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Circumambulatory rearrangements of cyclopolyenes containing element-centred migrants

V I Minkin, I E Mikhailov, G A Dushenko, A Zschunke

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Abstract. Data on circumambulatory rearrangements caused by rapid migrations of substituents formed by Group 13 – 17 elements around three- to nine-membered cyclopolyenes are generalised and systematised. Depending on the ring size, the nature of the migrating group, substituents in the ring and the medium, the rate constants of circumambulatory rearrangements vary over a wide range from 10^6 to 10^{-8} s^{-1} at room temperature. Particular attention is given to analysis of the mechanisms of these rearrangements ([1, *j*]-, [2,3]- and [3,3]-sigmatropic shifts, haptotropic rearrangements and ionisation – recombination) and to the correlation of these mechanisms with the structural characteristics of the compounds that undergo rearrangements. The bibliography includes 241 references.

I. Introduction

The molecular structure theory is closely related to the notions of space and time continuity. The three-dimensional space is insufficient for a detailed description of molecular structures; the fourth dimension is required to characterise the internal dynamics of a molecule, *i.e.*, the distribution of the times of occurrence of this molecule in different conformational, topomeric or isomeric states. The most detailed information on the internal dynamics can be gained from the data on energy barriers to various intramolecular processes.

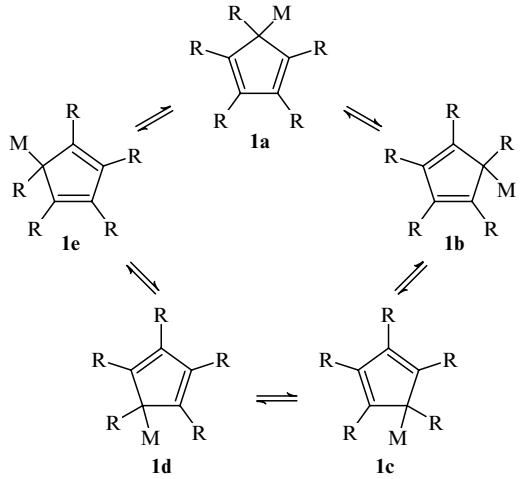
Hindered rotations about single bonds and the related conformational transitions characterised by particular energy barriers were among the first dynamic processes which have been studied extensively due to the development of IR spectroscopy and radiospectroscopy.[1,2] Internal rotations leave sequences of bonds in molecules unchanged. These rotations are characterised by relatively low energy barriers. An insight into these processes can be gained within the framework of conventional models of molecular structures, including mechanical models. In the 1950s, reports were published on the fluxional behaviour of organometallic and organic compounds associated with rapid and reversible degenerate intramolecular rearrangements, which are accompanied by the cleavage and formation of covalent bonds (some of these rearrangements are characterised by rate constants of $10^6 - 10^9$ s^{-1} at room temperature; these processes have been surveyed in Refs 3 – 7). These data radically change the views of the degree of rigidity of molecular structures. The decisive breakthrough has been achieved due to the development of methods of dynamic NMR spectroscopy,[3,8–10] which allowed the researchers to reveal the diversity of molecular fluxional structures and mechanisms of main intramolecular processes. It appeared that the stereochemical non-rigidity rather than rigidity of molecules is the most general characteristic of molecular structures. When speaking about NMR spectroscopy as the main method for studying the structural (or stereochemical) non-rigidity, it should be emphasised that the detection of structural non-rigidity is directly associated with the characteristic NMR time scale. It was suggested[11] that the term 'structurally non-rigid molecules' be used for molecules which undergo reversible rearrangements characterised by energy barriers (ΔG) no higher than the values determined by conventional methods of dynamic NMR spectroscopy ($\Delta G^{\neq}_{25} \leqslant 25$ kcal mol^{-1}).

The structural non-rigidity of the molecules of organometallic compounds was first discovered by Wilkinson and Piper,[12,13] who described very rapid migrations of the Fe(η^5-Cp)$(CO)_2$ (Cp is cyclopentadienyl) and Hg(η^1-Cp) groups around the five-membered ring in the π-cyclopentadienylirondicarbonyl-σ-cyclopentadiene and dicyclopentadienylmercury molecules, respectively. At that time, the techniques at hand did not enable Wilkinson and Piper to observe directly the migration, but they recorded the only averaged signal for the protons of the η^1-Cp ring and correctly attributed this fact to rapid (on the NMR time scale) migrations of the metal-centred groups around the five-membered ring.

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Only ten years later, this assumption was confirmed [14] by the data from complete analysis of line shapes of the temperature-dependent ^{1}H NMR spectra of the MC_5R_5 compounds (**1**), where M is the migrating group (this discovery has been described in detail in the study [15]).

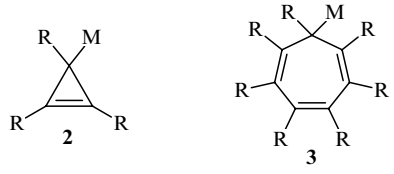


M = Fe(η^5-Cp)(CO)$_2$.

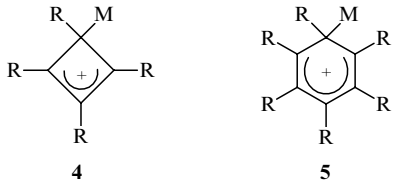
Rapid circumambulatory migrations of metal-centred groups M (formed by both transition and main-group metals) around the ring have been found in numerous cyclopentadiene derivatives containing such groups as substituents in the ring.[4, 15–17] The term 'circumambulatory rearrangements' has gained acceptance as the most general term for describing rearrangements in the course of which an atom or a group of atoms migrates around the ring in such a way that they can finally be bound to any carbon atom of the ring.[18] There are also alternative terms for these rearrangements, such as 'merry-go-round', 'walk', 'ring-whizzing', and 'ring runners'.[4, 15–18]

The tendency of σ-bound (η^1) cyclopentadienyl derivatives of transition metals **1a**–**e** to fluxionality correlates well with the polarity of the C_{Cp}–metal bonds, the ease of their ionisation and the ability of transition metal ions to form multicentre bonds. It was demonstrated that rapid circumambulatory rearrangements are typical also of cyclopentadiene derivatives containing covalently bound substituents formed by Group 13–15 elements in the ring (see comprehensive reviews published earlier [17–22]). Investigations which we carried out in the last decade in cooperation with researchers from Rostov-on-Don, Berlin and Novosibirsk extended the range of fluxional η^1-cyclopentadienes by including not only derivatives of Group 13–15 elements but also compounds in which migrating substituents are formed by Group 16 and 17 elements.

Circumambulatory rearrangements of cyclopentadiene derivatives belong to one of the most extensively studied areas of the dynamic stereochemistry of structurally non-rigid compounds. By contrast, analogous rearrangements of derivatives of the preceding and following members of the family of conjugated carbocyclic structures, *viz*., cyclopropene (**2**) and cycloheptatriene (**3**), respectively, were poorly studied. In recent years, our research group has obtained new data on the fluxional behaviour of cyclopropenyl and cycloheptatrienyl derivatives of Group 15 and 16 elements.



Circumambulatory rearrangements are typical also of cyclic carbocationic systems **4** and **5** containing an even number of carbon atoms.



In the present review, particular attention is given to mechanisms of circumambulatory rearrangements, structures and estimates of the relative energies of transition states and intermediates for different reaction pathways. An important role of theoretical simulation in the identification of the major reaction pathway is demonstrated. Compounds in which groups M exhibit high ability to migrate in conjugated rings can serve as convenient carriers of functional groups in intermolecular reactions with substrates possessing higher affinity for migrating groups than the molecules of the starting compound. The possibilities of using compounds **1**–**5** as efficient soft carrier reagents are illustrated in Section X. The non-degenerate rearrangements of cyclopentadiene derivatives **1** discovered recently extend the range of functionalised Cp ligands involved in metal complexes, which can serve as catalysts for various stereospecific reactions (see Section X).

In the present review, we restrict ourselves to thermal rearrangements of derivatives of compounds **1**–**5** and some higher cyclopolyenes containing Group 13–17 elements. Data on the rearrangements of analogous derivatives of transition metals are considered only for comparison. Circumambulatory rearrangements of migrating substituents formed by Group 13 and 14 elements (B, Si, Ge, Sn) and phosphorus were studied in detail. Excellent comprehensive reviews [17–19] devoted to this problem surveyed the data published up to 1985 inclusive. In the discussion of the rearrangements, we focus our attention on nitrogen-, oxygen-, chalcogen- and halogen-centred groups, whose migrations around the periphery of conjugated cyclopolyenes were discovered and studied primarily in the last 10–15 years. For cyclopentadiene derivatives, which belong to the most extensively studied fluxional cyclopolyene systems, the elements serving as centres of migrating groups are given below (according to their positions in the Periodic table); the central atoms of the groups, whose migrations were unknown before the mid-1980s (when we began our investigations) are shaded.

B	C	**N**	**O**	**F**
Al	Si	P	**S**	**Cl**
Ga	Ge	As	**Se**	**Br**
In	Sn	Sb	**Te**	**I**

The review is arranged as follows. It is known that the tendency of a molecule to undergo structural rearrangements depends on the presence of several stationary points on the potential energy surface (PES), which are comparable in energy, belong to two or more isomeric forms and are related by trajectories containing low-energy saddle points of transition states. Hence, we begin with the consideration of the structural types of isomers of conjugated cyclopolyenes. The tendency of these structures to undergo ionisation or $\eta^1 - \eta^n$ transformations dictates the pathway of circumambulatory rearrangements. Alternative possible pathways of circumambulatory rearrangements of compounds **1**–**5** depending on the ring size, nature of the migrating group M and substituents in the ring are considered in Section III. In subsequent sections, the experimental and theoret-

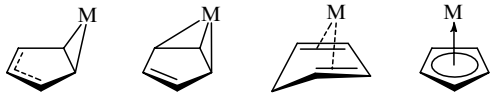
ical results are discussed in the order of increasing structural complexity, starting from the smallest cyclopropene derivatives.

II. Structural types of monosubstituted cyclopolyenes

Two main factors responsible for the mutual orientation of the fragments in cyclopolyenyl–M systems **1**–**5** and the type of the resulting structure are Coulombic and covalent interactions between these fragments. Cyclopentadienyl derivatives of alkali and alkaline-earth metals occur as ionic compounds containing aromatic cyclopentadienyl anions. In the solid state, these salts generally form polymeric structures. By contrast, the C–M bond in cyclopropene derivatives **2** and cycloheptatriene derivatives **3**, which are stable in the cationic form due to requirements for aromaticity, undergoes ionisation only if the group M possesses high electron affinity.

The multicentre mode of binding giving rise to sandwich (metallocene) structures is most common to transition metal complexes with cyclopolyenyl ligands. Although only the s and p orbitals of Group 13–17 elements can be involved in binding with the cyclopolyene fragment, their compounds of general formulae **1**–**3** are also characterised by considerable structural diversity. The usual covalent two-centre two-electron (2c–2e) binding is the dominant interaction in the cyclopolyenyl–M system. However, numerous stable π complexes with the cyclopentadienyl ligands in which the migrating groups M are formed by main-group elements are known (see the reviews [23–27]).

Hoffmann and co-workers [28] analysed the role of covalent binding for cyclopentadiene derivatives in terms of projections of the centre M bound to the five-membered ring onto the plane of this ring. Taking into account the isolobal analogy,[29] this approach allows one to extend analysis to all CpM compounds, where M is a transition metal or a main-group element.[26] The position of the projection point is considered as a structural parameter based on which the compound is assigned to one of the η^n structural types (n is the number of p_π centres of the ligand involved in the multicentre bond with the substituent). σ-Bound (η^1) compounds **1** (as well as compounds **2**–**5**) generally belong to the most stable structural type of cyclopolyenyl derivatives of Group 13–17 elements, and η^2–η^n structures (for cyclopentadiene derivatives, $n_{max} = 5$) **6**–**9** are possible isomeric forms. Different simple models for electronic calculations, which enable one to predict the structures of the energetically most favourable η^n isomers, were developed.[30, 31]



6 (η^2) **7** (η^3) **8** (η^4) **9** (η^5)

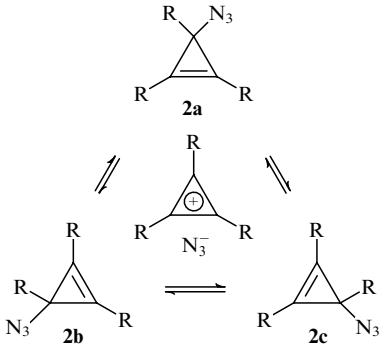
For some cyclopolyenyl, particularly, cyclopentadienyl, derivatives of Group 13–17 elements, the energy differences between various η^n-isomeric structures are very small. Tris(1,2,3,4-tetramethylcyclopentadienyl)aluminium is a prominent example.[32] In the solid state, all three tetramethylcyclopentadienyl ligands in this compound are η^1-coordinated, but signals in the ^{1}H and ^{13}C NMR spectra of its solutions are completely averaged, which reflects the rapid exchange of the Al centre between all positions of the ligands even at low temperatures (about −110 °C). The results of *ab initio* calculations at the RHF/3-21G* level for model compounds, *viz*., cyclopentadienylaluminium derivatives, are indicative of the flat potential energy surface in the region of existence of isomers with different modes of η-binding (η^1, η^2, η^3 and η^5). Thus, the energy differences between the η^2 and η^5 structures are in the range of 1–2 kcal mol^{-1}.

III. Mechanisms of circumambulatory rearrangements

The structural diversity of cyclopolyenyl compounds of Group 13–17 elements is a prerequisite for their fluxional behaviour. The choice between different mechanisms of rearrangements of a particular compound is determined by the relative stabilities of intermediate or transition state structures with different modes of η-binding as well as by the ease of ionisation of the cyclopolyenyl–M bond. We classify the possible pathways of circumambulatory rearrangements according to the modes of η-binding for energetically favourable transition state structures, including the η^1–η^2 (η^1–η^3, ... η^n) and η^2–η^3 (η^2–η^3, ... η^n) rearrangements, where n is the coordination number of the central atom in the transition state. In addition to haptotropic rearrangements (this term is used for generalisation of all types of [i,j]-sigmatropic rearrangements and isomerisation processes in multicentre π complexes **7**–**9** [19]), an intramolecular shift of the migrating group around the periphery of the cyclopolyene ring can occur due to successive events of the cleavage and recombination of the cyclopolyenyl–M bonds within a tight ion pair generated upon ionisation of this bond. We restrict ourselves to a brief discussion and characteristic examples of each specific mechanism responsible for circumambulatory rearrangements of derivatives of main-group elements in conjugated cyclopolyene systems.

1. Ionisation–recombination mechanism

The ionisation–recombination mechanism is most common to cyclopropene derivatives **2** and cycloheptatriene derivatives **3**, whose ionisation is facilitated by the formation of stable aromatic cations. This mechanism has been proposed for the first time in the study [33] as an explanation of rapid randomisation of the position of the chlorine atom in 3-chlorocyclopropene molecule **2** (M = Cl, R = H). More recent studies of migrations of the azido group (M = N_3) in 3-azido-1,2,3-trimethyl- [34] and 3-azido-1,2,3-tri-*tert*-butylcyclopropenes [35] demonstrated that the rate of these rearrangements is independent of the concentration of the solution, but it is substantially influenced by the polarity of the solvent. For instance, the energy barrier to the rearrangement of compound **2** (M = N_3, R = Bu^t) in non-polar tetrachloromethane is 16.5 kcal mol^{-1}, whereas this barrier in polar deuteriomethanol is lower by 4.5 kcal mol^{-1}.[35] These data provide evidence supporting the ionic mechanism (formation of a tight ion pair), which can be represented as a disordered (random) circumambulatory rearrangement of migrating groups in molecules **2**.



The dependence of the ^{1}H NMR spectrum of tropyl azide **3** (M = N_3, R = H) on the temperature and solvent was also accounted for by the intermediate formation of the ion pair, *viz*., tropylium azide ion.[36] Randomisation of the position of the isothiocyanate group in the cycloheptatriene ring was also observed in solutions of compound **3** (M = NCS, R = H) in CD_3CN.[37]

Unlike the cyclopropenyl and cycloheptatrienyl ions, the aromatic cyclopentadienyl ions bear a negative charge. Hence,

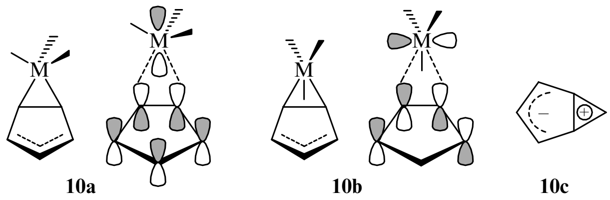
the electronic requirements for the ionisation mechanism of shifts of migrating groups M around the five-membered cyclopentadiene ring differ from those typical of three- and seven-membered cyclopolyenes **2** and **3**. Ionisation of the Cp–M bond is favoured by the presence of substituents, which facilitate delocalisation of the negative charge in the ring, as well as by the presence of groups M, which form stable cations M^+. This combination occurs in 5-arylazo-1,2,3,4,5-pentamethoxycarbonylcyclopentadienes. The latter compounds are the first cyclopentadiene derivatives for which the ionisation–recombination mechanism was observed (see Section VI.3.a).[38,39]

2. 1,2-Shifts of migrating groups

The migration of the substituent M to the adjacent position of the cyclopolyene ring is the most common pathway of circumambulatory rearrangements of compounds **1**–**5** proceeding through a series of successive 1,2-shifts. In terms of sigmatropic rearrangements, 1,2-shifts are classified as $[1,j]$-sigmatropic shifts, where $j = n$ (n is the ring size).

Until recently, examples of 1,2-shifts for sigmatropic rearrangements of cyclopropenyl compounds **2** remained unknown. The evidence supporting this mechanism was presented in the study of the rearrangements of S-substituted 1,2,3-triphenylcyclopropenes[40] (see Section IV.3). By contrast, the 1,2-shift ([1,5]-sigmatropic shift) is the most common and well-studied mechanism of circumambulatory rearrangements of cyclopentadiene derivatives **1**. The 1,2-shift of the hydrogen atom in the cyclopentadiene ring was first described in 1963.[41] Two years later, rapid migrations of Si-, Ge- and Sn-centred groups around the Cp ring were discovered.[42] Ustynyuk and co-workers[43,44] made a considerable contribution to investigations of [1,5]-sigmatropic shifts in cyclopentadienylsilanes, -germanes and -stannanes. In the cited studies, it was demonstrated that the shifts of Si-centred groups around the five-membered ring are accompanied by the competitive migration of the hydrogen atom, which should be taken into account to gain a precise estimate of the kinetics of these rearrangements. The cited studies gave impetus to investigations of cyclopentadienes containing methyl, phenyl or methoxycarbonyl substituents in all positions of the ring in view of the fact that their migration ability is lower than that of the hydrogen atom.

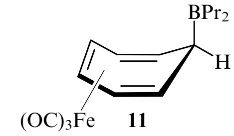
According to the Woodward–Hoffmann rules, the [1,5]-sigmatropic shifts in cyclopentadienylsilanes, -germanes and -stannanes proceed with retention of stereochemical configuration of the central atom of the migrating group.[45] Consequently, transition state structure **10a** should be energetically more favourable than structure **10b** corresponding to inversion of stereochemical configuration of the central atom of the migrating group. This prediction is consistent with the results of semi-empirical calculations for the rearrangement in the cyclopentadienylsilane molecule.[46] The transition state for 1,2-shifts in cyclopentadiene derivatives is structurally analogous to bicyclo[3.3.0]hexatriene (**10c**), which is the lowest homologue of azulene. The electron density distribution in molecule **10c** gives a clue to an explanation of the influence of the nature of migrating groups and substituents in the ring on the kinetics of rearrangements.[47]



10a **10b** **10c**

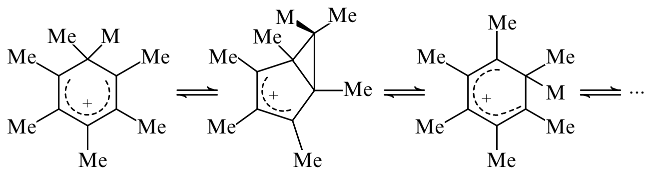
In the case of migrating substituents formed by elements of Groups 13 (B, Al) and 15 (P, As, Sb), the rearrangements also proceed predominantly as 1,2-shifts (see Sections VI.1, VI.3.b and c).

Thermal rearrangements of various cycloheptatriene derivatives caused by 1,2-shifts of the hydrogen atom, which correspond to the mechanism of [1,7]-sigmatropic shift, were described in sufficient detail.[17] In the presence of bulky substituents in the ring, symmetry-allowed suprafacial [1,5]-shifts of hydrogen atoms become energetically more favourable (see Section III.4). However, theoretical and experimental studies demonstrated[48] that photochemical rearrangements of monosubstituted cycloheptatrienes associated with the migration of the hydrogen atom around the ring proceed as the [1,7]-sigmatropic shift. This mechanism was established also for rapid migrations of the $Re(CO)_5$ and $RuCp(CO)_2$ groups around the cycloheptatriene ring.[49] Recently, ^{1}H and ^{13}C 2D EXSY NMR spectroscopic studies revealed[50] rapid 1,2-shifts ([1,7]-sigmatropic shifts) of the dipropylboryl group in the [1-4-η^4-*exo*-7-(dipropylboryl)cycloheptatriene]tricarbonyliron molecules (**11**) (E_a = 17 kcal mol^{-1}), which were accompanied by the simultaneous 1,2-shift of the $Fe(CO)_3$ group.



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For the 1,2-shifts of the hydrogen atom and various migrating substituents formed by Group 13–17 elements to occur in rings containing an even number of carbon atoms, it is requisite that the unsaturated portion of the ring should be either ionic or radical. In the four-membered ring of compound **4**, such migrations can be assigned to the η^2–η^3 type (see Section III.5), whereas the rearrangements in benzenium ions **5** proceed as a series of successive 1,2-shifts to form cations **5a**,**b**, *etc*. The kinetics and stereochemistry of this type of rearrangement were studied in detail.[51–53]



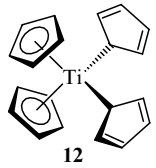
5a **5b**

3. 1,3-Shifts

According to the principle of conservation of orbital symmetry for [1,3]-sigmatropic shifts, the suprafacial pathway of the reaction with inversion of stereochemical configuration of the central atom of the migrating group is preferable. The transition state structures for these rearrangements are substantially sterically hindered, and this mechanism is untypical of circumambulatory rearrangements of migrating substituents formed by Group 13–17 elements. As a result, the 1,3-shift of the migrating group generally involves two successive 1,2-shifts (symmetry-allowed suprafacial [1,5]-sigmatropic shifts).[17,54] As an example we refer to the major mechanism of the rearrangement of tris(3-indenyl)-allylsilane studied by dynamic two-dimensional NMR spectroscopy.[55] The exceptions are the 1,3-shifts of the dipropylboryl group in 9-cyclononatetraenyldipropylborane[56] and compound **11**.[50] In the latter case, the rearrangement, which is presumably accompanied by the inversion of configuration of the boron atom, proceeds more slowly than the 1,2-shifts of the dipropylboryl group.

Studies by ^{13}C CP/MAS NMR spectroscopy and the results of magnetisation transfer experiments showed that the 1,3-shifts of the Ti(η^5-Cp)$_2$(σ-Cp) group occur in the σ-bound cyclopentadiene rings of the Ti(η^5-Cp)$_2$(σ-Cp)$_2$ compound (**12**) both in the solid state and solution at 165 K.[57] However, 1,2-shifts

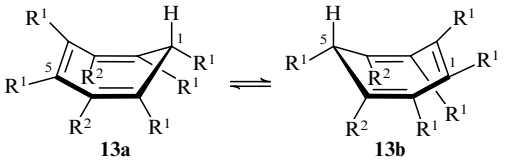
($E_a \approx 7.9$ kcal mol^{-1}) are still the major pathway of this rearrangement.



