Russian Chemical Reviews **69** (8) 683 – 704 (2000) © 2000 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2000v069n08ABEH000589

Inter-ring haptotropic rearrangements in π-complexes of transition metals with polycyclic aromatic ligands

Yu F Oprunenko

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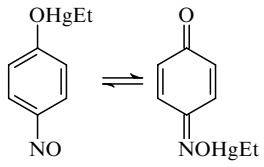
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Abstract. The results of studies of inter-ring haptotropic rearrangements in π-complexes of transition metals with polycyclic aromatic ligands are discussed. Syntheses and structures of model compounds are surveyed and the classification of dynamic processes in these compounds is proposed. The major regularities, mechanisms and kinetics of inter-ring haptotropic rearrangements in these systems are analysed. The bibliography includes 143 references.

I. Introduction

Diversified dynamic processes occur in molecules of different heteroorganic compounds (HOC) and, in particular, organometallic compounds (OMC), due to changes in the mutual arrangement of various groups in HOC molecules (rotation, small-amplitude oscillation, formation and cleavage of agostic bonds, inversion, *etc*.). Generally, these processes are degenerate and occur rather rapidly and hence, they are studied primarily by dynamic NMR spectroscopy.[1]

One of the dynamic processes most commonly observed in HOC and OMC involves rapid migration of an element (metal) together with the ligand environment from one position in the organic fragment to another. For this type of tautomerism, Academician A N Nesmeyanov introduced the term 'metallotropic tautomerism' (metallotropy). He was the first[2] to find metallotropic rearrangements in nitrosophenyl and quinoxime compounds of mercury.



Hoffmann[3] extended the term 'sigmatropic rearrangements' to π-complexes of transition metals and introduced the term 'haptotropic' rearrangements for these processes. Metallotropy is among the most important problems of chemistry because the reactivities and catalytic activities of OMC are to a large extent determined by the tautomer ratio.[4]

Metallotropic tautomerism has been studied for more than 40 years. A rich variety of metallotropic rearrangements have been thoroughly studied and a number of basic concepts have been offered, for example, the concepts of dual reactivity and σ,π-conjugation,[5] stereochemically nonrigid organometallic compounds[6] and catalytic and intramolecular activation of CH bonds,[7] which made a noticeable impact on the development of the general theory of chemical bonds, catalytic activity and reactivity of OMC.

Degenerate σ,σ- and π,π-rearrangements in HOC and OMC were among the first to be discovered.[8,9] For example, σ,σ-rearrangements in allylic complexes of magnesium,[10] boron[11] and silicon[12] ([1,3]-sigmatropic rearrangements according to Woodward – Hoffmann) proceed through an intramolecular mechanism.[13]

$$R_nMCH_2CH=CH_2 \rightleftharpoons CH_2=CHCH_2MR_n$$

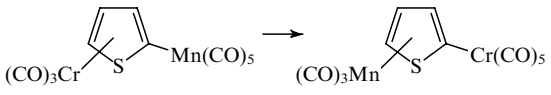
$n = 1$, M = Mg; $n = 2$, M = B; $n = 3$, M = Si.

Rearrangements of *C*- and *O*-substituted derivatives of carbonyl compounds containing MR^1_3 groups (M = Ge or Sn)[14,15] as well as the nitrosophenol – quinoxime rearrangement of mercury compounds described above (the first metallotropic rearrangement observed experimentally)[2] may also be assigned to this type of rearrangements.

$$R^1_3MOC(R^2)=CH_2 \rightleftharpoons R^1_3MCH_2C(=O)R^2$$

M = Ge, Sn.

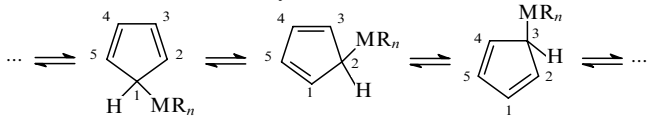
Migration of the organometallic group in the compounds described above is accompanied by rearrangement of the system of multiple bonds. Cross experiments demonstrated that these processes can occur both according to intramolecular and intermolecular mechanisms, but an intramolecular mechanism prevails. Formally, σ,σ-rearrangements are analogues of prototropic rearrangements in organic compounds, whereas σ,π- and π,π-rearrangements have no analogues because migrations of organometallic groups in the latter cases lead to a change in the character of a delocalised multicentre bond. For example, an interesting diotropic σ,π-rearrangement was observed in a binuclear thiophene complex.[16]



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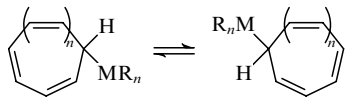
Received 4 April 2000
Uspekhi Khimii **69** (8) 744 – 766 (2000); translated by T N Safonova

The [1,5]-sigmatropic rearrangements in cyclopentadienyl and indenyl compounds of many main-group and transition metals have received the most study.[17]



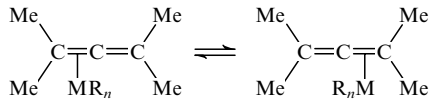
M = Si, Sn, Ge.

These rearrangements were also observed in cycloheptatrienyl [18] and cyclononatetraenyl [19] compounds.

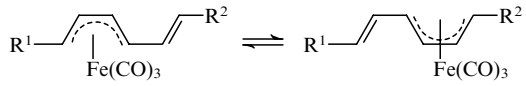


n = 1, 2.

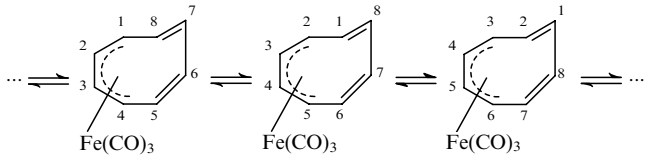
Generally, the activation barriers to these migrations are rather low and the migrations are degenerate in the sense that the molecule either undergoes internal conversion or is converted into a mirror image. Hence, these migrations are studied by dynamic NMR spectroscopy.[20] Molecules of this type can be described as 'stereochemically nonrigid' in terms proposed by Muetterties.[21] Cotton [22] introduced the term 'fluxional molecule' for their description. Haptotropic rearrangements in monocyclic π-complexes were considered in numerous reviews and monographs.[23–25] For π-complexes of open polyenes, rearrangements of η^2-allene [26] and η^4-triene [27] derivatives have been studied most extensively.



MR_n = $Fe(CO)_4$, $Fe(CO)_2(\eta^5\text{-}C_5H_5)^+$.

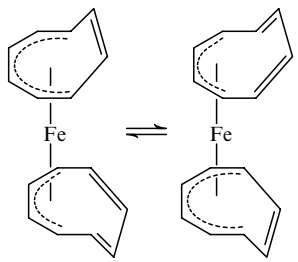


π,π-Rearrangements are often observed in π-complexes of open or cyclic conjugated polyenes with transition metals. These rearrangements are very diverse.[28] The η^4,η^4-rearrangement of the tricarbonyliron complex of cyclooctatetraene provides a typical example. In the course of isomerisation, the $Fe(CO)_3$ group migrates along the system of the conjugated double bonds of the ligand.[29]



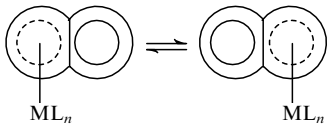
It should be noted that haptotropic rearrangements occur in π-complexes in which the π-ligand can be coordinated to the metal atom through several coordination sites and not all these sites are used, *i.e.*, some double bonds are not involved in coordination.

In (η^4-cyclooctatetraene)(η^6-cyclooctatetraene)iron, migration of the metal atom is accompanied by a change in the mode of bonding in each ligand (*i.e.*, the η^4,η^6-rearrangement).[30]



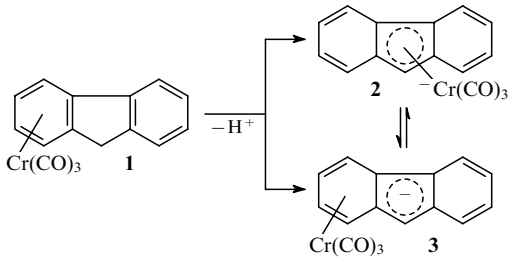
In early studies, metallotropy in OMC, including metallotropic rearrangements with the participation of the hydrogen atom and alkyl groups, was investigated primarily in open or monocyclic compounds.[30–34] Much later, inter-ring rearrangements, rapid within the NMR time scale, were found, for example, in nickel complexes of naphthalene [35] and anthracene,[36] phenalenyl palladium complex [37] and dibenzenepentalenyl manganese complex.[38]

Formally, π-complexes of transition metals (in particular, carbonyl chromium complexes, which are the most readily available and well-studied compounds) with polycyclic aromatic neutral ligands (naphthalene, acenaphthene, acenaphthylene, biphenylene, biphenyl, fluoranthene, *etc.*) are promising models for searching for and revealing new types of haptotropic rearrangements. In these systems, inter-ring haptotropic rearrangements (IHR) involving migration of the transition metal atom together with the ligand environment between the rings of the polyaromatic ligand can proceed.[39]



Studies of the general regularities of IHR are of considerable importance because they can allow one to obtain further insight into the nature of the transition metal–ligand bond and to elucidate the mechanisms of catalytic processes occurring in solution under the action of metal-complex catalysts because IHR are involved as particular elementary stages in these processes.

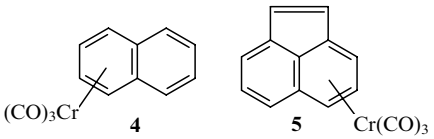
In 1971, Nicholas *et al.*[40] found for the first time nondegenerate IHR. Thus deprotonation of a solution of tricarbonyl(η^6-fluorene)chromium (**1**) in DMSO with potassium *tert*-butoxide afforded tricarbonyl(η^5-fluorenyl)chromium (**2**). The authors suggested that tricarbonyl(η^6-fluorenyl)chromium (**3**) formed in the initial step of the reaction underwent a η^6,η^5-rearrangement. The anion **3** was not detected by spectral methods and the kinetics and mechanism of its conversion into the isomeric η^5-anion **2** were not studied in detail.



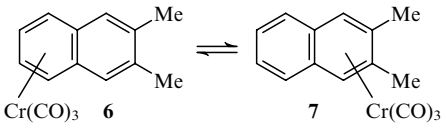
Later, inter-ring haptotropic rearrangement in the η^6-anion **3** was studied in detail by Russian [41–43] and Italian [44] researchers using IR and NMR spectroscopy and the kinetic and thermodynamic parameters of this rearrangement were determined. It was found that deprotonation of the complex **1** with a base gave rise to the η^6-anion **3**, which was isomerised to form the η^5-anion **2**. This rearrangement is reversible and entropy-controlled. The kinetic and thermodynamic parameters (E_a = 16.29 kcal mol^{-1} and $\Delta S^{\neq} = -19.62$ e.u.) are to a large extent determined by the equilibrium between different ion pairs of the corresponding fluorenyl salts [contact ion pairs (CIP), separated ion pairs (SIP) and ionic associates]. More recently, analogous η^6,η^5-rearrangements were found in complexes of a series of carbo- and heterocyclic analogues of fluorene.[45]

Nondegenerate inter-ring migrations in fluorenyl complexes are fairly well studied by stationary kinetic methods. Inter-ring migrations in complexes of naphthalene and related unsubstituted polyaromatic systems are degenerate and cannot be studied by conventional procedures. The researchers hoped to find rapid

migrations of the $Cr(CO)_3$ group between two equivalent rings in the simplest model complexes, *viz*., tricarbonyl(η^6-naphthalene)-chromium (**4**)[40,46] and related (η^6-acenaphthylene)tricarbonyl-chromium (**5**),[47] by NMR spectroscopy. Specimens were heated to rather high temperatures; however, no dynamic processes were observed in the spectra. Until the mid-1980s, procedures for the investigation of these degenerate processes were lacking.



As early as 1966, Deubzer, a coworker of the Nobelist Fischer, found[48] that isomeric tricarbonylchromium π-complexes of 2,3-dimethylnaphthalene **6** and **7** underwent reversible η^6,η^6-IHR ($E_a \approx 30$ kcal mol^{-1}) at 90–110 °C. Both complexes involved in the rearrangement have been isolated from the reaction mixture in pure form (by fractional recrystallisation) and identified for the first time.



However, these pioneering results were not published and remained unknown over 17 years until they were cited in Ref. 47.

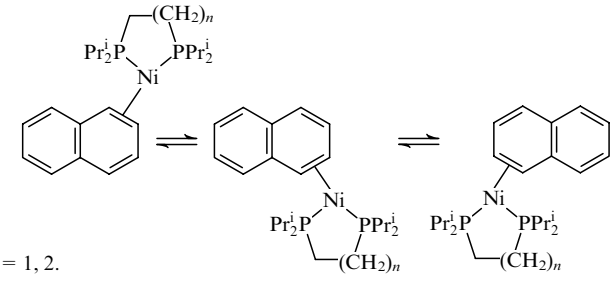
In succeeding years, inter-ring haptotropic rearrangements were studied by several research groups. Teams headed by P M Treichel (USA), E P Kündig (Switzerland), A Ceccon (Italy), Ch Elschenbroich (Germany), T A Albright (USA), M J McGlinchey (Canada), Yu A Ustynyuk and N A Ustynyuk (both from Russia) have made the major contribution to this line of investigation.

II. Classification and major regularities of inter-ring haptotropic rearrangements

The classification of IHR is as yet inadequate. I shall follow the classification of IHR depending on the type of bonding of the metal atom with the ligand proposed by N A Ustynyuk,[43] which is, in my opinion, the most reasonable and convenient one. According to this classification, the **3**⇌2 and **6**⇌**7** rearrangements are assigned to η^6,η^5- and η^6,η^6-IHR, respectively.

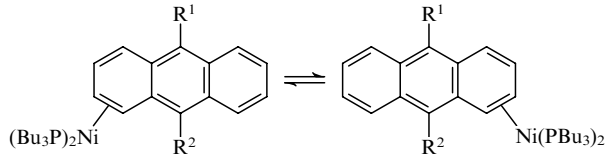
1. η^2,η^2-Rearrangements in nickel complexes of naphthalene and anthracene

Recently, this type of rapid reversible degenerate rearrangement has been observed in phosphine complexes of nickel(0) with naphthalene[35] and anthracene.[36] The reactions of $[Pr^i_2P(CH_2)_nPPr^i_2]_2Ni$ (n = 2 or 3) with naphthalene[49,50] in THF afforded complexes, which have η^2-structures [according to the solid-state ^{13}C NMR spectra measured with the use of cross-polarisation and the magic-angle-spinning technique (CP MAS NMR)]. Solid-state and solution-phase two-dimensional exchange ^{13}C NMR spectra measured with magnetisation transfer demonstrated that the organonickel group migrates between double bonds both within one six-membered ring (E_a are 6 and 23 kcal mol^{-1} in solution and in the solid state, respectively) and between the rings. The migration between the rings is observed only in solution (E_a = 15 kcal mol^{-1}).



n = 1, 2.

The reactions of $(Bu_3P)_3Ni$ with 5-alkyl- and 5,10-dialkylanthracenes[49] in benzene gave rise to η^2-complexes whose structures were established by CP MAS ^{13}C NMR spectroscopy.

