements. From the table it is apparent that cyclopentadienyls of Si, Ge and Sn have positive $D_e^{\ddagger}$ values and rearrange fluxionally in a non-dissociative manner. Both by estimation, and observation, the $D_e^{\ddagger}$ of the cycloheptatrienyl stannane is positive.[62,63]

A third, but specialized method for identification of the non-dissociative nature of the fluxional metal migration exists. This is observation of nuclear couplings between the averaged sites and the migrating group. Thus germylcyclopentadiene,[92] trimethyl pentamethylcyclopentadienyl stannane[27] and trimethylstannylindene[28] all rearrange in a non-dissociative manner.

Most of the metallotropic rearrangements occur with a negative, or very small $\Delta S^{\ddagger}$, indicative of a non-dissociative rearrangement.

None of the rearrangements are known to be dissociative. But none are known to be concerted. In terms of testing Woodward-Hoffmann rules, we propose that in these fluxional systems this does not really matter. What matters is what can be tested. Utilizing dissociation as the criteria allows new configurations of reality, depicted in Figure 3 below as Reality 4 and Reality 5.

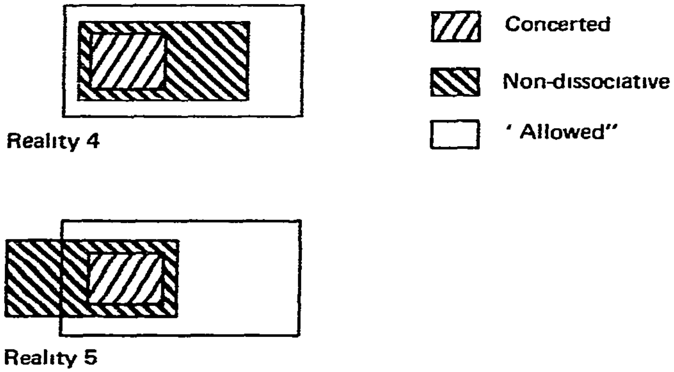


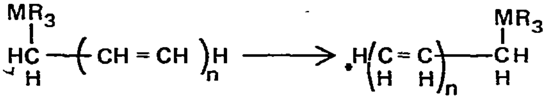
Figure 3. Configurations of reality relevant to chemical predictions from orbital symmetry.

What matters, and what determines the "truth" or utility of the predictive rules cast in this way is the degree of overlap between non-dissociative reactions, and those following the predicted pathway.

8. PREDICTIONS OF MIGRATORY PATHWAY FROM MOLECULAR ORBITAL SYMMETRY

It has been proposed that the directions of concerted reactions can be predicted through application of symmetry, or group theory to bonding models for transition states.[104] In this way the migration pathways for the fluxional rearrangements can be predicted and the observations in the systems reviewed stand as a test of the predictions.

Migration of organometallic groups between termini along one side of linear polymers are predicted to occur with retention at the migrating metal where n is even (29). Where n is odd, migration with inversion is predicted to occur. These processes are designated "symmetry allowed."[12,105]

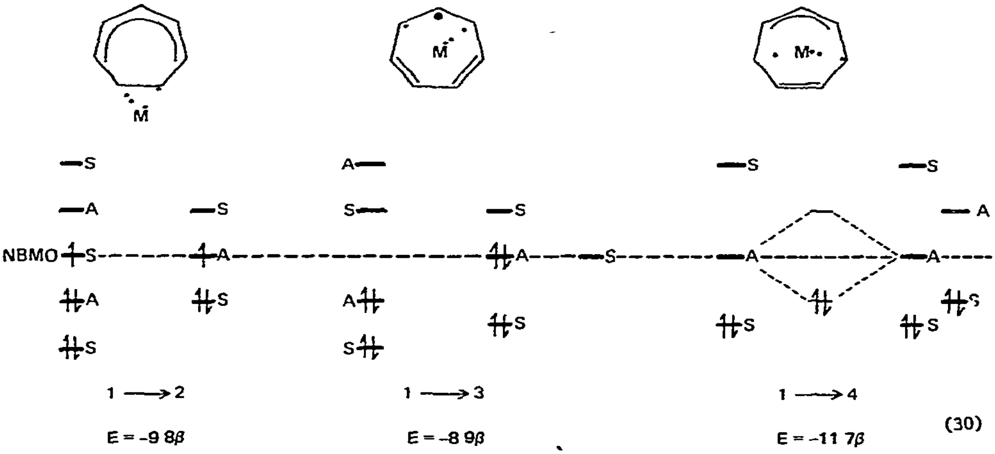


$$\underset{H}{\overset{MR_3}{HC}}-(CH=CH)_nH \longrightarrow {}^{\bullet}H\left(\underset{H}{C}=\underset{H}{C}\right)_n-\underset{H}{\overset{MR_3}{CH}} \qquad (29)$$

In actuality, of a set of possible reactions, those observed are those which occur with lowest $\Delta G^{\ddagger}$. Symmetry rules predict the reaction pathway of lowest $\Delta H^{\ddagger}$. These are the pathways of maximum bonding, or maximum $D_e^{\ddagger}$. Of course, symmetry arguments themselves never allow an estimation of the magnitude of the bonding in the transition state. They allow the conclusion to be made that the bonding energy is either zero, or non-zero. Exact calculations are required for a more quantitative prediction.

The prediction of the allowed pathway in cyclopentadienes, cycloheptadienes and cycloheptatrienes is identical with that for linear systems. This is illustrated for the seven-ring system in Scheme (30). Depicted are the 1' → 2', 1' → 3' and 1' → 5' migration pathways. Below each of the model transition states is a Grotian energy level diagram of the orbital energies, considering the polyenes, the 3-center bond with the migrating metal,[105] and the radical center as distinct interacting basis sets. The p orbital energy, or non-bonding orbital is the reference or zero line. Orbital energies are substantially lowered only in the case of the 1' → 5' migration, and this is the allowed pathway. Also shown in the diagram, in the 1' → 5' path the ethylene fragment does not contribute to the energy of the reaction pathway. Thus the energy lowering in the

1' → 5' rearrangement in cycloheptatrienes, cycloheptadienes and linear dienes is predicted to be quite similar.



(30)

Utilizing the explicit 3-center C-M-C bond in the transition state leads to prediction of migration to the adjacent carbon in indene (1' → 5') and in cyclopentadiene. Those predictions are verified in the semi-quantitative calculations of Anastasiou,[1] Chan-Cheng Su[93] and Dalton.[24] Thus in all systems observed to be fluxional, the migratory pathway is predicted to be 1' → 5'.

9. CONCLUSIONS

The fluxional behavior in the main group IV systems displays a commonality due to a common mechanism. In every instance, there is an intramolecular (non-dissociative) metallotropic migration unaffected by solvent polarity. The rates of migration are first-order and probably unimolecular. Rearrangement rates increase, and activation energies decrease as the atomic number of the migrating atom increases. Where possible, rearrangement occurs to the fifth carbon from the migration origin. The rates of the various systems increase in the order: propene < cycloheptatriene < cyclopentadiene. The rate trends are understandable in terms of the degree of bond breaking and bond making at the transition state; and in terms of the bond energy of the bond making at the transition state; and in terms of the bond energy of the bonds being made and broken.

The least sterically demanding reactions are the fastest. Despite this, the migratory pathway is not selected on the basis of the Principle of Least Motion. The fluxional pathways observed support, in a singular way, the predictions of orbital symmetry regarding sigmatropic rearrangements. No contrary behavior has been observed. To this extent, the predictive power of orbital symmetry rules is affirmed.

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