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4. 1,4-Shifts and 1,5-shifts

As mentioned in Section III.2, the migration of hydrogen atoms in sterically hindered cycloheptatrienes proceeds according to the mechanism of [1,5]-sigmatropic shifts, *i.e.*, as the 1,4-shift. For this rearrangement to occur, the migrating group must be present in the axial position. This rearrangement proceeds at a higher rate than the ring inversion in cycloheptatrienes **13** whose energy barrier is higher by 25 kcal mol^{-1}.[58]



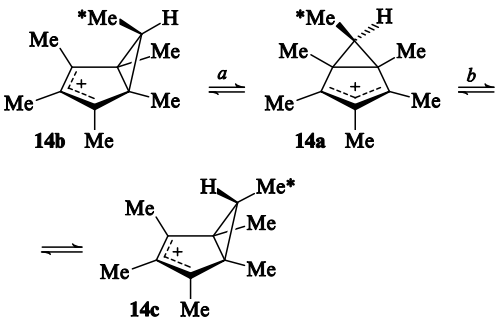
13a **13b**

R^1 = Ph; R^2 = Me, 4-MeC_6H_4.

According to the data from dynamic ^{13}C NMR spectroscopy, the migrations of the triphenylsilyl, -germyl and -stannyl groups in the cycloheptatriene ring also proceed as successive [1,5]-sigmatropic shifts.[59,60] In 7-triphenylstannylcycloheptatriene adopting a boat conformation, the Sn···C(5) distance (3.61 Å)[61] is approximately 0.3 Å smaller than the sum of the van der Waals radii of the tin and carbon atoms, which is indicative of the presence of strong attractive interaction between these centres even in the ground state. Recently, the ^{1}H 2D EXSY NMR spectroscopic study provided evidence that the mechanism of circumambulatory rearrangements in 7-trimethyltin- and 7-chlorodimethyltincycloheptatrienes involves a series of rapid successive 1,5-shifts of the tin-centred groups.[62]

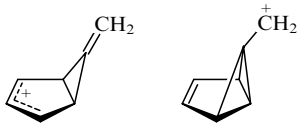
5. $\eta^2 - \eta^3$-Shifts

Compounds with bicyclic structures **6** (η^2 structures) are prone to undergo [1,3]-sigmatropic shifts resulting in the circumambulatory migration of the group M. One of the first examples of such shifts was presented in the elegant study of the low-barrier ($\Delta G_{25}^{\neq} = 10.1$ kcal mol^{-1}) rearrangement of hexamethylbicyclo[3.1.0]hex-3-en-2-yl cation **14a**.[63] The major reaction pathway (*a*) corresponds to retention of stereochemical configuration of the migrating carbon centre to form cation **14b**, whereas the pathway involving the inversion of configuration (*b*) to give cation **14c** is energetically less favourable (the energy difference is 4.6 kcal mol^{-1}).



14b **14a** **14c**

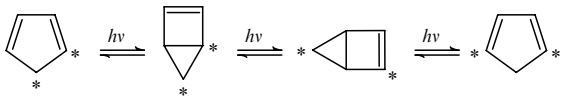
In the transition state structure for the rearrangement, the migrating group is bound to three adjacent atoms of the ring. Hence, this rearrangement can be assigned to the $\eta^2 - \eta^3$ type. It should be noted that an analogous rearrangement in 6-methylidenebicyclo[3.1.0]hexenyl cation **14d** (its energy barrier is 10.6 ± 0.2 kcal mol^{-1}) proceeds more than 10^7 times faster than that in cation **14a**. This was accounted for by the fact that intermediates with the structures of η^3-dicyclopropylcarbinyl cations **14e** are readily formed.[64]



14d **14e**

The η^3-transition state structure for the rearrangement of Dewar thiophene derivatives, which leads to a rapid exchange between the positions of the sulfur atom or the S=O group in the four-membered ring (see Section V),[65] was confirmed by semiempirical calculations using the PRDDO method.[66]

In uncharged systems, the ring-walk $\eta^2 - \eta^3$ rearrangements proceed rather slowly and do not satisfy the condition $\Delta G_{25}^{\neq} \leqslant 25$ kcal mol^{-1}. One way of increasing the rate of such rearrangements is to irradiate a solution with UV light. For example, the photoinduced rearrangement of doubly ^{13}C-labelled cyclopentadiene was attributed[67] to the migration of the cyclopropane fragment around the four-membered ring in bicyclo[2.1.0]pentene (**15**).

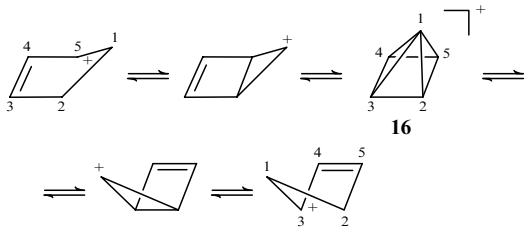


15a **15b**

It is believed that many photoinduced migration processes in aromatic five-membered heterocycles proceed as $\eta^2 - \eta^3$-rearrangements.[68,69]

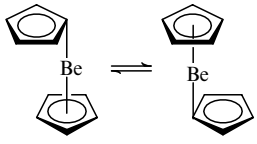
6. σ,π Rearrangements

The mechanism of bond switching in η^1 or η^2 structures with the intermediate formation of isomeric π complexes (η^n structures at $n \geqslant 3$) belongs to the σ,π type.[5,53] However, this mechanism of exchange between the positions of the carbon atoms in antiaromatic cyclopentadienyl cation **16** was not confirmed, although a series of derivatives of the pyramidal $(CH)_5^+$ cation, which has been predicted by Stohrer and Hoffmann,[70] were prepared (see the study[30] and references cited therein).



16

It should be noted that the σ,π rearrangements resulting in the shift of the migrating group around the cyclopolyene ring are known for cyclopentadienyl complexes of alkaline-earth metals. For example, the beryllium atom in beryllocene is equally disordered over two positions both in the solid state and the gas phase. This corresponds to unique asymmetric structure **17** in which very rapid ligand exchange takes place (see the study[26,71] and references cited therein).



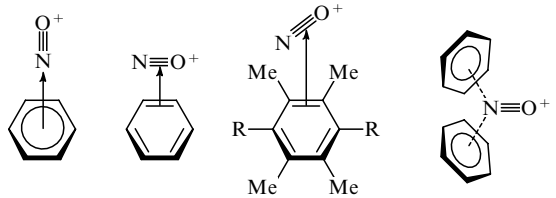
17a **17b**

Analogous rearrangements were also observed for di(1,2,3,4,5-pentamethylcyclopentadienyl)zinc, which has a 'slip sandwich' structure. In solutions, this compound undergoes very rapid reversible ligand exchange. The ^{1}H NMR spectrum of this compound has only one sharp singlet common to all methyl groups even at -135 °C.[72] Apparently, this process is controlled by two concerted isomerisation mechanisms with energy barriers of $\sim$1.2 kcal mol^{-1} (for rotation of the ring, which is displaced from the axis passing through the centre of another Cp ring; the so-called gear mechanism) and $\sim$2 kcal mol^{-1} (for the σ,π rearrangements; molecular inversion).

7. π,π Rearrangements

In asymmetric π complexes with the cyclopolyene ligands, the coordination centre can undergo reversible shifts above the plane of the ligands, which is associated with interconversions of isomeric or topomeric π complexes. Haptotropic rearrangements of this type are well-known for transition metal complexes.[73] A few examples of such shifts for π complexes of Group 13–17 elements were also described. Of the latter processes, the rearrangements of π complexes of the nitrosonium cation with arenes have received the most study (see the comprehensive review [74]). High-symmetry (C_{6v}) structure **18a**, which was expected based on experimental data [75] and *ab initio* calculations,[76] was in doubt because, according to the results of semiempirical calculations [77] and calculations by the density functional theory,[78,79] this structure corresponds not to a minimum but to a hilltop on the potential energy surface of $C_6H_6NO^+$. Structure **18b** with the symmetry C_s is a stable form of the π complex. This structure undergoes rapid topomerisation (the calculated energy barrier is $<$ 3 kcal mol^{-1}) due to sliding of the nitrosonium cation above the plane of the six-membered ring.

X-Ray diffraction studies of the $NO^+AlCl_4^-$ complexes with durene and hexamethylbenzene, the $NO^+AsF_6^-$ or $NO^+SbCl_6^-$ complexes with hexamethylbenzene and toluene [74] and the $NO^+PF_6^-$ complex with hexamethylbenzene [80] demonstrated that the nitroso group in these complexes does not lie on a sixfold symmetry axis. The structure of π complex **18c** corresponds to the η^2 arrangement although the nitroso group deviates from the plane of the ring by approximately 50°. The ^{13}C CP/MAS NMR spectrum [74] and ^{13}C NMR spectrum of the complex of the nitrosonium cation with durene revealed a rapid rearrangement (E_a = 10.2 kcal mol^{-1}). This process was described as the rotation of the six-membered ring about the nitroso group.[81] Analogous π complexes of the nitrosonium cation with fluorene, methyl-substituted naphthalenes [82] and 1,2-bis(pentamethylphenyl)bicyclo[2.2.2]octene (the latter is called a 'Venus flytrap') [83] as well as the triple π complex of the cene type **18d** (see Ref. 84) were prepared and structurally characterised.

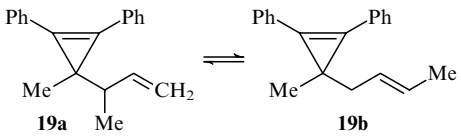


18a **18b** **18c** **18d**

18c: R = H, Me.

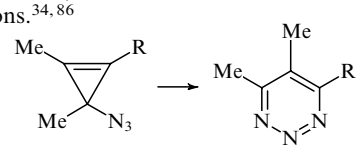
8. [3,3]-Sigmatropic shifts

If a migrating group consists of three atoms with a terminal π bond, circumambulatory rearrangements can proceed by a mechanism involving concerted [3,3]-sigmatropic shifts of this group around the cyclopolyene ring. This mechanism is supported by the transformations of 3-allylcyclopropene derivative **19a** into isomer **19b** upon heating,[85] which is indicative of the [3,3]- rather than [1,3]-sigmatropic shift of the migrating group.



19a **19b**

The mechanism of [3,3]-sigmatropic shifts is considered as an alternative to the ionisation–recombination pathway for the circumambulatory migrations of the azido group in the cyclopropene ring (see Section III.1). This mechanism is confirmed by the fact that a series of 3-azidocyclopropene derivatives **2** (M = N_3) were transformed into ν-triazines under mild conditions.[34,86]



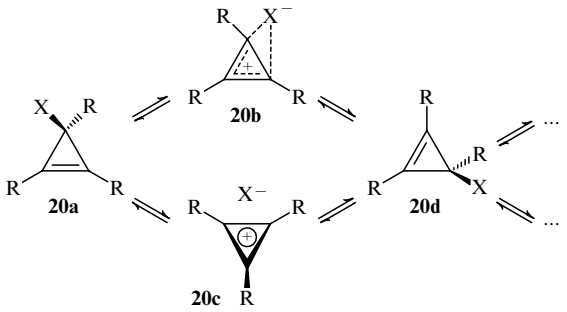
Direct evidence for [3,3]-sigmatropic shifts as a mechanism of migration of the azido group around the seven-membered cycloheptatriene ring was obtained [87,88] by dynamic ^{15}N NMR spectroscopy (see Section VIII.6).

Rapid circumambulatory migrations of the heteroallyl groups X–C(R^1)=X (X = NR^2, O, S) around three- and five-membered rings proceeding as successive [3,3]-sigmatropic shifts of these groups are considered in Sections IV.2, VI.3.a, VI.4.a and b.

IV. Circumambulatory rearrangements of cyclopropene derivatives

1. Rearrangements proceeding by the ionisation–recombination mechanism

Section III.1 covers the circumambulatory rearrangements of chloro- and azido-substituted cyclopropenes, involving heterolysis of the C–Cl and C–N bonds followed by recombination of the resulting ion pairs. Rapid degenerate and non-degenerate intramolecular migrations of the isothiocyanate groups around the three-membered ring in 1,2,3-triphenyl- and 1-(4-methoxyphenyl)-2,3-diphenylcyclopropene derivatives (**20a**) are other examples of this type of rearrangement.[89] According to the data from ^{13}C NMR spectroscopy in the temperature range of 10–80 °C, the activation free energies ($\Delta G_{25}^{\neq}$) of the rearrangements of compound **20a** (X = NCS, R = Ph) in benzene and chlorobenzene are 15.6 and 14.4 kcal mol^{-1}, respectively. The reaction pathways corresponding to the non-dissociative [1,3]-sigmatropic shift and the ionisation–recombination mechanism were simulated [89,90] by semiempirical AM1 and MNDO/PM3 methods taking into account solvation (polarisation continuum model).[91] It was demonstrated that transition state structure **20b** (X = NCO, R = H) for the 1,3-shift is energetically less favourable than tight ion pair **20c** even in non-polar solvents.



20a **20b** **20c** **20d**

The energy barrier (15.4 kcal mol^{-1}; estimated as the relative energy of ion pair **20c**) which was calculated for the randomisation of the position of the isothiocyanate group in the course of the rearrangement **20a** ⇌ **20d** ⇌ ... (X = NCS, R = Ph) in chloroform, is in good agreement with the experimental value $\Delta G_{25}^{\neq}$. The calculations carried out in the studies [89,90] demonstrated that in

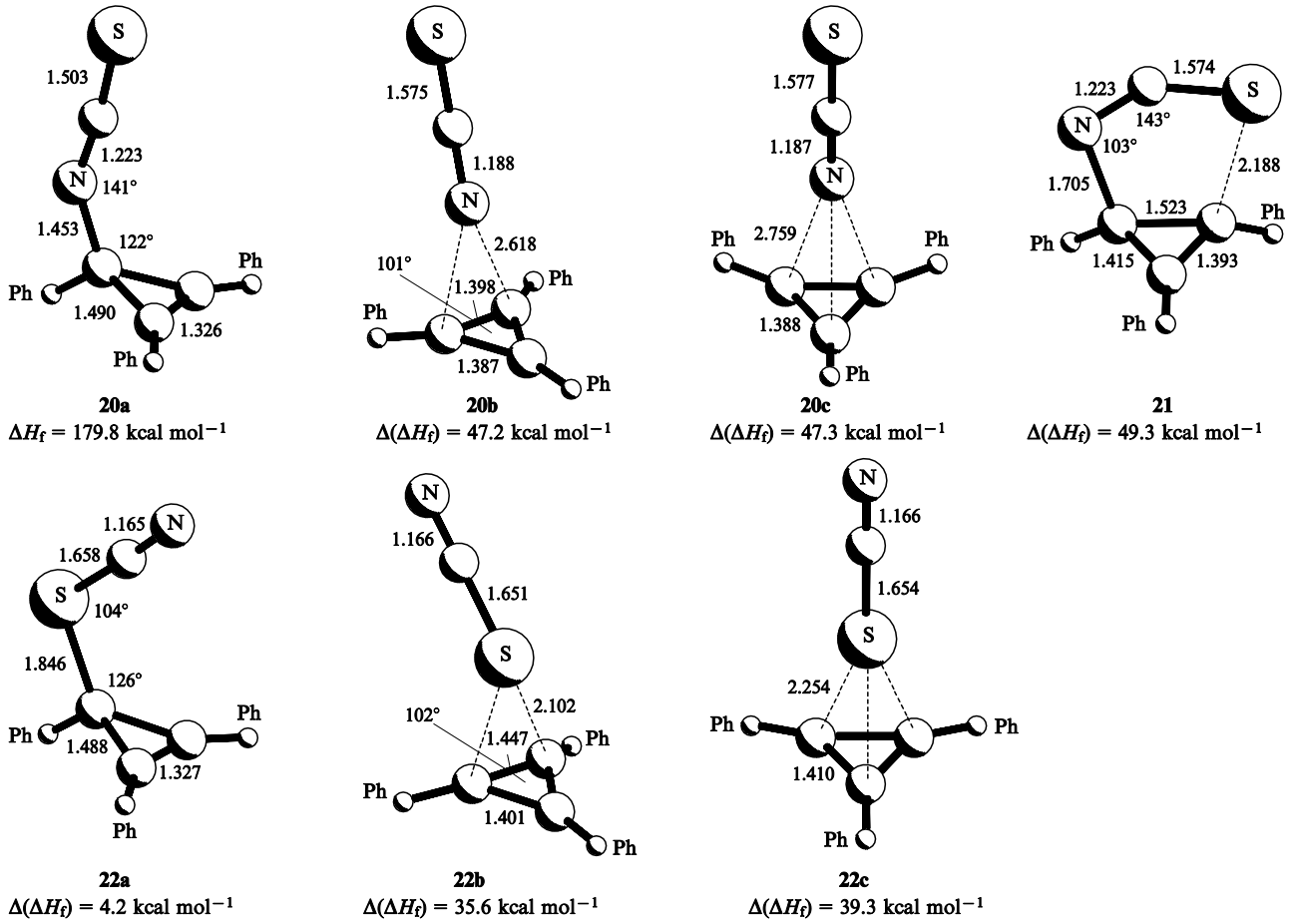


Figure 1. Geometric parameters and heats of formation of the ground state structures of 1-isothiocyanato-1,2,3-triphenylcyclopropene (**20a**) and 1,2,3-triphenyl-1-thiocyanatocyclopropene (**22a**), the transition state for the [1,3]-sigmatropic shift of the isothiocyanate (**20b**) and thiocyanate groups (**22b**), tight ion pairs (**20c** and **22c**) and transition state **21** for the interconversion **20a** ⇌ **22a** *via* [3,3]-sigmatropic shifts calculated by the MNDO/PM3 method.[90]

Hereinafter, the bonds in the figures are given in Å; the bond angles and dihedral angles are also presented.

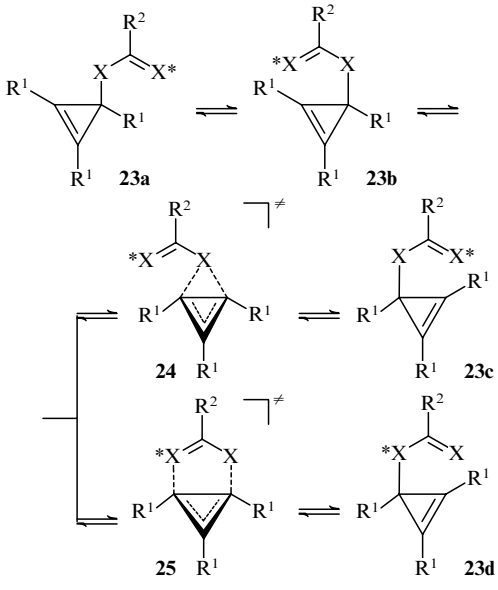
addition to the above-considered reaction mechanisms, the pathway through transition state **21** (Fig. 1) is also possible. The latter pathway corresponds to the [3,3]-sigmatropic shift in the course of interconversions of isomeric isothiocyanate **20** and thiocyanate **22**. Although MNDO/PM3 calculations demonstrated that compound **21** is less stable than isothiocyanate (the energy difference is 4.2 kcal mol^{-1}), it was detected [89] (0.4%) in the gas phase by mass spectrometry. The calculated relative energy of transition state structure **21** (49.3 kcal mol^{-1}) is too high and its value depends only slightly on the polarity of the solvent. Therefore, in this case the [3,3]-sigmatropic shift seems to be unlikely.

2. Rearrangements *via* [3,3]-sigmatropic shifts

For cyclopropene derivatives, rapid circumambulatory rearrangements proceeding through a series of successive [3,3]-sigmatropic shifts were first discovered in the study of the migration of the dithioacyl group [S−C(OEt)=S] around the three-membered ring of 1,2,3-triphenylcyclopropenyl *O*-ethyl dithiocarbonate **23a** (X = S, R^1 = Ph, R^2 = OEt).[92]

According to the results of X-ray diffraction study, molecule **23a** (X = S, R^1 = Ph, R^2 = OEt) in the crystal is characterised by the *exo* conformation of the dithioacyloxy group with respect to the three-membered ring. Based on the results of MNDO/PM3 calculations, this conformation is energetically more favourable (by 0.7 kcal mol^{-1}) than *endo* form **23b**. The transformation into the latter form requires the migration event. According to the data from NMR spectroscopy, the energy barrier to interconversion of the conformers in solutions is lower than 12 kcal mol^{-1}. The kinetic parameters of the degenerate rearrangement (Scheme 1), which were determined based on analysis of line shapes in the ^{13}C NMR spectra, are as follows: $\Delta G^{\neq}_{25}$ ($C_6D_5CD_3$) = 17.8 kcal mol^{-1}, $\Delta H^{\neq} = 14.8 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\neq} = -10.0 \pm 0.3$ cal mol^{-1} deg^{-1}, $k_{25} = 0.43$ s^{-1}. These parameters

Scheme 1



are virtually independent of the concentration of the solution, which is indicative of the intramolecular character of the migration of the dithioacyloxy group around the cyclopropene ring.

To decide between two possible competitive mechanisms of migration, *viz*., [3,3]- and [1,3]-shifts, the rearrangements of model compounds **23** (X = NH, O, S; $R^1 = R^2 = H$) were calculated by the semiempirical MNDO/PM3 method [90, 92] and the *ab initio* MP2/6-31G** method.[93] Selected results of these calculations are given in Table 1 and Figs 2 and 3.

Table 1. Relative energies (ΔE/kcal mol^{-1}) and relative heats of formation (ΔH_f/kcal mol^{-1}) of the structures of intermediates and transition states (TS) compared to the parameters of ground state structure **23a** for the hetero-Cope rearrangements of cyclopropene derivatives **23** ($R^1 = R^2 = H$).[90, 93]

Structure	X = NH		X = O		X = S	
	ΔE (see [a])	ΔH_f (see [b])	ΔE	ΔH_f	ΔE	ΔH_f
24 (TS for [1,3]-shift)	64.9	64.4	47.4	58.2	46.4	43.9
25 (TS for [3,3]-shift)	27.2 [c]	19.9	26.5	42.4	14.5	10.8
26	27.6	19.3	see [d]	see [d]	13.6	9.3
27	25.5	10.8	38.9	34.8	−5.0	−9.2

[a] Energies calculated by the *ab initio* MP2 (fc)/6-31G** method.
[b] Heats of formation were calculated by the MNDO/PM3 method.
[c] Without consideration of zero-point vibrations, the structure of TS **25** (X = NH) is energetically less favourable than structure **26** (X = NH); the energy difference is 0.3 kcal mol^{-1}.
[d] The structure was not localised on the corresponding potential energy surface.

It should be noted that the energy barriers predicted for the [3,3]-sigmatropic shifts of the dithioacyloxy group in molecule **23a** (X = S, $R^1 = R^2 = H$; see Table 1) are in good agreement with the barriers determined experimentally for compound **23a** (X = S, R^1 = Ph, R^2 = OEt), whereas the energies calculated for the migration mechanism involving the [1,3]-shift (with transition state structure **24**) are approximately 30 kcal mol^{-1} higher and seem to be inconsistent with the results of dynamic NMR spectroscopy. The conclusion that the [3,3]-sigmatropic shift is

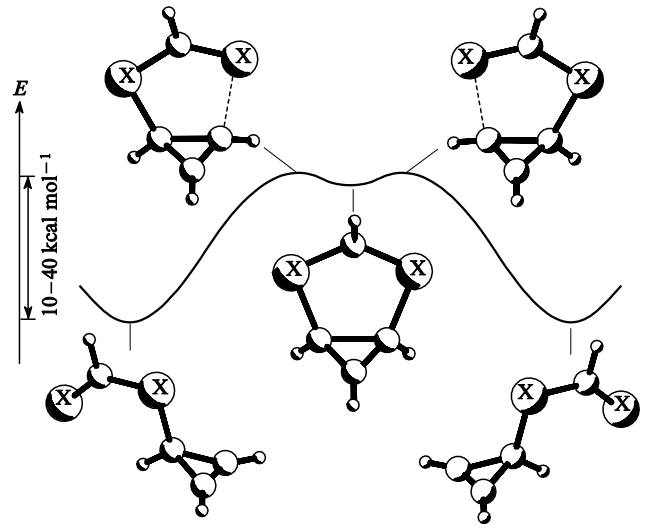


Figure 2. Energy profile of the pathway of [3,3]-sigmatropic shifts for the migrations of the allyl and heteroallyl groups around the cyclopropene ring in compound **23** (X = CH_2, O, NH, S).