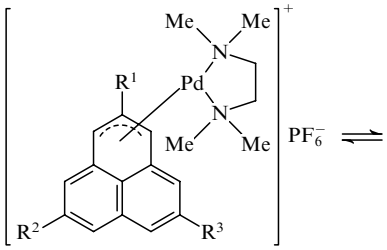


R^1 = Me, Et; R^2 = H, Me, Et.

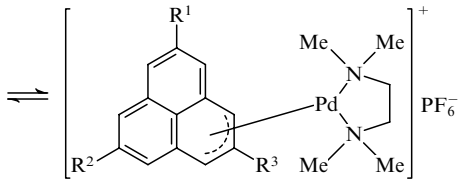
Based on the data of ^1H and ^{13}C NMR spectroscopy, these complexes in solutions in benzene-d_6 underwent rapid η^2,η^2-rearrangements, the organometallic group 'running around' the perimeter of the polycyclic ligand. The dynamic behaviour of these systems was studied using the spin saturation transfer technique and total line-shape analysis. In anthracene complexes, as in naphthalene complexes, the organonickel group was demonstrated to migrate within one ring and between the terminal rings both through intramolecular ($\Delta H^{\neq}$ = 8 kcal mol^{-1}) and intermolecular ($\Delta H^{\neq}$ = 20 kcal mol^{-1}) mechanisms.

2. η^3,η^3-Rearrangements in phenalenyl complexes of palladium and rhodium

η^3,η^3-Rearrangements were studied in most detail for η^3-phenalenyl complexes. Thus the reactions of di-μ-chlorobis(η^3-phenalenyl)dipalladium complexes dissolved in acetone with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and KPF_6 afforded cationic palladium complexes of the allylic type **8a**–**c**.[37,51] At 160 °C, coalescence of the signals for the aromatic protons was observed in the ^1H NMR spectrum of the complex **8a**, which is indicative of a dynamic process, *viz*., a haptotropic shift of the organometallic group between the six-membered rings.[37]



8a–**c**

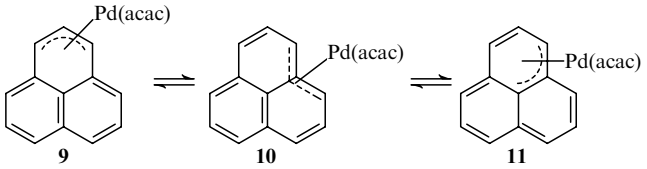


$R^1 = R^2 = R^3$ = H (**a**); $R^1 = R^2 = R^3$ = Me (**b**); R^1 = Me, $R^2 = R^3$ = H (**c**).

In the ^{13}C NMR spectrum of the compound **8b**, the signals for the allylic carbon atoms also coalesce at 102 °C. In this complex, the rate of the haptotropic rearrangement is higher and coalescence starts at lower temperature due apparently to the electronic effect of the methyl groups. The following activation parameters (at 90 °C) were determined from total line-shape analysis of the signals for the methyl groups in the spectra of the compounds **8b**,**c**.

Compound **8**	$\Delta H^{\neq}$ /kcal mol^{-1}	$\Delta G^{\neq}$ /kcal mol^{-1}	$\Delta S^{\neq}$ /e.u.	E_a /kcal mol^{-1}
b	20.9 ± 0.4	21.4 ± 0.1	−1.3 ± 0.3	21.6 ± 0.4
c	23.1 ± 0.7	21.6 ± 0.1	4.1 ± 1.9	23.8 ± 0.7

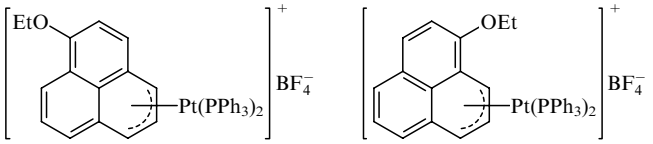
The reaction of phenalene with Li_2PdCl_4 gave rise to the η^3-phenalenyl palladium complex in 90% yield. Subsequent treatment of the latter with a solution of acetylacetone in benzene afforded η^3-phenalenyl complex **9** in 50% yield.[52, 53] The possibility of η^3,η^3-IHR occurring in the complex **9** was examined.



9 **10** **11**

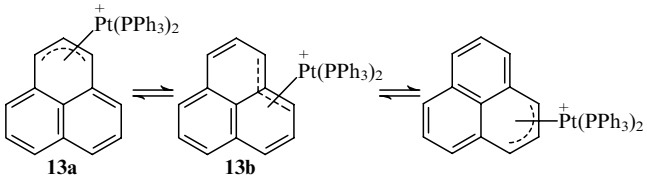
Calculations by the extended Hückel method demonstrated that structure **10** is less stable than structure **11** as the possible transition state. The difference between their energies is 1.21 kcal mol^{-1}. The energy of the structure **9** is 15.77 kcal mol^{-1} lower than that of the structure **11**. Based on the results of calculations, it was concluded that the inter-ring haptotropic shift should occur through the transition state **10**. However, no dynamic processes were observed in the complex **9** by NMR spectroscopy, although η^3,η^3-IHR would be expected to occur by analogy with the complexes **8**.

η^3-Phenalenyl platinum complexes **12a**,**b** were prepared as yellow crystals by the reaction of 1-ethoxyphenalenium tetrafluoroborate with bis(triphenylphosphine)(η^3-ethylene)platinum (the **12a** : **12b** ratio was 10 : 1).[54] The structures of the complexes **12a**,**b** were determined by ^{31}P NMR spectroscopy and X-ray diffraction analysis, but their dynamic behaviour in solution was not studied and the possibility of interconversion of the complexes **12a** and **12b** through inter-ring haptotropic rearrangements was not proved.



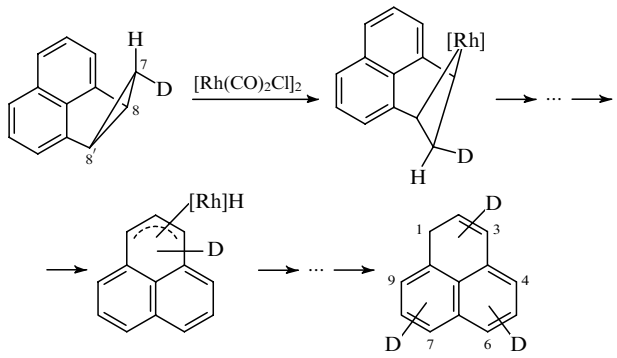
12a **12b**

Calculations by the extended Hückel method demonstrated that the inter-ring haptotropic rearrangement in the η^3-phenalenyl platinum complex **13a** should occur according to an intramolecular mechanism with a relatively low activation energy (20.1 kcal mol^{-1}) through transition state **13b**.[55] The difference between the energies of the complexes **13a** and **13b** was found to be 3.83 kcal mol^{-1}.



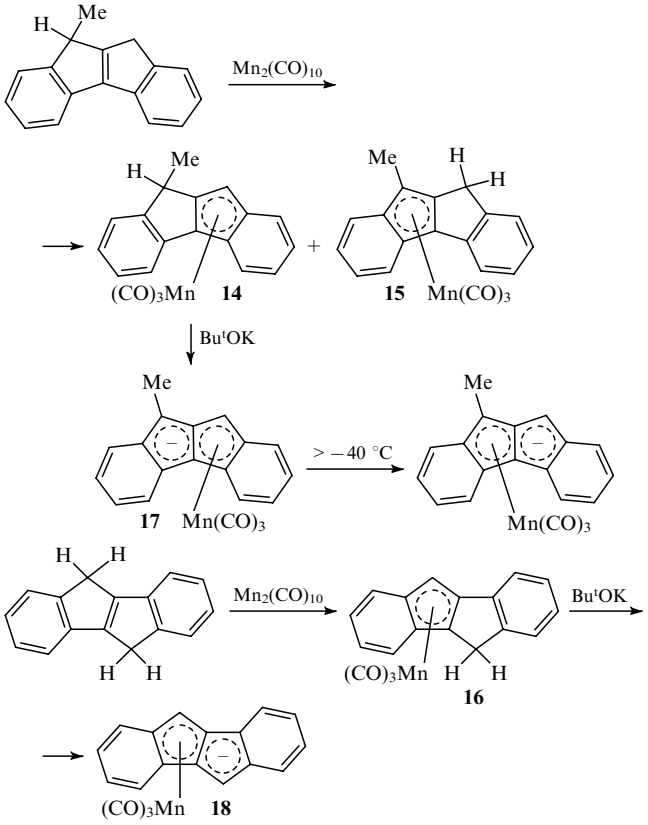
13a **13b**

It was postulated that the η^3-phenalenyl rhodium complex was formed in the reaction of the catalytic conversion of cycloprop[*a*]acenaphthylene into phenalene in the presence of the complex $[Rh(CO)_2Cl]_2$.[56] The deuterium label introduced in the starting compound, for example, at position 7, is statistically distributed over positions 1, 3, 4, 6, 7 and 9 in the final product, *viz*., in phenalene. This is attributable to the fact that the intermediate η^3-phenalenyl rhodium complex undergoes η^3,η^3-IHR involving migration of the metallohydride group between the six-membered rings with the 'ricochet' elimination of hydrogen.

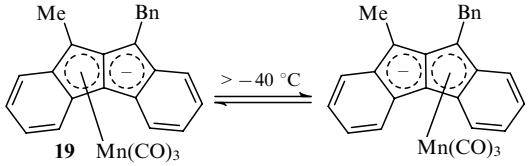


3. η^5,η^5-Rearrangements in dibenzopentalenyl complexes of manganese

Only one example of η^5,η^5-IHR is available in the literature. Refluxing of 9-methylindeno[1,2-*a*]indene or indeno[1,2-*a*]indene with $Mn_2(CO)_{10}$ in dodecane for 1.5 h afforded isomeric dibenzopentalenyl complexes **14**–**16**, which differ in the type of fusion of the indene fragments.[57]



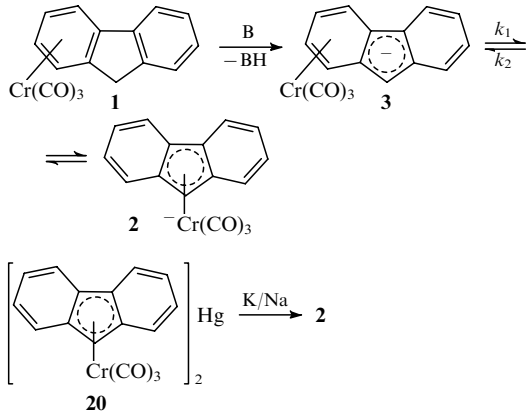
Deprotonation of the complexes **14** and **16** with potassium *tert*-butoxide gave rise to complexes **17** and **18**, respectively. In the compound **18**, no migration of the $Mn(CO)_3$ group, rapid within the NMR time scale, was observed, whereas the complex **17** and the related benzyl complex **19** underwent rearrangements (in the case of the benzyl derivative, the rearrangement was reversible) to form the corresponding isomeric η^5-complexes at temperatures above −40 °C.



The difference in the behaviour of the complexes **17** – **19** was explained based on analysis of the node properties and energies of the highest occupied π-MO of the dibenzopentalenyl complexes **17** and **18** calculated by the INDO method.[43]

4. η⁶,η⁵-Rearrangements in fluorenyl complexes of chromium

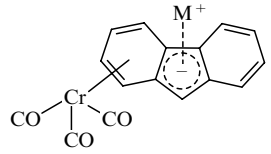
η⁶,η⁵-Inter-ring haptotropic rearrangements have been studied comprehensively for indenyl and fluorenyl complexes of transition metals of the chromium and iron subgroups. For example, isomerisation in the anionic complexes of such ligands as indene, fluorene, their analogues containing different substituents in five- and six-membered rings and heterocyclic analogues of fluorene was considered in detail in reviews.[41–43] In the present review, these data are briefly discussed and supplemented with new results. Thus tricarbonyl(η⁶-fluorene)chromium (**1**) is readily deprotonated with different bases, such as phosphoranes (for example, $Ph_3P=CH_2$), proton sponges, alkali metals in hexamethylphosphoramide (HMPA), BuLi and Bu^{t}OM (M = Na, K, Rb or Cs),[58] in THF, ether, HMPA, dioxane and some other polar solvents. In these cases, the anion **3** is initially formed at rather low temperatures. At temperatures above −20 °C, the η⁶-form **3** undergoes rapid rearrangement into the η⁵-form **2**. This accounts for the fact that Nicholas *et al.*[40] failed to detect the anion **3** at room temperature after deprotonation of the neutral complex **1**.



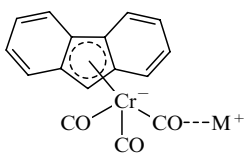
B is base.

The isomeric η⁵-anion **2** was also generated in the pure form by an independent synthesis involving reduction of symmetric mercury derivative **20** with a potassium – sodium alloy in ethereal solutions.

According to the data of IR spectroscopy, salts of the isomeric anions **2** and **3** exist in solution as equilibrium mixtures of contact ion pairs (CIP) and separated ion pairs (SIP) (Tables 1 and 2).[59–62] In the IR spectra of these salts, the absorption bands in the region of ν_{CO} stretching vibrations of the $Cr(CO)_3$ fragment are very characteristic, which allows one to obtain data on the type of ion pairs and to infer the position of the cation. In particular, no splitting of the *E* band of antisymmetric vibrations was observed in the IR spectrum of the contact ion pair formed by the anion **3**. Therefore, it can be concluded that the cation in this ion pair is located above the plane of the five-membered ring of the anion in the *trans* position with respect to the chromium atom.



In the contact ion pair formed by the anion **3**, the negative charge in the ring is substantially decreased due to the strong Coulomb cation – anion interaction. As a result, the symmetry C_{3v} of the $Cr(CO)_3$ fragment is retained and the *E* band is degenerate (see Table 1). On the contrary, splitting of the *E* band is pronounced in the IR spectra of the contact ion pair formed by the anion **2**, the degree of splitting depending on the nature of the cation (see Table 2). Such splitting indicates that the counterion is coordinated to the oxygen atom of one of the CO groups.



The anions **2** and **3** and bulky cations characterised by high charge delocalisation, such as Rb^+, Cs^+, $Bu^n_4N^+$ and Ph_3P^+Me, form predominantly contact ion pairs.

The η⁶,η⁵-inter-ring haptotropic rearrangement of the anion **3** into the anion **2** and the reverse rearrangement were studied by ^{1}H NMR[44, 60, 63] and IR spectroscopy.[59, 64] For these rearrangements, the equilibrium constants (K_{eq}) and the rate constants of the forward and back reactions (k_1 and k_2, respectively) were determined (Tables 3 and 4). The K_{eq} values (see Table 3) indicate that the metallotropic η⁶,η⁵-equilibrium studied for a wide range

Table 1. IR spectra of salts of the η⁶-anion **3** (ν_{CO}).

