

Fluxional η^1 -Cyclopentadienyl Compounds of Main-Group Elements

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I. Introduction

There is no doubt that the introduction of the cyclopentadienyl (cp) ligand has significantly influenced the fascinating development of the chemistry of the transition metals, lanthanides, and actinides; since the beginning of the 1950s a huge number of cp compounds have been synthesized and investigated. Until recently, on the other hand, the investigation of cyclopentadienyl chemistry of main-group elements was restricted to group 4 species and some other isolated examples. This situation has changed radically during the last decade; a variety of new cp compounds with main-group elements has been developed, and the knowledge of the possible bonding modes in σ -bonded (η^1) species as well as in π -bonded (η^n) complexes¹ has increased. One of the most interesting features in η^1 -cp compounds is the fluxionality often or usually observed. At present, there is no other class of fluxional molecules that has been so intensively studied. The comparison of experimental results with theoretical calculations turned out to be especially useful in understanding the basic principles of the dynamic behavior.

This paper reviews the latest work on the fluxionality of cp compounds of main-group elements.



Peter Jutzi was born in 1938 in Duisburg, West Germany. He received his Diplom-Chemiker from the Technische Hochschule München in 1962 and his Dr. rer. nat. degree from the University of Marburg in 1965. After his "Habilitation" at the University of Würzburg, he became professor in 1974. In 1979 he moved to the University of Bielefeld, where he is full professor in Inorganic Chemistry. Jutzi's research interests are in the field of experimental organometallic chemistry with emphasis on the synthesis of π complexes with main-group elements as central atoms and of compounds containing nonclassical (p-p) π bonds. Other interests include fluxional organometallic compounds and silicon-containing drugs.

II. Fluxional Compounds of the Type C_5H_5EI and C_5Me_5EI

A. Introductory Discussion

The fluxionality of compounds of transition metals and main-group elements with σ -bonded (η^1) cyclopentadienyl rings is caused by concerted sigmatropic rearrangements. To prepare for the elucidation of the latest developments in the following sections, a brief history of important earlier work is useful.

The first fluxional σ -cyclopentadienyl compounds were discovered in 1956 by Piper and Wilkinson;³ for species such as $(\eta^1-C_5H_5)_2Hg$ and $(\eta^5-C_5H_5)(\eta^1-C_5H_5)-Fe(CO)_2$ they discussed in an undetailed, but essentially correct, way fast intramolecular 1,2 migrations of the metal moiety around the cyclopentadienyl ring. The first observation of a 1,2 hydrogen shift in cyclopentadiene itself and in some of its organic derivatives was reported in 1963 by Mironov and co-workers;⁴ a more detailed description of the kinetics and mechanism of these processes was presented in 1964 by Roth.⁵ The 1,2 migration of main-group elements in cp compounds was first discussed by Fritz and Kreiter⁶ in 1965 for silicon-, germanium-, and tin-substituted cyclopentadienes; the important conclusion that a competitive prototropic rearrangement occurs in silicon cy-

clopentadienyls was presented in 1968 by Ustynyuk and co-workers.⁷ In 1966 the hypothesis of fluxional behavior in Wilkinson's compounds was substantiated by Cotton and co-workers,^{8,9} who characterized the rearrangement pathway by variable-temperature NMR studies and line-shape analysis. From these and other investigations it is evident that η^1 -cyclopentadienyl compounds of main-group elements or transition metals are all fluxional in qualitatively the same sense.

The use of modern NMR techniques such as variable-temperature measurement and line-shape analysis has greatly increased our understanding of fluxionality. In review articles by Sergeev and Abel¹¹ in 1973, by Larrabee¹² in 1974, by Cotton¹³ in 1975, and by Spangler¹⁴ in 1976 as well as in newer textbooks,^{15,16} the difficulties in identifying the pathway by which an atom migrates around a cyclopentadienyl ring are already explained in detail. The limitations of those NMR techniques need to be addressed. The described methods are applicable only in a rather narrow range of activation energies for rearrangement. Processes outside of these energies cannot be determined accurately. From there, cp systems with ΔE^\ddagger values lower than ≈ 5 kcal/mol are qualitatively described as "highly fluxional"; compounds with ΔE^\ddagger values higher than ≈ 35 kcal/mol must be treated carefully to determine the rearrangement mechanism.

According to an earlier review,¹⁰ average ¹³C chemical shifts and ¹³C-¹H coupling constants observed under fast-exchange conditions for a η^1 -cyclopentadienyl compound should differ significantly from those of a π complex. But, since then Fischer¹⁷ has presented some counter examples among the main-group element cyclopentadienyls. Thus, the only NMR technique still valid for the identification of a ground-state structure in the fast-exchange limit is the Saunders isotopic perturbation method.¹⁸ Other methods to define ground-state structures of highly fluxional molecules include IR and Raman spectroscopies as well as X-ray crystal structure analysis.

In all cases discussed in this paper it will be assumed that the rearrangements in question occur intramolecularly, following a unimolecular, concerted mechanism. Rearrangements that occur by dissociation-recombination processes—i.e., intermolecular exchange—are excluded.

Recent developments have shown that drastic differences in the fluxional behavior exist among the cp compounds of main-group elements. These differences may be ascribed to (i) the nature of the main-group element, (ii) the other ligands bonded to the main-group element, and (iii) the substituents on the cyclopentadienyl ring. These factors influence the rate of prototropic shifts and the proportion of allylic and vinylic isomers present in equilibrium enormously. Furthermore, they determine specifically the activation energy for the circumambulatory migration of the relevant main-group element. These phenomena will be discussed below in detail together with newer results concerning the mechanism of sigmatropic rearrangements and the stereochemistry at the migrating atom.

B. Influence of Main-Group Elements on the Isomer Ratio in C_5H_5EI -Type Compounds

In cyclopentadienyl compounds of the type C_5H_5EI

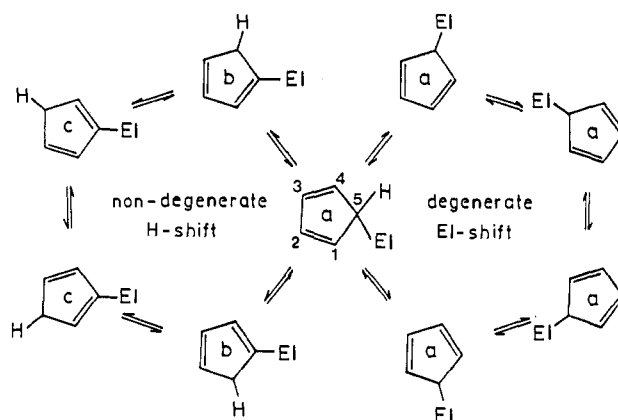


Figure 1. Sigmatropic processes in C_5H_5EI compounds.

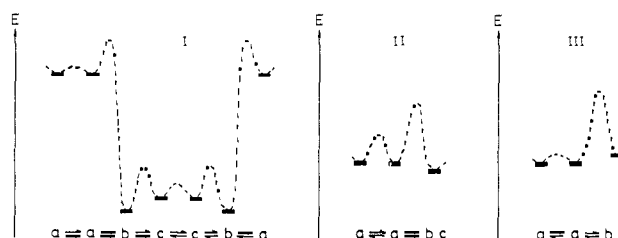


Figure 2. Schematic energy profiles for sigmatropic rearrangements in C_5H_5EI compounds.

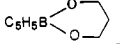
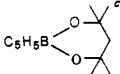
two different sigmatropic processes are possible; these are portrayed in Figure 1. First, a nondegenerate 1,2 hydrogen shift—corresponding to a 1,5 sigmatropic rearrangement—may occur, producing isomers with the element fragment in an allylic (a) or vinylic (b, c) position of the cyclopentadiene system. Second, a degenerate 1,2 shift of the element fragment may take place, producing only identical compounds (a) with the element in an allylic position.

Complete characterization of the dynamic processes in these compounds, considering both 1,2 H shifts and 1,2 EI shifts, is only possible by a rather complicated kinetic scheme including many rate constants. So far, only a few systems have been fully analyzed, although many compounds have been investigated partially in well-designed experiments.^{10,16} The thermodynamic data available from these investigations allow us to differentiate, on a qualitative scale, three situations whose energy profiles are displayed in Figure 2 and can be explained as follows:

Situation I: Due to strong back-bonding from the vinylic π system into a vacant orbital at the main-group element, the vinyl isomer is considerably lower in energy than the allylic isomer. In addition, the activation energy for the 1,2 element shift is lower than that for the 1,2 hydrogen shift. The above situation is common for cyclopentadienylboranes and well documented for the compound $C_5H_5BMe_2$.¹⁹ at $-80^\circ C$ only the allylic isomer, which is highly fluxional, is present; above $-15^\circ C$ apparently irreversible 1,2 H shifts occur to produce the vinylic isomers, which are the only ones present at ambient and at higher temperature. To obtain the allylic isomer, the temperature must be kept low throughout the reaction. The other boron compounds collected in Table 1 have not yet been investigated in detail but seem to exhibit similar behavior.

Situation II: The allylic and vinylic isomers of cp compounds have nearly the same energy; for element

TABLE 1. Fluxional Cyclopentadienylboranes and Derivatives

compound	dynamic behavior	compound	dynamic behavior
$C_5H_5BMe_2^{19}$	I	$C_5H_5BCl_2^a$	I
$C_5H_5BEt_2^{66}$	I	$C_5H_5B(OMe)_2^b$	I
$C_5H_5BEt_2 \cdot py^{66}$	I		I
$C_5H_5BEt_2 \cdot N(Et)_3^{66}$	I		I

^a Lockmann, B.; Onak, T. *J. Org. Chem.* 1973, 38, 2552.
^b Mikhailov, B. M.; Baryshnikova, T. K.; Bogdanov, V. S. *Akad. Nauk SSSR* 1972, 202, 358. ^c Mikhailov, B. M.; Baryshnikova, T. K. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1976, 2399.