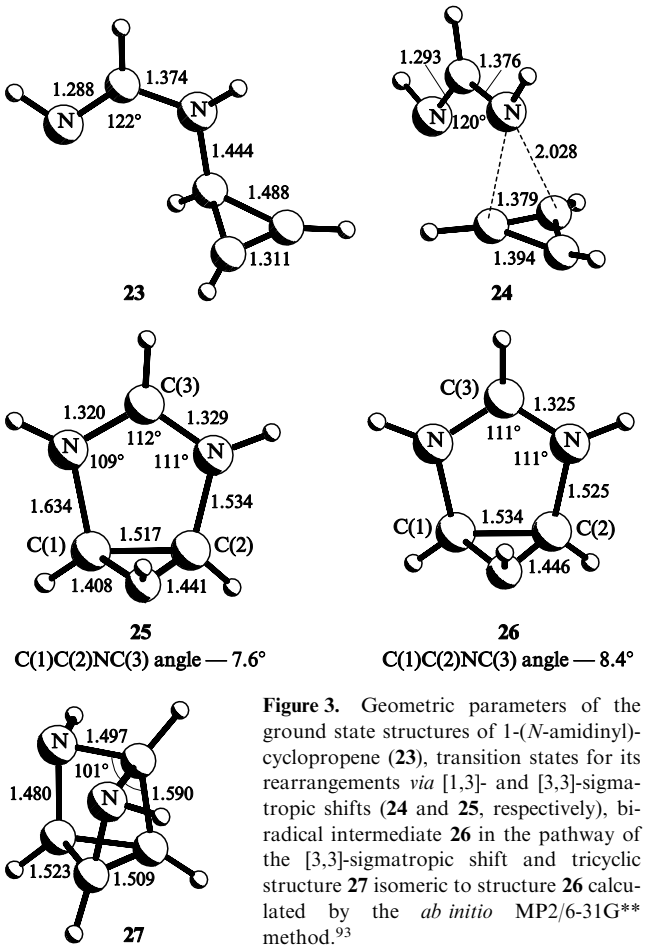
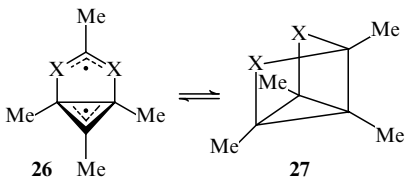


Figure 3. Geometric parameters of the ground state structures of 1-(*N*-amidinyl)-cyclopropene (**23**), transition states for its rearrangements *via* [1,3]- and [3,3]-sigmatropic shifts (**24** and **25**, respectively), biradical intermediate **26** in the pathway of the [3,3]-sigmatropic shift and tricyclic structure **27** isomeric to structure **26** calculated by the *ab initio* MP2/6-31G** method.[93]

energetically more favourable is also true for circumambulatory migrations of other heteroallyl substituents in the cyclopropene ring. The energy barriers calculated for this reaction pathway (transition state structure **25**) are 15–45 kcal mol^{-1} lower than the barriers to the [1,3]-shifts.[90, 93] According to the results of calculations, the Cope rearrangement (X = CH_2) and its heteroanalogue (X = NH, O, S) proceed in cyclopropene derivatives **23** as two-step reactions to give stable singlet biradical intermediates **26** (see Fig. 3). Unlike transition state structures **25**, biradical intermediates **26** have the symmetry C_s. The typical energy profile of the reaction pathway for [3,3]-sigmatropic shifts is shown in Fig. 2. Figure 3 presents the geometric parameters of the structures, *viz*., the starting structure, the transition state structure and the structure of the biradical intermediate, generated through the [3,3]- and [1,3]-sigmatropic shifts in the course of the circumambulatory rearrangements of 1-(*N*-amidinyl)cyclopropene **23** (X = NH, $R^1 = R^2 = H$).

Calculations predicted that biradicals **26** should readily be transformed into more stable tricyclic structures **27**.

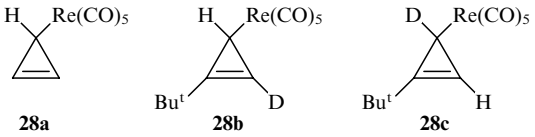


Actually, the investigation of thermolysis of 3-allylcyclopropene derivatives **19** (see Section III.8 and Refs 94 and 95) demonstrated [84] that the equilibrium mixture of products contained > 50% of the corresponding tricyclo[2.2.0.0]hexane derivative **27** (X = CH_2). The interconversion **26** ⇌ **27** can be

considered as an example of isomerisation of the bond-stretching type.[70,96]

3. Rearrangements proceeding by a mechanism of [1,3]-sigmatropic shifts

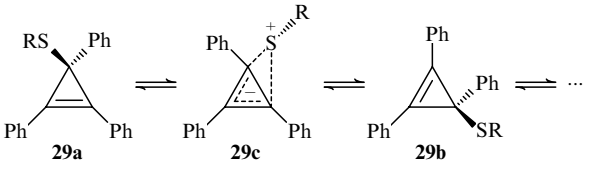
The non-dissociative rearrangement pathway involving the forbidden suprafacial [1,3]-sigmatropic shift is untypical of cyclopropene derivatives, even of those containing organometallic groups, which exhibit very high ability to undergo circumambulatory migrations in the cyclopentadiene ring. For example, 3-(pentacarbonylrhenium)cyclopropene (**28a**), like its derivatives **28b**,**c**, is a structurally rigid compound. The transformations **28b** ⇌ **28c** do not proceed in solution even at high temperature.[73]



28a **28b** **28c**

There is a high energy barrier (~32 kcal mol^{-1}) to the migration of the trimethylsilyl group in the 1,2-dimethyl-3-phenyl-3-trimethylsilylcyclopropene molecule.[97] By contrast, 3-phenylthio-1,2,3-triphenylcyclopropene **29a** (R = Ph) and di(1,2,3-triphenylcyclopropenyl) sulfide **29a** (R = C_3Ph_3) possess dynamic properties, and the ^{1}H and ^{13}C NMR spectra of their solutions in $C_2D_2Cl_4$ are temperature-dependent (but are concentration-independent).[40]

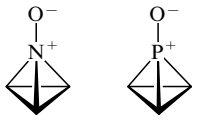
The energy barriers ($\Delta G^{\neq}_{25}$) to the migration of the phenylthio- and triphenylcyclopropenylthio groups calculated based on analysis of the line shapes of indicator signals in the ^{13}C NMR spectra are 24.4 and 24.1 kcal mol^{-1}, respectively, which are 5–10 kcal mol^{-1} higher than the barrier to migration of the phenylthio group in the cyclopentadiene system (see Section VI.4.b). This can be attributed to unfavourable conditions for delocalisation of the negative charge in the three-membered fragment of transition state structure **29c**.



29a **29c** **29b**

R = Ph, C_3Ph_3.

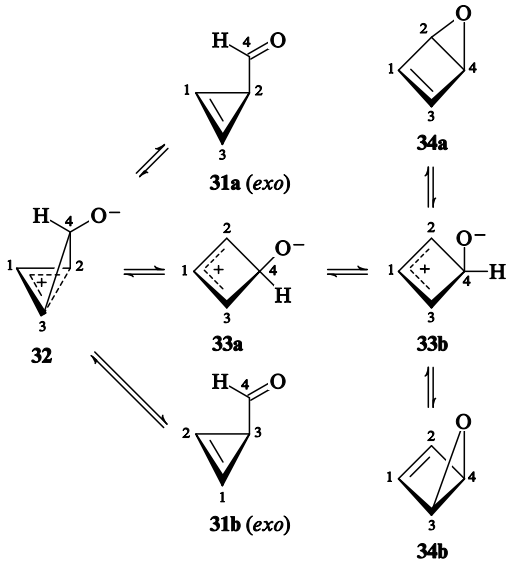
The rearrangements of cyclopropene derivatives containing π bonds in the migrating groups M = X = Y are of interest. Semiempirical (MINDO/3, MNDO/PM3 and AM1)[98] and *ab initio*[90] calculations demonstrated that the potential energy surfaces for C_3H_3NO and C_3H_3PO involve several alternative pathways of intramolecular rearrangements due to secondary orbital interactions between the migrating groups of this type and the ring; however, the relative energy of bicyclic structure **20b** (X = NO, R = H) corresponding to the transition state or intermediate for the 1,3-shift of the nitroso group around the cyclopropene ring is very high [35.3 kcal mol^{-1}; MP2(full)/6-31G**]. After the replacement of the nitrogen atom in the migrating group by the phosphorus atom, the local minimum of structure **20b** (X = PO, R = H) on PES calculated by the RHF/6-31G** method is only 5.1 kcal mol^{-1} higher than the minimum of structure **20a** (X = PO, R = H). Interestingly, calculations[90,98] revealed local minima corresponding to rather stable pyramidal azatetrahedrane oxide **30a** [ΔE(RHF/6-31G**) = 89.0 kcal mol^{-1}] and pyramidal phosphatetrahedrane oxide **30b** [ΔE (RHF/6-31G**) = 55.4 kcal mol^{-1}]. However, these highly strained structures are not involved in the rearrangements of the η^1 isomers **20a** ⇌ **20d**.



30a **30b**

The possibility of the circumambulatory intramolecular migration for formylcyclopropene **31**, which is another isoelectronic analogue of nitrosocyclopropene, was considered theoretically at the MP2/6-31G** level[99] using the intrinsic reaction coordinate calculations[100] for the identification of reaction trajectories. It was found that η^2 structure **32** is a high-energy intermediate ($\Delta G^{\neq}_{25}$ > 42 kcal mol^{-1}) for this rearrangement (Scheme 2).

Scheme 2



It was expected that *exo* conformer **32** would undergo isomerisation into the *endo* form *via* ring inversion. However, it appeared that the transformation of structure **32** into the planar form involves the formation of two successive transition states **33a** and **33b**, and the local minimum corresponds not to *endo* conformer **32** but to the energetically more favourable isomers of Dewar furan **34**. It should be noted that conformer **33b** corresponds to the transition state structure for the circumambulatory $\eta^2-\eta^3$ rearrangement of compound **34** involving the migration of the oxygen atom around the four-membered ring. An analogous rearrangement is also known for derivatives of Dewar thiophene (see Section III.5) but this rearrangement was not observed for derivatives of Dewar furan **34** (see Scheme 2). Therefore, the results of these calculations[99] led to the conclusion that the formyl group in the cyclopropene ring possesses low migration ability. Hence, it is beyond reason to expect that the rearrangement of compound **31** or its derivatives, unlike the rapid migration of the formyl group around the cyclopentadiene ring (see Section VI.2), is detectable by dynamic NMR spectroscopy.

4. Rearrangements of acylcyclopropenes catalysed by protonation

The intramolecular migration of acyl groups in cyclopropene derivatives is substantially accelerated under conditions of general or specific acid catalysis.[5,101] The complex formation with Lewis acids has the same or an even stronger effect (see Section VI.2).

According to MP2/6-31G** calculations,[99] protonation of formylcyclopropene **31** proceeds at the carbonyl oxygen atom to give four isomeric cations of which the *exo* conformer of 4-hydroxycyclobutenyl cation **35a** is most stable (Table 2, Fig. 4). The tetra-*tert*-butyl derivative of the 4-hydroxycyclobutenyl cation (**36**), which was prepared by oxidation of tetra-*tert*-butyltetrahedrane, has precisely this structure.[102] It was demon-

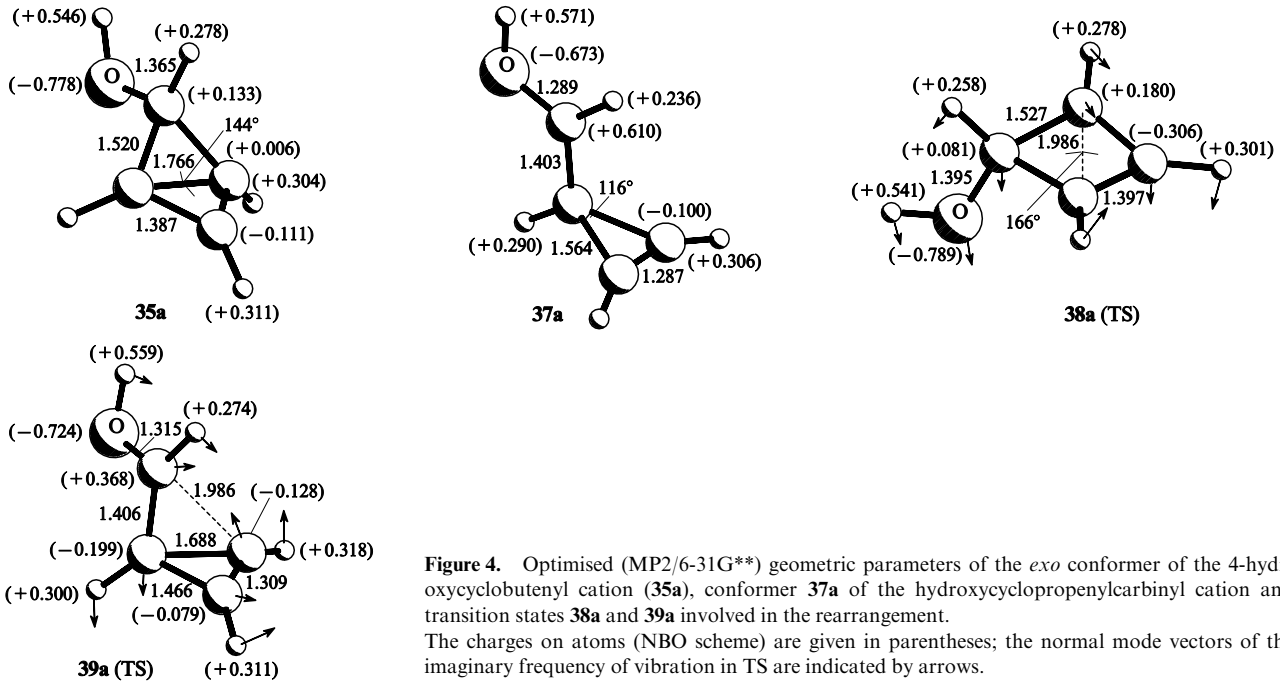


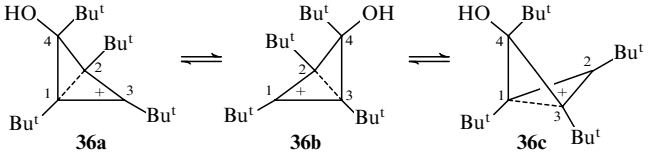
Figure 4. Optimised (MP2/6-31G**) geometric parameters of the *exo* conformer of the 4-hydroxycyclobutenyl cation (**35a**), conformer **37a** of the hydroxycyclopropenylcarbinyl cation and transition states **38a** and **39a** involved in the rearrangement.
The charges on atoms (NBO scheme) are given in parentheses; the normal mode vectors of the imaginary frequency of vibration in TS are indicated by arrows.

Table 2. Relative energies (ΔE) of structures **35** and **37**–**39** (see Ref. 99) involved in the rearrangement of the 4-hydroxycyclobutenyl cation and the values of the only imaginary frequency (ν_{im}) of normal vibrations for structures of transition states (TS).

Structure	ν_{im} /cm^{-1}	ΔE /kcal mol^{-1}
35a	–	0
39a (TS)	272	10.1
37a	–	3.7
35b	–	8.1
39b (TS)	431	18.4
37b	–	4.9
38a (TS)	267	13.1
38b (TS)	266	20.1

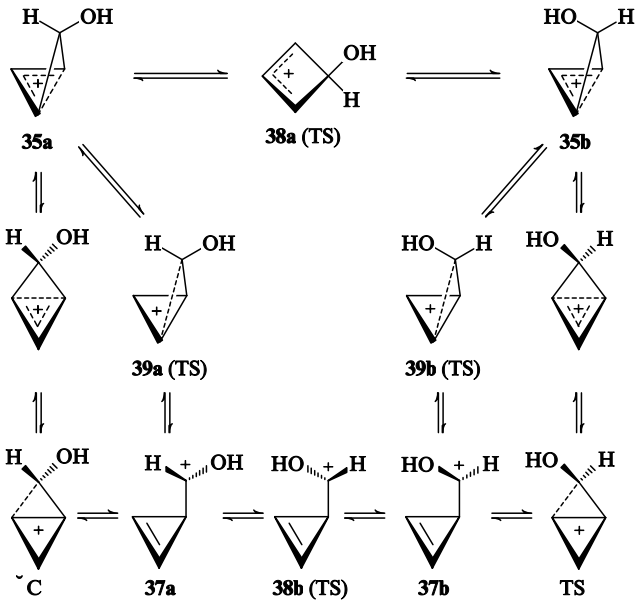
Note. The energies were calculated by the *ab initio* MP2/6-31G** method.

strated that cation **36** undergoes a low-barrier rearrangement ($\Delta G^{\neq} \approx 15$ kcal mol^{-1}) as a result of successive 1,2-shifts of the hydroxymethylene group around the cyclopropene ring. It was found that the chemical shift of the migrating sp^3-hybridised carbon atom in the NMR spectrum of cation **36** remains unchanged over a broad temperature range. This is indirect evidence that only *exo* isomer **36** is involved in the reaction, and, consequently, the configuration of the migrating carbon centre undergoes inversion because the reaction pathway with retention of configuration would require the interconversion between the *exo* and *endo* conformers to occur in each step of the rearrangement.



This assumption was confirmed by *ab initio* calculations,[99] which demonstrated that the rearrangement of the 4-hydroxycyclobutenyl cation **35** proceeds in two steps through the intermediate formation of classical hydroxycyclopropenylcarbinyl cations **37**. All main structures corresponding to local minima on PES of the $C_4H_5O^+$ cation, which are involved in degenerate circumambulatory rearrangements of the conformers of the 4-hydroxycyclobutenyl cation, are shown in Scheme 3. The migrations of the protonated formyl group around the three-membered ring in the *exo* (**35a**) and *endo* conformers (**35b**) of the 4-hydroxycyclobutenyl cation proceed as non-concerted two-step reactions to give the *exo* (**37a**) and *endo* (**37b**) conformers of the hydroxycyclopropenylcarbinyl cation, respectively, as intermediates.

Scheme 3



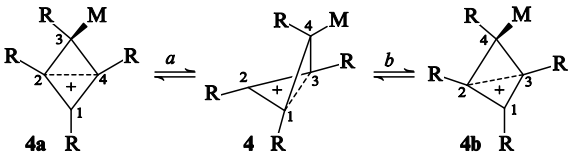
The calculated energy barriers to the 1,2-shifts of the hydroxymethylene groups (10.1 and 10.3 kcal mol^{-1} for conformers **35a** and **35b**, respectively) are in satisfactory agreement with the experimental activation free energy for the circumambulatory rearrangement of tetra-*tert*-butyl derivative **36** of cation **35a**. The eclipsed conformer of hydroxycyclopropenylcarbinyl cation **38b**, whose formation as an intermediate or transition state in the rearrangement would lead to retention of stereochemical configuration of the migrating carbon atom, lies on PES off this pathway. The intersection of the reaction pathways through the

ring inversion mechanism **35a** ⇌ **38a** ⇌ **35b** requires that the higher energy barrier be overcome compared to that calculated for the rearrangement **35a** ⇌ **39a** ⇌ **37a**. Therefore, the two-step circumambulatory rearrangement of the *exo* isomer of 4-hydroxycyclobutenyl cation **35a** accompanied by the inversion of configuration of the migrating carbon centre is the intramolecular rearrangement pathway corresponding to the minimum energy.

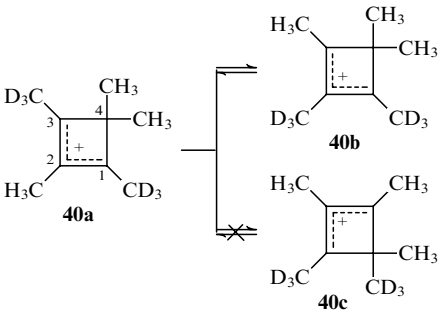
V. Circumambulatory rearrangements in a four-membered ring

High-level *ab initio* calculations [99, 103, 104] and X-ray diffraction study [105] of cyclobutenyl cation **4** showed that this cation has a non-planar homoaromatic structure intermediate between the planar and bicyclo[1.1.0]butyl forms.

The migration of the group M in derivatives **4** can, in principle, proceed as a series of successive 1,2-shifts ([1,4]-sigmatropic shifts) of the migrating group around the four-membered ring (path *a*) or as [1,3]-sigmatropic shifts of the cyclopropyl fragment around the three-membered ring of the homoaromatic cyclobutenyl (homocyclopropenyl) cation (path *b*).



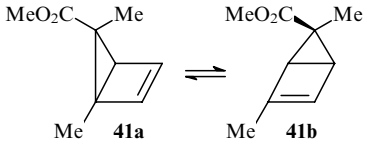
Koptyug and co-workers [106] found that cation **40a** containing deuterated methyl groups at positions 1 and 3 underwent intramolecular exchange resulting in the distribution of the labelled groups between positions 1, 2 and 3, but not 4, of the ring. Hence, the mechanism associated with path *a* can be excluded.



The sigmatropic rearrangements of a series of other carbon-centred groups (alkyl, aryl and allyl) and the hydrogen atom around the cyclobutene ring, which are characterised by energy barriers higher than 15–25 kcal mol^{-1}, were reported.[53, 107] By contrast, the migration of the anionic trichloroaluminium group in the permethylated σ complex of cyclobutadiene **4** (M = $AlCl_3^-$, R = Me) proceeded rather rapidly ($\Delta G_{25}^{\neq}$ < 25 kcal mol^{-1}).[105] Unlike the rearrangements of the cyclobutenyl cations with the carbon-centred migrating groups, this dynamic process involves successive 1,2-shifts of the $AlCl_3^-$ group.

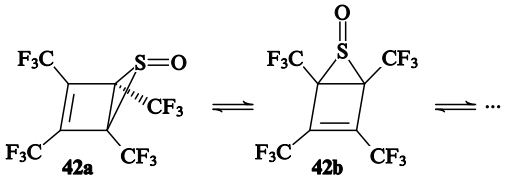
The formation of isomers of 2-azapyrylium salts in the reactions of σ complexes of dichloroethylene-, trichloroethylene- and tetraalkylcyclobutadienyldialuminium hexabromide with nitrosyl chloride [108] stimulated the examination of the possibility of the σ,π-mechanism for the rearrangement of nitrosocyclobutenyl cations **4** (M = NO, R = H). Semiempirical [109] and *ab initio* [110] calculations demonstrated that the intermediate pyramidal cation with the η^4-coordinated nitroso group corresponds to a local minimum on PES of the $C_4H_4NO^+$ cation. However, alternative reaction pathways proceeding through the intermediate formation of structures such as N,O-substituted Dewar benzene and bullvalene are energetically more favourable.[105, 109]

As demonstrated in Section III.5, circumambulatory rearrangements in neutral four-membered rings proceed by the $\eta^2-\eta^3$ mechanism corresponding to the [1,3]-sigmatropic shift. The interconversion of isomers of bicyclopentene **41** is one of the first and most well-studied examples of this type of thermal rearrangement.[111] This rearrangement is highly stereoselective and proceeds according to the Woodward–Hoffmann rules with the inversion of stereochemical configuration of the migrating carbon atom in the cyclopropyl fragment.



$\Delta G^{\neq}$ (**41a** → **41b**) = 21.7 kcal mol^{-1}

Unlike the rearrangements of bicyclopentenes **41**, an analogous degenerate rearrangement of the *exo* conformer of the tetrakis(trifluoromethyl) oxide derivative of Dewar thiophene **42** (see Ref. 65) proceeds in solution very rapidly even at low temperatures: $\Delta G_{-124}^{\neq}$ = 6.8 kcal mol^{-1}.