Cation	Solvent	Solvating additive	ν_A /cm^{-1}	ν_E /cm^{-1}	Type of ion pair
Li^+	THF	–	1927	1820, 1839	SIP
	HMPA	–	1928	1820, 1844	SIP
Na^+	THF	–	1925	1812, 1835	SIP
	HMPA	–	1928	1820, 1844	SIP
	THF	DCH-18-C-6	1925	1821, 1840	SIP
K^+	THF	–	1927	1817, 1841	SIP
	HMPA	–	1928	1820, 1844	SIP
	THF	[2.2.2]-cryptand	1905	1822, 1842	SIP
Rb^+	THF	–	1930	1840	CIP
	HMPA	–	1928	1819, 1843	SIP
	THF	[2.2.2]-cryptand	1927	1820, 1844	SIP
Cs^+	THF	–	1929	1840	CIP
	HMPA	–	1927	1821, 1843	SIP
	THF	[2.2.2]-cryptand	1928	1821, 1843	SIP
$Bu^n_4N^+$	THF	–	1924	1829	CIP
Ph_3P^+Me	THF	–	1927	1832	CIP
	HMPA	DCH-18-C-6	1927	1820, 1842	SIP

Note. DCH-18-K-6 is dicyclohexyl-18-crown-6.

Table 2. IR spectra of salts of the η⁵-anion **2** (ν_{CO}).

Cation	Solvent	Solvating additive	ν_A /cm^{-1}	ν_E /cm^{-1}	Type of ion pair
Li^+	THF	–	1915	1733, 1820	CIP
	HMPA	–	1904	1799	SIP
Na^+	THF	–	1907	1762, 1811	CIP
	HMPA	–	1904	1798	SIP
	THF	DCH-18-C-6	1903	1800	SIP
K^+	THF	–	1905	1766, 1807	CIP
	HMPA	–	1904	1798	SIP
	THF	[2.2.2]-cryptand	1905	1800	SIP
Rb^+	THF	–	1904	1766, 1804	CIP
	HMPA	–	1904	1798	SIP
	THF	[2.2.2]-cryptand	1905	1800	SIP
Cs^+	THF	–	1904	1778, 1798	CIP
	HMPA	–	1904	1789	SIP
	THF	[2.2.2]-cryptand	1905	1800	SIP
$Bu^n_4N^+$	THF	–	1903	1778, 1798	CIP
Ph_3P^+Me	THF	–	1905	1802	CIP

Table 3. Equilibrium constants for η^6,η^5-IHR of salts of anions **2** and **3**.

Cation	Solvent	Type of **3** ⇌ **2** equilibrium	$K_{eq} = 2k_1/k_2$
Li^+	HMPA	SIP ⇌ SIP	5.40
	THF	SIP ⇌ SIP	see [b]
Na^+	HMPA	SIP ⇌ SIP	5.00
	THF	SIP ⇌ SIP	13.7
K^+	HMPA	SIP ⇌ SIP	4.92
	THF	SIP ⇌ SIP	14.3
Rb^+	THF [a]	SIP ⇌ SIP	4.40
	THF	CIP ⇌ CIP	5.0
Cs^+	THF [a]	SIP ⇌ SIP	4.60
	THF	CIP ⇌ CIP	1.40
$Ph_3\overset{+}{P}Me$	THF	CIP ⇌ CIP	3.40

[a] HMPA was used as the solvating additive. [b] The K_{eq} value was not determined because the lithium salt of the anion **3** in a solution in THF was unstable.

Table 4. Rate constants and equilibrium constants of the **3** ⇌ **2** rearrangement.[59]

T/K	$10^{-4}k_1$ /s^{-1}	$10^{-4}k_2$ /s^{-1}	$K_{eq} = 2k_1/k_2$ (see [a])
THF			
273	1.11	0.2	11.1
280	1.22	0.21	11.62
288.5	4.0	0.63	12.7
298	8.9	1.28	13.9
301	17.1	2.4	14.3
THF with a DCH-18-C-6 additive			
273	0.62	0.4	3.1
285.5	2.75	1.12	4.91
298	18.5	6.86	5.4

[a] The possibility of the **3** ⇌ **2** rearrangement occurring in both directions was ignored in the study [59] and, hence, only the refined K_{eq} values for the doubly degenerate process are given.

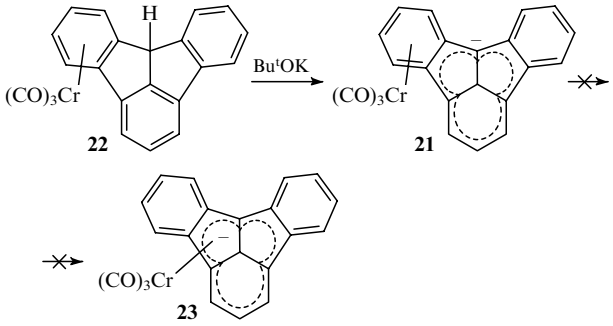
of systems is very sensitive to the structure of the ion pairs. The thermodynamic data given below testify that these η^6,η^5-IHR are entropy-controlled processes. It should be noted that many reactions involving ion pairs are entropy-controlled, which is attributed to the fact that several solvent molecules are coordinated about the cation (solvate coat) in separated ion pairs resulting in a substantial decrease in the entropy of this state.[62] The activation parameters of the **3** ⇌ **2** rearrangement in THF in the presence and in the absence of the solvating additive (DCH-18-C-6) are given below:

Solvent	E_a /kcal mol^{-1}	$\Delta H^{\neq}$ /kcal mol^{-1}	$\Delta S^{\neq}$ /e.u.
THF	16.3 ± 2.18	15.7 ± 2.04	-19.6 ± 2.55
THF + DCH-18-C-6	21.9 ± 2.13	21.3 ± 2.10	0.2 ± 0.02

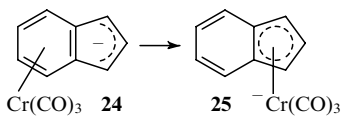
Cross experiments demonstrated that at moderate temperatures η^6,η^5-IHR in the anions **2** and **3** proceed through an intramolecular mechanism. In these processes, the tricarbonylchromium group is not eliminated and does not go into solution to form a complex with the solvent (for example, with THF).[41]

5. Rearrangements in anionic tricarbonylchromium η^6- and η^5-complexes of carbo-and heterocyclic analogues of fluorene

By going from the unsubstituted tricarbonylchromium complex of fluorene to its carbo- and heterocyclic analogues, one can substantially extend the range of systems in which η^6,η^5-IHR occur and study the dependence of these processes on the electronic and steric effects of the substituents and heteroatoms.[65] The introduction of a heteroatom or a substituent into one of the rings of the π-ligand leads to a substantial change in the electron density in the latter. The isomer in which the organometallic group is bound to the ring possessing a higher electron density is thermodynamically more stable resulting in an increase in the content of this isomer in the equilibrium mixture. In the case of carbocyclic analogues of 9-substituted fluorenes (9-methyl-, 9-*tert*-butyl- and 9-phenylfluorenes), the ratio between the η^5 and η^6-isomers depends on the electronic and steric effects of the substituent. The donor effect of the methyl group leads to an increase in the electron density in the five-membered ring of the fluorenyl anion and, correspondingly, to an increase in the proportion of the η^5-isomer ($K_{eq} = [\eta^5]/[\eta^6] = 10$). On the contrary, the electron-withdrawing effect of the phenyl substituent leads to a decrease in the electron density in the five-membered ring and, correspondingly, to a decrease in the portion of the η^5-isomer in the equilibrium mixture ($K_{eq} = [\eta^5]/[\eta^6] = 0.35$). Tricarbonyl($\eta^6$-fluoradenyl)chromium (**21**) formed upon deprotonation of fluoradene complex **22** does not undergo rearrangement to form the η^5-anion **23**.[66] This is attributable to the fact that the negative charge is delocalised over two five-membered rings and the six-membered ring fused with these rings.

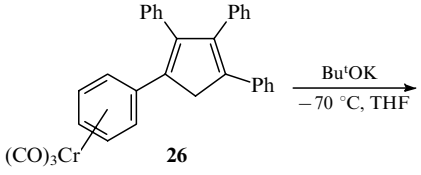


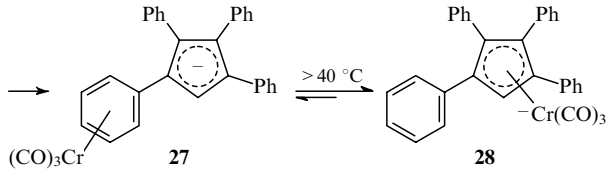
On the contrary, delocalisation of the negative charge in the five-membered ring in (η^6-indenyl)tricarbonylchromium (**24**) is smaller than that in the fluorenyl analogue and hence, the anion of **24** is completely rearranged into the η^5-isomer **25** in THF even at temperatures above −40 °C. The rate of the η^6,η^5-inter-ring haptotropic **24** → **25** rearrangement is noticeably higher than that of the **3** → **2** rearrangement.



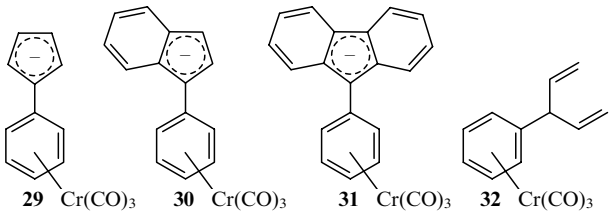
The phenyl substituent in the five-membered ring of the complex **24** (like that in the 9-phenylfluorenyl complex) decreases the electron density in the ring and hence, the equilibrium is shifted toward the η^6-anion.[43]

The Öfele reaction of tetraphenylcyclopentadiene with $Py_3Cr(CO)_3$ afforded tricarbonyl[(η^6-1-phenyl)-2,3,4-triphenylcyclopentadiene]chromium (**26**),[67] which is the nonannelated open analogue of (η^6-indenyl)tricarbonylchromium. Deprotonation of the latter giving rise to the η^6-anion **27** and the ability of the tricarbonylchromium group to migrate from the six-membered ring to the five-membered ring to form the η^5-anion **28** were examined.





Ceccon *et al.* studied irreversible η^6,η^5-IHR in the phenylcyclopentadienyl (**29**), 1-phenylindenyl (**30**) and 9-phenylfluorenyl (**31**) complexes of chromium [68] and the rearrangement in the very interesting open phenylpentadienyl system **32**.[69]



The activation parameters and the rate constants (k) of η^6,η^5-IHR in the anions **29**–**31** are given below.

29: $\Delta S^{\neq} = -7.1 \pm 1.1$ e.u., $\Delta H^{\neq} = 22.7 \pm 0.4$ kcal mol^{-1},

T/K	325	332	337	342
$10^4 k$ /s^{-1}	1.03 ± 0.03	2.32 ± 0.01	3.85 ± 0.02	6.21 ± 0.02

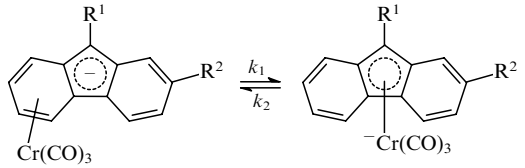
30: $\Delta S^{\neq} = -7.6 \pm 0.6$ e.u., $\Delta H^{\neq} = 22.3 \pm 0.4$ kcal mol^{-1},

T/K	324	325	341	346
$10^4 k$ /s^{-1}	1.3 ± 0.02	4.32 ± 0.02	7.86 ± 0.03	12.5 ± 0.2

31: $\Delta S^{\neq} = 2.6 \pm 0.7$ e.u., $\Delta H^{\neq} = 24.3 \pm 0.02$ kcal mol^{-1},

T/K	338	343	348	353
$10^4 k$ /s^{-1}	1.08 ± 0.01	1.84 ± 0.01	3.15 ± 0.06	5.20 ± 0.06

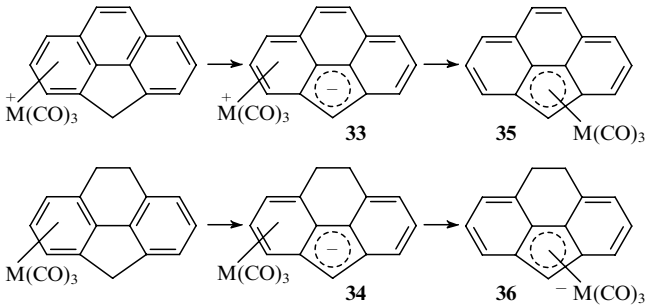
The kinetic parameters (298 K) of η^6,η^5-IHR in 2-acetyl, 9-methyl- and 9-phenylfluorenyl complexes of chromium were determined.[64]



R^1 = H, R^2 = COMe; R^1 = Me, R^2 = H; R^1 = Ph, R^2 = H.

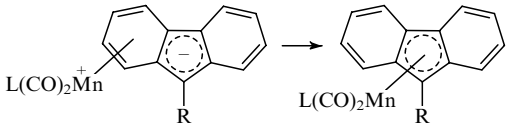
R^1	R^2	K_{eq}	$10^4 k_1$ /s^{-1}	$10^4 k_2$ /s^{-1}
H	H	6.37	4.0	0.63
Me	H	5.73	5.82	1.02
H	COMe	3.03	5.76	1.9

McGlinchey and coworkers studied [70] the rearrangements of the zwitterionic tricarbonylmanganese complexes and the anionic tricarbonylchromium complexes containing a very interesting ligand, *viz.*, 4*H*-cyclopenta(phenanthrene), or the corresponding hydrogenated ligand. The possible paths of these rearrangements and the transition states were investigated experimentally as well as theoretically by the extended Hückel method. The η^6,η^5-inter-ring haptotropic rearrangements both in the manganese and chromium complexes **33** with the completely fused ligand proceed much more readily than those in the anions **34** prepared from the corresponding hydrogenated complexes. The η^6-anions **33** are kinetically stable at temperatures below −40 °C. At higher temperatures, these anions undergo rearrangements into the η^5-anions **35**, whereas the rearrangements of the hydrogenated anions **34** into anions **36** occur at high temperatures. The authors attributed this fact to the retention of the stable naphthalene system of the aromatic anion in the course of IHR.

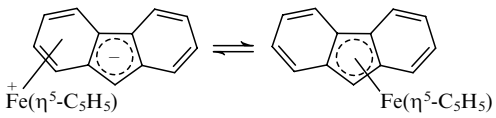


M = Mn, Cr.

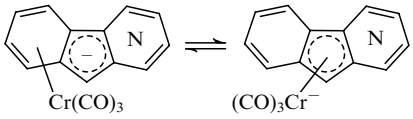
Relatively rapid η^6,η^5-inter-ring rearrangements in the fluorenyl complexes of manganese,[71] iron,[72] molybdenum and tungsten [73] were studied. The E_a values of these processes were demonstrated to depend substantially on the nature of transition metal. The $\Delta H^{\neq}$ values are in the range of 24–25 kcal mol^{-1} and the $\Delta S^{\neq}$ values vary from 2 to −1.6 e.u. The rearrangements in the manganese complexes are irreversible.[71]



R = H, Bu^t; L = CO, PBu$^n_3$.



Investigations of azafluorenyl systems by the INDO method demonstrated [43, 74] that the introduction of the electronegative nitrogen atom into the six-membered ring leads to a decrease in electron density in the five-membered ring compared to that in the fluorenyl system, *i.e.*, the inter-ring haptotropic rearrangement results in a decrease in the portion of the η^5-isomer.