TABLE 2. Fluxional Cyclopentadienylsilanes

compound	dynamic behavior	compound	dynamic behavior
$C_5H_5SiH_3^{a,b,38}$	II	$C_5H_5SiMe_2-$	II
$C_5H_5SiH_2Cl^b$	II	(1-piperidyl) ⁱ	
$C_5H_5SiHCl_2^b$	II	$(C_5H_5SiMe_2)_2O^i$	II
$C_5H_5SiMe_2^{a,c-e,72}$	II	$[C_5H_5(SiMe_2O)]_2-$	II
$C_5H_5SiMe_2Cl^{23}$	II	$SiMe_2C_5H_5^i$	
$C_5H_5SiMe_2Cl_2^{23}$	II	$C_5H_5SiMe_2OSiMe_2Ph^m$	II
$C_5H_5SiEt_3^{h,j}$	II	$C_5H_5SiMe_2(OSiMe_2)_2Ph^m$	II
$C_5H_5SiEt_2Cl^{h,j}$	II	$C_5H_5SiMe_2(OSiMe_2)_3Ph^m$	II
$C_5H_5SiEtCl_2^{h,j}$	II	$C_5H_5SiMe_2OSiMe_3^m$	II
$C_5H_5SiPrCl_2^{h,j}$	II	$C_5H_5SiMe_2OSiMe_2-$	II
$C_5H_5Si(i-Pr)Cl_2^h$	II	$(C_6H_3Cl)_2^m$	
$C_5H_5SiBuCl_2^h$	II	$C_5H_5SiMe_2OSiPh_3^m$	II
$C_5H_5Si(i-Bu)Cl_2^h$	II	$C_5H_5SiMe_2OSiMe_2Cl^m$	II
$C_5H_5Si(CH=CH_2)_2-$	II	$C_5H_5SiMe_2(OSiMe_2)_2Cl^m$	II
$Cl_2^{h,i}$	II	$C_5H_5Si(OEt)_3^n$	II
$C_5H_5SiPhCl_2^{h,i}$	II	$C_5H_5Si(OBu)_3^n$	II
$C_5H_5SiMe_2H^n$	II	$C_5H_5SiMe(OEt)_2^i$	II
$C_5H_5SiMe_2-$	II	$C_5H_5SiMe_2OEt^i$	II
$(CH_2CH=CH_2)^j$		$C_5H_5SiCl_3^{b,23}$	II
$C_5H_5SiEt_2H^k$	II	$C_5H_5SiF_3^c$	II
$C_5H_5SiMePhCl^h$	II	$(C_5H_5)_2SiH_2^b$	II
$C_5H_5SiMe_2-$	II	$(C_5H_5)_2SiMe_2^{o,p}$	II
$(CH_2SiMe_3)^q$		$(C_5H_5)_2SiHCl^b$	II
$(C_5H_5SiMe_2)_2CH_2^q$	II	$(C_5H_5)_3SiH^c$	II

^a Hagen, A. P.; Russo, P. J. *J. Organomet. Chem.* 1973, 51, 125.
^b Bonny, A.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* 1980, 224.
^c Kisin, A. V.; Korenevsky, V. A.; Sergeyev, N. M.; Ustynyuk, Yu. A. *J. Organomet. Chem.* 1972, 42, 47. ^d Ashe, A. J., III *J. Am. Chem. Soc.* 1970, 92, 1233. ^e McLean, S.; Reed, G. W. B. *Can. J. Chem.* 1970, 48, 3110. ^f Avramenko, G. J.; Sergeyev, N. M.; Ustynyuk, Yu. A. *J. Organomet. Chem.* 1972, 37, 89. ^g Sergeyev, N. M.; Avramenko, G. J.; Ustynyuk, Yu. A. *J. Organomet. Chem.* 1970, 22, 63. ^h Shologon, L. M.; Romantsevich, M. K.; Kul'kova, S. V. *Zh. Obshch. Khim.* 1967, 37, 2315. ⁱ Shologon, L. M.; Romantsevich, M. K. *Ah. Obshch. Khim.* 1966, 36, 1846. ^j Maksimova, L. N.; Koshutin, V. J.; Smironov, V. A. *Zh. Obshch. Khim.* 1973, 43, 1198. ^k Nametkin, N. S.; Chernysheva, T. I.; Babare, L. V. *Zh. Obshch. Khim.* 1964, 34, 2258. ^l Schaaf, R. L.; Kan, P. T.; Lenk, C. T. *J. Org. Chem.* 1960, 26, 1790. ^m Schaaf, R. L.; Kan, P. T.; Lenk, C. T.; Deck, E. P. *J. Org. Chem.* 1960, 25, 1986. ⁿ Olson, M. M.; Christenson, R. M.; U.S. Patent 2957 901, 1960; *Chem. Abstr.* 1961, 55, 18628. ^o Frisch, K. C. *J. Am. Chem. Soc.* 1953, 75, 6050. ^p Martin, R. W. U.S. Patent 2667 501, 1954; *Chem. Abstr.* 1955, 49, 2493. ^q Kumada, M.; Tsunemi, H.; Iwasaki, S. *J. Organomet. Chem.* 1967, 10, 111. ^r Koshutin, V. J.; Maksimova, L. N.; Emyashev, V. J.; Smironov, V. A. *Zh. Obshch. Khim.* 1976, 46, 146.

fragments with electron-acceptor properties the vinylic isomers may be energetically preferred. The activation energies for the degenerate and nondegenerate shifts are also very similar, though in most cases the rate for the 1,2 H shift is lower than for the E1 shift. As a consequence, a mixture of isomers is present, and the two sigmatropic processes may be observed simultaneously in the usual temperature range. This situation is typical for all cyclopentadienylsilanes (see Table 2)

TABLE 3. Fluxional Cyclopentadienylgermanes

compound	dynamic behavior	compound	dynamic behavior
$C_5H_5GeH_3^{a,b,69}$	II	$C_5H_5GePh_3^{c,d}$	II
$(C_5H_5)_2GeH_2^{67}$	II	$(C_5H_5)_2GeMe_2^{73,f}$	II
$C_5H_5GeH_2Me^b$	II	$C_5H_5Ge(OMe)_3^{24}$	II
$C_5H_5GeMe_3^{73,24}$	II	$C_5H_5Ge(OCH_2CH_2)_3N^{24}$	II
$C_5H_5GeMe_2Et^f$	II	$C_5H_5GeMeCl_2^e$	II
$C_5H_5GeEt_3^{73,f}$	II	$C_5H_5GeEtCl_2^e$	II
$C_5H_5GeBu_3^{73}$	II	$C_5H_5GeCl_3^{24}$	II

^a Hagen, A. P.; Russo, P. J. *Inorg. Nucl. Chem. Lett.* 1970, 6, 507. ^b Stobart, S. R. *J. Organomet. Chem.* 1971, 33, C11. ^c Lesbre, M.; Mazerolles, P.; Manuel, G. C. R. *Hebd. Seances Acad. Sci.* 1962, 255, 544. ^d Seyferth, D.; Hoffmann, H. P.; Burton, R.; Hellinger, J. F. *Inorg. Chem.* 1962, 1, 227. ^e Kocheskov, K. A.; Zemlyanski, N. N.; Shiro, V. S.; Ustynyuk, Yu. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1976, 2407. ^f Mironov, V. F.; Gar, T. K.; Leites, L. A. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1962, 1387.

TABLE 4. Equilibrated Isomer Ratios in Cyclopentadienylsilanes $C_5H_5SiMe_{3-x}Cl_x$

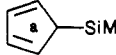
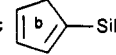
	ratio (a:b,c)		ratio (a:b,c)
x	ratio (a:b,c)	x	ratio (a:b,c)
0	90:10	2	50:50
1	79:21	3	35:65

TABLE 5. Cyclopentadienylphosphanes and Derivatives

compound	dynamic behavior	compound	dynamic behavior
$C_5H_5PF_2^{25,26}$	II	$(C_5H_5)_2PSPH^b$	I/II
$(C_5H_5)_2PF^{26}$	II	$(C_5H_5)_2PMe_2^+I^-^b$	I/II
$C_5H_5P(OBu)_2^a$	I/II	$C_5H_5PPh_2 \cdot Fe(CO)_4^c$	I/II
$C_5H_5PPh_2^b$	I/II	$C_5H_5PCL_2 \cdot W(CO)_5^{27}$	II
$C_5H_5PSPH^b$	I/II	$(C_5H_5)_2PBr \cdot W(CO)_5^{27}$	II
$C_5H_5POPPh_2^b$	I/II	$C_5H_5PPhCl \cdot W(CO)_5^{27}$	II

^a Kabachnik, M. J.; Tsvetkov, E. N. *Zh. Obshch. Khim.* 1960, 30, 322. ^b Mathey, F.; Lampin, J. P. *Tetrahedron* 1975, 31, 2685. ^c Mathey, F.; Lampin, J. P. *J. Organomet. Chem.* 1977, 128, 297.

and has been described in detail for the compound $C_5H_5SiMe_3^{20-22}$

The influence of ligand effects on the isomer ratio is best documented by a series of cyclopentadienylsilanes of the type $C_5H_5SiMe_{3-x}Cl_x$: The relative abundance of vinylic isomers increases with an increase in the number of chlorine ligands and/or in temperature²³ (see Table 4). Presumably, situation II is also typical for cyclopentadienylgermanes (see Table 3), but so far, detailed investigations have not been performed. In the germanium compounds $C_5H_5GeCl_3$ and $C_5H_5Ge(OMe)_3$ the relative abundance of vinylic isomers in the equilibrium is very small,²⁴ compared to the abundance in the silicon compounds.

Situation II can also be anticipated for most of the cyclopentadienyl compounds of phosphorus (see Table 5), although they have not yet been investigated in detail, partly due to their pronounced thermal instability. Both allylic and vinylic structures have been assigned. Fluxionality due to PR_2 migration has been found for $C_5H_5PF_2$ and $(C_5H_5)_2PF^{25,26}$. A prototropic rearrangement at ambient temperature has been proved only for the complex $C_5H_5P(C_6H_5)ClW(CO)_5^{27}$. The behavior of those compounds where only vinylic structures have been observed is on the borderline between situations I and II. In any case, allylic structures

TABLE 6. Cyclopentadienylarsanes and Derivatives

compound	dynamic behavior	compound	dynamic behavior
C ₅ H ₅ AsMe ₂ ²⁸	II	(C ₅ H ₅) ₃ As ^a	II/III
C ₅ H ₅ As(<i>t</i> -Bu) ₂ ⁶⁵	I/II	C ₅ H ₅ AsMe ₂ ·Cr(CO) ₅ ²⁹	II
C ₅ H ₅ AsMeCl ²⁸	II	C ₅ H ₅ AsMe ₂ ·W(CO) ₅ ²⁹	II
C ₅ H ₅ AsF ₂ ²⁸	III	C ₅ H ₅ As(<i>t</i> -Bu) ₂ ·W(CO) ₅ ²⁹	I/II
C ₅ H ₅ AsCl ₂ ²⁸	III	C ₅ H ₅ AsMe ₃ ⁺ I ⁻²⁹	II
C ₅ H ₅ AsBr ₂ ²⁸	III	C ₅ H ₅ As(<i>t</i> -Bu) ₂ Me ⁺ I ⁻²⁹	I/II

^aDeubzer, B.; Elian, M.; Fischer, E. O.; Fritz, H. P. *Chem. Ber.* 1970, 103, 799.