The possibility of the dynamic behaviour of the starting derivative of Dewar thiophene, which is the only known bicyclic isomer of aromatic five-membered heterocycles, was not examined. However, recent *ab initio* calculations (MP2/6-31 G**) and calculations at the B3LYP/6-31G** level [112] demonstrated that 1,3-sigmatropic shifts of the oxygen and chalcogen atoms around the four-membered ring can occur in metastable Dewar isomers of furan, thiophene, selenophene and tellurophene **43** (X = O, S, Se, Te). The energy barriers estimated for these processes are no higher than 25 kcal mol^{-1}. The results of these calculations are given in Table 3 and Fig. 5.

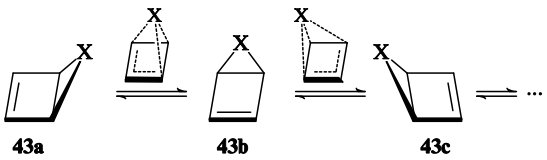


Table 3. Relative energies (Δ*E*) (compared to the aromatic structure) and energy barriers ($\Delta E^{\neq}$) for the rearrangements of the Dewar isomers of five-membered heterocycles **43**.[112]

X in **43**	ΔE /kcal mol^{-1}		$\Delta E^{\neq}$ /kcal mol^{-1}	
	MP2/6-31G**	B3LYP/6-31G**	MP2/6-31G**	B3LYP/6-31G**
O	66.6	67.8	23.2	16.1
S	57.2	57.2	26.4	16.0
Se	50.8	52.0	21.7	13.9
Te[a]	50.0	50.3	21.2	10.2

[a] The energy parameters for tellurium compounds were calculated using the LanL/2DZ orbital basis set.

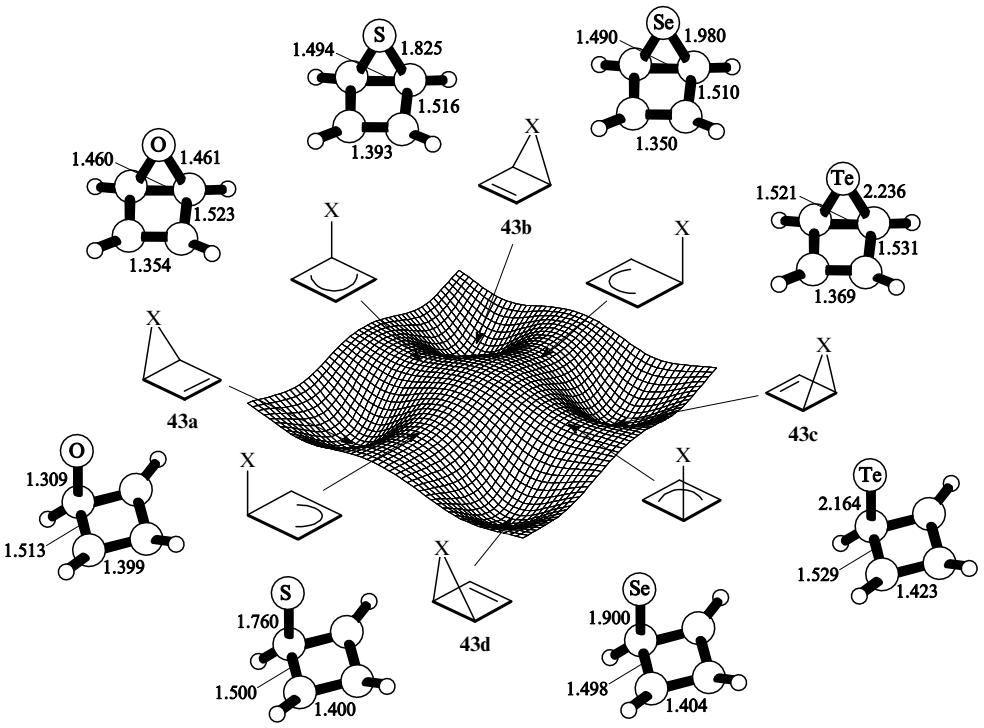


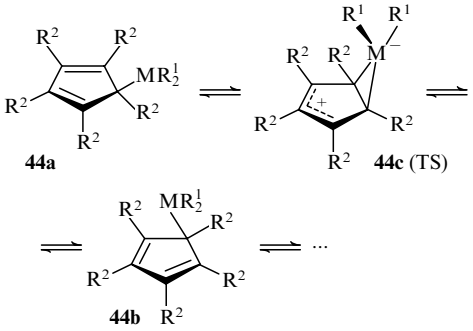
Figure 5. Topology of PES for the 1,3-sigmatropic rearrangements of Dewar isomers of furan, thiophene, selenophene and tellurophene according to the results of *ab initio* calculations (MP2/6-31G**) [112] and geometric parameters of the starting (at the top) and transition (at the bottom) structures.

VI. Circumambulatory rearrangements of element-centred migrating groups in the cyclopentadiene ring

Cyclopentadiene and its derivatives belong to the most important group of ligands in the chemistry of coordination compounds. That is the reason why their structures and dynamic behaviour associated with circumambulatory rearrangements were studied in close detail. Let us consider these rearrangements by classifying them according to the position of the central atom of the migrating group in the Periodic table.

1. Migrating substituents formed by Group 13 elements

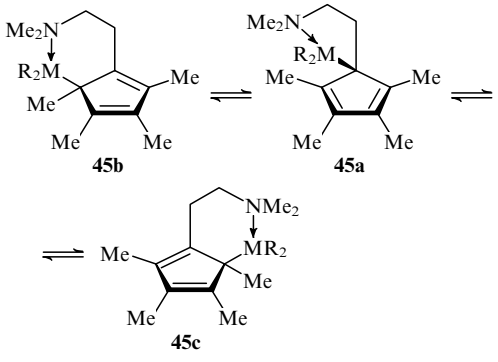
Circumambulatory rearrangements of the migrating groups BR_2, AlR_2, GaR_2 and InR_2 (R = Alk, F, Cl, Br, I) in unsubstituted and transmethylated cyclopentadiene rings proceed rather rapidly ($\Delta G^{+} \leqslant 20$ kcal mol^{-1}). Consequently, completely averaged ^{1}H or ^{13}C NMR spectra of compounds **44** were recorded at normal temperatures.[16, 20, 26, 113] Although direct experimental evidence supporting the mechanism of these rearrangements is lacking, one can say with a fair degree of assurance that each step involves the 1,2-shift ([1,5]-sigmatropic shift) of the migrating group. This conclusion was confirmed by MNDO calculations.[114]



R^2 = H, Me.

In the presence of electron-releasing groups R in the migrating centre, the rate of rearrangements substantially decreases. As a result, the energy barriers to migration of the $B(NMe_2)_2$, $B(OMe)_2$ and $B(SEt)_2$ groups in the pentamethylcyclopentadienyl ring become measurable on the NMR time scale ($\Delta G^{\neq}_{25}$ = 17.2, 14.4 and 10.2 kcal mol^{-1}, respectively).[115] In pentamethylcyclopentadienylboranes in which the boron atom is coordinated by the pyridine molecule (lone electron pair on the nitrogen atom of the pyridine ring fills the unoccupied p orbital of the boron atom), the rearrangement is completely decelerated ($\Delta G^{\neq}_{25}$ > 25 kcal mol^{-1}).

An interesting rearrangement of a series of aluminium, gallium, and indium derivatives of 1-dimethylaminoethyl-2,3,4,5-tetramethylcyclopentadiene **45** was described.[116] The ^{1}H and ^{13}C NMR spectra of compound **45** have two singlets in a ratio of 1 : 1 belonging to four Me groups at the carbon atoms of the cyclopentadiene ring, the spectral pattern being temperature-independent. The presence of the intramolecularly coordinated $Me_2NCH_2CH_2$ substituent restricts the shifts of the migrating substituents formed by Group 13 elements to only the adjacent carbon atoms. Hence, the dynamic behaviour is determined by



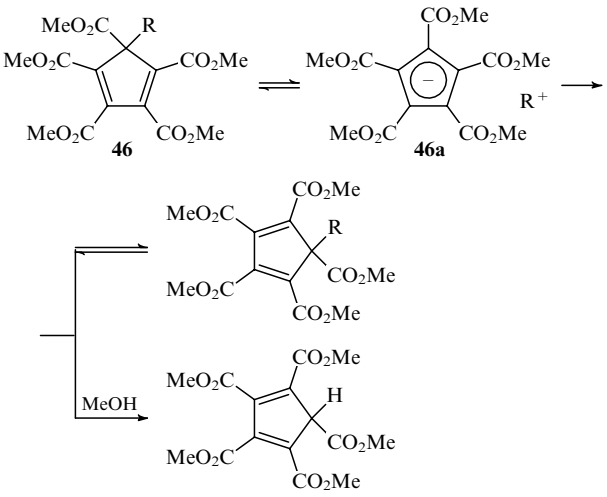
M = Al, R = H, Me, Et, Cl, Br, I; M = Ga, R = Cl; M = In, R = Cl.

rearrangements between isomers **45a–c**, which allowed the authors of the study [116] to compare this mechanism with the movement of windscreen wipers.

2. Migrating substituents formed by Group 14 elements

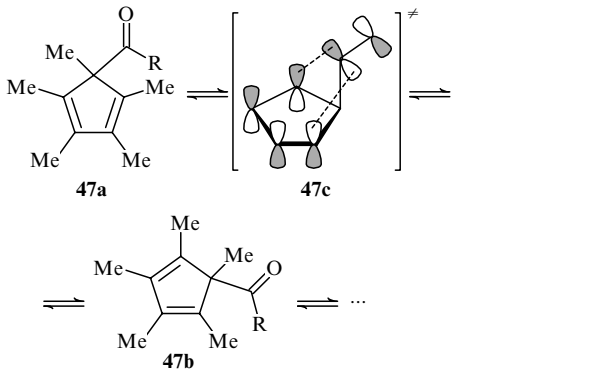
1,2-Alkyl shifts in the cyclopentadiene ring can be observed at temperatures higher than 300 °C, which corresponds to activation free energies higher than 40 kcal mol^{-1}.[18] According to more accurate data obtained for the rearrangement of hexamethylcyclopentadiene containing one trideuteriomethyl group, the activation barrier to migration of the CH_3 or CD_3 group is 43.1 kcal mol^{-1}.[117] In 5-(*p*-nitrobenzyl)-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene, the migration of the *p*-nitrobenzyl group requires that the energy barrier of 30 kcal mol^{-1} should be overcome, [118] which is close to the condition of structural non-rigidity ($\Delta G^{\neq}_{25} \leqslant 25$ kcal mol^{-1}).

It was hypothesised [119] that circumambulatory rearrangements of 5-R-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene derivatives **46** in polar solvents can be controlled by the ionisation–recombination mechanism involving heterolysis of the $C_{sp^3}-C_{Cp}$ bond. Actually, compounds **46** dissociate in methanol to form solvated ion pairs **46a**. Apparently, the collapse of the ion pairs giving rise to topomers **46** (degenerate circumambulatory rearrangement) can compete with the irreversible reaction with the solvent.

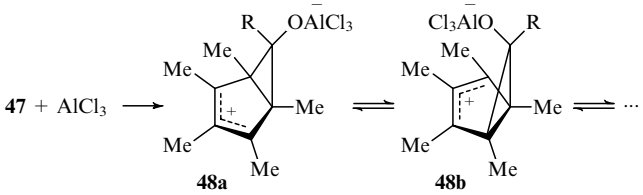


R = CH_2OMe, $CHPh_2$, $CH_2C_6H_4OMe$-4, adamantan-1-yl.

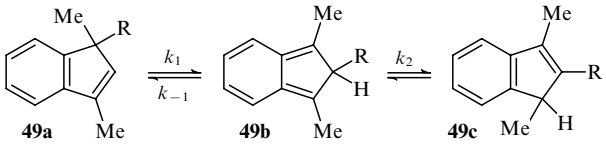
C_{sp^2}-Centred groups have higher ability to migrate around the five-membered ring as compared to C_{sp^3}-centred groups. The energy barrier ($\Delta G^{\neq}_{25}$) to the 1,2-shift of the phenyl group in 5-deuteriomethyl-1,2,3,4-tetramethyl-5-phenylcyclopentadiene is 37.8 kcal mol^{-1}.[120] Thermal rearrangements of a series of 5-substituted pentamethoxycarbonylcyclopentadienes [121, 122] proceed as successive 1,2-shifts of the substituent, the energy barrier to this migration is only slightly higher than 25 kcal mol^{-1}. At 25 °C, the migration of the formyl group in 5-formyl-1,2,3,4,5-pentamethylcyclopentadiene **47** (R = H) proceeds much more rapidly ($k = 90$ s^{-1}); its energy barrier is only 14.8 kcal mol^{-1}.[123] This rearrangement is favoured by a secondary orbital interaction involving π-HOMO of the cyclopentadiene fragment and π*-LUMO of the carbonyl group in transition state structure **47c**. Semiempirical calculations by the MINDO/3 method [124] confirmed that the orbital interaction of this type makes a substantial contribution to stabilisation of transition state structure **47c**.



In compound **47** (R = H), the formyl group undergoes rapid circumambulatory rearrangements in the five-membered ring, whereas other 5-acyl derivatives of 1,2,3,4,5-pentamethylcyclopentadiene are structurally rigid. To decrease the energy barrier to migration of the above-mentioned groups, powerful electron-withdrawing substituents, such as the trifluoro- or trichloromethyl group, should be introduced into the acyl fragment. The energy barriers ($\Delta G^{\neq}_{25}$) to migration of these groups around the pentamethylcyclopentadiene ring are 20.6 (hexachlorobutadiene) and 25.4 kcal mol^{-1} (DMF-d_7), respectively.[125] The coordination of the acyl oxygen atom by Lewis acid provides an alternative and more efficient way of accelerating the migration of the acyl group.[126] Upon the formation of complexes with $AlCl_3$, compounds **47** form bicyclic zwitterions **48**, which undergo circumambulatory rearrangement involving a series of 1,3-shifts of the cyclopropane fragment ($\eta^2-\eta^3$ mechanism). The energy barriers to this rearrangement depend on the ability of the substituent R in zwitterion **48** to stabilise the positive charge and their values vary from ~5 (R = $C_6H_4CF_3$) to 10.9 (R = Me) and then to 18.2 kcal mol^{-1} (R = C_6H_4OEt).[126]



Annelation of the benzene ring onto cyclopentadiene leads to an increase in the energy barrier to 1,2-shifts of carbon-centred groups by 9–11 kcal mol^{-1}. Because of this, thermal rearrangements in indene derivatives cannot be detected on the NMR time scale. In studies,[127–129] the migration abilities of various C_{sp^3}-, C_{sp^2}- and C_{sp}-centred groups were examined using optically active 1,3-dimethylindenes **49**.



If the migration of the groups R proceeds more slowly than the migration of the hydrogen atom in 2*H*-indene **49b** ($k_2 > k_{-1}$), the rate of formation of compound **49c** can serve as a measure of the migration ability. If the group R undergoes more rapid migration compared to the hydrogen atom in molecule **49b** ($k_{-1} > k_2$), as in the case of R = CHO or Ar, the constant k_1 can be estimated based on the racemisation rates of optically active indenes. The migration ability of the groups R thus estimated decreases in the following series: CHO > Acyl > H > $CH=CH_2$ > CO_2Me > $C\equiv N$ > $C\equiv CH$ > Ph > 1-naphthyl > Alk.[127–129]

The migration ability of groups increases with increasing atomic number of the element within the same group of the Periodic table, as evidenced by a substantial acceleration of the rearrangements of the SiR_3, GeR_3, SnR_3 and PbR_3 migrating groups as compared to alkyl groups. Even a qualitative analysis of the ^1H NMR spectra of 5-trimethylsilylcyclopentadiene[42] revealed the pronounced fluxional behaviour of this compound. More recent studies demonstrated that the energy barriers to migration of the trimethylsilyl group around the cyclopentadiene ring are ~ 15 kcal mol^{-1}. These energies are most convenient for studying the kinetics and permutation mechanisms by dynamic NMR spectroscopy. This is the reason why the migration processes in silylcyclopentadienes have attracted particular attention in early studies of circumambulatory rearrangements (see, for example, the reviews[15–17,19,20]). Generally, the 1,2-shifts of tin- and lead-containing migrating groups in the five-membered ring of various cyclopentadiene derivatives proceed at very high rates, which cannot be measured directly using standard techniques of ^1H or ^{13}C NMR spectroscopy.[130–132] The energy barriers to 1,2-shifts of substituents formed by Group 14 elements are given in Table 4.

Table 4. Energy barriers ($\Delta G^{\neq}$) to the 1,2-shifts of Si-, Ge- and Sn-centred groups (M) in cyclopentadiene derivatives C_5R_5M.

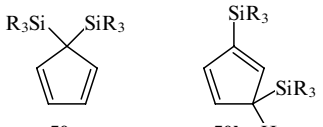
M	R	$\Delta G^{\neq}_{27}$ /kcal mol^{-1}	Ref.
SiH_3	H	13.6	133
SiH_2Cl	H	12.9	133
$SiHCl_2$	H	13.5	133
$SiMe_3$	H	15.2	20
$SiMe_2Cl$	H	15.5	20
$SiMeCl_2$	H	15.9	20
$SiCl_3$	H	16.3	20
$SiMe_3$	Me	15.3[a]	134
$SiCl_3$	Me	13.1[a]	134
$GeMe_3$	H	13.9	135
$GeMe_3$	Me	<11	136
$GeCl_3$	Me	11.9	136
$SnCl_3$	H	7.5	135

[a] The activation energy (E_a).

Unlike the rearrangements of cyclopentadiene derivatives in which the migrating fragments are formed by Group 13 elements, the barriers to rearrangements of cyclopentadienylsilanes, -germanes and -stannanes are only slightly affected by substituents at the central atom of the migrating fragment. This is attributed to the absence of the low-lying unoccupied p orbital in the sp^3-hybridised central atoms of the SiR_3 and GeR_3 groups (transition state structure **10a**), which plays an important role in stabilisation of the transition state structures of the migrating fragments of Group 13 elements.

The mechanism of rearrangements of η^1-indenyl derivatives of main-group elements was analysed in the review,[137] where the reactivities of these compounds and indenyl derivatives of transition metals were surveyed and their use as precursors of chiral metallocene catalysts was discussed. The conclusion that migrations of the Si-, Ge-, Sn- and Pb-centred groups around the ring proceed as [1,5]-sigmatropic shifts giving rise to short-lived isoindene intermediates was demonstrated to be of general character.

Rearrangements of cyclopentadiene derivatives containing two or three SiR_3 groups in the ring were studied in detail by Ustynyuk and co-workers[44] and other researchers.[26] The equilibrium mixtures of di-SiR_3-substituted cyclopentadienes bearing no other substituents in the ring can contain up to seven isomers, which are generated as a result of a series of 1,2-shifts of hydrogen atoms and SiR_3 groups in the ring. However, only two isomers, *viz*., **50a** and **50b**, are usually observed. These isomers are produced by successive 1,2-shifts of the SiR_3 groups, the first isomer being the major product. The high stability of compound **50a** results from the hyperconjugative π-aromaticity of 5,5-disubstituted cyclopentadienes containing electropositive groups, such as SiR_3, GeR_3 or SnR_3.[138]

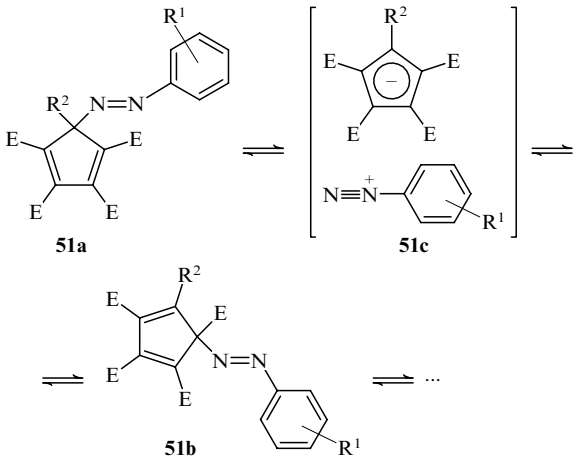


50a **50b**

3. Migrating substituents formed by Group 15 elements

a. Nitrogen-centred migrating groups

Ionisation–recombination mechanism. Circumambulatory migrations of N-centred substituents around the five-membered ring were first studied for arylazocyclopentadienes **51** whose rearrangements proceed through the ionisation–recombination mechanism.[38,39]



E = CO_2Me; R^2 = CO_2Me, Me (for notations of R^1, see Table 5).

The design of these rearrangements is based on the strategy opposite to that used for cyclopropene derivatives (see Sections III.1 and IV.1). It was demonstrated that there is a rather fine balance between the relative stabilities of covalent (**51a**, **51b**) and ionic (**51c**) isomers of arylazocyclopentadienes. To stabilise intermediate ion pair **51c**, the negative charge of the aromatic cyclopentadienyl anion should be additionally delocalised by introducing π-acceptor substituents into the Cp ring. For example, heating of arylazopentamethylcyclopentadienes **51** ($R^1 = NO_2$, R^2 = E = Me) did not lead to the heterolysis of the $C_{Cp}-N$ bond; instead, the rearrangement involved the migration of the arylazo group to the adjacent carbon atom.[139] At the same time, electron-releasing substituents in the benzene ring stabilise excessively ion pair **51c**, which becomes the major form of existence of compounds **51** (E = CO_2Me). In the solid state, such isomers of arylazopentamethoxycarbonylcyclopentadienes prevail even in the case of $R^1 = 4'$-NO_2 (Fig. 6).

At low temperature, mono-, di- and trinitrophenylazo derivatives **51** exist in benzonitrile as covalent compounds, which readily dissociate to form ion pairs **51c** upon heating. The collapse of the latter leads to the randomisation of the position of the arylazo group in the ring and, consequently, to the circumambulatory migration around the cyclopentadiene ring. The rate constants and activation parameters for the rearrangements of compounds **51** proceeding according to the ionisation–recombination mechanism are given in Table 5. For solutions of arylazo derivatives **51** in acetonitrile, these parameters are concentration-independent in the range of 0.03–0.30 mol litre^{-1}, which is indicative of the intramolecular nature of these rearrangements.