The η^6,η^5-inter-ring haptotropic rearrangements do not proceed in tricarbonylchromium complexes of carbazolyl and indolyl, which is difficult to explain within the framework of the above-decribed simplified approach because the electron density in the five-membered rings of these compounds is very high. Apparently, these rearrangements do not occur due to the fact that the electron pair at the nitrogen atom in the pyrrolyl, indolyl and carbazolyl anions occupies an MO orthogonal to the π-MO of the cyclic system, whereas the electron pair at the carbon atom in the cyclopentadienyl, indenyl and fluorenyl anions is involved in a π-MO participating in bonding with the metal atom.

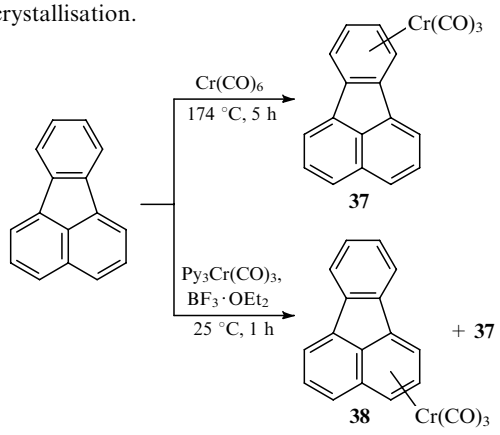
Experimental investigations of the structures and properties of isomeric η^6- and η^5-fluorenyl complexes and their analogues and examination of the mechanism of η^6,η^5-IHR have been summarised.[74–79] Analysis of the above-considered data demonstrates that the structure of the π-ligand, the nature of the metal atom and its ligand environment affect substantially the metallotropic equilibrium, the site of location of the organometallic group depending to a large extent on the electron density in the five-membered ring. Apparently, the determination of enthalpies of isomeric complexes and transition states using high-level quantum-chemical calculations can improve the reliability of the prediction of the results of IHP.[80]

6. η^6,η^6-Rearrangements in tricarbonylchromium complexes of naphthalene and its analogues

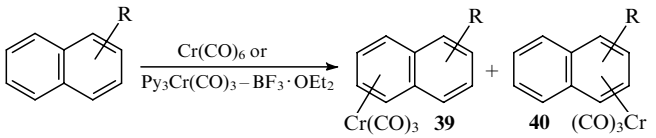
Deubzer[48] demonstrated that isomerisation of tricarbonylchromium complexes of 2,3-dimethylnaphthalene, which is the first example of η^6,η^6-IHR available in the literature, proceeds slowly and is characterised by a high activation barrier. These results were indirectly confirmed in studies performed by Nicholas,[40] Kündig[46] and Albright[47] with their coworkers. The authors failed to detect the haptotropic rearrangement in tricarbonylchromium complexes of η^6-naphthalene and η^6-acenaphthylene by dynamic NMR spectroscopy upon heating of specimens in the probe of an NMR spectrometer. Analogously, inter-ring rearrangements, rapid within the NMR time scale, were not detected at relatively high temperatures in some other naphthalene complexes, for example, in $[(\eta^6\text{-}C_{10}H_8)Ir(\eta^5\text{-}C_5Me_5)]^{2+}$ (70 °C, CF_3CO_2H)[77] and $(\eta^6\text{-}C_{10}H_8)_2Cr$ (130 °C, C_6D_6).[46]

Hence, the only possible strategy for studying η^6,η^6-rearrangements in π-complexes of naphthalene involves the removal of degeneration in these systems, *i.e.*, the use of unsymmetrically substituted compounds, and their study by stationary kinetics methods. This approach was developed in detail only in the mid-1980s.[81–84] Initially, procedures have been proposed for the regioselective synthesis of tricarbonylchromium complexes of substituted naphthalenes containing a label at a particular position of the coordinated or uncoordinated ring of the naphthalene ligand.

Substituted naphthalenes can form tricarbonylchromium complexes upon heating with $Cr(CO)_6$,[85] including reactions in the presence of polar additives[86] as catalysts. For example, boiling of $Cr(CO)_6$ with naphthalene in decalin in the presence of ethyl formate afforded $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$ in 88% yield.[87] Tricarbonylchromium complexes of substituted naphthalenes were also formed in the reactions of the ligand with $(NH_3)_3Cr(CO)_3$ (the Rausch reaction[88]) and with the $Py_3Cr(CO)_3$–$BF_3\cdot OEt_2$ system (the Öfele reaction[89,90]). Thus the reaction of fluoranthene with $Cr(CO)_6$ performed under conditions of thermodynamic control gave rise to η^6-complex **37** in which the $Cr(CO)_3$ is located at the benzene ring.[91] The synthesis with the use of the $Py_3Cr(CO)_3-BF_3\cdot OEt_2$ system yielded complex **38** in which the $Cr(CO)_3$ is located at the naphthalene fragment. The latter reaction also afforded a small admixture (< 5%) of the compound **37**, which was readily separated from the complex **38** by recrystallisation.



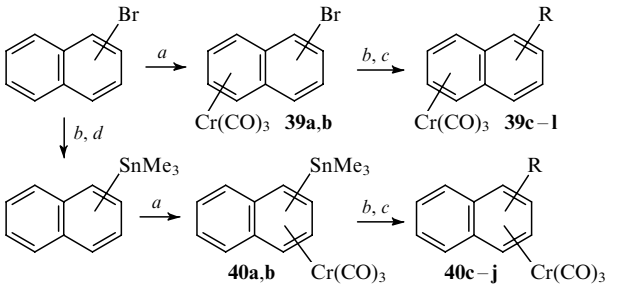
A convenient alternative procedure was developed for the synthesis of substituted naphthalenes. This procedure involves the migration of the tricarbonylchromium group from readily accessible $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$ to another polyaromatic ligand.[46] The result of this complexation reaction depends on the conditions of control (either kinetic or thermodynamic), which can be used for preparative purposes. However, these methods for the synthesis of complexes of monosubstituted naphthalenes generally give rise to mixtures of both possible isomers **39** and **40** containing the tricarbonylchromium group either in the substituted or unsubstituted rings.



For alkyl-substituted complexes, the **39** : **40** ratio is close to unity and the isomers can be separated by chromatography (TLC or HPLC[92]). It was demonstrated[93] that the very high regioselectivity of the Öfele reaction can be achieved if the substituent possesses pronounced electron-withdrawing or electron-donating properties. This behaviour agrees well with the results of calculations of the relative energies of isomeric tricarbonylchromium complexes of monosubstituted naphthalenes within the framework of density functional theory (DFT).[80]

Thus under the conditions of the Öfele reaction, complexes of the type **39** are predominantly formed if R = Br, whereas complexes of the type **40** are obtained as the major products if R = $SiMe_3$ and, particularly, if R = $SnMe_3$. A thorough search for the reaction conditions enables one to achieve satisfactory yields (50% and higher)

The most general and versatile procedure for the regioselective synthesis of substituted complexes **39** and **40** involves the following reaction sequence. Initially, 1- and 2-bromo- or 1- and 2-trimethylstannylnaphthalenes are converted into the corresponding tricarbonylchromium complexes **39a**,**b** or **40a**,**b**, respectively, by the Öfele reaction.



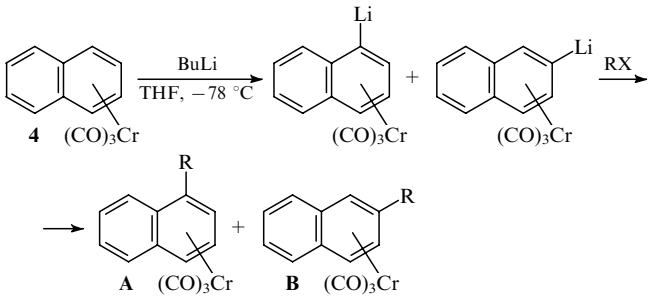
39: R = 1-Br (**a**), 2-Br (**b**), 1-D (**c**), 2-D (**d**), 1-Me (**e**), 2-Me (**f**), 1-$SiMe_3$ (**g**), 2-$SiMe_3$ (**h**), 1-$SnMe_3$ (**i**), 2-$SnMe_3$ (**j**), 1-Cl (**k**), 2-Cl (**l**);

40: R = 1-$SnMe_3$ (**a**), 2-$SnMe_3$ (**b**), 1-D (**c**), 2-D (**d**), 1-Me (**e**), 2-Me (**f**), 1-$SiMe_3$ (**g**), 2-$SiMe_3$ (**h**), 1-Cl (**i**), 2-Cl (**j**);

(*a*) $Py_3Cr(CO)_3-Et_2O\cdot BF_3$; (*b*) BuLi; (*c*) RX; (*d*) Me_3SnCl.

In the reactions of these complexes with BuLi in ether at −70 °C, the Br or $SnMe_3$ substituents are readily replaced by lithium. Under these conditions, the resulting organolithium compounds neither decompose nor undergo isomerisation. Subsequently, the latter compounds react with various electrophilic reagents to give the complexes **39c**–**l** or **40c**–**j** in yields varying from 50% (R = Cl) to 90% (R = D). It appeared that the reaction must be performed in ether because this reaction in THF is essentially complicated by intramolecular and intermolecular Li–H exchange (see below).[94]

One of procedures for the selective introduction of a substituent into the coordinated ring involves direct metallation of tricarbonyl(η^6-naphthalene)chromium (**4**) followed by treatment of the resulting organolithium compound with an electrophilic reagent.[93] It is known that coordination with the tricarbonylchromium group leads to a substantial increase in the acidity of the arene protons (the pK_a values decrease by 6–7[95]). The reaction with the use of BuLi as the metallating agent in THF at −78 °C proceeded nonselectively both at positions 1 and 2 of the coordinated ring to form mixtures of complexes following reactions with electrophiles.

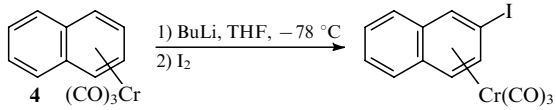


RX = D_2O, MeI, Me_3SiCl, Me_3SnCl.

If lithium salts are generated at a temperature below −78 °C, the ratio between the isomers **A** and **B** in the mixture depends on the nature of the substituent.

RX	Total yield (%)	The ratio **A** : **B**
D_2O	87	0.80
MeI	66	0.56
Me_3SnCl	74	0.44
Me_3SiCl	45	0.31

The replacement proceeded regioselectively at position 2 (the yield was 20%) only in the reactions of lithium salts with I_2.



Kündig *et al.* demonstrated[83] that the use of sterically hindered 2,2,6,6-tetramethylpiperidyllithium instead of BuLi made it possible to perform regioselective metallation of tricarbonyl(η⁶-naphthalene)chromium. In this case, the replacement occurred exclusively at position 2, which may be due to steric hindrances to electrophilic attack at position 1.

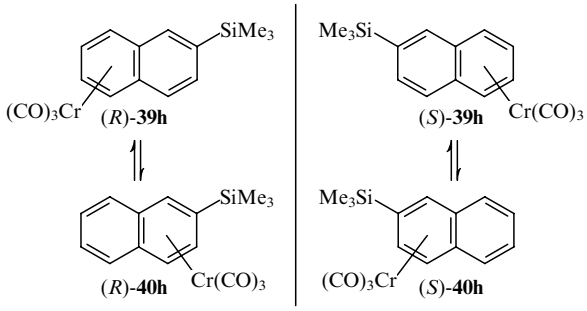
III. Studies of mechanisms and kinetics of rearrangements in tricarbonylchromium complexes of polycyclic arenes

Elucidation of the mechanism is the vital problem in studies of chemical processes. For inter-ring haptotropic rearrangements in tricarbonylchromium complexes of polycyclic arenes, it is important to determine whether the reaction proceeds through an intramolecular or intermolecular dissociation mechanism. In the first case, the migration of the $Cr(CO)_3$ group along the ligand plane occurs without the cleavage of bonds with the ligand. In the second case, the $Cr(CO)_3$ group is eliminated from one ring of the ligand and passes into solution. Then this group is coordinated by solvent molecules containing a heteroatom followed by addition to another ring of the same ligand or to another ligand. Bimolecular reactions of the complexes can proceed as well (either with each other[96] or with free ligands formed upon thermal destruction of the complexes). The latter are accompanied by the migration of the tricarbonylchromium group in the ligand, *i.e.*, IHR can occur through an intermolecular exchange mechanism.

Previously, the intramolecular mechanism of η⁶,η⁵-IHR in isomeric fluorenyl complexes **2** and **3** was confirmed by cross experiments.[42,43] An analogous approach was used in studies of the mechanism of η⁶,η⁵-IHR in tricarbonylchromium complexes of naphthalene derivatives. For this purpose, the redistribution of the tricarbonylchromium group between naphthalene and perdeuterionaphthalene was examined.[93] It was found that even prolonged heating (90 °C, > 40 h) of the complex **39e** with perdeuterionaphthalene in anhydrous decane did not lead to migration of the tricarbonylchromium group to perdeuterionaphthalene. Although the **39e** ⇌ **40e** inter-ring haptotropic migration occurred under these conditions, the $(\eta^6\text{-}C_{10}D_8)Cr(CO)_3$ complex was not formed. According to the data of mass spectrometry with the use of chemical ionisation, heating of $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$ in the presence of perdeuterionaphthalene at 130 °C (*i.e.*, at a temperature which is substantially higher than that required for IHR to proceed at a noticeable rate) for 6 h afforded only a small amount (< 5%) of $(\eta^6\text{-}C_{10}D_8)Cr(CO)_3$.[93] However, in the reactions with the use of benzene derivatives (which coordinate the tricarbonylchromium group much more readily than polycyclic aromatic compounds) as the solvent, the migration of the $Cr(CO)_3$ group to monocyclic arene was observed even at 90–130 °C and monocyclic complexes were obtained in yields of up to 20%. The complete replacement of naphthalene by monocyclic arene was achieved only upon heating of $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$ in unsubstituted benzene (140 °C, 6 h).

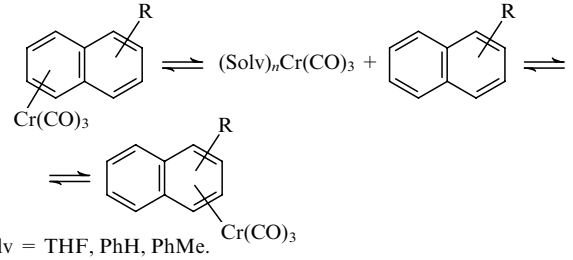
Therefore, even before IHR were found to occur in naphthalene complexes, investigations of these compounds have demonstrated that isomerisation can proceed according to both intramolecular and intermolecular mechanisms depending on the nature of the solvent. Later, the most convincing evidence that IHR in tricarbonylchromium complexes of monosubstituted naphthalenes proceeds through an intramolecular mechanism was obtained with the use of enantiomerically pure compounds.