TABLE 7. Fluxional Cyclopentadienylstannanes

compound	dynamic behavior	compound	dynamic behavior
C ₅ H ₅ SnMe ₃ ^{a,72,b}	III	(C ₅ H ₅) ₂ SnMe ₂ ⁸²	III
C ₅ H ₅ SnEt ₃ ^{6f}	III	(C ₅ H ₅) ₂ SnEt ₂ ^{6,62,f}	III
C ₅ H ₅ SnBu ₃ ^{6,b}	III	(C ₅ H ₅) ₂ SnBu ₂ ⁶	III
C ₅ H ₅ SnMe ₂ Cl ⁸²	III	(C ₅ H ₅) ₂ SnPh ₂ ⁶	III
C ₅ H ₅ SnMeCl ₂ ^d	III	(C ₅ H ₅) ₂ SnMeCl ^d	III
C ₅ H ₅ Sn(CH=CH ₂)Cl ₂ ^g	III	(C ₅ H ₅) ₂ SnEtCl ^d	III
C ₅ H ₅ SnPhCl ₂ ^d	III	(C ₅ H ₅) ₃ SnCl ^{d,35}	III
C ₅ H ₅ SnEtCl ^d	III	(C ₅ H ₅) ₃ SnPh ⁶	III
C ₅ H ₅ SnPh ₂ Cl ^d	III	(C ₅ H ₅) ₃ SnMe ⁸²	III
C ₅ H ₅ SnCl ₃ ^g	III	(C ₅ H ₅) ₂ SnCH=CH ₂ ³⁵	III
C ₅ H ₅ Sn(O ₂ CR) ₃ ^e	III	(C ₅ H ₅) ₄ Sn ^{d,6,35}	III

^aKisin, A. V.; Korenevsky, V. A.; Sergeyev, N. M.; Ustyniuk, Yu. A. *J. Organomet. Chem.* 1972, 34, 93. ^bJones, K.; Lappert, M. F. *J. Organomet. Chem.* 1968, 3, 295. ^cCotton, F. A.; Musco, A.; Yagupsky, G. *J. Am. Chem. Soc.* 1967, 89, 6136. ^dKolosova, D. D.; Zemlyanskii, N. N.; Azizov, A. A.; Ustyniuk, Yu. A.; Barminova, N. P.; Kocheshkov, K. A. *Dokl. Akad. Nauk. SSSR* 1974, 218, 117. ^eKocheshkov, K. A.; Zemlyanskii, N. N.; Kolosova, N. D.; Azizov, A. A.; Subbstin, O. A.; Ustyniuk, Yu. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1974. ^fKatsumare, T. *Nippon Kagaku Zasshi* 1962, 83, 727; *Chem. Abstr.* 1963, 59, 5184. ^gRamsden, H. E. U.S. Patent 2873 287, 1959; *Chem. Abstr.* 1959, 53, 13108.

TABLE 8. Fluxional Cyclopentadienylplumbanes

compound	dynamic behavior	compound	dynamic behavior
(C ₅ H ₅) ₄ Pb ⁶	III	(C ₅ H ₅) ₂ PbMe ₂ ⁷³	III
C ₅ H ₅ PbPh ₃ ³⁶	III	C ₅ H ₅ PbEt ₃ ⁷³	III
(C ₅ H ₅) ₂ PbPh ₂ ³⁶	III	(C ₅ H ₅) ₂ PbEt ₂ ⁷³	III
C ₅ H ₅ PbMe ₃ ⁷³	III		

must serve as intermediates along pathways using cp transfer. Situation II is typical also for most of the cyclopentadienyl compounds of arsenic (see Table 6). Vinylic isomers have been detected at ambient temperature to a small extent for the cyclopentadienylarsanes C₅H₅AsMe₂ and C₅H₅AsMeCl²⁸ and exclusively for the di-*tert*-butylarsino-substituted cyclopentadienes,²⁹ which once more are on the borderline between situations I and II.

Situation III: The energies of the allylic and vinylic isomers are similar to those described in situation II, but in contrast a very low activation energy exists for the 1,2 El shift in comparison to that for the 1,2 H shift. As a consequence, only the highly fluxional allylic isomers can be observed under normal conditions; the H shift will become important only at higher temperatures, if at all. This is the typical situation for the majority of cp compounds of the heavier elements in main groups 3–5, as documented in Tables 7–10. η^1 ground-state structures can be assumed for all of these compounds and have been proved by X-ray crystallography in the case of C₅H₅AlMe₂,³⁰ C₅H₅GaMe₂,³¹ (C₅H₅)₃Ga,³² [(C₅H₅)₂GaOEt]₂,³³ (C₅H₅)₃In,³⁴ (C₅H₅)₄Sn,³⁵ C₅H₅PbPh₃,³⁶ and (C₅H₅)₃Sb.³⁷

TABLE 9. Cyclopentadienylstibanes, -bismutanes, and Derivatives

compound	dynamic behavior	compound	dynamic behavior
C ₅ H ₅ SbMe ₂ ^{73,a}	III	C ₅ H ₅ Sb(<i>t</i> -Bu) ₂ ·W(CO) ₅ ²⁹	III
C ₅ H ₅ Sb(<i>t</i> -Bu) ₂ ⁶⁵	III	C ₅ H ₅ SbMe ₃ ⁺ I ⁻²⁹	III
C ₅ H ₅ SbCl ₂ ⁷⁶	III	(C ₅ H ₅) ₃ Sb ^{b,37}	III
C ₅ H ₅ SbMe ₂ ·Cr(CO) ₅ ²⁹	III	C ₅ H ₅ BiMe ₂ ^a	III
C ₅ H ₅ SbMe ₂ ·W(CO) ₅ ²⁹	III		

^aKrommes, P.; Lorberth, J. *J. Organomet. Chem.* 1975, 88, 329.

^bDeubzer, B.; Elian, M.; Fischer, E. O.; Fritz, H. P. *Chem. Ber.* 1970, 103, 799.

TABLE 10. Cyclopentadienyl Compounds of Aluminum, Gallium, Indium, and Thallium

compound	dynamic behavior	compound	dynamic behavior
C ₅ H ₅ AlMe ₂ ^{a,b,17}	III	C ₅ H ₅ GaEt ₂ ^b	III
C ₅ H ₅ AlEt ₂ ^a	III	[(C ₅ H ₅) ₂ GaOEt] ₂ ³³	III
C ₅ H ₅ Al(<i>t</i> -Bu) ₂ ^a	III	(C ₅ H ₅) ₃ Ga ³²	III
C ₅ H ₅ AlEt ₂ ·OEt ^b	III	C ₅ H ₅ InEt ₂ ^b	III
(C ₅ H ₅) ₂ AlMe ^b	III	(C ₅ H ₅) ₃ In ³⁴	III
C ₅ H ₅ GaMe ₂ ^{b,31}	III	C ₅ H ₅ TlMe ₂ ^d	III

^aKnoll, B. R.; Naegle, W. *J. Chem. Soc., Chem. Commun.* 1969, 246. ^bStadelhofer, J.; Weidlein, J.; Haaland, A. *J. Organomet. Chem.* 1975, 84, C1; 1976, 116, 55. ^cKrommes, P.; Lorberth, J. *J. Organomet. Chem.* 1975, 88, 329. ^dLee, A. A. *J. Chem. Soc. A* 1970, 2157.

The main conclusion to be drawn from this chapter is that both the main-group element itself and its substituents have a drastic influence on the isomer ratio of cyclopentadienyl compounds and, correspondingly, on the rate of 1,2 hydrogen and 1,2 element shifts.

C. Fluxional Behavior owing to Element Migration

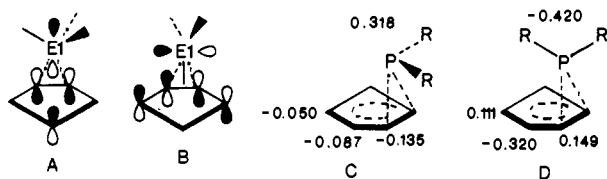
1. Mechanisms: Stereochemistry at the Migrating Atom

The intramolecular dynamics in many cyclopentadienyl compounds have become clear with the help of modern variable-temperature NMR techniques. Asymmetric collapse of olefinic signals (¹H, ¹³C) during coalescence rules out a random migration, but the inference of 1,2 or 1,3 shifts remained far from simple due to the uncertainty of the assignment of signals to atoms in 1/4 or 2/3 position⁹¹ of the cyclopentadiene system. It is now very probable that 1,2 shifts indeed occur: clear evidence stems from different NMR criteria under slow-exchange conditions.^{9,15,16,38} As mentioned already, NMR data allow no conclusion to be drawn when—even at low temperatures—only averaged signals (fast-exchange limit) are observed.

For a detailed mechanistic discussion it is necessary to know the stereochemistry at the migrating center. The symmetry-allowed 1,5 sigmatropic rearrangements (1,2 shifts) in η^1 -cyclopentadienyl compounds can only occur suprafacially.³⁹ Because the frontier orbitals in a cp fragment are degenerate, these migrations can in principle take place either with retention or with inversion of configuration at the migrating center. Which stereochemistry will be more favorable depends on the element and on the substituents.

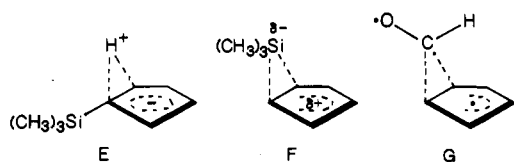
In an important contribution, Stobart and co-workers⁴⁰ demonstrated experimentally that in cyclopentadienylsilanes, -germanes, and -stannanes the 1,5

sigmatropic rearrangements occur with retention of configuration at the group 4 element. For the chiral compounds of the type $C_5H_5ElR(i-Pr)(Ph)$ ($El = Si, Ge, Sn$) 1H and ^{13}C NMR spectra show magnetically non-equivalent methyl resonances for the prochiral isopropyl substituent; this anisochronicity is temperature invariant, thus establishing the retention of configuration at the migrating center. Hence, by qualitative MO arguments, transition-state geometry A is much more favorable than geometry B. This agrees with an MNDO calculation.⁴¹



Interesting theoretical arguments have recently been elaborated by Schoeller^{42,43} concerning the stereochemistry at the migrating atom in cyclopentadienyl compounds of the group 5 elements (N, P, As, Sb). According to energy-optimized MNDO calculations, the 1,5 sigmatropic process in cyclopentadienylphosphanes can occur either with retention (geometry C) or with inversion (geometry D) of configuration at phosphorus, depending on the ligands within the PR_2 fragment; electropositive ligands R favor inversion, whereas electronegative ligands promote retention. The stereochemistry in these rearrangements is also influenced by electron-withdrawing or -donating substituents attached to the cyclopentadienyl ring. According to MNDO calculations,⁴³ the cyclopentadienyl unit in $C_5H_5PH_2$ is differently polarized in the transition state for retention and inversion processes, as portrayed in C and D ($R = H$). This results in various substituent effects on the magnitude of the energy difference between the two transition-state geometries. Given the same ligands, the tendency to favor retention over inversion of configuration has been found to increase with increasing principal quantum number of the group 5 element, i.e. in order $N < P < As < Sb$.^{42,43} On the other hand, in the sigmatropic rearrangements in cyclopentadienylboranes inversion over retention at the boron atom is clearly favored.⁴⁴ Unfortunately, all these predictions could not yet be substantiated experimentally.