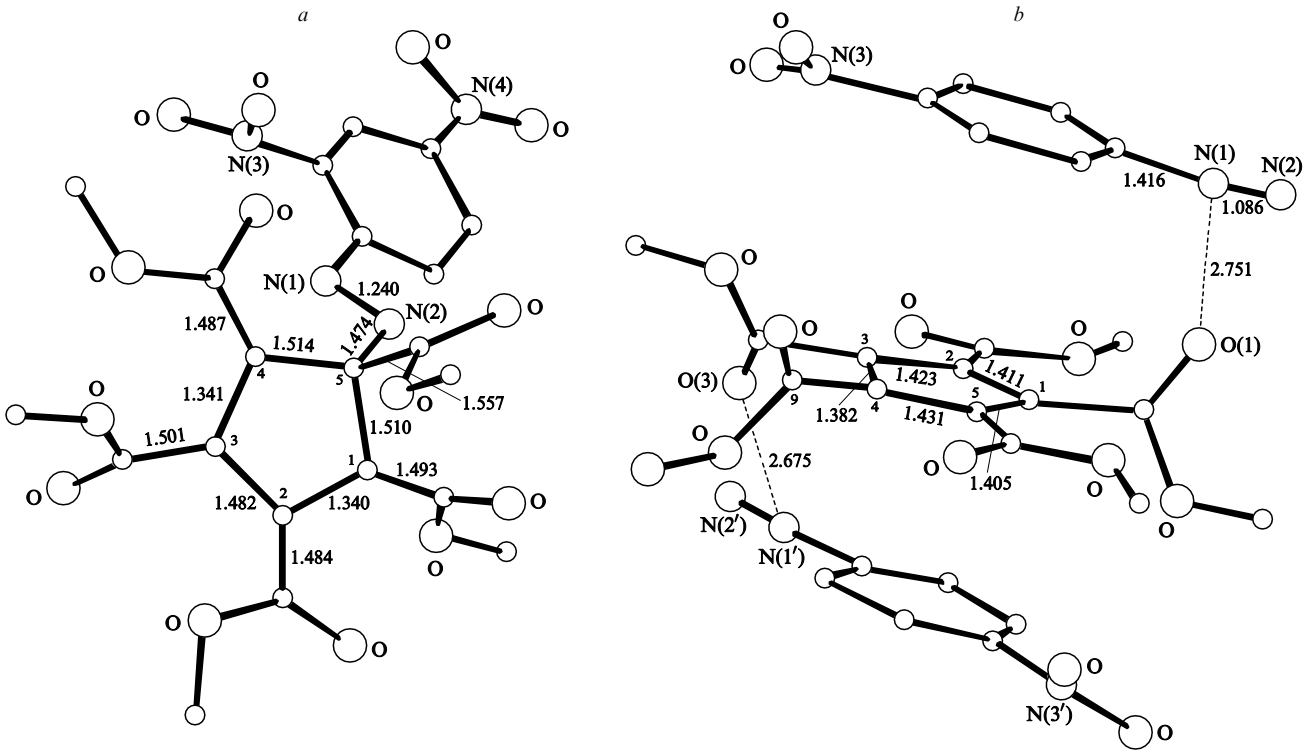
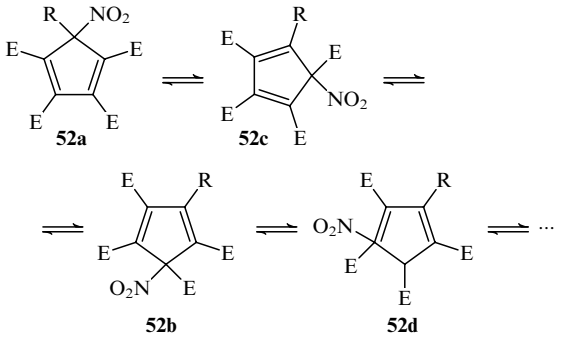


Figure 6. Molecular structures of 5-(2,4-dinitrophenylazo)-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene (*a*) and 5-(4-nitrophenylazo)-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene **51** (*b*) according to the results of X-ray diffraction analysis.[38, 39]

Heating of solutions of arylazopentamethoxycarbonylcyclopentadienes led to elimination of molecular nitrogen followed by rearrangements of the resulting arylpentamethoxycarbonylcyclopentadienes caused by 1,2-shifts of the methoxycarbonyl group around the five-membered ring.[121, 122, 140]

1,2-Shifts. The slow degenerate circumambulatory rearrangements of 1,2,3,4,5-pentamethyl-5-nitrocyclopentadiene ($\Delta G^{\neq}_{172}$ = 25.1 kcal mol^{-1} in DMSO)[141] and 1,2,3,4,5-pentamethoxycarbonyl-5-nitrocyclopentadiene ($\Delta G^{\neq}_{25}$ = 24 kcal mol^{-1} in chlorobenzene) and non-degenerate rearrangements of 5-alkyl(benzyl)-5-nitro-1,2,3,4-tetramethoxycarbonylcyclopentadienes **52a**[142] proceed as 1,2-shifts ([1,5]-sigmatropic shifts) around the periphery of the cyclopentadiene ring. Compounds **52a** were prepared as mixtures with their isomers **52b** (in a ratio of $\sim$ 1 : 1) by nitration of the corresponding cyclopentadienes in acetic anhydride at 50 °C and were then separated by chromatography. The energy barriers to the 1,2-shifts of the nitro group ($\Delta G^{\neq}_{25}$ = 24.0–26.6 kcal mol^{-1}) were determined from the kinetics of establishment of an equilibrium between these isomers, which involves two successive 1,2-shifts of the nitro group proceeding through the intermediate formation of isomer **52c** (which was not observed by ^{1}H NMR spectroscopy due to its low equilibrium concentration).



R = CO_2Me, Me, $CHMe_2$, CH_2Ph.

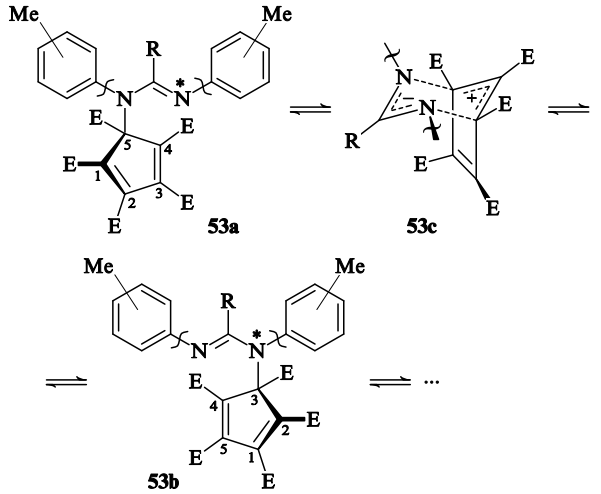
Table 5. Kinetic and activation parameters for the migration of the arylazo groups in 5-arylazo-1,2,3,4,5-pentamethoxycarbonylcyclopentadienes **51** (R^2 = CO_2Me) in benzonitrile.[38, 39]

R^1 in compound **51**	k_{25} /s^{-1}	$\Delta H^{\neq}$ /kcal mol^{-1}	$\Delta S^{\neq}$ (see [a])	$\Delta G^{\neq}_{25}$ /kcal mol^{-1}
4′-NO_2	9×10^2	11.1 ± 0.8	−7.7 ± 1.2	13.4
2′-NO_2	6.3×10^2	13.3 ± 0.7	−0.9 ± 1.0	13.6
2′-I, 4′-NO_2	6.3×10^2	14.2 ± 0.6	−1.3 ± 1.1	13.6
2′-Cl, 4′-NO_2	5.4×10^2	11.3 ± 0.5	−8.2 ± 1.0	13.7
2′-Br, 4′-NO_2	4.6×10^2	11.7 ± 0.6	−7.0 ± 1.1	13.8
2′,4′-$(NO_2)_2$	1.0×10^2	9.9 ± 0.5	−16.1 ± 1.0	14.7
2′,6′-$(NO_2)_2$	7.2×10^1	11.5 ± 0.7	−11.4 ± 1.3	14.9
2′,4′,6′-$(NO_2)_3$	7.8	11.4 ± 0.7	15.4 ± 1.3	16.0

[a] $\Delta S^{\neq}$ are given in cal mol^{-1} deg^{-1}.

All attempts to synthesise nitrosocyclopentadiene derivatives failed. The rearrangements of these compounds were theoretically simulated by the semiempirical MINDO/3 method.[143] These calculations revealed two energetically almost equivalent transition state structures corresponding to the 1,2- and 1,3-shifts of the nitroso group. The relatively high stability of the latter structure is attributed to the fact that it conforms to the rules of electron calculation for pyramidal structures of this type.[30, 31]

[3,3]-Sigmatropic shifts. *N*,*N*′-Diaryl-*N*-(1,2,3,4,5-pentamethoxycarbonylcyclopentadienyl)amidines **53** generated by the reactions of *N*,*N*′-diarylamidines with compounds **52** (R = CO_2Me) underwent rapid degenerate rearrangements involving successive [3,3]-sigmatropic shifts of the amidinyl groups.[144, 145]



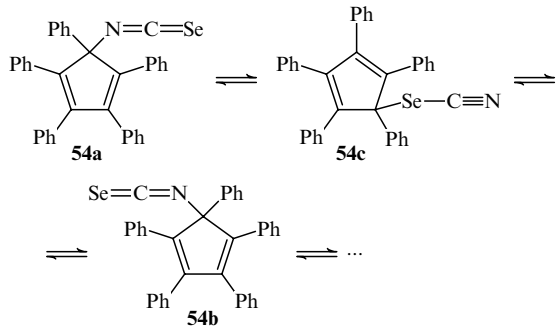
The fact that the rearrangements proceed as successive 3,3-shifts rather than as 1,2-shifts of the amidinyl groups is confirmed by the simultaneous averaging of the signals of the methyl groups of the aryl and methoxy fragments in the ^{1}H NMR spectra of solutions of diarylamidines **53** in hexachlorobutadiene observed at high temperatures. The kinetic parameters (Table 6) of the rearrangements, which were calculated based on analysis of full line shapes of both groups of indicator signals, are identical to each other. Quantum-chemical calculations (see Section III.8) provide additional evidence supporting the [3,3]-sigmatropic shifts (hetero-Cope rearrangement) in the amidinylcyclopentadiene molecules.

Table 6. Kinetic and activation parameters for the circumambulatory rearrangements of amidinylcyclopentadienes **53** in hexachlorobutadiene.[145]

R, position of Me in compound **53**	k_{90} /s^{-1}	$\Delta H^{\neq}$ /kcal mol^{-1}	$\Delta S^{\neq}$ (see [a])	$\Delta G^{\neq}_{90}$ /kcal mol^{-1}
Ph, 4-Me	0.17	22.5 ± 0.4	−1.5 ± 0.5	22.7
1-Naphthyl, 4-Me	3.9	15.1 ± 0.3	−14.7 ± 0.3	20.4
1-Naphthyl, 3-Me	2.0	15.7 ± 0.4	−14.3 ± 0.9	20.9

[a] $\Delta S^{\neq}$ are given in cal mol^{-1} deg^{-1}.

The thermal rearrangement of 5-isoselenocyanato-1,2,3,4,5-pentaphenylcyclopentadiene (**54a**,**b**) is an example of non-degenerate circumambulatory rearrangements in the cyclopentadiene system proceeding as [3,3]-sigmatropic shifts.[146] In solutions, this compound is in equilibrium with isomeric selenocyanate **54c** (in ratios of 3 : 2 and 2 : 3 in $CDCl_3$ and toluene-d_8, respectively). The isothiocyanate derivative of pentaphenylcyclopentadiene does not exhibit fluxional behaviour in solutions (as well as 5-isothiocyanato-1,2,3,4,5-pentamethylcyclopentadiene [147]), whereas the ^{1}H and ^{13}C NMR spectra of an equilibrium mixture of selenium-containing analogues **54a**–**c** are temperature-dependent. This indicates that two different competitive circumambulatory rearrangements proceed simultaneously. The more rapid rearrangement involves 1,2-shifts of the selenocyanate group around the five-membered ring (see Section VI.4.3), whereas the slower rearrangement ($\Delta G^{\neq}_{135}$ = 22 kcal mol^{-1}) is associated with interconversions of isomers as a series of successive [3,3]-sigmatropic shifts involving all carbon atoms of the ring.



b. Phosphorus-centred migrating groups

In the unsubstituted cyclopentadiene ring, migrations of phosphorus-centred groups and hydrogen atoms proceed at similar rates, although in most cases the rates of 1,2-shifts of the P-centred migrating groups are higher than those of the hydrogen atoms.[26,148] The ability of phosphorus-centred groups to migrate was estimated by studying the kinetics of circumambulatory rearrangements of compounds in which non-migrating substituents are bound to all carbon atoms of the cyclopentadiene ring. The energy barriers (E_a) to 1,2-shifts of selected phosphorus-centred groups M in the C_5Me_5M molecules are given below.[149]

M	E_a /kcal mol^{-1}	M	E_a /kcal mol^{-1}
P=C(SiMe$_3$)$_2$	<8	PCl_2	12.0 ± 1.6
PH_2	31.3 ± 1.8	PBr_2	5.2 ± 3.1
PMe_2	23.0 ± 0.5	$P(CN)_2$	16.4 ± 0.3
PMeCl	16.4 ± 1.1	$P(OMe)_2$	21.2 ± 0.4
PBu^{t}Cl	21.3 ± 1.5	$P(SMe)_2$	17.5 ± 1.3
PPh_2	24.3 ± 1.5	PMe_3^+	>35
PF_2	16.7 ± 0.7	$PR_2Cr(CO)_5$	>35

Compounds containing two-coordinate phosphorus atoms exhibit a pronounced fluxional behaviour, whereas compounds containing four-coordinate phosphorus atoms are structurally rigid. The migration ability of the P(III)-centred groups sharply increases with increasing electronegativities of the ligands bound to the phosphorus atom. This fact can be explained taking into account the stabilising interaction between the orbitals of the lone electron pair on the P(III) centre and LUMO of the cyclopentadiene fragment: the electronegative ligands decrease the energy level of the orbital of the lone pair, and the energy gap between the above orbitals is narrowed. According to the results of MNDO calculations,[150] the 1,2-shifts of P(III)-centred migrating groups can proceed either with retention or inversion of configuration at the phosphorus atom depending on the type of the ligands bound to this atom. Thus, electropositive ligands facilitate the inversion of configuration at the migrating centre, whereas electronegative ligands are favourable for the retention of configuration. The tendency to retention of configuration increases in the series P < As < Sb.

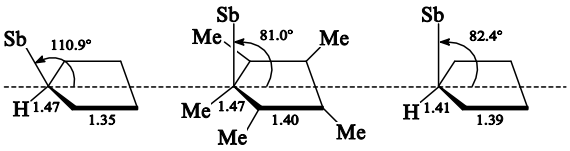
c. Arsenic- and antimony-centred migrating groups

It was found that ligands bound to Group 15 elements have an analogous effect on the ability of these elements to undergo migration in cyclopentadienyl compounds of arsenic and antimony. The 1,2-shifts of the $AsMe_2$ groups in $C_5H_5AsMe_2$ and the shifts of the $AsCl_2$ group in $C_5H_5AsCl_2$ are characterised by the energy barriers E_a = 15.0 kcal mol^{-1} and E_a < 7 kcal mol^{-1}, respectively. There is a pronounced tendency for a substantial increase in the migration ability of the groups formed by heavier elements on going from P- to As- and Sb-centred migrating groups. The activation energies for the circumambulatory rearrangements of dimethyl(1,2,3,4,5-pentamethylcyclopenta-

dienyl)phosphane, -arsane and -stibane are 23.0, 17.1 and 11.3 kcal mol^{-1}, respectively.[26]

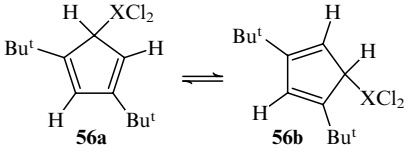
1,2,3,4,5-Pentamethylcyclopentadienyldihaloarsanes C_5Me_5.$AsHal_2$ (Hal = F, Cl, Br, I) are characterised by pronounced structural non-rigidity. Even at −90 °C, the ^{1}H NMR spectra of these compounds have only narrow singlets for the protons of the Me groups. In the ^{13}C NMR spectra, the sp^3- and sp^2-hybridised carbon atoms and the carbon atoms of the Me groups [151] also give common singlets. Moreover, attempts to freeze the migration of the AsHal[N(SiMe$_3$)$_2$] group in monoamide-substituted arsanes on the NMR time scale failed.[152]

High rate constants of 1,2-shifts of migrating heavy Group 15 elements are attributed to the fact that there are favourable conditions for interactions between the π orbitals of the central atom and the cyclopentadienyl fragment in these compounds.[152, 153] A comparison of the structures [153] of three fluxional stibanes **55a**–**c**, for which an increase in non-rigidity would be expected on going from unsubstituted compound **55a** to dichloride **55c**, showed that the mode of binding gradually changes from $\eta^1(\sigma)$ to $\eta^3(\pi)$. In molecule **55c**, the C−C bond lengths in the five-membered ring are equalised, which is indicative of an increase in the ionicity of the compound giving rise to the symmetrical cyclopentadienyl anion. The sequence of structures **55a**–**55c** reflects a part of the pathway of the 1,2-shift of heavy migrating substituents formed by Group 15 elements in cyclopentadiene systems.



55a [$(C_5H_5)_3Sb$] **55b** ($C_5Me_5SbCl_2$) **55c** ($C_5H_5SbCl_2$)

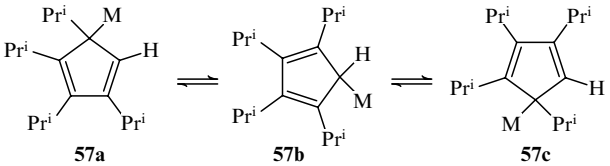
The bulky substituents in the cyclopentadiene ring influence both the relative stabilities of isomers generated in the course of circumambulatory rearrangements and the energy barriers to 1,2-shifts of the migrating groups M = XR_2 (X = P, As, Sb). For example, di-*tert*-butylcyclopentadienyl derivatives of arsanes and stibanes **56** occur primarily as isomers containing the substituent M in the allyl position and two *tert*-butyl groups in vinyl positions. The rearrangements involve shifts of the migrating groups between two vicinal carbon atoms of the ring.[154]



56a **56b**

X = As, Sb.

5-M-(1,2,3,5-Tetraisopropyl)cyclopentadienes **57** (M = PCl_2, PBr_2, $AsCl_2$ and $SbCl_2$) have different dynamics.[155] Analysis of the ^{1}H NMR spectra showed that the rearrangements caused by migrations of the PCl_2 (E_a = 13.1 ± 0.3 kcal mol^{-1}) and PBr_2 (E_a = 13.2 ± 0.3 kcal mol^{-1}) groups proceed as 1,2-shifts of the phosphorus atoms in space limited only by the carbon atoms of the ring adjacent to the CH centre, whereas the C(1) and C(2) atoms remain intact.

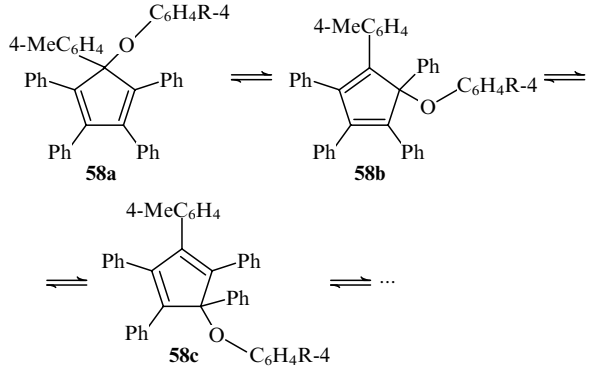


57a **57b** **57c**

4. Migrating substituents formed by Group 16 elements

a. Oxygen-centred migrating groups

1,2-Shifts of oxygen-centred migrating groups around the cyclopentadiene ring proceed too slowly to be detected by dynamic NMR spectroscopy. Investigation of the kinetics of migrations of aryloxy groups is based on measurements of the lifetimes of individual isomers of 1,2,3,4,5-pentaaryl-5-aryloxycyclopentadienes **58**. For this purpose, a weak disturbance of degeneration of the rearrangement is required, which can be achieved, for example, by replacing one of the phenyl groups in the ring by the *p*-tolyl group.[156]



58a **58b** **58c**

The energy barriers (averaged for the 1,2-OAr-shifts **58a** → **58b** and **58b** → **58c**) for the rearrangement of isomers of 5-aryloxy-1,2,3,4-tetraphenyl-5-*p*-tolylcyclopentadiene (180 °C, in diphenyl oxide) are given below.[156]

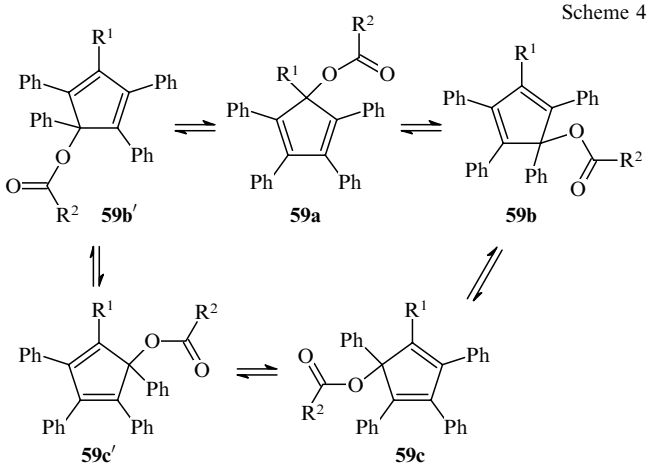
R	NH_2	OMe	Me	H	Cl	NO_2
$\Delta G^{\neq}_{180}$ /kcal mol^{-1}	23.8	24.6	24.8	25.5	26.3	31.6

It can be seen that the presence of electron-releasing substituents in the migrating groups facilitates this rearrangement, whereas electron-withdrawing substituents lead to its deceleration. These results provide evidence supporting polar transition state **10c**, which was proposed for [1,5]-sigmatropic shifts in cyclopentadiene molecules. Semiempirical quantum-chemical calculations [143] of the rearrangement of compound **58** also confirmed that the three-membered ring of the η^2-transition state structure bears a positive charge. Semiempirical calculations showed the occurrence not only of the expected η^2 structure but also of the second η^3-type transition state structure for the symmetry-forbidden 1,3-shift of the aryloxy group; the latter is energetically less favourable than the 1,2-OAr-shift (the energy difference is 8–10 kcal mol^{-1}).

The circumambulatory rearrangements caused by [3,3]-sigmatropic shifts of O-centred migrating groups are also characterised by high-energy barriers, which do not satisfy the conditions of structural non-rigidity.[157, 158] The kinetic parameters for the rearrangements of acyloxycyclopentadienes **59** (R^1 = C_6H_4Me-4) were determined from the rate at which the equilibrium between isomers **59a**, **59b** and **59c** (which were prepared by treatment of a mixture of isomers of bromo-*p*-tolyltetraphenylcyclopentadiene with silver carbonates) was established in solution (Scheme 4). These parameters are given in Table 7.

The equilibrium ratios between isomers **59** correspond to the statistical distribution **59a** : **59b** : **59c** = 1 : 2 : 2. The rearrangement rate is concentration-independent. No paramagnetic intermediate species were detected in the temperature range of 25–160 °C, which is indicative of the concerted intramolecular mechanism of the reaction. The fact that the rearrangement proceeds *via* [3,3]-sigmatropic shifts, *i.e.*, as the sequence **59a** ⇌ **59b** ⇌ **59c** ⇌ **59c′** ⇌ **59b′** ⇌ **59a** (see Scheme 4), rather than *via* the alternative [1,5]-sigmatropic shift as the sequence **59a** ⇌ **59c′** ⇌ **59b** ⇌ **59b′** ⇌ **59c** ⇌ **59a** was proved in the study of the time dependence of the ^{1}H NMR spectra of 5-ben-

Scheme 4



zyl-1,2,3,4-tetraphenyl-5-trifluoroacetoxycyclopentadiene **59a** (R^1 = Bn, R^2 = CF_3) (Fig. 7).