Since chiral organometallic compounds are used in asymmetric synthesis and catalysis, they attract growing interest of researchers in organometallic chemistry.[97] Although the use of chiral compounds for studying the mechanisms of purely organic reactions has long been a classical method, this approach to investigation of the mechanism of IHR has been used only recently.[98] With the aim of elucidating the mechanism of η⁶,η⁶-IHR in tricarbonylchromium complexes of naphthalene derivatives possessing planar chirality, the ability of their individual enantiomers to retain or lose optical activity in the course of the rearrangements was examined. If η⁶,η⁶-IHR proceeds according to an intramolecular mechanism, the optical activity should be retained and isomeric complexes, for example, **39h** and **40h** (for which this process was studied in most detail), should be present in the equilibrium mixture only as either *R* or *S* forms.



Mirror plane

If the rearrangement proceeds through either a dissociation or exchange intermolecular mechanism, the individual enantiomer should undergo racemisation due to the equally probable attacks of the tricarbonylchromium group [free ('hot'), σ-bonded to the solvent molecule containing a heteroatom or π-bonded to the solvent molecule, which does not contain a heteroatom (benzene or toluene)] on the arene from opposite sides. In this case, both



Solv = THF, PhH, PhMe.

isomeric complexes containing the $Cr(CO)_3$ group in either substituted or unsubstituted ring should be present in the equilibrium mixture both as the *R* and *S* forms.

Some planar-chiral tricarbonylchromium complexes of substituted naphthalenes can be separated by HPLC on an optical Chiracel OD column (Diacel, Japan).[99] Previously,[100] it had been demonstrated that this column, with modified cellulose as the support, is very efficient for separation of enantiomers of transition metal complexes, including tricarbonylchromium complexes of arenes.[101] For a number of complexes of monosubstituted naphthalenes, very high selectivity factors of separation (α)

$$\alpha = \frac{t_2 - t_0}{t_1 - t_0},$$

were achieved, where t_0 is the retention time of the compound not retained (3.35 min) and t_1 and t_2 are the retention times of the enantiomers, which are eluted successively. For example, the selectivity for the complex **40b** was 5.23! The results of HPLC are given in Table 5.

Table 5. Data on separation of enantiomers of tricarbonylchromium complexes of naphthalene derivatives by HPLC on a Chiracel OD column.

Complex **39**	t_1 /min	t_2 /min	α	Complex **40**	t_1 /min	t_2 /min	α
l	13.32	14.00	1.07	**j**	9.65	10.35	1.11
f	11.30	11.30	1.00	**f**	11.53	12.32	1.09
h	7.33	8.66	1.33	**h**	6.00	14.66	4.27
j	8.65	10.64	1.37	**b**	6.53	20.00	5.23
k	12.00	17.37	1.62	**i**	10.00	14.30	1.65
e	12.2	14.69	1.28	**e**	11.66	18.00	1.76
i	7.34	8.00	1.16	**a**	8.53	15.20	2.29
g	6.26	8.06	1.62	**g**	6.66	9.35	1.81

Note. The rate of the mobile phase [9 : 1 (*v*/*v*) n-hexane – propan-2-ol] was 10 ml min^{-1}.

To elucidate the mechanism of IHR in the tricarbonylchromium complexes of monosubstituted naphthalenes, **39h** and **40h**, the possibility of their enantiomers retaining optical activity in the course of the rearrangements (85 °C, C_6F_6 or toluene or C_6F_6 with 5% of THF) was examined. The chromatogram (Fig. 1 *a*) of one of the enantiomers of the complex **39h** in C_6F_6 was obtained. [It should be noted that the absolute configuration was determined (for example, by X-ray diffraction analysis) for none of the complexes.] As the inter-ring haptotropic rearrangement proceeds (C_6F_6, 85 °C, 40 h), two intense peaks appear on the chromatogram. One of them corresponds to an enantiomer of **39h** (peak *1*) and the second peak corresponds to an enantiomer of **40h** (peak *2*), *i.e.*, the **39h** ⇌ **40h** equilibrium occurs (K_{eq} = [**40h**]/[**39h**] = 17.26). The portions of enantiomers of **39h** (peak *3*) and **40h** (peak *4*) with another configurations were ⩽ 1% (Fig. 1 *b*). Analogous results were obtained in the case of the **39h** ⇌ **40h** rearrangement in decane.

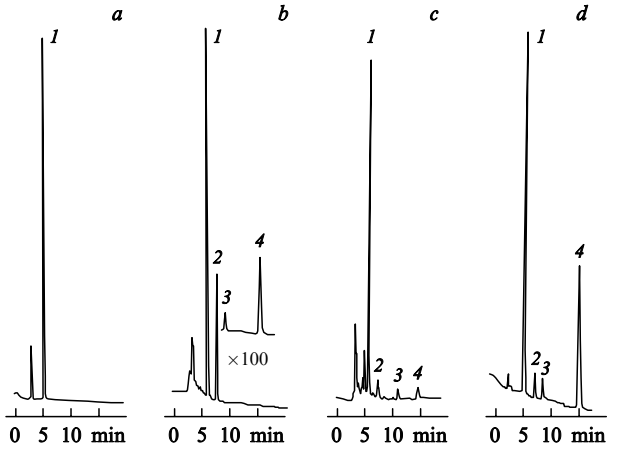
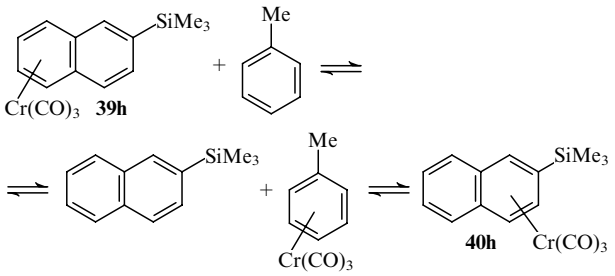


Figure 1. Chromatograms (HPLC on a Chiracel OD column) of the enantiomers of **39h** in C_6F_6 without heating (*a*) and with heating at 85 °C for 40 h in C_6F_6 (*b*), toluene (*c*) and the C_6F_6 – THF system (95 : 5) (*d*). Peaks (*1*) and (*4*) correspond to enantiomers of **39h** and peaks (*2*) and (*3*) correspond to enantiomers of **40h**. The integrated intensities of peaks (*1*) and (*4*) and of peaks (*2*) and (*3*) on the chromatogram (*d*) are equal.

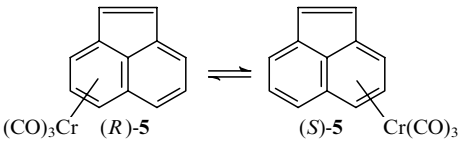
The absence of racemisation proves that IHR in inert non-solvating solvents proceeds through an intramolecular mechanism without participation of dissociation and exchange processes. In this case, the $Cr(CO)_3$ group 'slips' along the plane of the π-ligand, bonding with the ligand being retained. However, the degree of racemisation in pure toluene under the same conditions is ~ 20% (Fig. 1 *c*), *i.e.*, IHP in aromatic solvents proceeds to some extent through an intermolecular exchange mechanism.



In the reaction performed under the same conditions but in C_6F_6 with the addition of 5% of THF, the complexes **39h** and **40h** underwent virtually complete racemisation (⩾ 75%) (Fig. 1 *d*). For some other complexes, analogous results were achieved upon addition of 10% of dibutyl ether to C_6F_6. Therefore, thermally induced η^6,η^6-IHR in tricarbonylchromium complexes of naphthalene derivatives in the presence of solvating solvents proceeds primarily by the dissociation intermolecular mechanism.

The use of chiral complexes shows considerable promise for elucidation of fine details of the mechanism of organometallic reactions, in particular, IHR. For example, studies of racemisation of some complexes in the course of their rearrangements made it possible to determine the kinetic and thermodynamic parameters of IHP in the cases where these parameters cannot be obtained by other methods.

Based on the results of calculations by the extended Hückel method, Albright *et al.*[47] suggested that the presence of an exocyclic double bond should substantially promote η^6,η^6-IHR in tricarbonylchromium complex of acenaphthylene **5**. The authors attempted to detect degenerate η^6,η^6-IHR by dynamic NMR spectroscopy upon heating of the complex **5** in deuteriodecalin to 160 °C. However, no broadening of lines caused by migration of the tricarbonylchromium group between the equivalent six-membered rings was observed. Apparently, the activation barrier is such that this rearrangement cannot be studied by two-dimensional NMR spectroscopy. However, the rearrangement can be examined without introduction of a label into the coordinated ring. The enantiomers of the complex **5** can be separated and each isomer should undergo racemisation in the course of IHR, which, in principle, allows one to determine the rate constant of the rearrangement as the rate constant of racemisation.



1. η^6,η^6-Rearrangements in tricarbonylchromium complexes of naphthalene derivatives

The kinetics of IHR in a number of tricarbonylchromium complexes of monosubstituted naphthalenes was studied by NMR spectroscopy. The rearrangements were performed in C_6F_6 at 85 °C.[94] The $^2H\{^1H\}$ NMR spectra of the deuterium-containing complexes **39c**,**d** and **40c**,**d** were measured. For the remaining complexes **39** and **40**, the ^1H NMR spectra were recorded. The signals in the NMR spectra were repeatedly integrated and averaged.

Kinetic studies demonstrated that the parameters obtained are well reproduced for pairs of the complexes, which differ in the position of the $Cr(CO)_3$ group, and are independent of a particular isomer chosen as the starting one. The typical kinetic curves for a pair of the complexes **39g** and **40g** are shown in Fig. 2.

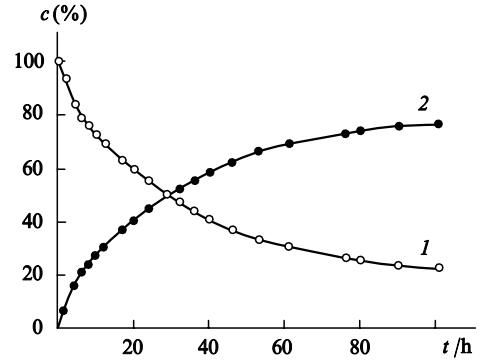
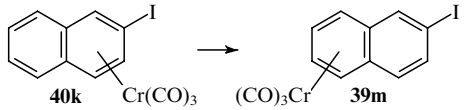


Figure 2. Kinetic curves of isomerisation of the tricarbonylchromium complexes of 1-trimethylsilylnaphthalene **39g** (*1*) and **40g** (*2*) (starting from **39g**).

The 2-iodonaphthalene complex **40k**, unlike the remaining tricarbonylchromium complexes of substituted naphthalenes, was demonstrated to be irreversibly rearranged to the isomeric complex **39m**. However, attempts to measure the kinetic parameters of the rearrangement failed due to instability of both complexes in all solvents under study.

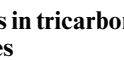


It should be noted that no noticeable destruction of the remaining compounds accompanied by the appearance of free ligands in the reaction mixtures was observed. In all cases, the rearrangements

Table 6. Rate constants, equilibrium constants and free activation energies of IHR in the complexes **39** (C_6F_6, 85 °C).[94]

Complex	$10^5 k_1$ /s^{-1}	$10^5 k_2$ /s^{-1}	K_{eq}	$\Delta G^{\neq}(358)$ /kcal mol^{-1}
39e	0.90 ± 0.01	0.51 ± 0.02	1.77	29.4 ± 0.6
39f	1.82 ± 0.10	1.01 ± 0.10	1.80	29.2 [a]
39f	3.02 ± 0.24	1.45 ± 0.07	2.09	28.5 ± 1.2
39g	2.40 ± 0.02	0.50 ± 0.02	4.80	28.7 ± 0.7
39h	1.93 ± 0.03	0.11 ± 0.01	17.26	29.1 ± 0.6
39i	0.70 ± 0.01	0.14 ± 0.01	5.00	29.5 ± 0.5
39j	2.24 ± 0.04	0.17 ± 0.01	13.26	28.8 ± 0.7
39k	0.15 ± 0.01	4.36 ± 0.06	0.034	30.6 ± 0.4
39l	0.40 ± 0.01	3.46 ± 0.06	0.12	30.2 ± 0.8

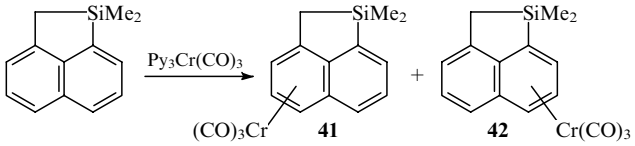
[a] Calculations were performed based on the data reported in Ref. 83; cyclohexane-d_{12} was used as the solvent.



are described with a high degree of accuracy by a model of a reversible first-order reaction. The kinetic and thermodynamic parameters of the rearrangements of the complexes **39** in solutions in C_6F_6 are given in Table 6.

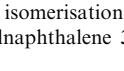
2. η^6,η^6-Rearrangements in tricarbonylchromium complexes of naphthalene-related ligands

The kinetics of rearrangements in isomeric (η^6-dimethylsilaacenaphthene)tricarbonylchromium complexes **41** and **42**, related to naphthalene complexes, was studied. The complexes **41** and **42** were prepared starting from dimethylsilaacenaphthene by the Öfele reaction in 76% yield.[102]



The **41** : **42** ratio was equal to 1 : 6. *i.e.*, as discussed above, the tricarbonylchromium group tends to occupy the position in the ring containing an electron-donating substituent. Under conditions of TLC, the complexes **41** and **42** are characterised by virtually identical mobilities due to which they were separated by HPLC.

At 75–130 °C, the kinetically less stable complex **41** in C_6F_6 underwent rearrangement to the thermodynamically more stable complex **42**.



The content of the complex **42** in the equilibrium mixture was higher than 70%, which made it possible to measure a large number of points for the time dependence of the concentration, thus improving the accuracy and reliability of the experimental data. The kinetic data measured for the forward and back processes agree well with each other.[103]

The relative concentrations of the complexes **41** and **42** were determined by repeated integration followed by averaging of the well-resolved signals for the protons of the methyl groups in the ^1H NMR spectra. The measurements were carried out in the temperature range of 105–118 °C because the rate of IHR at temperatures below 100 °C is very low, whereas at temperatures above 118 °C the complexes decompose (in the NMR spectrum, a signal for the protons of the methyl groups of the ligand appears at δ 0.52). The dependence of the concentration of the isomer **42** on the time (t) was calculated according to the equation for a reversible first-order reaction:[104]

$$\ln\left(\frac{A_0 - A_e}{A_t - A_e}\right) = (k_1 + k_2)\Delta t,$$

where A_e, A_0 and A_t are the equilibrium, initial and actual concentrations of the complex **42**, respectively. The linear kinetic dependences were processed by the least-squares method. The kinetic dependences in the above-mentioned temperature range are shown in Fig. 3. The rate constants for the back and forward reactions **41** ⇄ **42** are given in Table 7. The activation parameters of this rearrangement are given below.