Insight into the structure of η^2 transition states passed during sigmatropic rearrangements has been given by le Noble and co-workers,⁴⁵ who have measured the volumes of activation for degenerate and nondegenerate processes in some cyclopentadienyl systems. In every case investigated the activation volumes were negative, as evidenced by the pressure-induced enhancements of rates. For the hydrogen migration in 5-(trimethylsilyl)cyclopentadiene the activation volume is -26.5 cm^3/mol at $30^\circ C$; this observation requires considerable charge separation in the transition state E. The



trimethylsilyl group in the same molecule migrates with

TABLE 11. Activation Energies for 1,2 Element Shifts in Some Cyclopentadienyl-Element Compounds

compound	E_A , kcal/mol	compound	E_A , kcal/mol
$H_5C_5CMe_3$	$>40^a$	$H_5C_5AsMe_2$	15.0 ± 0.3^{28}
$H_5C_5SiMe_3$	13.0 ± 1^b	$H_5C_5SbMe_2$	8.5 ± 1^d
$H_5C_5GeMe_3$	9.2 ± 1^b	$Me_5C_5NMe_2$	$\geq 25^e$
$H_5C_5SnMe_3$	7.8 ± 1	$Me_5C_5PMe_2$	23.0 ± 0.5^{27}
$Me_5C_5CMe_3$	$>40^a$	$Me_5C_5AsMe_2$	17.1 ± 0.4^c
$Me_5C_5SiMe_3$	15.3 ± 0.2^c	$Me_5C_5SbMe_2$	11.3 ± 1.4^c
$Me_5C_5GeMe_3$	11.4 ± 1.3^c		
$Me_5C_5SnMe_3$	$<5^c$		

^a Estimated value. ^b Kisin, A. V.; Korenevsky, V. A.; Sergeev, N. M.; Ustyniyuk, Yu. A. *J. Organomet. Chem.* **1972**, *34*, 93. ^c Jutzi, P.; Hielscher, B.; Saleske, H., unpublished results. ^d Jutzi, P.; Kuhn, M. *J. Organomet. Chem.* **1979**, *173*, 221. ^e Boche, G., unpublished results.

an activation volume of -12.5 cm^3/mol at $68^\circ C$ according to a minor degree of charge separation, probably in the opposite sense, as indicated in F. Finally, in 5-formylcyclopentadiene (activation volume -4 cm^3/mol at $-4^\circ C$) there is no evidence for charge separation; the transition state G has been formulated as a radical pair.

It can be concluded from these experiments that in sigmatropic rearrangements of cp compounds various transition states can be passed ranging from highly dipolar ones to those that are completely dissociated into radical pairs.

2. Influence of the Main-Group Element on the Migration Rates

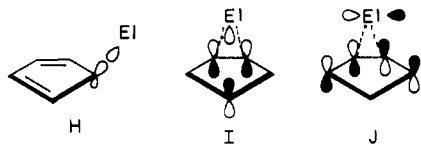
As mentioned already, cyclopentadiene systems with main-group elements in allylic positions can undergo 1,5 sigmatropic rearrangements of the corresponding element fragments (see Figure 1). The rates for these migrations vary over a wide range, as it has been demonstrated by investigation of cyclopentadienyl and various substituted cyclopentadienyl compounds mainly of elements in main groups 3–5. The comparatively high thermal stability of the pentamethylcyclopentadienyl compounds makes them most suitable for the study of element migration. Furthermore, nondegenerate methyl migrations, which can complicate the analysis of element migration processes, are not observed in the usual NMR temperature range.

Providing the substituents are the same, the heavier elements in each main-group exhibit lower activation barriers for migration. This has been demonstrated qualitatively in many cases^{10,16} and in a more quantitative fashion in the series $C_5H_5ElMe_3$, $C_5Me_5ElMe_3$ ($El = C, Si, Ge, Sn$) and $C_5H_5ElMe_2$, $C_5Me_5ElMe_2$ ($El = N, P, As, Sb$). The relevant activation energies are summarized in Table 11.

Cyclopentadienyl compounds of the heavier atoms in the main groups 3–5 (Al, Ga, In, Te, Sn, Pb, Sb, Bi) are generally so highly fluxional that it is impossible to ascertain the mechanism for the rearrangements with low-temperature NMR; estimated activation energies are lower than 5 kcal/mol. In analogy with the dynamic behavior of the lighter elements, a 1,2 shift can be anticipated, but other mechanisms are also possible because for the heavier atoms the η^1 , η^2 , and η^5 structures are very close in energy⁴⁶ and might represent ground or transition states in rearrangement processes.

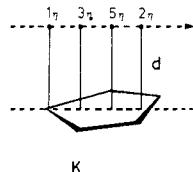
Several theoretical calculations have been published that explain the experimentally observed fluxionality of cyclopentadienyl compounds and the differences in

activation energies caused by variation of the main-group element. A priori, the rates for sigmatropic rearrangements are determined by the relative differences between η^1 ground states (represented by H) and η^5 transition states (represented by I and J).



The bond strength between the cyclopentadienyl carbon atom and the main-group element decreases in the ground-state structures H going to the heavier congeners in the periodic system, whereas it increases in the transition-state structures I and J in the same direction due to better overlap. The result is an overall lowering of the relevant activation energies for the heavier homologues.

Ground- and transition-state energies have been calculated by different methods including qualitative arguments based on symmetry and overlap—supported by extended Hückel calculations—and on CNDO/2, MINDO/2, and *ab initio* molecular orbital calculations.^{42–44,46,47} Hoffmann and co-workers have considered the passage of a fragment EI [$\text{EI} = \text{H}^+, \text{CH}_3^+, \text{SiH}_3^+, \text{GeH}_3^+, \text{SnH}_3^+, \text{CH}_2^{2+}$ (serving as a model for BR_2^+ and AlR_2^+)] across the face of a C_5H_5^- ring moving in a plane parallel to the ring at a distance d where sizable interaction between the frontier orbitals of the fragment EI and the π system can be anticipated.⁴⁶ The various sites along the transit line in these “haptotropic shifts” have been labeled as 1η , 2η , 3η , and 5η (see K)



in contrast with the true geometrically relaxed η^x states. These considerations show that the energies for the haptotropic shifts depend strongly on the nature of the fragment EI. In the case of $\text{EI} = \text{H}^+, \text{CH}_3^+$, and SiH_3^+ , the calculated $1\eta - 2\eta$ differences, which can be related to the activation energy for the 1,5 sigmatropic shift, have been found to be qualitatively correct; CNDO/2 and MINDO/2 calculations, which allow all geometrical parameters to vary, order the activation energies more correctly.⁴⁷ The consideration of correlation effects would lead to an even better fit between observed and calculated activation energies.⁴⁸

Hoffmann and co-workers have postulated in their calculations an η^2 ground state for cyclopentadienylboranes and -alanes.⁴⁶ In contrast, Schoeller argues for an η^1 structure in the ground state of cyclopentadienylboranes from the results of energy-optimized MNDO calculations.⁴⁴ Experimentally, η^1 structures have been established for some (pentamethylcyclopentadienyl)boranes of the type $\text{Me}_5\text{C}_5\text{BR}_2$ ($\text{R} = \text{NMe}_2, \text{OEt}, \text{SEt}, \text{F}$) by their ^1H and ^{13}C NMR data^{49,50} and for $(\text{Me}_5\text{C}_5)_2\text{BF}$ by an X-ray diffraction study.⁵⁰

An interesting correlation of ionization potentials with fluxional behavior has been published.^{51–53} $\sigma-\pi$ hyperconjugation of the relevant $\text{H}_5\text{C}_5-\text{EI}$ bond ($\text{EI} = \text{H}, \text{SiMe}_3, \text{GeMe}_3, \text{SnMe}_3, \text{CH}_3, \text{SiH}_3, \text{GeH}_3, \text{SiF}_3, \text{PF}_2$)

with the ring diene system in the ground-state structures of cyclopentadienyl compounds appears to be an important factor in controlling the rates of sigmatropic rearrangements. The degree of $\sigma-\pi$ hyperconjugation can be estimated from the photoelectron spectra.

3. Substituent Effects on the Migration Rate

a. Substituents at the Migrating Center. Recent investigations have clarified a sometimes surprisingly large influence of the further substituents at the relevant main-group element on the rate of sigmatropic rearrangements. Systematic investigations have been done with cp compounds of the elements boron, carbon, silicon, germanium, phosphorus, and arsenic. The most pronounced substituent effects have been observed in pentamethylcyclopentadienyl phosphorus compounds. The activation energies for sigmatropic processes lie within the region of ≤ 5 and ≥ 35 kcal/mol (see Table 12); i.e., the structures of the relevant molecules have to be classified within a range from highly fluxional to rigid.


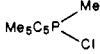
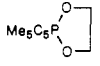
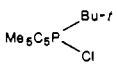
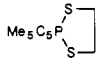
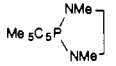
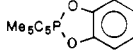
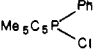
It is evident from the activation data in Table 12 that the dynamic behavior of cyclopentadienyl phosphorus compounds depends on the coordination number at phosphorus. Whereas molecules with coordination number 2 [i.e., 1-(pentamethylcyclopentadienyl)-2,2-bis(trimethylsilyl)-1-phosphaethene⁵⁴ and bis(pentamethylcyclopentadienyl)diphosphene⁵⁵] are highly fluxional, those with coordination number 4 (phosphonium salts, phosphane sulfides and selenides, and pentacarbonyl metal phosphane complexes with cyclopentadienyl²⁷ or pentamethylcyclopentadienyl⁵⁶ ligands) are rigid on the NMR time scale.^{27,56}

Surprisingly large differences in fluxionality are found in phosphorus compounds with coordination number 3. From the activation data for the latter species the following trends have been observed:⁵⁷ (1) Elongation of the carbon skeleton in alkyl substituents leads to higher activation energies. (2) Substitution of an alkyl or aryl group by a halogen atom leads to lower activation energies. (3) Among compounds containing pseudo-halogen and halogen substituents, a decrease of E_A values is observed in the following order: $\text{CN} \sim \text{F} > \text{Cl} > \text{Br}$; similar effects are observed when the substituents contain elements of main group 6 (O, S); (4) Fixing oxygen-, sulfur-, or nitrogen-containing substituents in a five-membered ring system leads to comparably lower activation energies. Finally, the high E_A value for the 1,2 PH_2 shift in the (pentamethylcyclopentadienyl)phosphane is remarkable.

Similar trends have been found for the few known cyclopentadienyl arsenic compounds;²⁸ activation energies for these molecules are collected in Table 13.