Due to the presence of the stereogenic C_{sp^3} centre in the ring of isomers **59c**,**c**′ (R^1 = Bn, R^2 = CF_3), the energetically favourable reaction pathway can be readily identified based on ^{1}H NMR spectra, which show diastereotopic splitting of the signals for the methylene protons of the benzyl substituent R^1 characteristic of the prochiral methylene group (AB spectrum, δ 2.88 and 3.97, ^2J = 14.5 Hz). In the ^{1}H NMR spectrum of isomers **59b**,**b**′ (R^1 = Bn, R^2 = CF_3) in which the stereogenic C_{sp^3} centre is most far removed from the prochiral group, this splitting is absent. The assignment of the singlets for the methylene protons at δ 3.48 and 3.62 to isomers **59a** (symmetry C_s) and **59b**, respectively, was made after their separation and was also based on the X-ray diffraction data for compound **59a** (R^1 = Bn, R^2 = CF_3).[157] In the course of storage of a solution of **59a** at 80 °C, a singlet (δ 3.62) assigned to the methylene protons of isomer **59b** appeared and gradually grew in its ^{1}H NMR spectrum. Further heating led to slow accumulation of isomer **59c** in the reaction mixture, which was detected from the appearance of the AB quartet of the methylene group. The equilibrium between interconvertible isomers of **59** (**59a** : **59b** : **59c** = 65 : 22 : 13) was established upon storage of a solution in *o*-dichlorobenzene at 80 °C for 2 h. This spectral behaviour is unambiguously indicative of a sequence of interconversions of isomers **59** corresponding to the mechanism of [3,3]-sigmatropic shifts (see Scheme 4). The activation free energies ($\Delta G^{\neq}_{80}$) of interconversions of different isomers **59** (R^1 = Bn, R^2 = CF_3) calculated from the time dependence of the intensities of the signals in the ^{1}H NMR spectra are in the range of 26.5 – 27.2 kcal mol^{-1}. The difference in the mechanisms of migrations of the aryloxy and acyloxy groups around the cyclopentadiene ring is manifested also in the difference in the influence of the substituents in the migrating group on the energy barrier for the rearrangement. As can be seen from Table 7, the

Table 7. Equilibrium ratios between the isomers at 130 °C, rate constants and activation parameters for the rearrangements of compounds **59** (R^1 = C_6H_4Me-4) in *o*-dichlorobenzene.[157]

R^2 in compound **59**	**59a** : **59b** : **59c**	k_{130} /s^{-1}	$\Delta H^{\neq}$ (see [a])	$\Delta S^{\neq}$ (see [b])	$\Delta G^{\neq}_{25}$ (see [a])
CF_3	85 : 10 : 5	1.0×10^{-2}	24.0 ± 0.5	−3.6 ± 0.7	26.6
CCl_3	85 : 5 : 10	1.7×10^{-3}	25.9 ± 0.6	−7.4 ± 0.8	28.1
$CHCl_2$	75 : 15 : 10	1.9×10^{-4}	28.7 ± 0.5	−5.0 ± 0.7	30.2
CH_2Cl	60 : 20 : 20	4.4×10^{-6}	31.1 ± 0.7	−6.6 ± 0.9	33.0
CH_3	55 : 30 : 15	5.9×10^{-7}	33.6±0.6	−4.1 ± 0.8	34.8

[a] $\Delta H^{\neq}$ and $\Delta G^{\neq}_{25}$ are given in kcal mol^{-1}.
[b] $\Delta S^{\neq}$ are given in cal mol^{-1} deg^{-1}.

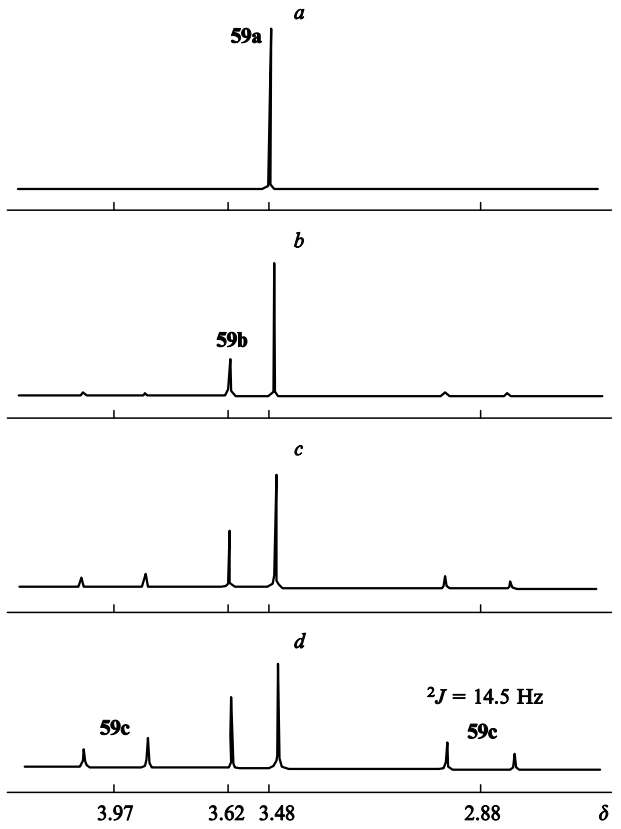


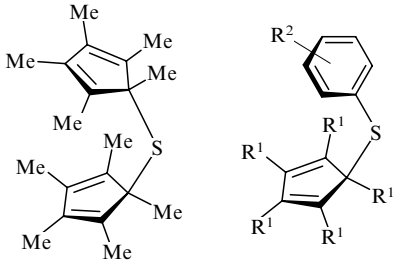
Figure 7. Time dependence of the ^{1}H NMR spectra of compounds **59** (R^1 = Bn, R^2 = CF_3) in *o*-dichlorobenzene in the region of signals for the protons of the benzyl group (δ 2.50 – 4.30) at 25 °C (*a*) and after heating at 80 °C for 0.5 (*b*), 1 (*c*) and 2 h (*d*).[157]

rearrangements of compounds **59**, unlike the analogous rearrangements of aryloxypentaarylcyclopentadienes **58**, are accelerated upon the introduction of electron-withdrawing substituents R^2 into the migrating group.

Unlike the [3,3]-sigmatropic rearrangements of allyl acetates catalysed by mercury or palladium salts,[159] the circumambulatory rearrangements of their oxygen analogues **59** are rather weakly catalysed [$\Delta(\Delta G^{\neq}_{80})$ = 1.3 – 2.9 kcal mol^{-1}] by $(CF_3CO_2)_2Hg$ and $[PdCl_2(PhCN)_2]$. This can be attributed to steric hindrance to the formation of complexes of these salts with oxygen centres in tetra- and pentaaryl-substituted compounds **59**.

b. Sulfur-centred migrating groups

1,2-Shifts. The rearrangement of bis(pentamethylcyclopentadienyl) sulfide **60** was not observed on the NMR time scale.[160] However, the replacement of one pentamethylcyclopentadienyl fragment in molecule **60** by the aryl group gives rise to fluxional compounds **61a**; the energy barriers to migration of the arylthio



61: R^1 = Me (**a**), CO_2Me (**b**) (for notations of R^2, see Table 8).

group around the cyclopentadiene ring are in the range $\Delta G^{\neq} = 22-24.5$ kcal mol^{-1}.[161, 162]

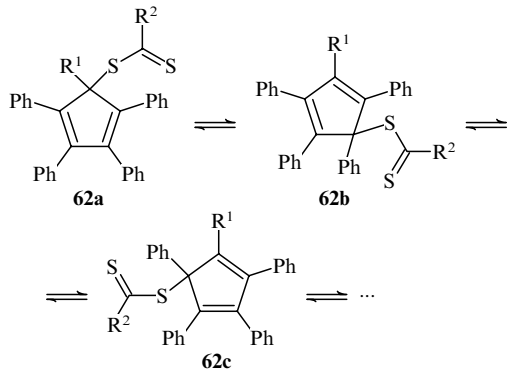
The replacement of the methyl groups in the cyclopentadienyl fragment of compound **61a** by the electron-withdrawing methoxycarbonyl groups leads to a substantial acceleration of the rearrangement.[161, 163–166] As can be seen from Table 8, the energy barriers for degenerate rearrangements of compounds **61b** are 5–8 kcal mol^{-1} lower than the corresponding barriers for sulfides **61a** containing the same migrating groups. This observation and the fact that the electron-releasing substituents in the aryl rings of the migrating groups promote the rearrangement are consistent with polar transition state structure **10c** for 1,2-shifts in the cyclopentadiene system. Analysis of line shapes in the temperature-dependent ^{1}H and ^{13}C NMR spectra of compounds **61a**,**b** and semiempirical (MINDO/3 and MNDO) calculations of the pathways of this rearrangement[167] demonstrated that 1,2-shifts are preferable for migrations of the arylthio groups.

Table 8. Energy barriers ($\Delta G^{\neq}_{25}$) to 1,2-shifts of the arylthio groups in the cyclopentadiene ring of compounds **61**.

Structure	R^2 in compound **61**	Solvent	$\Delta G^{\neq}_{25}$ /kcal mol^{-1}	Ref.
61a	4-OMe	*o*-dichlorobenzene	24.5	161, 163
61a	H	"	23.0	161, 163
61a	3-NO_2	"	22.1	161, 163
61a	2,3,4,5,6-F_5	DMSO-d_6	23.2	162
61b	4-OMe	chlorobenzene	16.1	161, 163
61b	H	"	17.4	161, 163
61b	3-NO_2	"	17.6	161, 163
61b	2-NO_2	"	18.5	161, 163
61b	4-NO_2	"	17.8	161, 163
61b	2,4-$(NO_2)_2$	"	19.0	161, 163
61b	4-CF_3	"	20.7	161, 163

An interesting feature of compounds **61** is their half-sandwich structures, *i.e.*, the *s-cis* conformation with respect to the $C_{Cp}-S$ bond. This conformation is favourable for sulfides **60**[160] and, according to the results of X-ray diffraction studies, for tetra- and pentamethoxycarbonyl derivatives **61b**.[164, 165] For the migration of the phenylthio group, not only the usual η^2-type transition state structure **6** for the 1,2-shift but also the alternative η^3-type transition state structure **7** were found to be possible. The latter structure is energetically less favourable (by 10 kcal mol^{-1}) than transition state structure **6** for the 1,2-shift. The opposite situation is observed for the migration of the disulfide (SSR) group. In the latter case, the transition state corresponding to the 1,3-shift is energetically more favourable (by 7 kcal mol^{-1}). This can be attributed to orbital interactions between the migrating group and the cyclic moiety of the molecule.[167, 168] Investigation of the rearrangement of bis(pentamethoxycarbonylcyclopentadienyl) disulfide in solution by ^{1}H and ^{13}C NMR spectroscopy demonstrated that it is characterised by a rather low energy barrier (15–17 kcal mol^{-1}).[164] However, no evidence in favour of the mechanisms of either 1,2- or 1,3-shifts for the migration of the RSS group was reported.

[3,3]-Sigmatropic shifts. To decide between the mechanisms of 1,2-shift ([1,5]-sigmatropic shift) and [3,3]-sigmatropic shift as the migration pathway of the dithioacyl groups around the cyclopentadiene ring, the prochiral group was introduced into the ring. The same approach was applied to acyloxycyclopentadienes (see Section VI.4.a). The circumambulatory rearrangement of *S*-(5-benzyl-1,2,3,4-tetraphenylcyclopentadienyl) *O*-ethyl dithiocarbonate **62a** ($R^1 = CH_2Ph$, $R^2 = OEt$) gave rise to two isomers **62b**,**c**. Taking into account that diastereotopic splitting of the peaks for the methylene protons in the ^{1}H NMR spectrum of isomer **62b** should be larger than that in the spectrum of isomer **62c** because the prochiral and stereogenic centres in molecule **62b** are in close proximity, the following sequence of rearrangement steps was revealed:[169]



$R^1 = CH_2Ph$, Ph, C_6H_4Me-4; $R^2 = OEt$, Ph.

In nitrobenzene-d_5, the equilibrium was established at 60 °C within 25 min; the isomer ratio **62a** : **62b** : **62c** = 45 : 25 : 30. The kinetic parameters for individual steps of the migration of the *O*-ethyl dithiocarbonate group in isomers **62** ($R^1 = CH_2Ph$, $R^2 = OEt$) are given in Table 9. The average rate constants and activation parameters for the slower migration of the dithiobenzoate group in solution of compound **62** ($R^1 = C_6H_4Me$-4, $R^2 = Ph$) in deuterionitrobenzene are as follows: $k_{130} = 1.8 \times 10^{-4}$ s^{-1}, $\Delta G^{\neq}_{130} = 30.7$ kcal mol^{-1}, $\Delta H^{\neq} = 28.9 \pm 0.7$ kcal mol^{-1}, $\Delta S^{\neq} = -4.5 \pm 1.0$ cal mol^{-1} deg^{-1}.

Table 9. Rate constants and activation free energies for the [3,3]-sigmatropic shifts of isomers of the *O*-ethyl dithiocarbonate group in isomers **62** ($R^1 = CH_2Ph$, $R^2 = OEt$) in nitrobenzene-d_5.[169]

Rearrangement	k_{60} /s^{-1}	$\Delta G^{\neq}_{60}$ /kcal mol^{-1}
62a → 62b	7.5	24.3
62b → 62a	13.2	23.9
62b → 62c	8.9	24.2
62c → 62b	7.2	24.3

It can be concluded that 1,3- or 3,3-shifts, but not 1,2-shifts characteristic of the migration of the arylthio groups (see Section VI.4.b), are energetically favourable for the migration of the dithioacyl group around the cyclopentadiene ring. Although it is necessary to introduce one labelled sulfur atom to make an unambiguous choice between the mechanisms involving 1,3- and 3,3-shifts, the latter mechanism seems to be most probable, as evidenced by the results of theoretical simulation.[170]

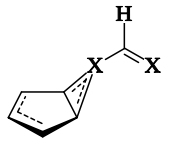
The results of calculations of the relative energies of transition state and intermediate structures for different pathways of migrations of heteroallyl groups in the cyclopentadiene ring are presented in Table 10.

Table 10. Relative (compared to the ground state structures) energies (ΔE) of the transition state and intermediate structures in different pathways of circumambulatory rearrangements of heteroallylcyclopentadienes calculated by the MINDO/3 method.[170]

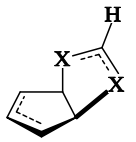
X	ΔE /kcal mol^{-1}				
	63a	**63b**	**63c**	**63d**	**63e**
NH	39.3	72.7	~48.5 [a]	46.4	40.1
O	44.1	85.8	~47.9 [a]	43.6	37.0
S	19.3	37.9	17.5	see [b]	1.9

[a] A saddle point was not found.

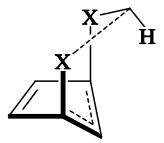
[b] A biradical intermediate was not detected.



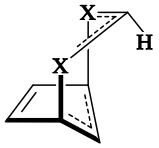
63a (TS, 1,2-shift)



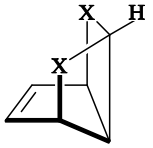
63b (TS, 2,3-shift)



63c (TS, 3,3-shift)



63d (intermediate, 3,3-shift)

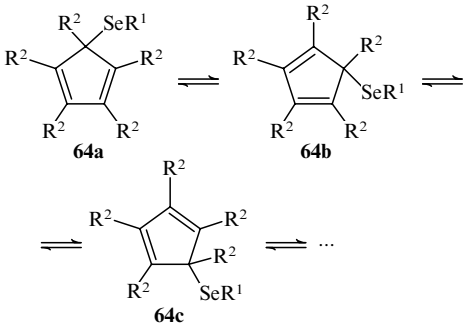


63e (intermediate)

In calculations (see Table 10), the effects of the substituents in the cyclopentadiene ring and the migrating groups in compounds **53**, **59** and **62** were ignored. Nevertheless, the results of these calculations indicate with a fair degree of consistency that the [2,3]-sigmatropic shifts (structure **63b**) of the heteroallyl groups in the cyclopentadiene ring are highly improbable. As in the case of hetero-Cope rearrangements in a series of cyclopropene derivatives (see Section IV.2), the reaction pathways assuming [3,3]-sigmatropic shifts involve the transition through symmetrical biradical structures (**63d**), which can undergo isomerisation into tricyclic structures (**63e**). The energy profile of these rearrangements is analogous to that shown in Fig. 2.

c. Selenium- and tellurium-centred migrating groups

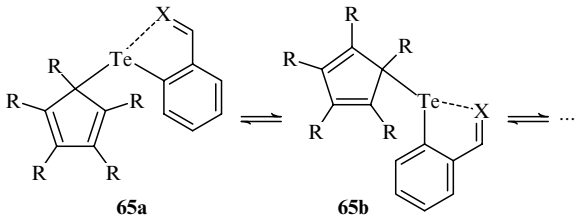
As mentioned in Section VI.3.a, 1,2,3,4,5-pentaphenyl-5-selenocyanatocyclopentadiene (**54c**) in solution undergoes two interrelated rearrangements, *viz*., a non-degenerate rearrangement to form isoselenocyanate isomer **54a** through [3,3]-sigmatropic shifts and a rapid degenerate circumambulatory rearrangement through 1,2-shifts of the selenocyanate group around the cyclopentadiene ring. The kinetic and activation parameters for this rearrangement and another degenerate circumambulatory rearrangement of organylselenocyclopentadienes **64** *via* 1,2-shifts of Se-centred migrating groups are given in Table 11. Migrations of selenium-centred groups around substituted cyclopentadiene rings proceed more rapidly [$\Delta(\Delta G^{\neq}) = 3-4$ kcal mol^{-1}] than migrations of analogous sulfur-centred groups (see Table 8). Both electron-releasing (R^1) and electron-withdrawing (R^2) substituents facilitate acceleration of the rearrangement.



64a ⇌ **64b** ⇌ **64c** ⇌ ...

Recently, bis(pentamethylcyclopentadienyl) selenide and bis-(pentamethylcyclopentadienyl) polyselenides $Se_n(C_5Me_5)_2$ ($n = 2-4$) have been synthesised.[172] Measurements of their high-temperature ^{1}H and ^{77}Se NMR spectra are made difficult because of thermal instability of these compounds. At room temperature, these polyselenides are structurally rigid on the NMR time scale.

High thermal sensitivity is also typical of substituted tellurocyclopentadienes. A few known representatives of this class of compounds contain intramolecular Te ← O or Te ← N coordination bonds, which provide substantial kinetic and thermodynamic stabilising effects in a series of organic compounds of low-oxidation-state tellurium.[173–175] The fluxional behaviour of several tellurocyclopentadienes **65** was studied. Based on analysis of line shapes in the ^{1}H NMR and ^{1}H 2D EXSY NMR spectra recorded for solutions of compounds **65** in deuteriochloroform, their dynamic behaviour can unambiguously be assigned to rapid intramolecular rearrangements involving 1,2-shifts of the aryltellurenyl groups around the cyclopentadiene ring.[166,176] The migration proceeds rapidly on the ^{1}H and ^{13}C NMR time scale even at −90 °C, and the protons of all five methoxycarbonyl groups are manifested as the only weakly broadened peak.



65a **65b**

R = CO_2Me.

X in compound **65**	k_{25} /s^{-1}	$\Delta H^{\neq}$ /kcal mol^{-1}	$\Delta S^{\neq}$ /cal mol^{-1} deg^{-1}	$\Delta G^{\neq}_{25}$ /kcal mol^{-1}
O	890	10.1 ± 0.7	−11.1 ± 1.0	13.4
NPh	–	–	–	7.0 ± 2.0

Therefore, the migration ability of substituents formed by Group 16 elements in the cyclopentadiene system increases in the series O < S < Se < Te.

5. Migrating substituents formed by Group 17 elements

The migration of the halogen atoms around the five-membered ring cannot proceed by the ionisation – recombination mechanism because heterolysis of the $C_{Cp}-Hal$ bond would give anti-aromatic cyclopentadienyl cations. Intramolecular migrations of the chlorine and bromine atoms in a series of 5-alkyl-5-chloro(bromo)-1,2,3,4-tetramethoxycarbonylcyclopentadienes[177–179] and 5-bromo-1,2,3,4,5-pentaphenylcyclopentadienes[178] proceed *via* successive 1,2-halogen shifts around the cyclopentadiene ring.

Isomers **66a**–**c** (Hal = Cl) were isolated from a mixture prepared by the reaction of 5-alkyl-1,2,3,4-tetramethoxycarbonylcyclopentadienes with *N*-chlorosuccinimide in the presence of catalytic amounts of benzoyl peroxide. Upon storage of solutions of individual isomers **66a**,**b** in dichlorobenzene, the equilibrium **66a** ⇌ **66b** ⇌ **66c** is established, which requires the energy barriers in the range of 25.7–27.3 kcal mol^{-1} to be overcome

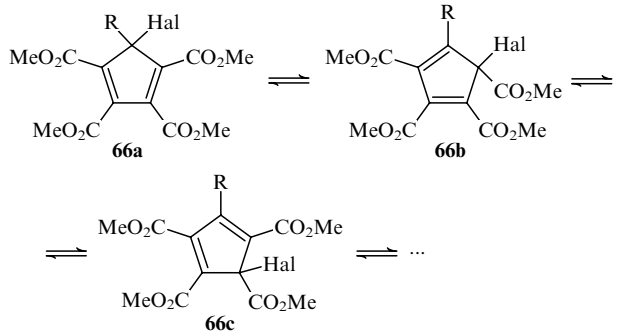
Table 11. Kinetic and activation parameters for the circumambulatory rearrangement **64a** ⇌ **64b** ⇌ **64c** ⇌ ...

R^1 in compound **64**	R^2 in compound **64**	Solvent	k_{25} /s^{-1}	$\Delta H^{\neq}$ /kcal mol^{-1}	$\Delta S^{\neq}$ /cal mol^{-1} deg^{-1}	$\Delta G^{\neq}_{25}$ /kcal mol^{-1}	Ref.
CN	Ph	toluene-d_8	3.4	14.2 ± 0.3	−8.4 ± 0.4	16.7	146
CF_3	CO_2Me	*o*-dichlorobenzene	1.8	11.1 ± 0.8	−20.1 ± 1.0	17.1	164
C_6H_4OMe-4	Me	"	1.5×10^{-1}	15.3 ± 0.5	−10.8 ± 0.8	18.5	168
Ph	Me	"	4.2×10^{-2}	13.9 ± 0.7	−18.4 ± 0.9	19.4	168
C_6F_5	Me	DMSO-d_6	1.1×10^{-2}	18.9 ± 0.5	−3.6 ± 0.7	20.0	171

Table 12. Equilibrium concentrations of isomers **66a** and **66b** (Hal = Cl) and the kinetic parameters of their interconversions in *o*-dichlorobenzene at 80 °C.[179]

R in compound **66**	**66a** : **66b**	k_{25} /s^{-1}		$\Delta H^{\neq}$ /kcal mol^{-1}		$\Delta S^{\neq}$ /cal mol^{-1} deg^{-1}		$\Delta G^{\neq}_{25}$ /kcal mol^{-1}	
		a → **b**	**b** → **a**	**a** → **b**	**b** → **a**	**a** → **b**	**b** → **a**	**a** → **b**	**b** → **a**
Me	11 : 89	4.3×10^{-7}	5.6×10^{-4}	25.1 ± 0.2	26.1 ± 0.2	-3.5 ± 0.3	-5.7 ± 0.3	26.1	27.3
Pr^{i}	35 : 65	5.0×10^{-7}	2.6×10^{-7}	23.9 ± 0.4	24.1 ± 0.3	-6.9 ± 0.5	-7.6 ± 0.5	26.0	26.4
CH_2Ph	25 : 75	9.1×10^{-7}	3.2×10^{-7}	24.1 ± 0.3	24.3 ± 0.4	-5.5 ± 0.4	-6.6 ± 0.6	25.7	26.3

(Table 12). Although isomers **66c** are present in equilibrium mixtures in benzene in concentrations comparable to those of compounds **66a**,**b**, they were not detected by NMR spectroscopy in *o*-dichlorobenzene.



R = Me, Pr^{i}, Bn; Hal = Cl, Br.

In molecule **66** (Hal = Br), 1,2-migrations of the bromine atom proceed more rapidly. The energy barriers for these rearrangements are in the range of 16.2–23.0 kcal mol^{-1}. In 5-bromo-1,2,3,4,5-pentaphenylcyclopentadiene, the energy barrier to intramolecular 1,2-bromine shifts is 16.7 kcal mol^{-1} (in 1,1,2,2-tetrachloroethane). The stable pentaphenylcyclopentadienyl radical, which could exist as an intermediate in the rearrangement proceeding by a homolytic mechanism, was not detected.[178] As in the case of migration of the thioaryl group (see Section VI.4.b), semiempirical quantum-chemical (AM1) calculations demonstrated that not only the low-energy reaction pathway corresponding to 1,2-halogen shifts in the ring but also alternative reaction pathways involving 1,3-shifts of migrating groups can take place. However, the transition state structures corresponding to these mechanisms are energetically much less favourable than the transition state structures corresponding to the mechanism of 1,2-shifts (the energy difference is 35–40 kcal mol^{-1}).