Reaction	E_a /kcal mol^{-1}	$\Delta H^{\neq}$ /kcal mol^{-1}	$\Delta S^{\neq}$ /e.u.	$\Delta G^{\neq}$ /kcal mol^{-1}
41 → **42**	26.9 ± 0.8	26.1 ± 0.8	−8.1 ± 0.2	30.0 ± 1.0
42 → **41**	26.7 ± 0.8	25.9 ± 0.8	−10.4 ± 0.2	30.5 ± 1.0

These results agree well with those reported in the literature for the related systems, in particular, for tricarbonylchromium complexes of methyl-[83] and methoxynaphthalenes.[84] The results of studies are unambiguously indicative of the absence of the

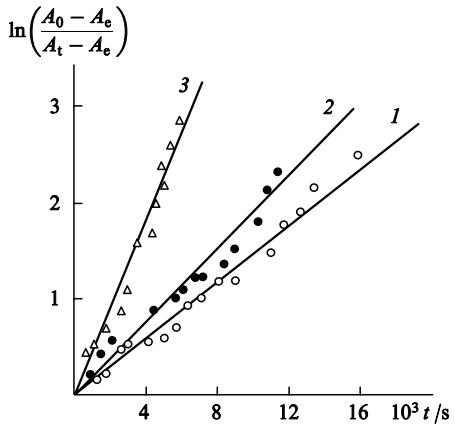


Figure 3. Kinetic first-order dependences obtained for IHR in the tricarbonylchromium complexes of η⁶-dimethylsilaacenaphthene **41** and **42** (starting from **41**) at 105 (*1*), 110 (*2*) and 118 °C (*3*).

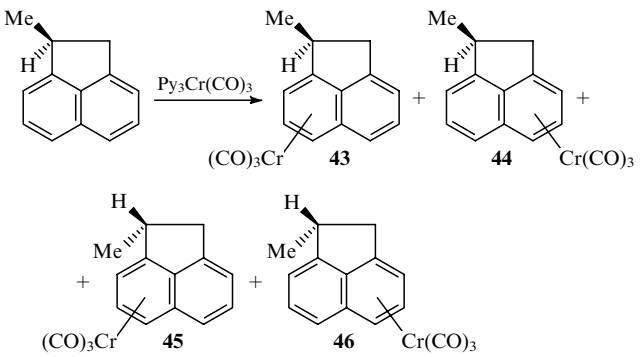
Table 7. Rate constants of IHR in the tricarbonylchromium complexes of η⁶-dimethylsilaacenaphthene **41** and **42**.

Rate constant /s^{-1}	Temperature /°C			
	85	105	110	118
$10^5 k_1$	1.15 ± 0.10 [a]	11.8 ± 0.4	14.0 ± 1.2	37.3 ± 1.1
$10^5 k_2$	0.64 ± 0.06 [a]	5.1 ± 0.2	5.80 ± 0.5	7.68 ± 0.8

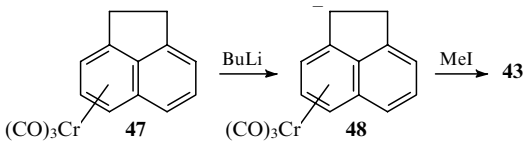
[a] The rate constants were calculated taking into account the thermodynamic parameters.

contribution of the intermolecular dissociation mechanism to the IHR under examination. This is also confirmed by the relatively small negative entropies of activation both of the back and forward reactions because dissociation processes are generally characterised by higher negative $\Delta S^{\neq}$ values.[61]

The η⁶,η⁶-inter-ring haptotropic rearrangements in a number of naphthalene-related tricarbonylchromium complexes in degassed anhydrous decane (an inert nonsolvating solvent) were examined.[105, 106] For example, four possible isomeric tricarbonylchromium η⁶-complexes **43**–**46** (two isomers with the *exo* configuration of the methyl group and two isomers with the *endo* configuration) were obtained starting from 1-methylacenaphthene under the conditions of the Öfele reaction [105] in 37% total yield; the **43** : **44** : **45** : **46** ratio was 1 : 1 : 0.8 : 0.7. The complexes **43** and **44** were isolated in the individual state by HPLC. Attempts to separate the complexes **45** and **46** failed, but their mixture enriched with the isomer **45** was obtained (**45** : **46** = 3 : 1).



The individual complex **43** was prepared by deprotonation of (η⁶-acenaphthene)tricarbonylchromium (**47**) followed by the reaction of the resulting anion **48** with MeI.



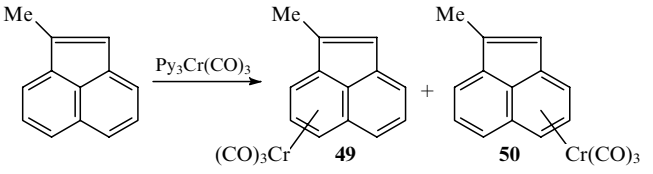
The electron-withdrawing tricarbonylchromium group substantially increases the acidity of the protons bound to the sp^3-hybridised carbon atoms as a result of which deprotonation proceeds regioselectively only at the CH_2 group that is located more closely to the substituted ring. The reaction of the anion **48** with MeI is stereoselective. The methyl group attacks the negatively charged carbon atom from the side opposite to the bulky tricarbonylchromium group. The low yield (23%) of the target product **43** indicates that the anion **48** is unstable and decomposes to form, apparently, the corresponding carbanion. This agrees with the fact that 1-methylacenaphthene was isolated from the reaction mixture in a substantial amount. Previously, the stereo- and regioselectivity of such reactions was established for derivatives of fluorene [78] and indene [79] by ^{1}H NMR spectroscopy (the ASIS effect) and X-ray diffraction analysis. In the case of the complex **43**, irradiation of the methyl multiplet in the nuclear Overhauser effect (NOE) experiment led to an increase in the intensity of the corresponding doublet for the protons of the coordinated ring, which proves that the methyl group is located in the vicinity of this ring. In addition, the signal for the protons of the methyl group in the complex **43** is observed at higher field than those in the complexes **44**–**46**. Based on the ASIS effect,[70, 79] this fact is indicative of the *exo* structure of **43**.

The η⁶,η⁶-inter-ring haptotropic rearrangement

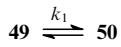


proceeded in solution in decane at 90 °C with a noticeable rate [$k_1 = 1.00 \times 10^{-5}$ s^{-1}, $K_{eq} = 1.13$, $\Delta G^{\neq}(363) = 29.7$ kcal mol^{-1}] with retention of the *exo* configuration of the methyl group. Under the same conditions, the rearrangements of the complexes **45** and **46** proceeded with retention of the *endo* configuration of the methyl group. Isomerisation was monitored by HPLC. The addition of 10% of THF to decane resulted in the formation of a mixture of all four possible stereoisomers without regard to the particular isomer used as the starting compound. This is unambiguous evidence that the rearrangements in a nonsolvating medium proceed through an intramolecular mechanism, whereas the rearrangements in the presence of solvating solvents occur according to an intermolecular mechanism.[105] These results agree with the data of more recent studies confirming the retention of optical activity of enantiomerically pure tricarbonylchromium complexes of naphthalene derivatives in the course of η⁶,η⁶-IHR.[98]

The η⁶,η⁶-inter-ring haptotropic rearrangements in isomeric tricarbonylchromium complexes of methylacenaphthylene (**49** and **50**) were examined.[106] A mixture of these complexes was obtained by the Öfele reaction in 78% yield (the **49** : **50** ratio was 45 : 55). The compounds **49** and **50** were isolated in pure form by HPLC.



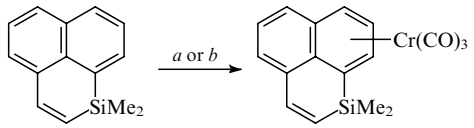
The necessity of studying IHR in methylated derivatives of tricarbonylchromium complexes of acenaphthylene stems from the fact that attempts to introduce a label directly into the six-membered ring of (η⁶-acenaphthylene)tricarbonylchromium (**5**) [107] [as in the case of tricarbonyl(η⁶-naphthalene)chromium] failed. The course of isomerisation



in solution in decane at 90 °C was monitored by NMR spectroscopy and HPLC. The rearrangement proceeded somewhat more rapidly [$k_1 = 2.29 \times 10^{-5}$ s^{-1}, $K_{eq} = 1.18$, $\Delta G^{\neq}(363) = 29.1$ kcal mol^{-1}] than those in the case of analogous acenaphthene or naphthalene complexes. This fact agrees with the results of theoretical analysis.[47] In the cited study, potential energy surfaces were calculated by the extended Hückel method and it was demonstrated that the presence of an exocyclic double bond in the polyaromatic ligand should lead to a decrease in the activation barrier to IHR.

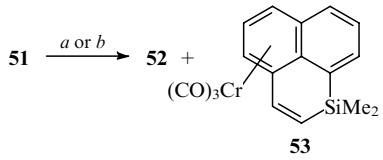
1,1-Dimethyl-1-silaphenalene (**51**) also contains an exocyclic double bond and two different aromatic fragments suitable for coordination to the transition metal atom. Hence, one would expect that η^6,η^6-IHR will also readily proceed in the corresponding isomeric tricarbonylchromium complexes.

The compositions of the products of the reaction of 1,1-dimethyl-1-silaphenalene (**51**) with chromium carbonyls performed under different conditions were examined.[108] It was found that the reaction of the compound **51** with $(NH_3)_3Cr(CO)_3$ in boiling dioxane or with $(MeCN)_3Cr(CO)_3$ in boiling THF afforded complex **52** as the only product. According to the data of ^1H and ^{13}C NMR spectroscopy, the tricarbonylchromium group in the complex **52** is coordinated at the silicon-substituted ring.



(*a*) $(NH_3)_3Cr(CO)_3$, dioxane, 100 °C (42%);
(*b*) $(MeCN)_3Cr(CO)_3$, THF, 64 °C (6%).

Both possible isomers **52** and **53** were formed only when the reaction temperature was decreased. The reaction of the compound **51** with $(MeCN)_3Cr(CO)_3$ at 34 °C gave rise to a mixture of the complexes **52** and **53** in a total yield of ⩽ 1%. The reaction of the compound **51** with $Py_3Cr(CO)_3$ at 0 °C afforded a mixture of the isomers in 54% yield with the complex **53** predominating.



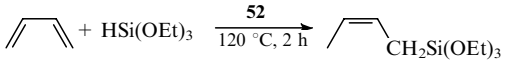
(*a*) $(MeCN)_3Cr(CO)_3$, 34 °C (1%) (**52** : **53** = 3 : 2);
(*b*) $(Py)_3Cr(CO)_3$, 0 °C, 1 h (54%) (**52** : **53** = 2 : 3).

This is yet another example of the effect of thermodynamic and kinetic factors on the formation of tricarbonylchromium complexes with polycyclic aromatic ligands.

The complexes **52** and **53** were identified by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. Since the complex **53**, unlike the complex **52**, is unstable under conditions of TLC, it was not isolated in pure form. The complex **52** decomposes upon storage of a mixture of the complexes even in the solid state.

Heating of a mixture of the complexes **52** and **53** in the $C_6F_6-C_6D_{12}$ system or in heptane to 90 °C for 5 h resulted in the complete rearrangement of the complex **53** to form the thermodynamically more stable complex **52**. The absence of traces of the free ligand in the reaction mixture and the fact that the rearrangement proceeds in nonpolar media are indicative of an intramolecular mechanism of IHR. The reverse **52** → **53** rearrangement was observed in none of the experiments.

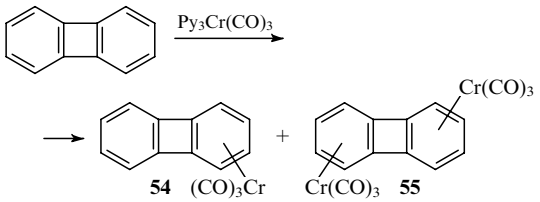
The rearrangements of silaphenalene complexes proceed under milder conditions than the rearrangements of silaacenaphthene complexes. This is indicative of a decrease in the activation energy of the process, although the rate constant of this process was not estimated. It should be noted that the isomer in which the tricarbonylchromium group is coordinated at the silicon-substituted ring is thermodynamically more stable in the case of the silaphenalene complexes **52** and **53** and the silaacenaphthene complexes **41** and **42**. The complex **52** acts as a catalyst of hydrosilylation of butadiene. The catalytic action is achieved upon addition of 0.2% of the compound **52** to an equimolar mixture of diene and silane.[109] The charactersitic feature of the reaction is its regio- and stereospecificity. Hydrosilylation afforded (*Z*)-1-triethoxysilylbut-2-ene as the only product in a yield of ⩾ 90%. Its structure was established by ^1H and ^{13}C NMR spectroscopy.[109]



The catalytic activity of tricarbonylchromium complexes of polycyclic arenes (naphthalene, phenanthrene and anthracene) in hydrogenation of conjugated dienes and acetylenes, isomerisation of dienes, Kharasch addition of CCl_4 to alkynes, *etc.* was attributed to the ability of the tricarbonylchromium group, which is η^6-bonded to the arene ring, to change the mode of bonding to form an η^4-intermediate.[110]

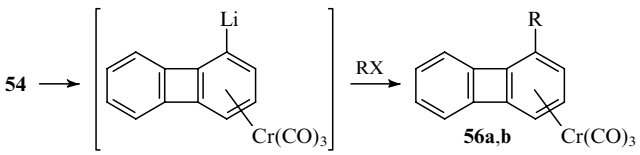
3. η^6,η^6-Rearrangements in tricarbonylchromium complexes of biphenylene

Tricarbonylchromium complexes of biphenylene are of considerable interest from the viewpoint of studies of η^6,η^6-IHR. The η^6-mononuclear (**54**) and η^6-binuclear (**55**) tricarbonylchromium complexes of biphenylene were synthesised by the Öfele reaction in 66% total yield (**54** : **55** = 15.5 : 1).[106] The individual complexes were isolated from the reaction mixture by TLC.



Previously, the complexes **54** and **55** were obtained in the reaction of biphenylene with $(NH_3)_3Cr(CO)_3$ in boiling dioxane in a similar ratio.[111,112] It was assumed that the binuclear complex **55**, like the structurally similar binuclear complex of fluorene,[78] contains the $Cr(CO)_3$ group in the *trans* position because such a structure was established for the biphenylene binuclear complex of molybdenum η^6,η^6-$C_{12}H_8[Mo(CO)_3]_2$ by X-ray diffraction analysis.[113]

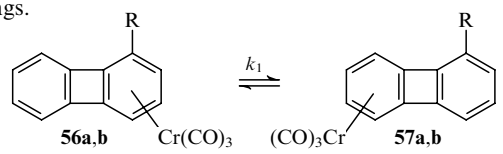
The directed introduction of substituents into the coordinated ring was performed by a procedure analogous to that used in the case of tricarbonyl(η^6-naphthalene)chromium. Metallation of the complex **54** with butyllithium in THF proceeded regio- and stereoselectively to form complexes **56a**,**b** in which the label is located exclusively at position 1 of the coordinated ring.



R = D (**a**), Me (**b**).

The η^6,η^6-inter-ring haptotropic rearrangements in tricarbonylchromium complexes of 1-substituted biphenylenes **56a**,**b** containing the planar ligand (according to the data of X-ray diffraction analysis) proceed more slowly than the corresponding

rearrangements in monosubstituted naphthalene complexes. Thus, the isomers **57a**,**b** were detected in the reaction mixture obtained upon heating of the complexes **56a**,**b** only at temperatures above 100 °C, IHR proceeding with a noticeable rate at 120 °C. In the course of the rearrangement, the tricarbonylchromium group migrates between the nonequivalent six-membered rings.