The experimental data for the dynamic behavior in cyclopentadienyl phosphorus compounds can be explained by somewhat sophisticated theoretical arguments. A priori, a change of energy barriers depends on the stabilization or destabilization of transition and ground states. In cyclopentadienyl phosphorus compounds these states can be described by the frontier orbital interaction of the corresponding phosphorus fragment with a cyclopentadienyl unit. The sigmatropic rearrangements in some relevant cyclopentadienyl compounds with trivalent phosphorus have been analyzed on the basis of differential frontier orbital theory

TABLE 12. Activation Energies for 1,2 Element Shifts in Pentamethylcyclopentadienyl Compounds of Phosphorus

compound	E_A , kcal/mol	compound	E_A , kcal/mol
$\text{Me}_5\text{C}_5\text{P}=\text{C}(\text{SiMe}_3)_2$	$<8.0 \pm 1^{a,54}$	$\text{Me}_5\text{C}_5\text{P}(\text{CN})_2$	16.4 ± 0.3^{57}
$\text{Me}_5\text{C}_5\text{P}=\text{PC}_5\text{Me}_5$	$<8^{a,55}$	$\text{Me}_5\text{C}_5\text{P}(\text{OMe})_2$	21.2 ± 0.4^{57}
$\text{Me}_5\text{C}_5\text{PMe}_2$	23.0 ± 0.5^{57}	$\text{Me}_5\text{C}_5\text{P}(\text{SMe})_2$	17.5 ± 1.3^{57}
	27.4 ± 1.2^{57}	$\text{Me}_5\text{C}_5\text{P}(\text{NMe}_2)_2$	19.0 ± 1.2^{57}
	16.4 ± 1.1^{57}		16.3 ± 1.6^{57}
	21.3 ± 1.5^{57}		15.2 ± 0.5^{57}
$\text{Me}_5\text{C}_5\text{P}(\text{Ph})_2$	24.3 ± 1.0^{57}		6.2 ± 0.6^{57}
$\text{Me}_5\text{C}_5\text{P}(\text{C}_6\text{F}_5)_2$	17.2 ± 3.2^{57}		12.3 ± 0.8^{57}
	13.4 ± 2.9^{57}	$\text{Me}_5\text{C}_5\text{PMe}_3^+\text{I}^-$	$>35^{a,56}$
$\text{Me}_5\text{C}_5\text{PH}_2$	31.3 ± 1.8^{57}	$\text{Me}_5\text{C}_5\text{P}(\text{S})\text{R}_2$	$>35^{a,56}$
$\text{Me}_5\text{C}_5\text{PF}_2$	16.7 ± 0.7^{57}	$\text{Me}_5\text{C}_5\text{PR}_2\cdot\text{Cr}(\text{CO})_5$	$>35^{a,56}$
$\text{Me}_5\text{C}_5\text{PCl}_2$	12.0 ± 1.6^{57}		
$\text{Me}_5\text{C}_5\text{PBr}_2$	5.2 ± 3.1^{57}		

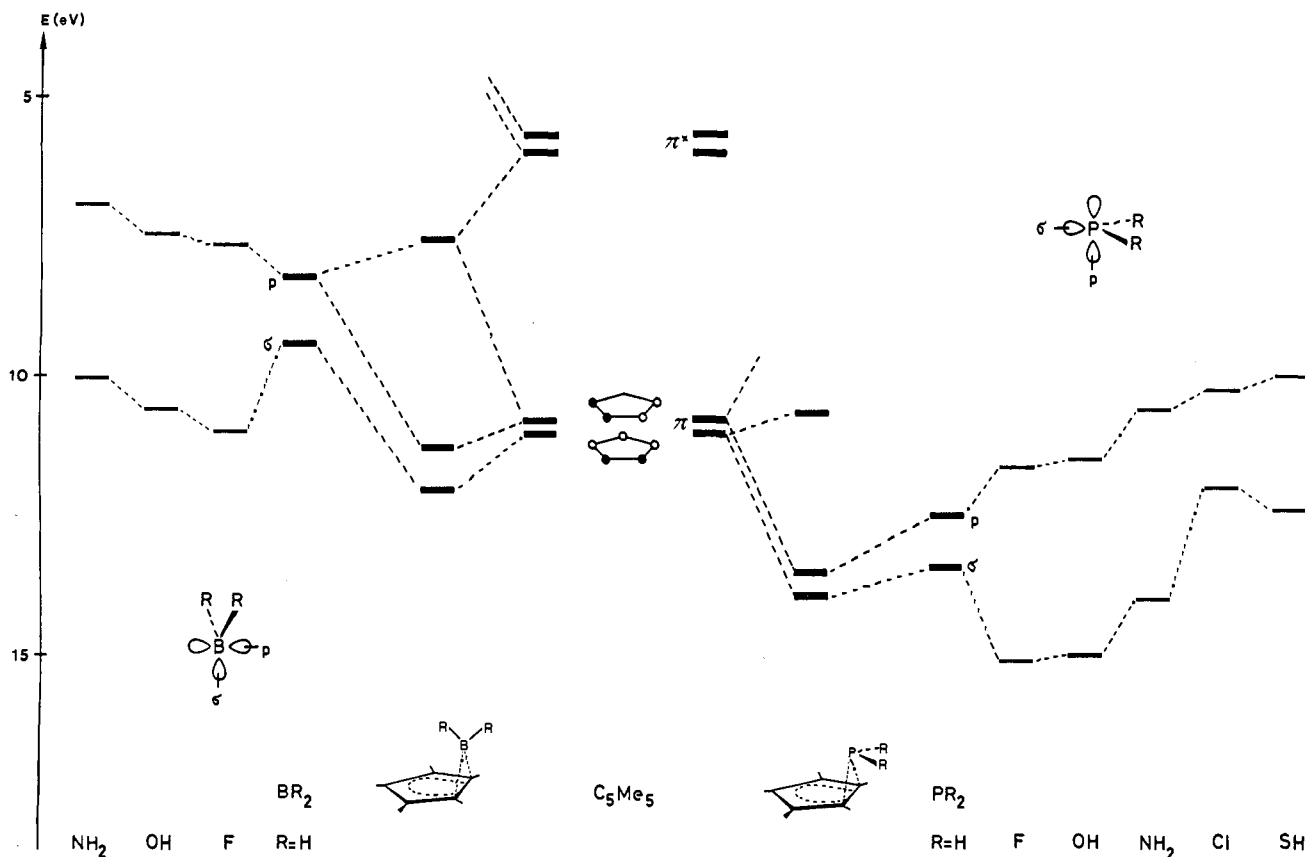
^a Estimated value.

Figure 3. Interaction diagram for the formation of η^2 structures from the frontier orbitals of a pentamethylcyclopentadienyl unit and of EIR_2 fragments ($\text{E} = \text{B}, \text{P}$).

using EH and energy-optimized MNDO calculations.⁴² The substituent effects on the frontier orbitals of the η^2 transition state will be considered first. They are illustrated in Figure 3 for the case of retention of configuration at phosphorus. It is important to note that PR_2 fragments possess a frontier orbital system analo-

gous to that of carbene anion radicals. The predominant orbital interaction occurs between the p orbital at the sp^2 -hybridized phosphorus in the pseudoallylic PR_2 fragment with one component (a' within C_s symmetry) of the degenerate cp set. The overlap of the σ orbital at phosphorus with the relevant cp set is less favorable.

TABLE 13. Activation Energies for 1,2 Element Shifts in Cyclopentadienyl Compounds of Arsenic

compound	E_A , kcal/mol	compound	E_A , kcal/mol
$H_5C_5AsMe_2$	15.0 ± 0.3^{28}	$H_5C_5AsMe_3^+I^-$	$>19^{29}$
$H_5C_5As(Me)Cl$	12.1 ± 0.3^{28}	$H_5C_5AsMe_2 \cdot Cr(CO)_5$	$>19^{29}$
$H_5C_5AsCl_2$	$<7^{a,28}$		

^a Estimated value.

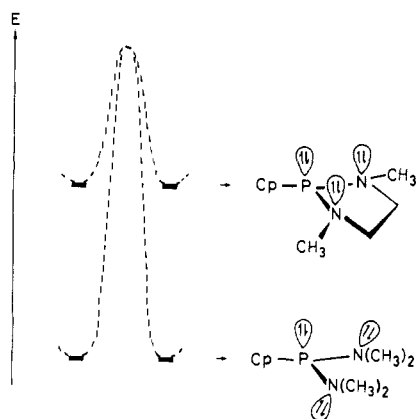


Figure 4. Schematic energy profiles for the 1,2 shift in CpPNR₂ systems.

Replacement of the hydrogens in PH₂ by other groups, especially by those bearing lone pairs (i.e. Hal, OH, SH, NH₂), changes the energy of the relevant p orbital and, therefore, has great influence on the energy of the transition state. If the ligands R belong to the same row in the periodic table, the energy of the SOMO (single-occupied molecular orbital) decreases with increasing atomic number, i.e. in the order R = NH₂ > OH > F or R = PH₂ > SH > Cl.⁵⁸ These changes in frontier orbital energy coupled with those in frontier orbital overlap determine the relevant energies of the transition states.

Let us now consider substituent effects on the ground-state energies of cpPR₂ compounds. In the ground state the phosphorus atom is hybridized as usual (~p³). As a consequence, mesomeric effects in the PR₂ unit cannot influence ground-state energies significantly, while lone-pair interactions within a PR₂ unit can. In compounds with alkoxy, thioalkoxy, or alkyl-amino ligands there is a tendency to minimize repulsion between the lone pairs at phosphorus and at the heteroatoms. There is much more repulsion when the lone pairs are forced into a nearly parallel orientation, which occurs when the ligands are part of a five-membered ring, as illustrated in Figure 4. The destabilization of the ground states reduces the overall energy barriers for migration (see Table 3). This explanation is best confirmed by comparison of the E_A values in cpPR₂ compounds with R = (NMe₂)₂ and NMeCH₂CH₂MeN.

The low activation energies observed for the sigmatropic rearrangements in cp compounds with divalent phosphorus can be explained by a pronounced stabilization of the η^2 transition state, caused by interaction of the cp π system with the π^* orbital at phosphorus. No marked stabilization of the relevant transition states can be expected for cp compounds with tetravalent phosphorus. Consequently, cp-substituted phosphonium salts, phosphane sulfides, and phosphanes bound to a transition metal possess high activation energies for rearrangements; rigid structures have been found

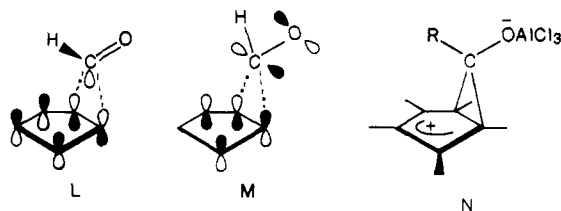
TABLE 14. Activation Energies for 1,2 Element Shifts in Cyclopentadienyl Compounds of Carbon, Silicon, and Germanium

compound	E_A , kcal/mol	compound	E_A , kcal/mol
$Me_5C_5CH_3$	40 ^a	$H_5C_5GeMe_3$	$<11^{24}$
Me_5C_5COCl	20 ^b	$H_5C_5Ge(OMe)_3$	$\sim 10^{24}$
Me_5C_5COMe	18 ⁶⁰	$H_5C_5Ge(OCH_2CH_2)_3N$	10.7 ²⁴
$Me_5C_5COR \cdot AlCl_3$	5–18 ⁶¹	$H_5C_5GeCl_3$	11.9 ²⁴
$Me_5C_5COOEt \cdot AlCl_3$	18 ⁶¹	$Me_5C_5SiMe_3$	15.3 ± 0.2^{63}
Me_5C_5CHO	13.8 ± 0.3^{60}	$Me_5C_5SiMe_2Cl$	13.8 ± 1.2^{63}
$H_5C_5SiH_3$	$13.6 \pm 0.1^{62,c}$	$Me_5C_5SiMeCl_2$	13.5 ± 0.5^{63}
$H_5C_5SiH_2Cl$	$12.9 \pm 0.1^{62,c}$	$Me_5C_5SiCl_3$	13.1 ± 1.1^{63}
$H_5C_5SiHCl_2$	$13.5 \pm 0.1^{62,c}$	$Me_5C_5GeMe_2Cl$	14.7 ± 1.0^{63}
$H_5C_5SiMe_3$	15.2 ^{23,c}	$Me_5C_5GeMe_2F$	15.2 ± 1.2^{63}
$H_5C_5SiMe_2Cl$	15.5 ^{238c}	$Me_5C_5GeMe_2I$	13.8 ± 0.7^{63}
$H_5C_5SiMeCl_2$	15.9 ^{23,c}	$Me_5C_5GeMe_2OMe$	15.7 ± 1.5^{63}
$H_5C_5SiCl_3$	16.3 ^{23,c}	$Me_5C_5GeMe_2SMe$	14.9 ± 1.4^{63}

^a Estimated value from C₅H₄Me₂: Mc Lean, S.; Findlay, D. M. *Can. J. Chem.* 1970, 48, 3107. ^b Kohl, F. X.; Jutzi, P., unpublished results. ^c ΔG_{300}^\ddagger .

for these compounds. However, fluxional structures have been observed in cp compounds of the congeners in the same bonding situation,²⁹ presumably due to comparable weaker El–C σ bonds in the ground-state structures and less steric hindrance in the η^2 transition states.