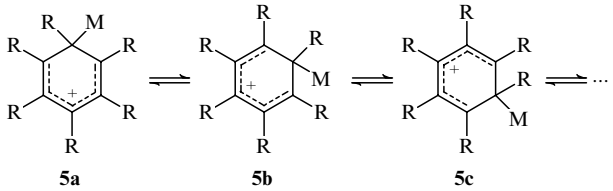
The rapid migration of the iodine atom around the cyclopentadiene ring proceeding, apparently, *via* 1,2-shifts was also observed.[180] It was found that in the isomers of deuterated iodocyclopentadiene, which was prepared in an ether–benzene mixture (2 : 1) at −15 °C, the deuterium atoms are distributed over all positions of the cyclopentadiene ring. This behaviour of the label indicates that the iodine atom rapidly migrates around the ring. This conclusion was supported by the data on magnetisation transfer at ∼ 20 °C,[180] which demonstrated that substantial deceleration of the rearrangement was achieved only upon a decrease in the temperature of a solution of deuterated CpI to −40 °C.

VII. Circumambulatory rearrangements in a six-membered ring

1. Rearrangements *via* 1,2-shifts

Circumambulatory rearrangements in six-membered rings in cationic systems proceed *via* 1,2-shifts ($\eta^1-\eta^2$-shifts) or $\eta^2-\eta^3$-shifts as well as *via* σ,π-shifts (see Sections III.2 and III.6). Rearrangements of the first type in a series of derivatives of the benzenium cation are among the first cationic rearrangements proceeding on the NMR time scale, which have received the most study. These rearrangements were comprehensively surveyed in the reviews.[17, 53, 181] In the present review, we briefly consider only selected, most important, results.

The mechanism of rearrangements of cations **5** involving sequences of 1,2-shifts of the migrating group M around the six-membered ring was confirmed by analysis of the line shapes in temperature-dependent ^{1}H and ^{13}C NMR spectra, spin-echo and magnetisation-transfer experiments and data from 2D NMR spectroscopy. The elucidation of the nature of the fluxional behaviour of heptamethylbenzenium cation **5a** (M = R = Me) as a result of a series of successive 1,2-shifts of the methyl group around the ring demonstrated that 2D NMR spectroscopy is a method of choice for elucidating permutation mechanisms of exchange reactions.[182]



The migration ability of various groups M in hexamethylbenzenium cations **5** (R = Me) decreases in the following series:[181] Br > H ⩾ CH_2Ph > NO_2 > Cl > SO_3H > Et > Ph > Me > CH_2Cl > $CHCl_2$.

The energy barriers to migrations of some of the above-mentioned groups in compounds **5** are given in Table 13.

Table 13. Energy barriers ($\Delta G^{\neq}_{25}$) for circumambulatory rearrangements in hexamethylbenzenium cations **5** (R = Me) *via* 1,2-shifts of the migrating groups M.[53, 181]

M in cation **5**	Solvent	$\Delta G^{\neq}_{25}$ /kcal mol^{-1}
Me	HSO_3Cl	17.9
Et	HSO_3Cl	16.0
SO_3H	HSO_3F	15.6
Cl	HSO_3F	14.7
OMe	HSO_3F	> 11.7
NO_2	$HSO_3F-SO_2Cl_2$	12.2
H	HSO_3Cl	10.3
Br	HSO_3F-SO_2ClF	9.2

To correlate the migration ability of various groups in carbocations, useful semiempirical equations were deduced.[53, 181] The main equation (1)

$$\Delta G^{\neq} = a + bE_1 + cE_2 \quad (1)$$

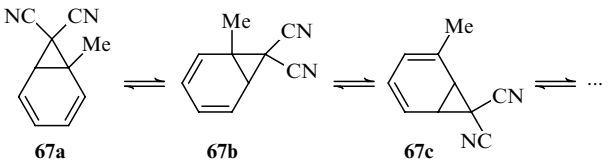
includes the following two parameters: E_1 is the energy required for the cleavage of the C(1)–M bond and deformation of the M–C(1)–C(2) bond angle and E_2 is the energy produced upon the formation of a new M–C(2) bond due to the shift of the migrating group M to the adjacent C(2) cationic centre. One approach to estimating the parameters E_1 and E_2 is to approx-

imate these parameters by the energies of the C–M bonds in the H_3C-M molecule and by the affinity for the proton or methyl cation, respectively.

It was found that circumambulatory rearrangements of some cations **5** in the solid state are as rapid as in solutions. For example, the energy barrier for the rearrangement of heptamethylbenzenium cation **5** (M = R = Me, $SbCl_6^-$ as the anion) in the crystal is 17.3 kcal mol^{-1} (see Ref. 183), which is 0.6 kcal mol^{-1} lower than that for its solution in dichloromethane. The energy barriers for the rearrangement of cation **5** in the solid state are very sensitive to the unit cell parameters. For example, the rearrangement of compound **5** (M = Ph, R = Me), which crystallises in lower-symmetry crystal lattice compared to its analogue with M = R = Me, is nonobservable in the solid state even at high temperature.

2. $\eta^2-\eta^3$-Rearrangements

Migrations of the cyclopropane fragment around the six-membered ring were found by Berson,[184] who attributed the exchange between the deuterium positions in 2,6-dideuterio-3,7,7-trimethylcycloheptatriene at high temperatures (300 °C) to the intermediate formation of norcaradiene derivatives, which undergo [1,5]-sigmatropic ($\eta^2-\eta^3$) rearrangements. Migration of this type was directly observed at 77 °C in the study of the rearrangement of the corresponding dicyano derivative for which norcaradiene valence tautomer **67** is energetically more favourable than the 7,7-dicyanocycloheptatriene form.[185, 186]



67a **67b** **67c**

Generally, such rearrangements are characterised by higher energy barriers compared to those corresponding to conditions of structural non-rigidity.[17, 69, 186] It was found that the migration of the methylene group around the aromatic ring is accompanied by the inversion of configuration of the migrating carbon atom[187] (contrary to the Woodward–Hoffmann rules). This result was explained based on the results of density functional theory calculations (UB3LYP/3-21G and UB3LYP/6-31G* + ZPE) for the pathways of the rearrangement of 7-cyano-7-methylnorcaradiene.[188] The transition state structures for both pathways, *viz*., both with inversion and retention of stereochemical configuration of the migrating centre, were localised, the first structure being energetically more favourable (by ~1 kcal mol^{-1}). This difference corresponds to the 97 : 3 ratio between the processes occurring with inversion and retention of configuration, which is consistent with the experimental ratio of 92 : 8.

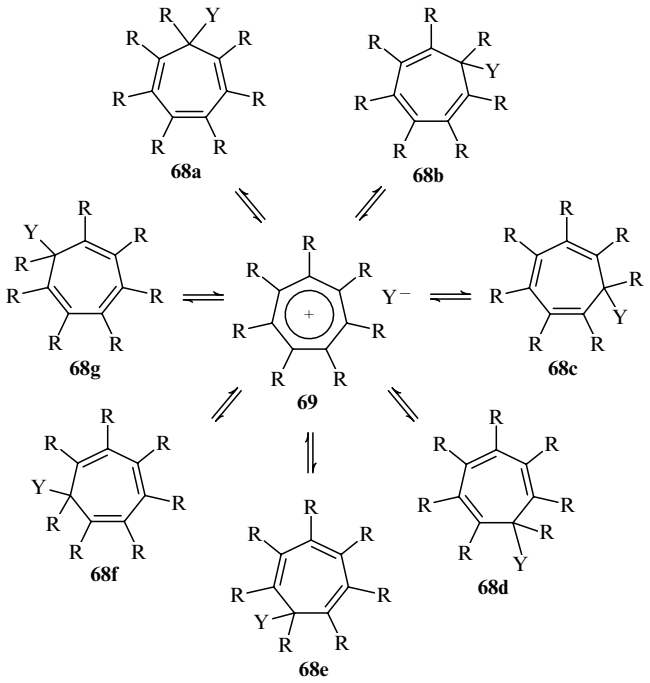
VIII. Circumambulatory rearrangements in a seven-membered ring

1. Rearrangements proceeding by the ionisation–recombination mechanism

Heterolysis of the C–M bond in 7-substituted cycloheptatriene **3** afforded the aromatic tropylium cation. This corresponds to rearrangements of compounds in which migrating groups M possess fairly high electron affinity, *i.e*., form stable anions in the ionisation–recombination pathway. Hence, it is not surprising that circumambulatory rearrangements[37, 189] of isothiocyanates and isoselenocyanates **68a–g** derived from cycloheptatriene proceed as random rearrangements involving preliminary ionisation of C–N bonds. The kinetic parameters of these rearrangements, which were calculated based on analysis of line shapes in temperature-dependent ^{1}H NMR spectra, are given in Table 14.

Table 14. Activation free energies for circumambulatory rearrangements of cycloheptatrienes **68**.

X in compound **68**	R in compound **68**	Solvent	$\Delta G_{25}^{\neq}$ /kcal mol^{-1}	Ref.
O	Ph	nitrobenzene-d_5	> 25	189
S	H	$CDCl_3-CD_3CN$ (1 : 3)	12.1	37
S	H	$CDCl_3$	14.3	37
S	H	CS_2-CDCl_3 (10 : 1)	14.8	37
S	Ph	nitrobenzene-d_5	24.3	189
Se	Ph	"	22.4	189



68a **68b** **68g** **68c** **69** **68f** **68d** **68e**

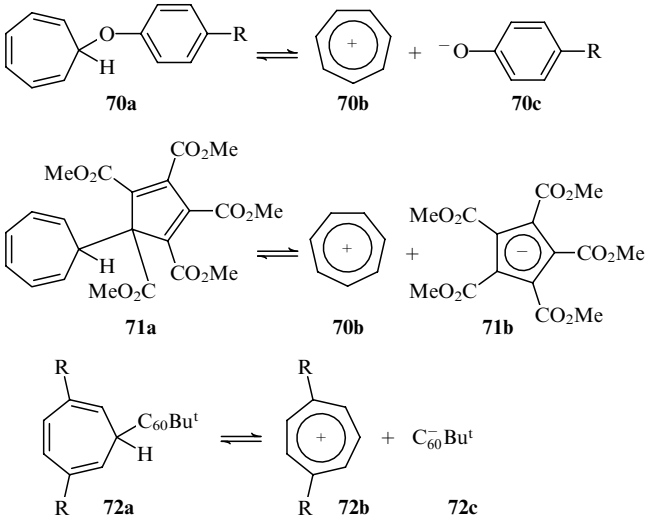
R = H, Ph; Y = NCX (X = S, Se).

An increase in the rate of the rearrangement of compound **68** (X = S, R = H) with increasing polarity of the solvent is indicative of the occurrence of the pre-equilibrium ionisation step. The migration of the isothiocyanate group in heptaphenylcycloheptatriene proceeds much more slowly than the analogous rearrangement in isothiocyanatocycloheptatriene, which may be associated with steric hindrance produced by the bulky phenyl groups in the recombination step. The energy barriers to hindered rotation of the phenyl groups in molecule **68** (R = Ph, X = O, S, Se) were estimated at ~16 kcal mol^{-1}.[189] The migration rates of the isothiocyanate and isoselenocyanate groups are independent of the concentration of the solution, which indicates that this rearrangement proceeds through the intermediate formation of tight ion pairs **69**.

Thermally induced heterolysis of the C–N bond in *N*-(cyclohepta-1,3,5-trien-7-yl)phthalimide also led to the circumambulatory rearrangement of the phthalimide group, which migrates around the cycloheptatriene ring through the intermediate formation of the tropylium cation–phthalimide anion tight ion pair ($C_6D_5NO_2$, $\Delta G_{180}^{\neq}$ = 24.8 kcal mol^{-1}).[190]

Examples of heterolytic dissociation of the $C_{tropyl}-O$, $C_{tropyl}-C$ and $C_{tropyl}-N$ bonds in compounds which are potentially prone to circumambulatory random rearrangements were offered.[191–197] In these studies, the possibility of these rearrangements occurring was not discussed, but the equilibria **70a** ⇌ **70b** + **70c**,[191] **71a** ⇌ **70b** + **71b** (see Ref. 192) and **72a** ⇌ **72b** + **72c** (see Ref. 193) were examined. The heats of

heterolysis (ΔH°) of 7-aryloxycycloheptatrienes **70a** depend substantially on the nature of substituents in the aryl ring. For example, the heat of heterolysis $\Delta H^{\circ} = 10.6$ kcal mol^{-1} for compound **70a** (R = 4-NO_2) is almost 10 kcal mol^{-1} lower than that for its methoxy-substituted analogue (R = 4-OMe). This difference is indicative of the importance of delocalisation of the negative charge in the anion favourable for ionisation of compounds **70a**. According to the dynamic ^{13}C NMR spectroscopic data, the activation free energies of heterolysis of fullerene derivatives **72a**, which dissociate into ions in dimethyl sulfoxide or the DMSO – SO_2 system, are rather low (7.7 – 9.3 kcal mol^{-1}).

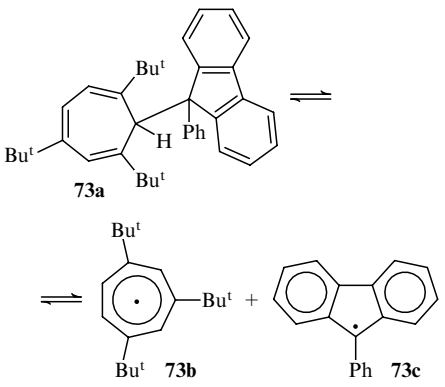


R = H, Bu^t, cyclo-C_6H_{11}.

Detropylation of *N*,*N*-dimethyltropylamine and *N*-tropylacetamide[198] and the dynamic equilibrium between 1-, 2- and 3-chloro-substituted 7-chlorocycloheptatrienes[199] are other examples of equilibria of this type involving, apparently, steps of ion recombination at an arbitrary position of the ring.

2. Homolytic reaction pathway

Thermal dissociation of C – C σ bonds in hydrocarbon molecules generally involves their homolytic cleavage. For instance, sterically overcrowded 1,3,5-tri-*tert*-butyl-7-(9-fluorenyl-9-phenyl)-cyclohepta-1,3,5-triene (**73a**) dissociates upon heating in *m*-xylene or cyclohexane to form the 1,3,5-tri-*tert*-butyltropyl (**73b**) and 9-phenylfluorenyl (**73c**) radicals ($\Delta H^{\neq} = 23$ kcal mol^{-1}, $\Delta S^{\neq} = 22.0$ cal mol^{-1} deg^{-1})[200] detected by EPR spectroscopy. Evidently, the recombination step proceeds randomly. This reaction is a first example of cycloheptatriene rearrangements proceeding by a radical mechanism.

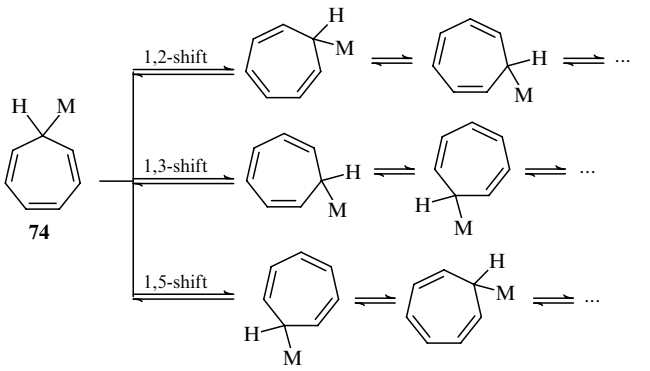


The formation of radical pairs whose subsequent recombination leads to shifts of the substituents in the ring can also be initiated photochemically, like in the rearrangements of 1-indenylcyclopropene derivatives.[95]

3. Rearrangements *via* 1,2(2,3)-shifts

As demonstrated in Section III.2, 1,2-shifts ([1,7]-sigmatropic shifts) of the dialkylboryl group lead to the rapid rearrangement of [1-4-η^4-*exo*-7-(dipropylboryl)cycloheptatriene]tricarbonyliron (**11**).[50] The question arises as to whether rearrangements of this type can proceed without coordination of the cycloheptatriene ring, for example, in compound **74** (M = BPr_2).[62] Studies of 7-dipropylborylcycloheptatriene by ^{1}H 2D EXSY NMR spectroscopy demonstrated that in solutions, an equilibrium between this compound and its 7-*exo*-(dipropylboryl)norcaradiene isomer is rapidly established, and migration of the dipropylboryl group occurs, the latter process being observed at temperatures higher than 293 K. According to the results of density functional theory calculations (B3LYP/6-311 + G*//B3LYP/6-31G*) for a model system, the energetically most favourable migration mechanism involves 1,2-shifts of the dipropylboryl group in the cycloheptatriene ring ($\Delta H^{\neq} = 18.4$ kcal mol^{-1}). The calculated energy barriers for the possible 1,5- and 1,3-shifts (Scheme 5) are 27.4 and 25.7 kcal mol^{-1}, respectively.

Scheme 5



The fact that the migration of the dialkylboryl group around the cycloheptatriene ring proceeds primarily *via* 1,2-shifts was attributed[62] to the characteristic features of the electronic structure of the transition state, which corresponds to a Moebius-type aromatic system containing eight electrons on eight active orbitals.[201] From this viewpoint, the 1,2-shift should be unfavourable for the migration of groups containing two additional electrons on active orbitals compared to boron-centred groups. However, this assumption was not confirmed in the case of rearrangements of sulfur-centred migrating groups. 7-Phenylthiocycloheptatriene **74** (M = SPh)[40,202] and cycloheptatrien-7-yl ethyl dithiocarbonate **74** [M = SC(OEt)=S][203] undergo circumambulatory rearrangements at rates comparable to those found for the migrations of boron-centred groups in compound **74** with M = BPr_2. According to the data from ^{1}H and ^{13}C 2D EXSY NMR spectroscopy, the phenylthio- and, probably, ethyldithiocarbonate groups migrate around the cycloheptatriene ring *via* successive 1,2-shifts ([1,7]-sigmatropic shifts). The kinetics of both rearrangements is independent of the concentrations of solutions, which is indicative of their intramolecular character. The kinetic parameters of these rearrangements are summarised in Table 15.

Since studies of the mechanisms by dynamic NMR elucidated only the type of the permutation mechanism, an alternative mechanism involving [2,3]-sigmatropic shifts for the rearrangement of compound **74** [M = SC(OEt)=S] cannot be excluded.

The theoretical simulation of the mechanism of rearrangement of model system **74** [R = H, M = SCH(=S)], which is an analogue of compound **3**, was carried out by *ab initio* calculations at the MP2/6-31G** level.[93] The optimised geometric parameters and energies of the transition state structures relative to the ground state of thioformylthionecycloheptatriene **74** are shown in Fig. 8. Calculations provided evidence that the 2,3-shift is the energetically most favourable channel of the rearrangement. The larger size of the cycloheptatriene ring as compared to that in lower cyclopolyenes allows more diverse pathways of circum-

Table 15. Kinetic and activation parameters for the circumambulatory rearrangements of 7-phenylthiocycloheptatriene **74** (M = SPh)[40, 202] and cycloheptatrien-7-yl ethyl dithiocarbonate **74** [M = SC(OEt)=S][203] calculated from the data of dynamic ^1H and ^{13}C NMR spectroscopy.

M in compound **74**	Solvent	$\Delta G^{\neq}_{25}$ (see [a])	$\Delta H^{\neq}$ (see [a])	$\Delta S^{\neq}$ (see [b])	k_{25} /s^{-1}
SPh	benzene-d_6	19.2	18.3 ± 0.4	-4.0 ± 0.4	2.9×10^{-2}
SPh	nitrobenzene-d_5	20.1	18.5 ± 0.5	-5.5 ± 0.4	1.1×10^{-2}
SC(OEt)=S	benzene-d_6	17.9	16.9 ± 0.3	-3.3 ± 0.4	4.5×10^{-1}
SC(OEt)=S	toluene-d_8	17.4	15.4 ± 0.2	-6.6 ± 0.3	1.1

[a] $\Delta G^{\neq}_{25}$ and $\Delta H^{\neq}$ are given in kcal mol^{-1}.
[b] $\Delta S^{\neq}$ are given in cal mol^{-1} deg^{-1}.

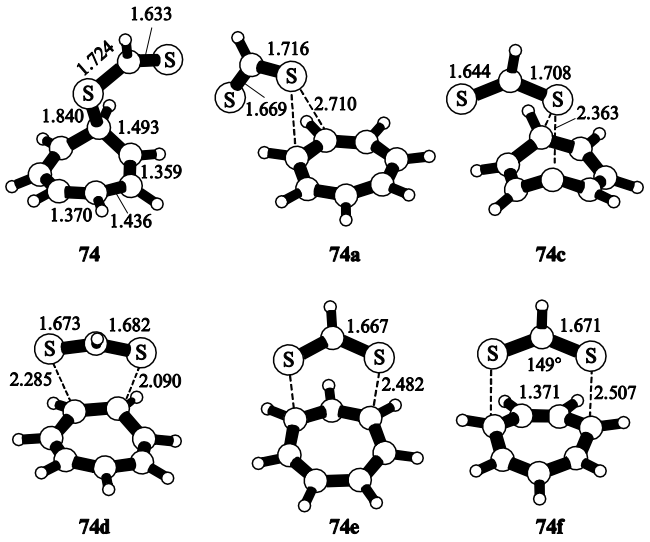
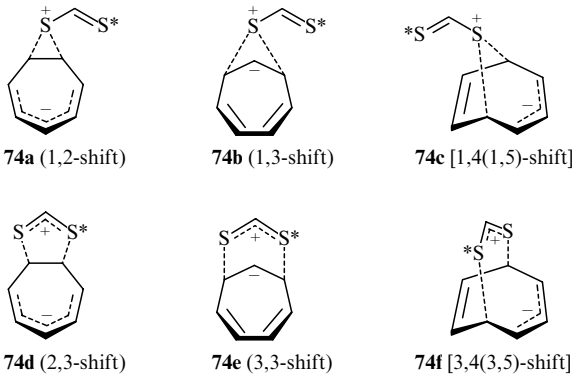


Figure 8. Optimised (MP2/6-31G**) structures of thioformylthionecycloheptatriene **74** and transition states **74a**,**c**–**f** for different mechanisms of circumambulatory sigmatropic rearrangements.[93]
The transition state structure for the mechanism of the [1,3]-sigmatropic shift (**74b**) was not localised.

ambulatory rearrangements, including the formation of transition states **74a**–**f**, to proceed.

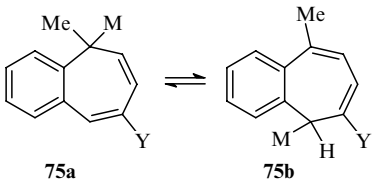


4. Rearrangements *via* 1,3-shifts

The presence of the $Fe(CO)_3$ group in molecule **11** facilitates the 1,3-migration of the dipropylboryl group observed by dynamic NMR spectroscopy. This migration along with the main reaction channel (1,2-shift) contributes to the mechanism of the circumambulatory rearrangement.[50] In uncoordinated compound **74** (M = BPr_2), the 1,3-migration proceeds much more slowly and is experimentally undetectable, although it is known that the boryl groups in polyunsaturated dialkylboranes can undergo rapid [1,3]-sigmatropic shifts.[204, 205]

5. Rearrangements *via* 1,4-shifts

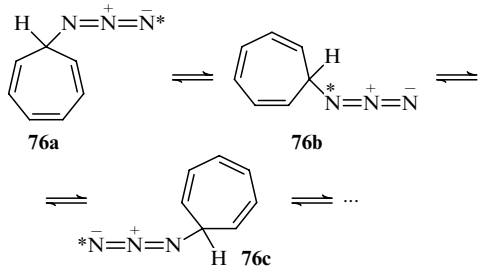
Unlike the cyclopentadiene system for which the energetically most favourable mechanism of circumambulatory rearrangements involves thermally allowed suprafacial [1,5]-sigmatropic shifts of the migrating group (1,4-shifts) (see Section VI), the rearrangements of this type in cycloheptatrienes are characterised by high energy barriers. For example, the migrations of silicon- or germanium-centred groups in compounds **74** [M = $SiPh_3$ (see Ref. 206) and $GePh_3$ (see Ref. 207)] are unobservable. At temperatures higher than 130 °C, [1,5]-sigmatropic hydrogen shifts take place in these cycloheptatriene derivatives. At 150 °C, the methoxy group in 7,7-dimethoxycycloheptatriene undergoes [1,5]-sigmatropic shifts characterised by fairly high activation barriers.[208] In cycloheptatrienes, rather rapid rearrangements *via* [1,5]-shifts were observed only for migrating substituents formed by Group 14 elements of a lower period of the Periodic table, *viz*., $SnPh_3$, $SnMe_3$ and $SnMe_2Cl$ (see Section III.4). This is attributed to the fact that [1,5]-sigmatropic shifts in the cyclopentadiene system proceed as 1,2-shifts along the pathways of the smallest motions of the migrating groups, whereas these shifts in the cycloheptatriene system do not correspond to this pathway (1,4-shifts). Additional arguments in favour of the 1,2-shift were obtained in calculations of the geometry of the transition state structures for various reaction pathways associated with the migration of the dimethylboryl group in compound **74** (M = BMe_2)[60] and the dithioformate group in its analogue with M = SCH(S) (see Fig. 8). If the rearrangement proceeds *via* 1,2-shifts ([1,7]-sigmatropic shift), the seven-membered ring in the transition state remains virtually planar, while the C–B and C–S bond lengths moderately increase. By contrast, the ring is forced to adopt a distorted conformation with substantially elongated C–B (1.859 Å) and C–S (2.363 Å) contacts if the rearrangement proceeds *via* 1,4-shifts ([1,5]-sigmatropic shifts). Therefore, it can be assumed that steric rather than electronic factors are predominantly responsible for fairly high energy barriers to [1,5]-sigmatropic shifts in the cycloheptatriene system. This accounts for the fact that the migration ability of various carbon-centred groups in benzocycloheptatrienes **75** depends to a much lesser extent on the nature of the migrating group compared to those in indene system **49**. The rearrangements **75a** ⇌ **75b** proceed upon heating of solutions of compounds **75** in benzene in sealed tubes.[209]



The migration ability of carbon-centred groups decreases in the following series: CHO > CN > C≡CH > C(O)Me > CO_2Me > Alk.