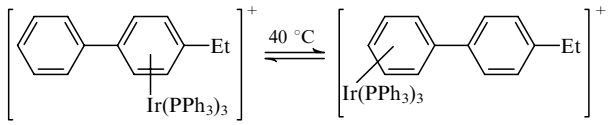


R = D (**a**), Me (**b**).

According to the data of ^{2}H NMR spectroscopy, the equilibrium for the deuterium-containing complexes **56a** and **57a** in decane was established at 120 °C in 6 h [$k_1 = 4.79 \times 10^{-5}$ s^{-1}, $K_{eq} = 1.00$, $\Delta G^{\neq}(393) = 31.00$ kcal mol^{-1}]. The η^6,η^6-rearrangements in the methyl-substituted complexes **56b** and **57b** proceeded somewhat more slowly [$k_1 = 3.41 \times 10^{-5}$ s^{-1}, $K_{eq} = 1.10$, $\Delta G^{\neq}(393) = 31.25$ kcal mol^{-1}].

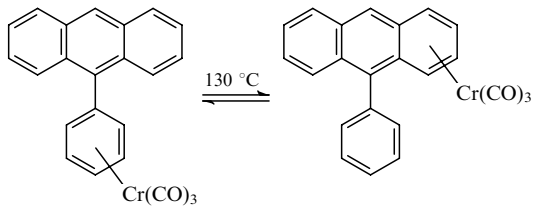
4. Synthesis of tricarbonylchromium complexes of substituted biphenyls and studies of the mechanism and kinetics of rearrangements in these complexes

Until the mid-1980s, the data on IHR in complexes with bi- or polycyclic open ligands were virtually lacking in the literature. Biphenyl complexes represent the simplest model systems.[114–116] More complex analogues, *viz*., tricarbonylchromium complexes of 1,3,5-triphenylbenzene,[117] triphenylene,[118] 9-phenylanthracene,[119] 9,10-dihydrophenanthrene,[120] silaoxaphenanthrene,[121] 9,9-dimethyl-9-silafluorene,[122] fluorene,[74] carbazole[74] and fluoranthene,[91,123] were also prepared. Procedures for the introduction of a label into tricarbonylchromium complexes of biphenyl derivatives are scarce. [The only procedure for the introduction of a label into (η^6-biphenyl)tricarbonylchromium involving the reaction of its stannylated derivative with butyllithium has been reported.[124]] Only two examples of rearrangements in complexes of biphenyl and its derivatives with transition metals were described before 1985. The inter-ring haptotropic rearrangement in the ethylbiphenyl complex of iridium was described in the study[125] with reference to the Ph. D. Thesis of Mellea.[126]

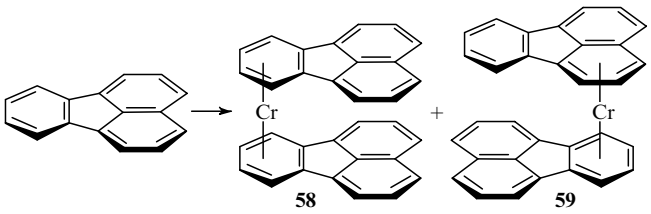


The reaction proceeded under mild conditions (40 °C) and the equilibrium ratio of the isomers was 1 : 1.

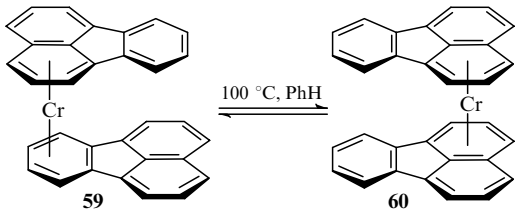
Isomerisation of tricarbonylchromium complexes of 9-phenylanthracene[119] proceeded under more drastic conditions (dibutyl ether, 130 °C). The tricarbonylchromium group successively migrates first over the biphenyl system and then over the fused system to the peripheral rings.[119] The mechanism of this rearrangement is not entirely known. Although the authors assumed that the rearrangement proceeds through an intermolecular mechanism, this statement is questionable and calls for special studies.



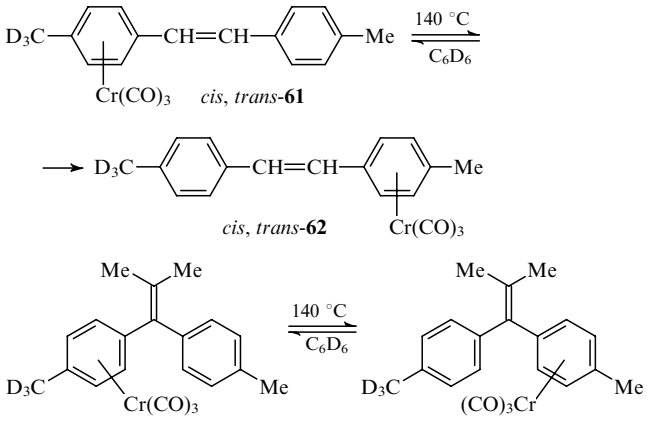
Recently, the first example of η^6,η^6-IHR in sandwich chromium complexes was reported.[127] The vapour-phase (350 °C) reaction of fluoranthene with metal vapour was demonstrated to afford complex **58** as the major product along with isomeric complex **59**. In the former complex, the chromium atom is located at the benzene rings, whereas one ligand in the complex **59** is coordinated at the 'naphthalene' fragment.



Prolonged heating (for several days) of the isomer **59** in deuteriobenzene at 100 °C resulted in the reversible rearrangement to form complex **60** in which both ligands are coordinated at the 'naphthalene' fragment, *i.e*., η^6,η^6-IHR of the biphenyl type occurred.



Migrations of the $Cr(CO)_3$ group in biphenyl-related open systems, *viz*., in tricarbonylchromium complexes of diphenylalkanes [(η^6-Ph)Cr(CO)$_3$](CH$_2$)$_n$Ph ($n = 1-4$), unsymmetrically substituted *cis*- and *trans*-stilbenes and 1,1-diarylethylenes, were observed.[128,129] At 140 °C, the $Cr(CO)_3$ group in complexes of substituted stilbenes (**61** and **62**) and diarylethylenes migrates between the rings containing the methyl and CD_3 groups.



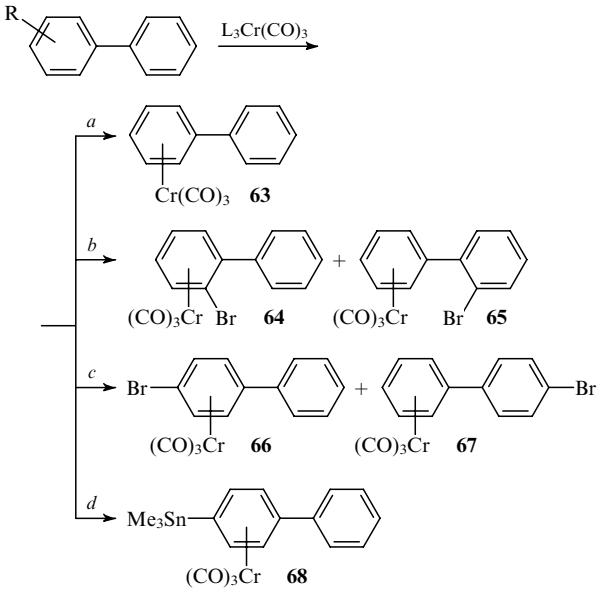
The rate of the intramolecular rearrangement is noticeably higher than that of the rearrangement proceeding through the dissociation mechanism, which is evidenced by an insignificant amount of products of replacement of the ligand in these complexes by the 'trapping' ligand.

The rate constants of IHR were determined for the *cis*- and *trans*-isomers of stilbene complexes at 140 °C. For the rearrangement **61** → **62** proceeding by an intramolecular mechanism, the rate constants are 4.20×10^{-5} s^{-1} and 6.95×10^{-5} s^{-1} for the *trans*- and *cis*-isomers, respectively. The rate constants of exchange through a dissociation mechanism are substantially smaller (0.18×10^{-5} s^{-1} and 0.066×10^{-5} s^{-1}, respectively).

a. Synthesis of tricarbonylchromium complexes of substituted biphenyls

It was not until 1985 that progress was achieved in the synthesis of tricarbonylchromium complexes of biphenyl derivatives labelled at one of the rings. For this purpose, insignificantly modified

procedures, which had been developed primarily for the synthesis of tricarbonylchromium complexes of monocyclic arenes, were used. The reactions of the ligands (biphenyl and 2-bromo, 4-bromo- and 4-trimethylstannylbiphenyls) with chromium carbonyls $L_3Cr(CO)_3$ (L = CO,[130] NH_3 [87] or Py;[88] $L_3 = C_{10}H_8$ [46]) afforded complexes **63–68** in moderate yields (30%–40%).[131]

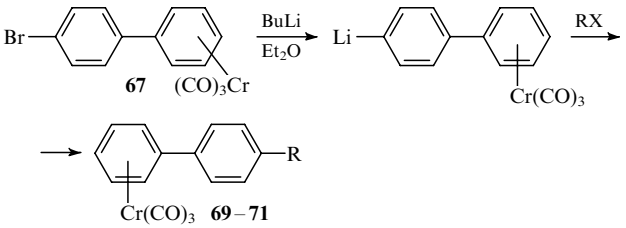


(*a*) L = CO, R = H, Bu_2O : THF = 1 : 6, 140 °C, 4 h; (*b*) L = CO, R = 2-Br, Bu_2O : THF = 1 : 5, 140 °C, 5 h; (*c*) L = CO, R = 4-Br, Bu_2O : THF = 1 : 7, 140 °C, 7 h; (*d*) L = NH_3, R = 4-$SnMe_3$, dioxane, 100 °C, 2 h.

Either both possible isomers or only one isomer are formed depending on the nature of the substituent in the ligand, its position and the type of chromium carbonyl used in the reaction. Thus the reaction of 4-trimethylstannylbiphenyl with $(NH_3)_3Cr(CO)_3$ gave rise exclusively to the complex **68**. Due to the strong electron-donating properties of the trimethylstannyl group, the electron density at the substituted ring increases resulting in coordination of the $Cr(CO)_3$ group at this ring. Analogously, the Rausch reactions of 2- and 4-bromobiphenyls with $(NH_3)_3Cr(CO)_3$ (dioxane, 100 °C, 2 h) afforded only the complexes **65** or **67** containing the $Cr(CO)_3$ group in the unsubstituted ring due to the electron-withdrawing properties of bromine (kinetic control). Prolonged heating of the bromo derivatives **65** or **67** with $Cr(CO)_3$ in a mixture of dibutyl ether and THF at 140 °C (thermodynamic control) yielded a mixture of the isomers **64** and **65** or **66** and **67**, respectively, with the complex containing the bromine atom in the uncoordinated ring predominating. Although the isomers can be readily isolated by TLC, the above-considered procedure cannot be used for the preparative synthesis of complexes containing halogen in the coordinated ring.

Based on analysis of the above-considered results, it can be stated with assurance that individual complexes containing a substituent either in the uncoordinated or coordinated rings can be selectively prepared starting from bromo- or trimethylstannyl derivatives of biphenyl by the Rausch reaction. Subsequently, the bromine atom or the $SnMe_3$ group can be first replaced by lithium under the action of BuLi and then by the R substituent by the reactions of the lithium derivatives with electrophilic reagents RX.

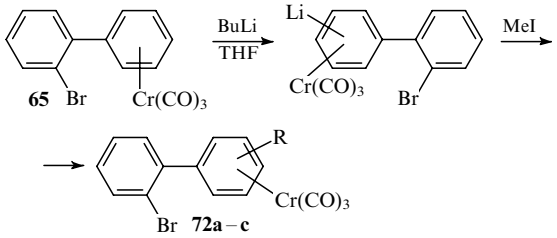
On the whole, the selective synthesis of tricarbonylchromium complexes of substituted biphenyls by the exchange reaction of bromine for lithium is analogous to the procedure used for the preparation of naphthalene derivatives. The reaction of the complex **67** containing the tricarbonylchromium group in the unsubstituted ring with BuLi in anhydrous ether at −78 °C led to the replacement of Br by Li. The lithium derivative is stable at low temperatures and reacts rather smoothly with electrophiles (D_2O, Me_3SnCl, MeI, *etc.*) at 0 °C to form selectively labelled complexes **69–71** containing the label at position 4 of the uncoordinated ring.[131]



RX = D_2O, Me_3SnCl, MeI; R = D (**69**), Me (**70**), Me_3Sn (**71**).

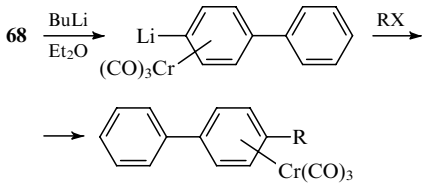
Attempts to prepare the corresponding complexes containing a label at position 2 of the uncoordinated ring starting from the compound **65** have not met with success even when the reactions were performed at room temperature, which is, apparently, due to steric hindrance to the replacement of Br by Li.

It should be noted that it is necessary to perform these reactions, like the synthesis of naphthalene complexes, in ether because direct metallation of the coordinated ring in THF proceeds more rapidly than the replacement of Br by Li. Thus the reaction of the derivative **65** with BuLi in THF followed by treatment of the reaction mixture with methyl iodide gave rise to the complexes **72a–c** (**72a** : **72b** : **72c** = 13 : 57 : 30). The low content of the complex **72a** in the mixture is attributable to steric hindrances, which appear either in the stage of metallation or, what is less probable, in the stage of the reaction of the lithium derivatives with MeI.



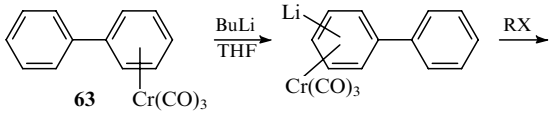
R = 2-Me (**a**), 3-Me (**b**), 4-Me (**c**).

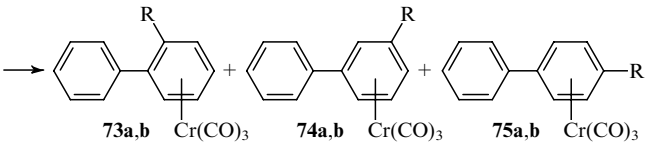
The replacement of the Me_3Sn group by lithium in the biphenyl complexes **68** was not performed. However, by analogy with the corresponding naphthalene complexes, complexes selectively substituted at the coordinated ring can be apparently prepared according to this procedure.



RX = D_2O, MeI, Me_3SiCl, *etc.*

The synthesis of tricarbonylchromium complexes of substituted biphenyls by direct metallation of (η^6-biphenyl)tricarbonylchromium was described. Thus the reaction of the complex **63** with BuLi in THF was accompanied by metallation of the coordinated ring. Then the reaction of the resulting lithium derivatives with the electrophile RX at −78 °C afforded a mixture of all three possible isomers.[131]



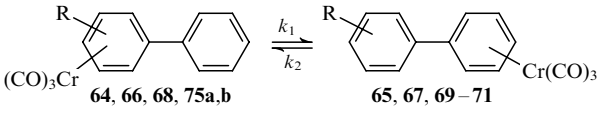


R = D (**a**), Me (**b**).