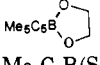
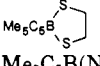
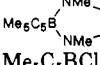
Pronounced substituent effects on the rate of sigmatropic rearrangements have been observed in pentamethylcyclopentadienyl carbon compounds; activation parameters are summarized in Table 14. A high activation energy can be estimated for the shift of a methyl group, but caution has to be exercised in assuming a concerted process.⁵⁹ According to Table 14 an sp²-hybridized carbon fragment migrates significantly faster than a sp³ carbon fragment. This has been explained by qualitative MO arguments for C₅H₅CHO. The frontier orbital interactions in an η^2 transition state for the migration of a formyl group are portrayed in L and M, indicating a stabilizing effect in M by electron



delocalization.⁶⁰ This situation is comparable to that in cp compounds with divalent phosphorus due to the isolobal relationship between —C(H)=O and —P=X fragments. For the Me₅C₅COR adducts with aluminum trichloride, it was suggested that a bicyclo[3.1.0]hexenyl zwitterion N likewise might be a high-energy intermediate in the migration, so that the observed rearrangements would not be truly sigmatropic.⁶¹

Much less dramatic substituent effects have been observed for cyclopentadienyl compounds of the group 4 elements silicon and germanium, although this class of compounds has been studied extensively. The activation energies for some relevant cyclopentadienyl and pentamethylcyclopentadienyl silicon and germanium compounds are summarized in Table 14. The substitution of hydrogen by halogen atoms in cyclopentadienylsilanes lowers the corresponding activation energy only to a small extent (~2 kcal/mol^{23,62}); the same is true for the substitution of halogen atoms by

TABLE 15. Activation Energies for the 1,2 Boron Shift in Some Pentamethylcyclopentadienyl Boron Compounds

compound	E_A , kcal/mol	ΔG_{298}^\ddagger , kcal/mol	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/deg·mol
$\text{Me}_5\text{C}_5\text{BMe}_2$	<5			
$\text{Me}_5\text{C}_5\text{BCl}_2$	<5			
$\text{Me}_5\text{C}_5\text{BBr}_2$	<5			
$\text{Me}_5\text{C}_5\text{BI}_2$	<5			
$\text{Me}_5\text{C}_5\text{BF}_2$	12.8 ± 2.0	11.4	12.2	2.8 ± 0.9
$\text{Me}_5\text{C}_5\text{B(OMe)}_2$	13.3 ± 0.5	14.4	12.7	-5.7 ± 2.8
	14.5 ± 0.6	10.9	13.9	10.0 ± 1.4
$\text{Me}_5\text{C}_5\text{B(SEt)}_2$	6.4 ± 0.7	10.2	5.8	-14.8 ± 2.8
	6.9 ± 0.9	11.3	6.3	-16.6 ± 1.1
$\text{Me}_5\text{C}_5\text{B(NMe)}_2$	20.6 ± 1.2	17.2	20.0	9.5 ± 0.3
	23.1 ± 2.1	21.1	22.5	5.0 ± 1.3
$\text{Me}_5\text{C}_5\text{BCl}_2 \cdot \text{py}$	>25			
$\text{Me}_5\text{C}_5\text{BI} \cdot 2\text{py}^+$	>25			

methyl groups,²³ but in pentamethylcyclopentadienyl compounds the sequence is reversed.⁶³ Similar weak substituent effects have been measured for cyclopentadienyl- and (pentamethylcyclopentadienyl)germanes.^{24,63}

An explanation for these observations in silicon and germanium chemistry can be given in terms of the bonding in the relevant ground and transition states. Mesomeric effects—mainly responsible for differences in the dynamic behavior of cp compounds with groups 3 and 5 elements—cannot occur in compounds with tetracoordinated or higher coordinated group 4 elements. Hence, a pronounced ligand influence on the speed of sigmatropic rearrangements is not expected.

Rather drastic substituent effects are found in a series of pentamethylcyclopentadienyl boron compounds.^{49,50} The measured activation energies for sigmatropic rearrangements are collected in Table 15. The migration rates can be correlated with the Lewis acidity of the relevant boron atom; e.g., rapid migrations are observed for the dichloro and the dimethyl boron compounds and rather low rates for the amino-substituted boranes. Finally, no dynamic behavior is found for some pyridine adducts of pentamethylcyclopentadienyl boron species. Differential frontier orbital calculations agree with experiment.⁴⁴ The predominant orbital interactions between a BR_2 and a C_5Me_5 fragment in the η^2 transition state are illustrated in Figure 3. Mesomeric ligand effects in a pseudoallylic BR_2 fragment can be transferred into the cp unit and, therefore, markedly influence relevant transition-state energies.

b. Substituents at the Cyclopentadienyl Ring.

So far only the influence of the main-group element itself and of the substituents at these main-group elements on the rate of sigmatropic rearrangements has been discussed. Experimental data and calculations show, however, that the substituents at the cyclopentadienyl ring also have an interesting influence.

Two different situations have to be discussed. In the first case, all five hydrogens in the cyclopentadienyl system are substituted by other atoms or groups of atoms; in the second case, substitution only takes place at certain ring positions.

As an example of the first situation, it has been shown experimentally that an increase in activation energy of about 2 kcal/mol takes place on going from the cyclopentadienyl to the pentamethylcyclopentadienyl system

TABLE 16. Activation Enthalpies (kcal/mol) for $\text{R}'_5\text{C}_5\text{BR}_2$ Systems, Determined by Energy-Optimized MNDO Calculations

R	R'				
	H	Me	F	Cl	
H	18.0	16.5	19.7	25.8	
F	33.6	31.8	37.5	38.8	
OH	36.3	30.5	39.8	39.4	
NH ₂	37.8	30.6	40.7	39.8	
SH	28.3	18.7	32.1	31.5	

TABLE 17. Activation Enthalpies (kcal/mol) for $\text{R}'_5\text{C}_5\text{PR}_2$ Systems, Determined by Energy-Optimized MNDO Calculations

R	R'				
	H	Me	SiH ₃	Cl	F
H	40.7	39.7	40.0	75.6	47.8
F	40.6	37.6		40.0	39.3
OH	38.1	32.8	32.5	33.4	33.9
NH ₂	34.8	27.4	26.9	25.4	26.0

in a comparable series of compounds (see Table 12). The ground and transition states of sigmatropic rearrangements may be differently influenced by substituent effects, so that whether these processes are accelerated or decelerated depends on the circumstances. Schoeller has calculated the activation enthalpies for a variety of substituted cyclopentadienylboranes and -phosphanes,^{42,44} replacing the hydrogens at the cp ring by alkyl or silyl groups or by halogen atoms. The results of these calculations are portrayed in Tables 16 and 17. In cyclopentadienylboranes, electron-withdrawing substituents (e.g., F and Cl) in the cyclopentadienyl unit raise and electron-donating substituents (e.g., CH_3) lower the overall reaction enthalpies. In cyclopentadienylphosphanes no comparable trends can be discerned. This can be understood by inspection of the interaction of the relevant frontier orbitals in both systems. These theoretical predictions will be difficult to be substantiated experimentally.

Of the second situation there are some examples in the literature that document the influence of the substitution of one or two hydrogen atoms in the cyclopentadienyl unit. These situations will be discussed in the following sections (IV, V).

D. Steric Constraints

In sigmatropic rearrangements of cyclopentadienyl and pentamethylcyclopentadienyl compounds, the steric repulsion of bulky ligands perturbs the higher coordinated transition states more than the ground states. Although this implies higher activation enthalpies and—even more characteristically—higher negative activation entropies, conclusive experimental verification has been rare. Ustynuk and co-workers²⁴ attributed the highly negative activation entropy of -36.2 eu to the steric effect of the triethoxyamine ligand in the germatrane $\text{H}_5\text{C}_5\text{Ge(OCH}_2\text{CH}_2)_3\text{N}$, where the germanium in the transition state is six-coordinated.

On the other hand, steric repulsion can occasionally raise the ground-state energies as well. This was documented, for example, by the distorted bond angles seen by X-ray diffraction in several pentamethylcyclopentadienyl silicon compounds.^{64,94} If the ground and transition states are raised by about the same amount, no pronounced changes in the activation data are to be expected.

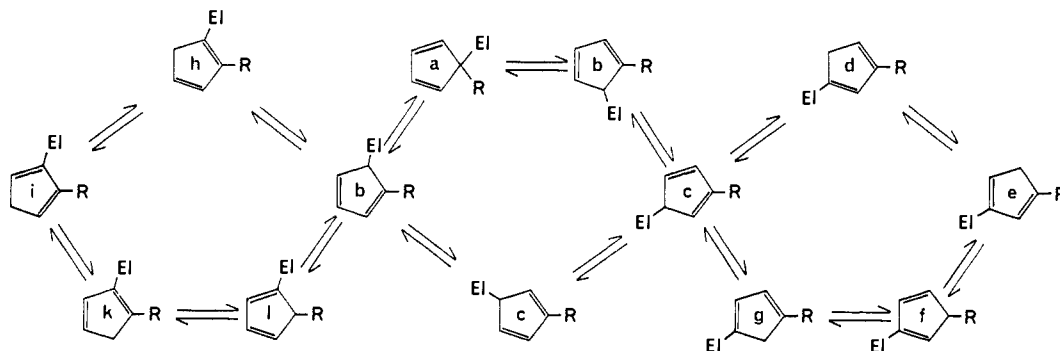


Figure 5. Sigmatropic rearrangements in C_5H_4REl compounds.

TABLE 18. C_5H_4REl -Type Compounds (R Nonmigrating)

$C_5H_4MeBEt_2$ ⁶⁶	$C_5H_4MeGeH_3$ ⁶⁸	$(C_5H_4Me)_2PbMe_2$ ⁷³
$C_5H_4MeBEt_2 \cdot py$ ⁶⁸	$C_5H_4MeGeMe_3$ ⁷²	$C_5H_4MePbEt_3$ ⁷³
$C_5H_4MeBCl_2$ ⁶⁷	$(C_5H_4Me)_4Ge$ ^{69,72}	$(C_5H_4Me)_2PbEt_2$ ⁷³
$C_5H_4MeSiH_3$ ³⁸	$C_5H_4MeSnMe_3$ ⁷²	$C_5H_4MePF_2$ ²⁶
$C_5H_4MeSiMe_3$ ⁷²	$C_5H_4MeSnMe-i-PrPh$ ⁷⁰	$(C_5H_4Me)_2PF_2$ ²⁶
$C_5H_4MeSiMe_2OSiMe_2Ph$ ^b	$C_5H_4(CPh_3)SnMe_3$ ⁷⁴	$C_5H_4MeAsMeCl$ ⁷⁵
$C_5H_4MeSiMe_2Cl$ ^b	$(C_5H_4Me)_4Sn$ ^{a,70,71}	$C_5H_4MeAsMe_2$ ⁷⁵
$C_5H_4(CPh_3)SiMe_3$ ⁷⁴	$C_5H_4MePbMe_3$ ⁷³	$C_5H_4MeSbMe_2$ ⁷⁶

^a Campbell, C. H.; Green, M. L. H. *J. Chem. Soc. A* 1971, 3282.