6. Rearrangements *via* [3,3]-sigmatropic shifts

The shifts of the isothiocyanate groups in tropyl isothiocyanate **69** belong to random processes, *i.e*., the positions of the migrating group after ionisation of the starting molecule is randomly chosen (see Scheme 5), whereas the energetically favourable mechanism of the rearrangement of tropyl azide **76** involves the selective 1,3-migration of the azide group.[87] Dynamic ^{15}N NMR spectroscopic studies confirmed that this migration is associated also with the exchange between the positions of the terminal nitrogen atoms in the azide group. Since the rate of this process is equal to the rate of circumambulatory migrations of the azide group around the seven-membered ring, 1,3-migrations should correspond to [3,3]-sigmatropic shifts.



Along with the [3,3]-sigmatropic shift, the following alternative reaction pathways take place: ionisation – recombination and [1,5]-sigmatropic shift. The contribution of the ionic mechanism increases as the polarity of the solvent increases (26% and 34% in THF and CD_3CN, respectively). The activation free energy barriers for various mechanisms of circumambulatory rearrangements of compound **76**, which were estimated based on analysis of line shapes in NMR spectra, are given in Table 16.

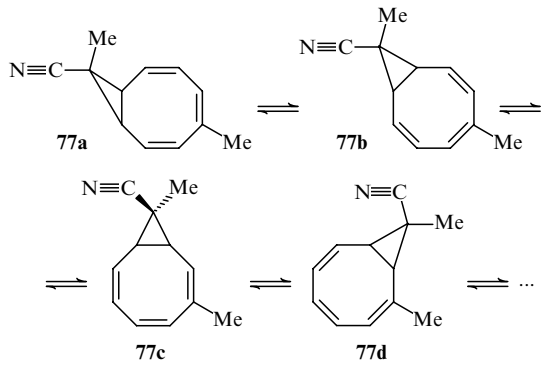
Table 16. Activation free energies ($\Delta G^{\neq}_{-48}$) for the circumambulatory rearrangements of tropyl azide **76**.[87,88]

Solvent	$\Delta G^{\neq}_{-48}$ /kcal mol^{-1}		
	random shift	[3,3]-shift	[1,5]-shift
CD_3CN	14.8 ± 0.2	14.0 ± 0.2	16.0 ± 0.5
$CDCl_3$	15.2 ± 0.5	14.9 ± 0.6	17.0
THF	16.5 ± 0.4	15.9 ± 0.4	17 ± 1

Although direct evidence of [3,3]-sigmatropic shifts of the isoselenocyanate groups in 7-isoselenocyanatocycloheptatriene **68** (Y = NCSe) is lacking, the presence of small amounts of selenocyanate isomer **68** (Y = SeCN), which was observed in the mass spectrum of the starting isoselenocyanate,[189] is indicative of the possibility of this rearrangement occurring in the gas phase.

IX. Circumambulatory rearrangements in multimembered rings

Circumambulatory migrations in the eight- and nine-membered cyclopolyene rings are virtually unknown. Rearrangements in neutral eight-membered systems can proceed only in bis-hapto compounds (see Section III.5). The only known example is interconversions of the isomers of 9-cyano-4,9-dimethylbicyclo[8.1.0]nonatriene (**77**) occurring as migrations of the cyclopropyl group.[210]

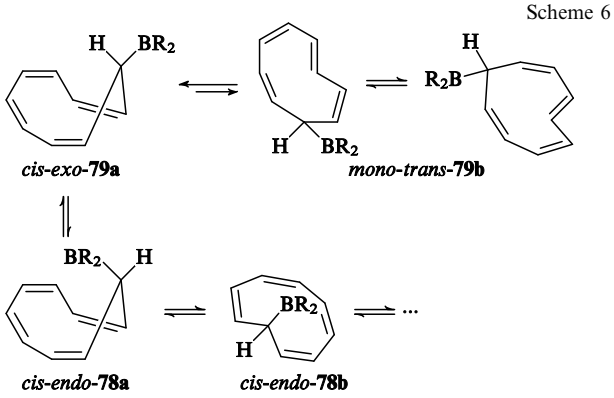


Compound **77**	**a**	**b**	**c**	**d**
Yield at 102 °C (%)	35	33	21	11

Heating of a solution of cyclopolyene **77a** afforded a mixture of all four isomers. The activation free energy of the rearrangement **77a** → **77b** is 29 kcal mol^{-1}. Each step of the circumambulatory rearrangement involves the inversion of stereochemical configuration at the C(9) centre. The thermal rearrangement of isomer **77a** attended by the exchange between the positions of the cyano and methyl groups proceeds analogously.

The rapid circumambulatory rearrangement of cyclononatrienyl(dipropyl)borane **78** was studied by Bubnov and co-workers.[56] The dynamic process associated with 1,3-shifts of the dipropylboryl group in molecule **78** (R = Pr) is detected by ^{1}H NMR spectroscopy even at −100 °C. The activation free energy barrier for migrations of the dipropylboryl group, which was calculated based on analysis of line shapes in the ^{13}C NMR spectra in the temperature range from −100 to −40 °C, is low ($\Delta G^{\neq}_{-78}$ = 8.8 kcal mol^{-1}). This value is well reproduced by calculations of model compounds **78** and **79** (R = Me) using the density functional method [211] by relating this barrier to the interconversions of the most stable *cis-endo* isomers **78a** ⇌ **78b** ⇌ .... According to the results of calculations, the dialkylboryl group in the energetically less favourable *cis-exo* isomer of **79** undergoes the 1,2-shift to form *mono-trans* conformer **79a**, which, in turn, can undergo 1,3-boron shifts. These rearrangements are shown in Scheme 6.

Scheme 6



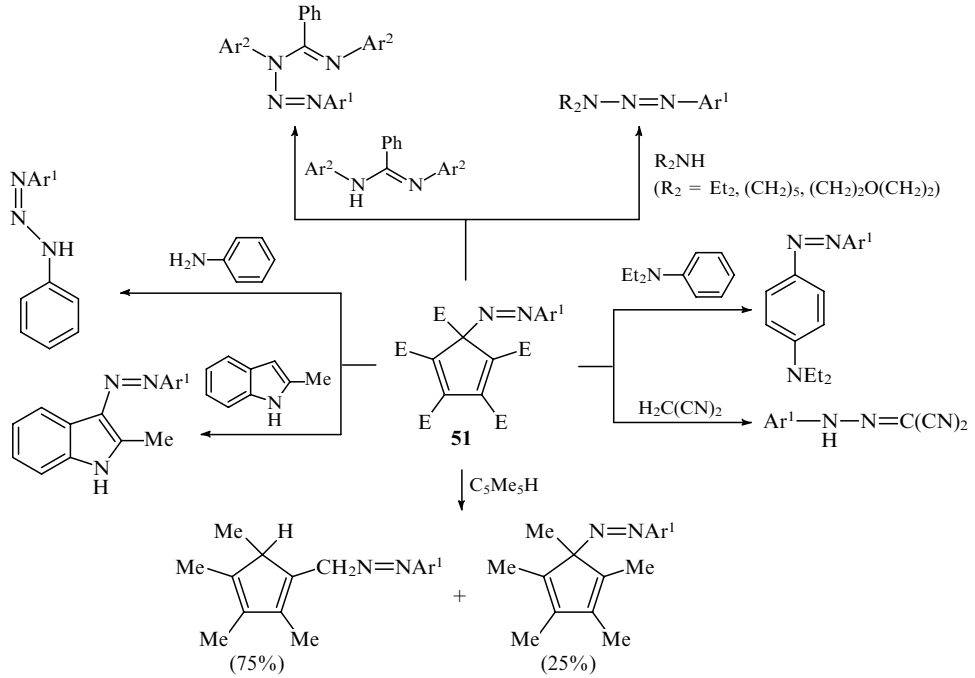
The fluxional behaviour of cyclononatrienyl(trimethyl)tin was studied in detail in the temperature range from −100 to −78 °C by ^{13}C–^{13}C EXSY NMR spectroscopy. The results of these studies demonstrated that the Me_3Sn group in the *exo* conformer undergoes 1,2-shifts ([1,9]-sigmatropic shifts) around the nine-membered ring.[212] The activation energy of this process (6.0 ± 0.6 kcal mol^{-1}) agrees well with the calculated (B3LYP/3-21G*) value.

X. Fluxional compounds as efficient carriers of groups and precursors of structurally rigid chiral ligands

Compounds whose fluxional behaviour is determined by the ionisation – recombination mechanism involving dissociation into ions can serve as soft carriers of functional groups. This takes place when the rearrangement proceeds in solutions containing another substrate, which possesses a fairly high affinity for the migrating group, thus competing with the starting counterion in the recombination step. For example, arylazo derivatives of 1,2,3,4,5-pentamethoxycarbonylcyclopentadiene **51** (see Section VI.3.a) serve as efficient carriers of arylazo groups facilitating their migration to the nucleophilic carbon and nitrogen centres in various acidophobic compounds.[38,39,213–216] The reactions proceed smoothly at room temperature in benzene to give various arylazo compounds in ~ 90% yields. The most important transformations of this type are shown in Scheme 7.

Not only ionisable arylazo compounds **51** but also 5-arylthio-1,2,3,4,5-pentamethoxycarbonylcyclopentadienes **61**, which are characterised by low energy barriers to circumambulatory migrations of the arylthio groups (see Section VI.4.b), behave as

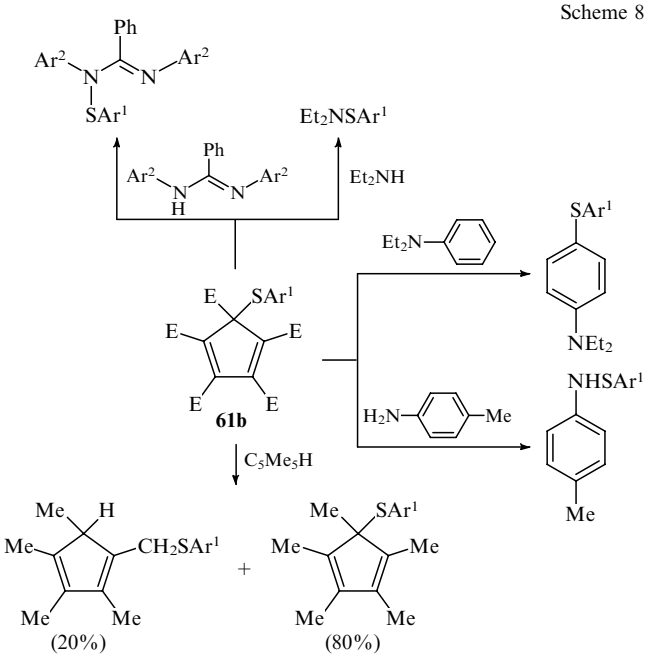
Scheme 7



E = CO_2Me; Ar^1 = $C_6H_4NO_2$-4, $C_6H_4NO_2$-2, $C_6H_4SO_2CF_3$-4; Ar^2 = C_6H_4Me-4, C_6H_4OMe-4.

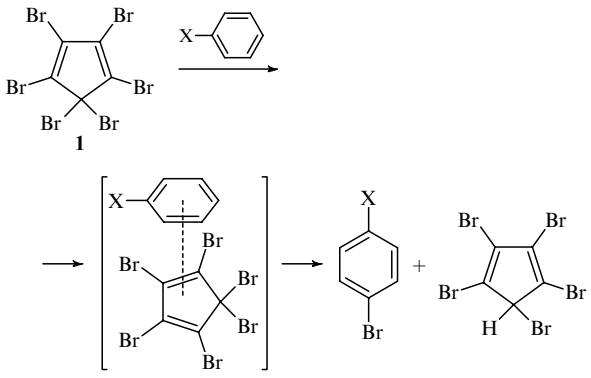
efficient carriers of these groups.[217–220] Intermolecular migrations of the arylthio groups are illustrated in Scheme 8.

Scheme 8



E = CO_2Me; Ar^1 = $C_6H_4NO_2$-4, $C_6H_4NO_2$-2;
Ar^2 = C_6H_4Me-4, C_6H_4OMe-4.

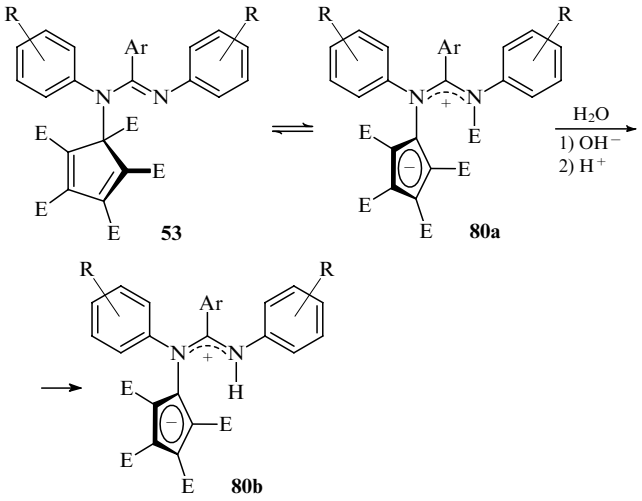
Potentially fluxional hexabromocyclopentadiene **1** (R = M = Br) is also able to undergo the intermolecular transfer of the bromine atom to the nucleophilic carbon centres.[221,222] This reagent brominates smoothly aromatic amines and alcohols, furans, thiophenes and ketones activated at the α-carbon atoms, the electrophilic substitution of aromatic compounds proceeding selectively at the *para* position due to formation of intermediate π complexes.



X = NMe_2, NMeCOMe, OH, OMe.

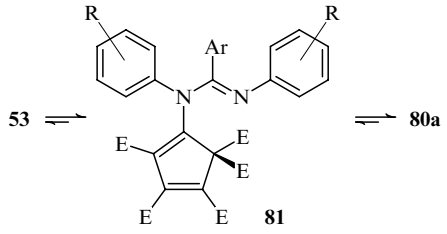
The cyclopentadienyl ligand exhibits properties of a readily leaving group in the exchange reactions of fluxional P-, Ga-, Si-, Sn- and Ge-centred pentamethylcyclopentadiene derivatives with nucleophiles.[223]

The migrations of groups analogous to those shown in Schemes 7 and 8 can also be carried out as intramolecular reactions, provided that the cyclopentadiene ring contains an additional nucleophilic centre, which can compete with the carbon atoms of the ring for the mobile migrating group bound to this ring. The correct choice of functional groups in the molecule of a fluxional compound allows one to perform the rational design of structures which are difficult to prepare according to conventional synthetic procedures. This approach can be exemplified by the new rearrangement of *N*-1,2,3,4,5-pentamethoxycarbonylcyclopentadienyl-*N*,*N*′-diarylamidines **53** observed in solutions at high temperatures.[224] This rearrangement afforded previously unknown *N*-methoxycarbonyl-*N*,*N*′,α-triarylamidinium *N*-cyclopentadienides **80a**, which readily eliminated the *N*-methoxycarbonyl group upon treatment with a methanolic solution of NaOH to give (after neutralisation of the solution) amidinium *N*-cyclopentadienyl ylides **80b**. The zwitterionic structures of the ylides were confirmed by X-ray diffraction analysis of a series of derivatives **80**.[224–226]



The rearrangement **53** → **80a** can proceed either *via* the direct 1,4-shift of the methoxycarbonyl group or as a two-step process involving an additional 1,2-shift to the carbon atom of the ring **53** → **81** followed by the 1,5-shift of this group. The possibility of the second mechanism is evidenced by rather low energy barriers to the 1,2-shifts ($E_a \approx 25$ kcal mol^{-1}) of the methoxycarbonyl group in 5-R-1,2,3,4,5-pentamethoxycarbonylcyclopentadienes.[119,122] However, simulation of the mechanisms of migration of the methoxycarbonyl group for a series of amidinylcyclopentadiene derivatives taking into account the methoxycarbonyl and aryl substituents in the cyclopentadiene and amidine fragments, respectively, by the MNDO quantum-chemical method provided theoretical evidence for the occurrence of the 1,4-shift of the methoxycarbonyl group.[227]

The presence of electron-releasing groups in the *C*-aryl ring facilitates the shift of the equilibrium **53** ⇌ **80a** toward *N*-ylide (Table 17).



The non-planar molecules of *N*-ylides **80b** are chiral, and the presence of both the amidine and cyclopentadiene residues in these molecules provides their bifunctional character. Hence, compounds **80b** hold promise as chiral N-functionalised cyclopentadienyl ligands in the synthesis of metal complexes serving as potential catalysts for asymmetric reactions.[228–233] In such complexes, the cyclopentadiene fragment and the nitrogen atom of the side chain coordinate the metal centre in a bidentate fashion giving rise to the rigidly coordinated chiral centre at the metal atom. Complexes of this type with N-centred functional groups, such as the aminoethyl and pyridyl groups, were studied.[234–237] Compounds **80b**, which contain the bulky 1-naphthyl group in the α position of the amidine triad and retain a stable chiral structure both in the crystals and solutions even upon heating to 180 °C (the energy barrier to rotation about the $C_\alpha - C_{Ar}$ bond $\Delta G^{\neq}_{180} > 26$ kcal mol^{-1}), are of particular interest. In gold(I) complexes with 1-naphthamidinium *N*-cyclopentadienides prepared recently, the rigidity of a chiral structure is provided by additional coordination of the gold atom by the π system of the cyclopentadiene ring.[238] Analogous thallium complexes retain stable chiral structures through coordination of the thallium atom both by the nitrogen atom of the side chain (N—Tl) and the π system of the cyclopentadiene ring (Tl—Cp, η^5-binding).[239]

Table 17. Equilibrium and rate constants of the rearrangement **53** ⇌ **80a** (*o*-dichlorobenzene, 120 °C).[224]

Ar in compounds **53**, **80a**	K = [**80a**]/[**53**]	$10^3 k$ /s^{-1}		$\Delta G^{\neq}$ /kcal mol^{-1}	
		53 → **80a**	**80a** → **53**	**53** → **80a**	**80a** → **53**
$C_6H_4NO_2$-4	0.25	0.8	3.2	28.8	27.6
C_6H_4Br-4	0.31	1.0	3.2	28.6	27.6
C_6H_5	0.40	1.2	3.0	28.4	27.7
C_6H_4Me-4	0.53	1.6	3.0	28.4	27.7
C_6H_4OMe-4	0.66	2.1	3.2	28.0	27.6

XI. Conclusion

Circumambulatory rearrangements can serve as models of many important chemical processes associated with migrations of functional groups, which allow one to prepare compounds with various structures. The elucidation of the mechanisms of such rearrangements, their driving forces and factors responsible for the energy barriers to shifts of the migrating groups around the ring helps in understanding the mechanisms and stereoelectronic requirements of a series of more complex reactions. The results surveyed in the present review demonstrate that circumambulatory rearrangements are not limited to shifts of mobile organometallic groups around the ring but involve also various migrating substituents of Group 13–17 elements. In particular cases, such Group 13–17 element-centred migrating substituents exhibit high ability to undergo intramolecular shifts comparable to the mobility of organometallic groups.

The circumambulatory rearrangements of cyclopentadiene derivatives were studied in sufficient detail. In most cases, these rearrangements proceed *via* successive 1,2-shifts ([1,5]-sigmatropic shifts) of the migrating group around the five-membered ring. The energy barriers to migrations of the substituents M whose central atoms belong to one and the same group of the Periodic table decrease with increasing atomic number of the element due primarily to a gradual decrease in the energy of the $C_{sp^3} - M$ bonds with increasing ordinal number of the period. In the presence of electron-withdrawing substituents in the five-membered ring, the migration rate increases. In the case that a migrating group can form a stable cation and the five-membered ring contains electron-withdrawing substituents, which facilitate delocalisation of the negative charge in the cyclopentadienide anion, the $C_{sp^3} - M$ bond readily undergoes ionisation and the rearrangement proceeds through the ionisation–recombination mechanism within the tight ion pair that formed. In the presence of nucleophiles possessing a higher affinity for a migrating group compared to the starting cyclopentadiene residue, the cationic migrating group can be shifted to the foreign nucleophilic centre. Such compounds serve as efficient soft carriers of functional groups.

The electronic requirements for circumambulatory rearrangements of derivatives of three- and seven-membered cyclopolyenes characterised by low energy barriers are opposite to those considered above for cyclopentadienes. Aromatic stabilisation of these cyclopolyene rings is achieved in their cationic forms and increases upon the replacement of the hydrogen atoms in the ring by electron-releasing groups. As a consequence, circumambulatory rearrangements of cyclopropene and cycloheptatriene derivatives containing electronegative migrating groups and electropositive substituents in the rings proceed by the ionisation–recombination mechanism. By contrast, the differences in the stereoelectronic requirements for migrations of heteroallyl groups in various cyclopolyenes are dictated primarily by steric factors.

The rate constants of circumambulatory rearrangements vary over a wide range characteristic of intramolecular migrations, *viz*., from 10^6 to 10^{-8} s^{-1} at room temperature, which corresponds to energy barriers of 5–40 kcal mol^{-1}. Depending on the ring size,

the nature of the migrating group, substituents in the ring and the medium, compounds **1**–**5** and their higher homologues can exhibit very high structural non-rigidity or, on the contrary, substantial rigidity, *i.e.*, according to the classification proposed in the study,[240] these compounds can be assigned to both fluxional structures and structures which undergo slow rearrangements. An interesting feature of circumambulatory rearrangements is a diversity of mechanisms responsible for simple intramolecular shifts of migrating groups around the cyclopolyene ring. Among these are various sigmatropic shifts of migrating groups, haptotropic rearrangements and ionisation pathways. Very fine variations in the structure can switch the reaction between possible pathways resulting in topomerisation or isomerisation of cyclopolyene derivatives. In this respect, circumambulatory rearrangements of substituted cyclopolyenes provide a good example of the limitations of the so-called 'principle of Ockham's razor',[241] which is often used as a qualitative criterion for analysis of reaction mechanisms. The Woodward–Hoffmann rules of the conservation of orbital symmetry are also non-universal for the prediction of mechanisms and stereochemistry of circumambulatory rearrangements of cyclopolyene compounds although these rearrangements belong to typical pericyclic processes. To account adequately for the electronic and steric factors, critical regions of potential energy surfaces should be calculated by quantum-chemical methods at a high level of theory.

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