^b Schaaf, R. L.; Kan, P. T.; Lenk, C. T.; Deck, E. P. *J. Org. Chem.* 1960, 25, 1986.

Steric effects must be responsible for the unusual fluxional behavior of some cyclopentadienylarsanes.^{29,65} Thus, the compounds with two *tert*-butyl groups at the arsenic atoms are the only ones that exist exclusively as rigid vinylic isomers, whereas the other cyclopentadienylarsanes mainly consist of fluxional allylic isomers, as documented in Table 6. In the first case, steric constraints lead to higher activation energies for the arsenic shift and, therefore, favor prototropic rearrangements leading to vinylic isomers, as already described in Chapter IIB.

III. Cyclopentadienyl Compounds of the Type C_5H_4REl [R Nonmigrating]

Dynamic processes in compounds of the type C_5H_4REl include degenerate and nondegenerate El shifts as well as nondegenerate H shifts, as documented in Figure 5.

Only 3 of the 11 possible isomers, namely a–c, are expected to be fluxional at ambient temperature due to sigmatropic El shifts. The other isomers d–l with the El group in vinylic position should be rigid; H shifts are expected only at higher temperature. In more detail, the equilibrium isomer contribution (a:b:c) as well as the rate of interconversion must be considered.

The C_5H_4REl compounds known so far with group 3–5 elements are collected in Table 18. In principle, the rules elaborated for C_5H_5El compounds (Chapter II) can be applied also for the C_5H_4MeEl compounds.

Boryl and alkyl ligands strongly prefer the vinylic positions of a cyclopentadiene skeleton. Therefore, in methylcyclopentadienyl boron compounds some isomers a priori can be excluded or should be observable only at rather high temperatures. Grundke and Paetzold⁶⁶ have shown that in (methylcyclopentadienyl)diethylborane and its pyridine complex only the isomers d and g are present at ambient temperature. Similar obser-

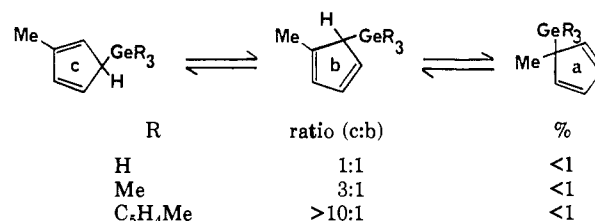


Figure 6. Isomer ratios in the rearrangement processes of some (methylcyclopentadienyl)germanes.

vations have been made for (methylcyclopentadienyl)dihaloboranes.⁶⁷

In well-designed experiments Stobart and co-workers have investigated some (methylcyclopentadienyl)silanes, -germanes, and -stannanes.^{38,68,69,71} Steric requirements of the substituents R in the ElR_3 group together with the size of El will control the equilibria and the activation energies in the rearrangement processes.

As expected, all tin and lead compounds of the type $C_5H_4MeElR_3$ are highly fluxional. Due to the rapidity of the R_3El shifts no conspicuous spectral changes occur within an accessible temperature range. Fast nondegenerate rearrangements involving predominance of the nongeminal isomers of type c have been discussed, leading to an AA'XX' type 1H NMR spectrum for the cp protons.^{69,70,72,73}

(Methylcyclopentadienyl)germanium compounds exhibit the full range of dynamic behavior in a convenient temperature range. A detailed analysis^{68,69,72} documents interesting steric effects on the isomer ratio in these rearrangements. In the compound $C_5H_4MeGeH_3$, nearly equal amounts of the isomers c and b have been found, whereas in $C_5H_4MeGeMe_3$ and—even more in $(C_5H_4Me)_4Ge$ —the nongeminal isomer c predominates (see Figure 6). Steric constraints grow in the direction $GeH_3 < GeMe_3 < Ge(C_5H_4Me)_3$ and seem to be responsible for the preference of isomer c. In all three cases the exchange processes have been discussed in terms of vanishingly small equilibrium concentrations for the geminal isomer a. Furthermore, hydrogen migration is not facile, although additional signals appear in the NMR spectra of samples stored for several months at room temperature.

The fluxional behavior of (triphenylmethyl)cyclopentadienyltrimethylsilane and -stannane has been investigated by Kläui and Werner.⁷⁴ Contrary to the methyl ligand the triphenylmethyl ligand prevents the nondegenerate rearrangements $c \rightleftharpoons b \rightleftharpoons a$, presumably due to steric constraints. The exchange mechanism in these compounds corresponds to the degenerate process

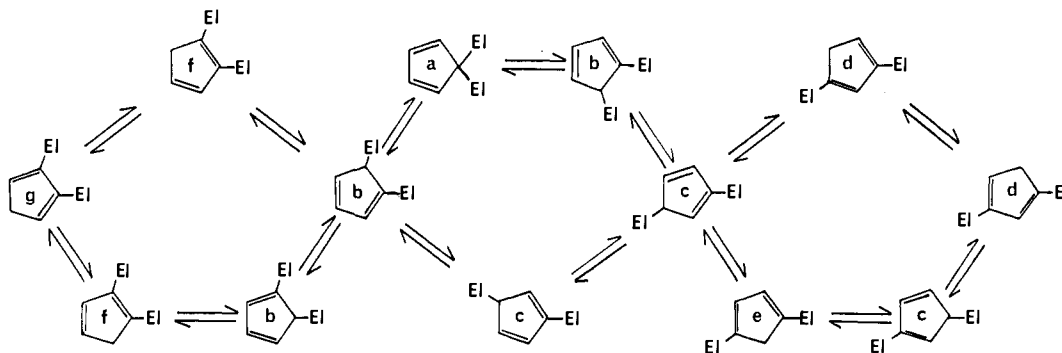


Figure 7. Sigmatropic rearrangements in $C_5H_4(EI)_2$ compounds.

$c \rightleftharpoons c$. The migratory aptitude for the trimethylsilyl and -stannyl group is as expected. For the silicon compound prototropic rearrangements have been observed at rather high temperature.

Only a few methylcyclopentadienyl compounds with group 5 elements are reported in the literature. The dynamic behavior of (methylcyclopentadienyl)difluorophosphate²⁶ and -dimethylarsane⁷⁵ is comparable to that of the trimethylgermyl species; that of the dimethylstibino compound⁷⁶ corresponds to the trimethylstannyl species.

IV. Cyclopentadienyl Compounds of the Type $C_5H_4(EI)_2$

In this and the following chapters the structures (isomer ratios) and fluxional behavior of polymetalated cyclopentadienes are described.

In compounds of the type $C_5H_4(EI)_2$, seven isomers can be formed by sigmatropic rearrangements of hydrogen or of the EI fragment if both elements are identical, as depicted in Figure 7; with different elements 10 isomers are in principle possible. The $C_5H_4(EI)_2$ compounds known so far are collected in Table 19. Considering the differing migratory aptitudes of EI fragments and the differing preference of vinylic positions, the most probable isomers for these cp compounds can be predicted. Typical situations will now be discussed in more detail.

Diborylcyclopentadienes $C_5H_4(BR_2)_2$ ($R = F, Cl, Br, I, NMe_2, Me$) and the pyridine adducts $C_5H_4(BR_2 \cdot py)_2$ ($R = Cl, Br$) all exist only as the vinylic isomer e; they are rigid in the usual temperature range. Isomers with allylic boron ligands that rearrange by rapid hydrogen shifts must have been passed during synthesis by cp transfer.⁷⁷ The situation in boryl and silyl substituted cyclopentadienes $C_5H_4(BR_2)SiMe_3$ ⁶⁷ is much more complicated. In all isomers present, the boryl group is found in vinylic position, whereas the trimethylsilyl group may occupy a vinylic or an allylic position. The latter compounds are fluxional due to sigmatropic shifts of the Me_3Si group.

The fluxionality of the group 4 compounds $C_5H_4-(EI)Me_3)_2$ ($EI = Si, Ge, Sn$) has been intensively studied by the group of Ustynyuk.

The ¹H and ¹³C NMR spectra of $C_5H_4(SiMe_3)_2$ ⁷⁸ recorded at -30 to +220 °C indicate a mixture of the isomers a, c, d and e, in the ratio 132:3.6:2.2:1 at -30 °C. Isomer c exhibits a degenerate metallotropic rearrangement that proceeds via the 1,2 shift of the allylic Me_3Si group [$E_A = 14.5 \pm 1.8$ kcal/mol]. The interconversion of a and c proceeds via two successive 1,2

TABLE 19. Main Isomers (30 °C) of $C_5H_4(EI)_2$ -Type Compounds

isomer	ref	isomer	ref
	77		84
$R = F, Cl, Br, I, NMe_2, Me$			84, 92
	77		
$R = Cl, Br$			79
	67		79, 80
$BR_2 = BCl_2, BBr_2, B(OEt)_2, BClMe, BBrMe, B(NMe_2)_2$			79, 82
	78		82
	79		79, 80
$SiR_3 = SiMe_2Cl, SiMeCl_2$			
	92		81
	87		29
	29		75
$As(t-Bu)_2$	29		29

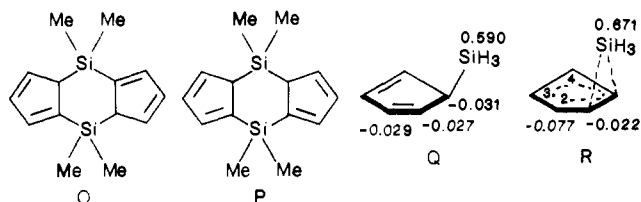
shifts of the Me_3Si group with the isomer b as a high-energy intermediate [$E_A(a \rightarrow c) = 18.6$ kcal/mol; $E_A(c \rightarrow a) = 15.8$ kcal/mol]. Above 120 °C hydrogen migration has been observed including the isomers c-e [$E_A(e \rightarrow c) = 21$ kcal/mol].

The NMR spectra of $C_5H_4(GeMe_3)_2$ and $C_5H_4-(SnMe_3)_2$ have been recorded in the range -130 to +190 °C.^{79,80} A nondegenerate rearrangement $a \rightleftharpoons c$ has been found to occur in both compounds. The equilibrium lies well toward the 5,5 isomer, especially in the tin compound, where the existence of the isomer c could only be proved chemically (metalation with an aminostannane).

Typical for the above compounds are AA'BB'-type ^1H NMR spectra that can represent (1) rigid isomers of type a, (2) a highly fluxional mixture of isomers $a \rightleftharpoons c$ with a high content of a in the equilibrium, and (3) a highly fluxional mixture with greater concentrations of c; in the latter case the AA'BB'-type spectrum is shifted to higher field and the methyl signal of the ElMe_3 group moves gradually downfield with increasing temperature due to the vinylic ElMe_3 character in c.

The presence of the geminal isomer has been shown for the tin compound $\text{C}_5\text{H}_4(\text{SnMe}_3)_2$ also by a crystal structure analysis.⁸¹ The cyclopentadiene ring has been found to be planar; the tin-carbon (cp) bond length is in the expected range (2.18 Å).

A complicated intramolecular dynamic process, presumably based on 1,5 sigmatropic rearrangements, has been discussed for the highly fluxional trimer $[\text{C}_5\text{H}_4\text{SnMe}_2]_3$,⁸² mainly existing as the 5,5 isomer (see Table 19). In contrast, a much less fluxional dimer has been found for the corresponding silicon species $[\text{C}_5\text{H}_4\text{SiMe}_2]_2$ existing as a mixture of the isomers O and P in solution; the isomer O has been investigated by X-ray crystallography⁸⁴ and is the only one present in the solid state.



The substitution of one of the hydrogen atoms in a cyclopentadienyl unit by another main-group fragment importantly influences the migration rates of sigmatropic rearrangements. This is documented in the literature by some interesting examples. The degenerate migration $c \rightleftharpoons c$ (see Figure 7) of a trimethylsilyl group is retarded by a further trimethylsilyl ligand in the 3-position of the cyclopentadiene system.⁷⁸ However, it is accelerated by a trimethylsilyl or by a boryl ligand in the 2- and/or 4-position;^{78,67} activation energies for the Me_3Si shift drastically decrease in the ligand order $\text{Me}_3\text{Si} > \text{B}(\text{OEt})_2 > \text{BClMe} > \text{BCl}_2$.⁶⁷ These effects can be understood from charge density data for the ground and the transition state in cyclopentadienylsilane,⁷⁹ as portrayed in Q and R. In the transition state, negative charge is accumulated in positions 2 and 4 of the cp ring. Consequently, the introduction of electron-acceptor substituents at position 2 and/or 4 should stabilize the transition state and accelerate the rearrangements. Just this effect results from the introduction of a trimethylsilyl or a boryl group, which acts as electron acceptors.

The effect of hydrogen substitution on the 1,2 hydrogen shift has also been studied in few examples. A methyl group in the allylic position has been found to accelerate the 1,2 H shift,⁸⁵ whereas a halogen substituent slows down this rearrangement.⁸⁶

V. Cyclopentadienyl Compounds of the Type $\text{C}_5\text{H}_3(\text{El})_3$

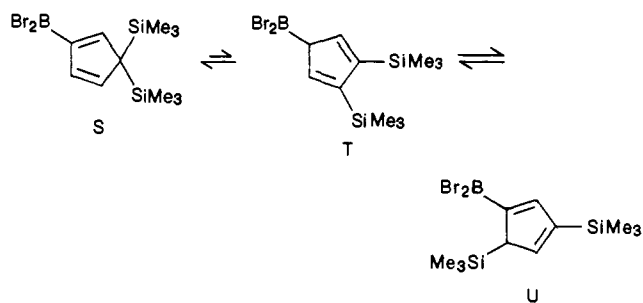
All compounds of the type $\text{C}_5\text{H}_3(\text{El})_3$ so far known in the literature possess at least two El fragments with

TABLE 20. Main Isomers (30 °C) of $\text{C}_5\text{H}_3(\text{El})_3$ - and $\text{C}_5\text{H}_2(\text{El})_4$ -Type Compounds

isomer	ref	isomer	ref
	67		87
R = Cl, Br, OEt, NMe ₂			87
	89		87
	82, 88		87
	82, 88		89, 90
	82, 88		82, 88
	82, 88		87
	82		

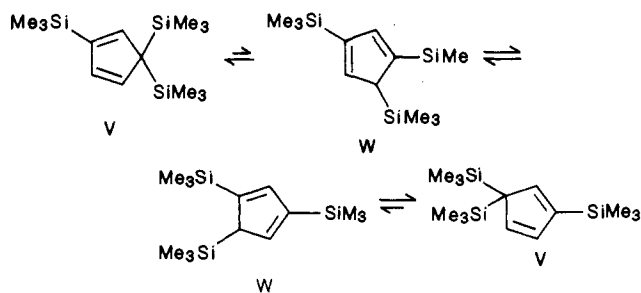
group 4 elements. The most stable isomers at ambient temperature are collected in Table 20. Their structure can be predicted by using the fact that the preference for the allylic over the vinylic position grows in the direction $\text{R}_2\text{B} < \text{R}_2\text{P} < \text{Me}_3\text{Si} < \text{Me}_3\text{Ge} < \text{Me}_3\text{Sn} < \text{Me}_2\text{Sb}$. Thus, the compounds $\text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{BR}_2$ ⁶⁷ and $\text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{PR}_2$ ⁸⁷ exist mainly as the isomer with a vinylic BR_2 or PR_2 group. In the compounds $\text{C}_5\text{H}_3(\text{Me}_3\text{Si})(\text{Me}_3\text{Ge})(\text{Me}_3\text{Sn})$ ^{38,88} and $\text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{SbMe}_2$ ⁸⁷ a Me_3Si group is bonded to a vinylic carbon atom. For steric reasons those vinylic positions not adjacent to the allylic ones are preferred in the most stable isomers.

Detailed investigations of the dynamic behavior of these compounds are scarce. Temperature-dependent ^1H NMR spectra have been described for the compound $\text{C}_5\text{H}_3(\text{Me}_3\text{Si})_2\text{BBr}_2$.⁶⁷ At -10 °C mainly the isomer S is present. With increasing temperature more of the isomers T and U are observed in a rapidly equilibrating system due to 1,2 migration of one of the allylic Me_3Si groups.



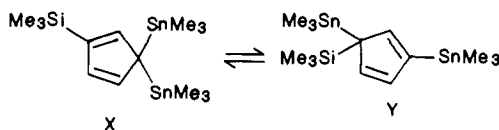
Similar observations have been made for the compound $\text{C}_5\text{H}_3(\text{SiMe}_3)_3$.⁸⁹ Clearcut temperature dependence of line shapes and line intensities in the ^1H and ^{13}C NMR spectra of this cp compound demonstrate that metallotropic and at higher temperatures also prototropic rearrangements do occur. A series of successive 1,2 shifts of the Me_3Si group is most probable, including the isomers V and W.

The process $\text{V} \rightleftharpoons \text{V}$ has been considered as quasi-degenerate;⁸⁹ the content of isomer W in the equilibrated mixture is low at ambient temperature. [Measured values for activation energies: $\text{V} \rightleftharpoons \text{W}$, 17.8 ± 0.3 kcal/mol; $\text{W} \rightleftharpoons \text{V}$, 14.1 ± 0.3 ; $\text{W} \rightleftharpoons \text{W}$, 12.3 ± 0.3].



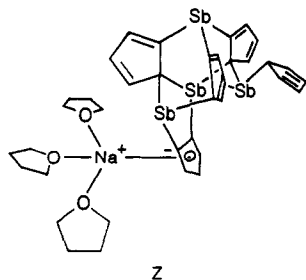
Concerning the activation energies for the trimethylsilyl shift in the compounds $C_5H_3(Me_3Si)_2BBr_2$ and $C_5H_3(Me_3Si)_3$, it is important to note that the BBr_2 group stabilizes the η^2 transition state more than a Me_3Si group, thus accelerating the rearrangement $T \rightleftharpoons U$ in comparison to $W \rightleftharpoons V$.

The dynamic processes in the compounds $C_5H_3-(Me_3Sn)_3$ and $C_5H_3(Me_3Si)(Me_3Sn)_2$ have been followed also by ^{119}Sn NMR spectroscopy.⁸² In $C_5H_3(Me_3Sn)_3$ two distinct resonances for the Me_3Sn groups in the vinylic and allylic positions (compare with V) of the cyclopentadiene have been observed at $-80^\circ C$ due to a nearly rigid structure on the ^{119}Sn NMR time scale. At ambient temperature an average signal indicates fast quasi-degenerate metallotropic rearrangements. In principle, the averaged chemical shift cannot be temperature dependent. However, if the process is non-degenerate, the chemical shift must exhibit strong dependence upon temperature, reflecting a displacement of the fast metallotropic equilibrium. This has been demonstrated for $C_5H_3(Me_3Si)(Me_3Sn)_2$. The observed change in chemical shift corresponds to a greater portion of the isomer Y with a vinylic Me_3Sn group in the equilibrium $X \rightleftharpoons Y$.



Finally, fast metallotropic rearrangements of the Me_2Sb group already at ambient temperature have been found for the compound $C_5H_3(Me_3Si)_2SbMe_2$.⁸⁷

An interesting example for the complexity of sigma-tropic rearrangements in polymetalated cp compounds has been presented by Becker.⁹³ Reaction of antimony trichloride with sodium cyclopentadienide in tetrahydrofuran as solvent leads to $Na(C_4H_8O)_3[Sb_4(C_5H_3)_4(C_5H_5)]$ whose surprising structure (see Z) has been



proved by an X-ray diffraction analysis. At about $60^\circ C$ fast degenerate rearrangements take place in this compound, leading to four equivalent C_5H_3 units, as

demonstrated by the appearance of only one doublet and one triplet in the ratio 2:1 in the 1H NMR spectrum.

VI. Cyclopentadienyl Compounds of the Type $C_5H_2(EI)_4$

Up to now, only four members of this class of compounds are known in the literature (see Table 20). The silyl compound $C_5H_2(SiMe_3)_4$ exists in form of the 2,3,5,5 isomer and is nonfluxional in the normal temperature range.⁹⁰ For the tin compound $C_5H_2(SnMe_3)_4$, an averaged ^{119}Sn NMR signal has been observed at $20^\circ C$, thus indicating fast sigmatropic rearrangements of Me_3Sn groups.⁸⁸ The mixed-substituted compounds $C_5H_2(SiMe_3)_3PMe_2$ and $C_5H_2(SiMe_3)_3P(Me)Cl$ both are nonfluxional at room temperature and exist mainly in the form of the isomers with the PR_2 and a Me_3Si group in vinylic and two Me_3Si groups in allylic positions.⁸⁷ Isomers with allylic PR_2 groups must have been formed first during synthesis; they rearrange in a complicated sequence of Me_3Si shifts to the final products.

VII. Concluding Remarks

In this paper I have attempted to cover the recent literature relevant to the fluxionality of cyclopentadienyl and various substituted cyclopentadienyl compounds of main-group elements.

It should now be apparent that several factors influence the dynamics of this class of compounds. Prototropic shifts favor isomers with the EIR_x group in allylic or vinylic position; their ratio as well as the rate of interconversion clearly depends on the nature of the fragment EIR_x . Furthermore, in most of the compounds described here the EIR_x fragment migrates. The rate depends drastically on the main-group element itself, on the substituents at this element, and also on the substituents at the cyclopentadienyl system. The migrations are characterized as 1,5 sigmatropic rearrangements, which can proceed either with retention or with inversion of configuration, depending on the circumstances.

Our understanding of the dynamic effects in η^1 -cyclopentadienyl compounds of main-group elements can be used as a basis for experimental and theoretical studies of circumambulatory rearrangements of main-group fragments also in other systems from the literature, where proton migrations have already been observed.⁴²

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Note Added in Proof. This review was written prior to circulation of the new periodic group recommendations of IUPAC. Under these recommendations the

main-group elements discussed in this review would be numbered 13–15, respectively.

IX. References and Notes

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