For example, the reactions of lithium derivatives with D_2O or MeI at −78 °C gave rise (according to the data of ^2H NMR spectroscopy) to a mixture of deuterated complexes **73a**–**75a** in 84% total yield (**73a** : **74a** : **75a** = 10 : 65 : 25) or a mixture of methyl derivatives **73b**–**75b** in 17.5% total yield (**73b** : **74b** : **75b** = 12 : 58 : 30), respectively. The ratios of the isomers of deuterio- and methyl-containing derivatives are rather similar, which does not allow one to consider the effects of kinetic and thermodynamic control on their formation. Storage of the reaction mixture at 0 °C for 1 h followed by treatment with MeI afforded only the isomer **73b**. Apparently, the 2-lithium-substituted derivative is the thermodynamically most stable compound and is predominantly formed through the replacement of H by Li. On the whole, the procedure for the synthesis involving metallation of the coordinated ring in the complex **63** is inferior to the above-described procedures (see Section III.1.b) in the preparative respect. However, the use of all available synthetic approaches enables one to prepare various tricarbonylchromium complexes of substituted biphenyls. It should be noted that in the general case these procedures are applicable to all polyaromatic arenes.

b. Studies of rearrangements in tricarbonylchromium complexes of substituted biphenyls

For all available tricarbonylchromium complexes of substituted biphenyls, the possibility of IHR was studied upon their heating in anhydrous oxygen-free decane in the temperature range of 140–174 °C for 4–20 h.[131]



R = 4-$SnMe_3$ (**68**, **71**), 2-Br (**64**, **65**), 4-Br (**66**, **67**), 4-D (**69**, **75a**), 4-Me (**70**, **75b**).

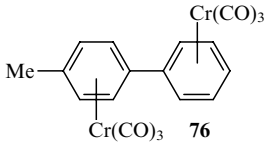
The course of the rearrangement was monitored by withdrawing samples every 30 min and recording the ^1H NMR spectra (^2H NMR spectra were measured for deuterated derivatives) to determine the isomer ratio. Heating was terminated if the isomer ratio ceased to change (according to the NMR data). In some cases, this approach made it possible to estimate the rate constants and equilibrium constants for IHR. The structures of the complexes were established by ^1H and ^{13}C NMR spectroscopy.

The inter-ring haptotropic rearrangements in the biphenyl complexes **64**, **66** and **68** are irreversible. Heating of the stannylated derivative **71** in boiling decane (174 °C, 5.5 h) resulted in the complete migration of the $Cr(CO)_3$ fragment from the unsubstituted ring to the substituted fragment to form the complex **68** [$k_2 = 6.42 \times 10^{-5}$ s^{-1}, $\Delta G^{\neq}(447) = 35.10$ kcal mol^{-1}], whereas the corresponding isomeric complex **68** did not undergo rearrangement under these conditions, *i.e.*, the reaction is actually irreversible. At 174 °C, the tricarbonylchromium group in the 2- and 4-bromophenyl derivatives (**64** and **66**) migrates irreversibly from the substituted ring to the unsubstituted one in 13 and 6 h, respectively [$k_1 = 2.23$ and 5.13×10^{-5} s^{-1}, $\Delta G^{\neq}(447) = 36.04$ and 35.3 kcal mol^{-1} for the complexes **64** and **66**, respectively]. Reverse migration of the tricarbonylchromium group was not observed, which is evidence in favour of the irreversibility of IHR. Analysis of the kinetic data demonstrated that the rearrangement in the 2-bromo derivative **64** proceeds much more slowly than that in the 4-bromo derivative **66**. Apparently, this is due to steric interactions in the complex **64** existing between the bulky bromine atom, on the one hand, and the *ortho*-proton of the adjacent ring and the organometallic group, on the other hand, resulting in the appearance of a twisting angle (a nonzero dihedral angle) and distortion of conjugation of the phenyl rings (see, for example, Refs 132 and 133). Ceccon *et al.*[134] also revealed the presence of the twisting angle and a noticeable degree of noncoplanarity of the five- and six-membered rings in the tricarbonylchromium complexes **29** and **30**. For the thermodynamically more stable (and, correspondingly, more populated) conformation of the *ortho*-derivatives of (η^6-biphenyl)tricarbonylchromium, the degree of noncoplanarity of the six-membered rings is higher than that in the corresponding *para*-derivatives. This effect is manifested in a substantial decrease in NOE between the protons of the coordinated and uncoordinated rings due to an increase in the average distance between their *ortho*-protons. The appearance of the nonzero dihedral angle between the benzene rings agrees with the data obtained by the DFT method for tricarbonyl(η^6-2-chlorobiphenyl)chromium containing the $Cr(CO)_3$ group in the unsubstituted ring, which was chosen instead of the 2-bromo derivative to simplify calculations. In this compound, the dihedral angle is 58.14° and the halogen and chromium atoms are oppositely directed.[135]

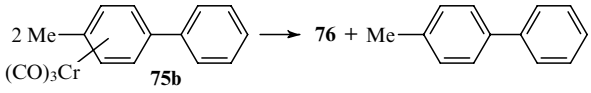
The results of quantum-chemical calculations with the use of the HyperChem program (the PM3 method) for uncoordinated biphenyl and 2-bromobiphenyl also confirm the above-considered experimental and theoretical data. According to these calculations, the biphenyl molecule is virtually planar (the dihedral angle is 0.2°), whereas the phenyl rings in 2-bromobiphenyl are essentially noncoplanar (the dihedral angle is 52.9°).

It should also be noted that the corresponding dihedral angle in the tricarbonylchromium complex of unsubstituted biphenyl (calculations by the DFT method) is 21.38°, *i.e.*, coordination to the transition metal atom leads to an increase in steric hindrance.[135]

The inter-ring haptotropic rearrangements in 4-deuterated and 4-methyl derivatives of tricarbonylchromium complexes of biphenyl, unlike those in the corresponding trimethylstannyl and bromo derivatives, are reversible. Heating of the complexes **75a**,**b** in decane at 174 °C for 5 and 8 h, respectively, resulted in reversible rearrangements to form the isomeric complexes **69** and **70**, respectively (K_{eq} = [**75a**]/[**69**] = 1.0 and K_{eq} = [**75b**]/[**70**] = 1.4). The binuclear complex **76** was isolated from a mixture of the 4-methylbiphenyl complexes **70** and **75b** (which was formed as a result of IHR) by TLC in 5% yield.



The structure of the compound **76** was established by mass spectrometry and ^1H NMR spectroscopy. The formation of **76** indicates that insignificant dissociation of the complexes with elimination of the tricarbonylchromium group that passes into solution did occur under drastic thermal conditions even in inert nonsolvating decane. An alternative explanation assumes that a bimolecular reaction proceeded giving rise to a molecule of the binuclear complex **76** and the ligand from two molecules of the complex **75b**.



Therefore, inter-ring haptotropic rearrangements in tricarbonylchromium complexes of biphenyl derivatives proceed through an intramolecular mechanism. However, due to the high temper-

atures of the reactions, an intermolecular mechanism is realised to a small extent. This conclusion is consistent with kinetic evidence that metallotropic rearrangements in tricarbonylchromium complexes of diphenylalkanes proceed predominantly by an intramolecular mechanism.[128, 129]

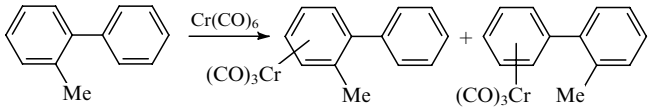
Analogous results were obtained upon heating of a mixture of the biphenyl complexes **73a**–**75a** containing deuterium in the coordinated ring in decane at 174 °C for 6 h. Under these conditions, the reversible rearrangement proceeded accompanied by migration of the tricarbonylchromium group from the deuterium-labelled ring to the deuterium-free ring. The ratio between the isomers containing deuterium in the coordinated and uncoordinated rings is close to unity in all three pairs of 2-, 3- and 4-deuterium-substituted complexes (according to the ^{2}H NMR data; acetone as the solvent).

When a mixture of complexes containing 2-, 3- and 4-methyl-substituted coordinated rings (**73b**–**75b**) was heated under the same conditions, only isomers **74b** and **75b** underwent rearrangements to form complexes containing substituents in the uncoordinated ring (K_{eq} is 1.6 and 1.4 for the isomers **74b** and **75b**, respectively).

The fact that IHR did not occur in the 2-methyl-substituted complex **73b**, as in the case of the corresponding bromo derivative, is attributable to the fact that the phenyl rings are essentially noncoplanar in the most populated rotamer. This is consistent with a decrease in NOE between the *ortho*-protons of the coordinated and uncoordinated rings in the complex **73b** (3%–4%) compared to the corresponding values obtained for the complexes **74b** and **75b** (7%–9%).

The dihedral angle in the 2-methylbiphenyl complex containing the $Cr(CO)_3$ group in the unsubstituted ring calculated by the DFT method is 62.01°.[135]

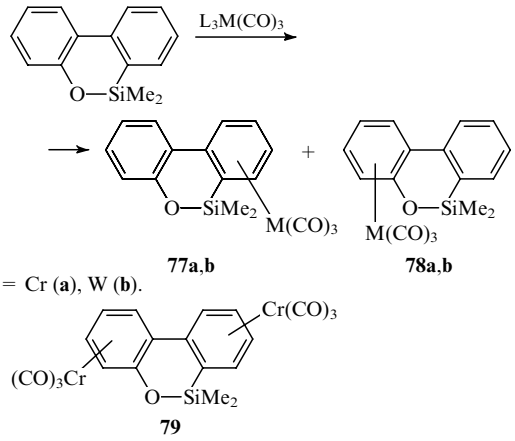
Interestingly, a mixture of 2-methyl-substituted complexes containing the $Cr(CO)_3$ group either in the coordinated or uncoordinated rings did form from 2-methylbiphenyl and $Cr(CO)_3$ upon refluxing in the dibutyl ether–THF system. The isomeric 2-methyl-substituted tricarbonylchromium complexes were separated by TLC. The isomer ratio (1.3 : 1) appeared to be similar to that obtained as a result of inter-ring haptotropic rearrangements in tricarbonylchromium complexes of 3- and 4-methyl-substituted biphenyls.



The absence of IHR in 2-methyl-substituted tricarbonylchromium complexes of biphenyl and the fact that their mixture can be readily obtained by the reaction of the ligand with chromium hexacarbonyl is additional evidence in favour of the intramolecular character of IHR. Therefore, a necessary condition of IHR to occur in complexes of substituted biphenyls and related ligands is a small degree of noncoplanarity of the rings (the dihedral angle should be smaller than 22°, as in the case of the biphenyl complex), which is impossible in 2-substituted complexes due to steric effects.

5. η^6,η^6-Rearrangements in tricarbonylchromium complexes of biphenyl-related ligands

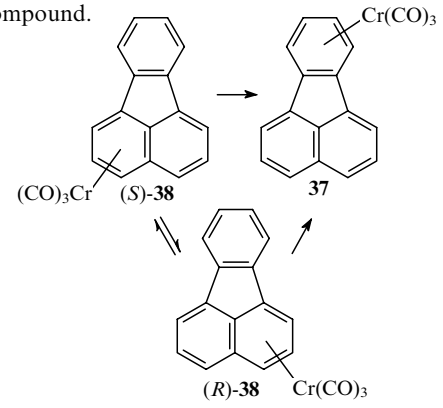
Biphenyl-related 10,10-dimethyl-10-sila-9-oxa-9,10-dihydrophenanthrene, which contains substituents possessing different electronic properties in both rings, is of interest. Tricarbonylchromium and -tungsten complexes of this compound were prepared by reactions with different chromium and tungsten carbonyls.[121, 136] In the case of M = Cr, the bis(tricarbonyl)chromium complex μ-η^6:η^6-$C_{12}H_8OSiMe_2[Cr(CO)_3]_2$ (**79**) was formed in a small amount.



The six-membered rings in the tricarbonylchromium complexes **77a** and **78a** are noncoplanar and the dihedral angles between these rings are (according to the X-ray diffraction data) 20.4° and 15.5°, respectively.[137]

Heating of the complex **77a** in anhydrous degassed decane at 130 °C led to IHR yielding the isomer **78a**. The equilibrium was established in 6 h. According to the data of ^{1}H and ^{13}C NMR spectroscopy, the **77a** : **78a** ratio was 12 : 1 (the same isomer ratio was obtained upon heating of the complex **78a**). In both cases, the ^{1}H NMR spectra of the equilibrium mixtures have low-intensity signals belonging to the ligand and the binuclear complex **79**. However, their total amount was no higher than 5% even after heating of the reaction mixture at 174 °C for 20 h. The binuclear complex and the ligand were formed due to either thermal destruction or bimolecular reactions proceeding in the complexes **77a** and **78a**. Analogously (but under substantially milder conditions), the inter-ring haptotropic rearrangement proceeded in the tricarbonyltungsten complex **77b**. After heating of **77b** in decane at 100 °C for 6 h, the ^{1}H NMR spectrum had additional signals, which were assigned to the isomer **78b** (**77b** : **78b** = 15 : 1). Attempts to isolate the complex **78b** from the reaction mixture by TLC failed and the ^{1}H NMR spectrum of the pure complex was not measured.[136]

Fluoranthene is of considerable interest because η^6,η^6-IHR both of the 'biphenyl' and 'naphthalene' types can proceed in this compound.



In this case, the complex **38** exists as two enantiomers, which are interconverted in the course of the 'naphthalene' rearrangement. Apparently, the kinetic parameters of such degenerate rearrangements may be determined from the rates of racemisation of the corresponding enantiomers in the future.

Heating of the η^6-fluoranthene complex **38** in which the $Cr(CO)_3$ group is located at the naphthalene fragment even at rather low temperature (in decane or benzene at 100 °C for 10 h) led to IHR to form the complex **37** in which the $Cr(CO)_3$ group is located at the benzene ring.[91, 123] On the contrary, prolonged heating (> 100 h) of the complex **38** under the same conditions did not give rise to the isomer **37**. The inter-ring haptotropic

rearrangement was not accompanied by substantial decomposition of the complexes or migration of the $Cr(CO)_3$ group to the benzene ring, which is consistent with the results of other studies.[46,90] It was demonstrated that when tricarbonyl(η^6-naphthalene)chromium was heated in benzene, the migration of the tricarbonylchromium group to the benzene ring proceeded with a noticeable rate ($k_{sub} = 1.73 \times 10^{-4}$ s^{-1})[46] only at 140 °C and was completed in 6 h.

The rate constant of the irreversible η^6,η^6-inter-ring haptotropic rearrangement **38** → **37** was determined from the data of ^{1}H NMR spectroscopy (C_6F_6 as the solvent). The corresponding kinetic curves are shown in Figs 4 and 5. The rate constant of the rearrangement is equal to $(5.5\pm0.2) \times 10^{-6}$ s^{-1}; $E_a = 30.13$ kcal mol^{-1}. The complexes **37** and **38** were separated by TLC and their structures were established by ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction analysis.

Therefore, IHR in planar fluoranthene complexes proceed under substantially milder conditions (80–90 °C) than those in open biphenyl complexes (even in the cases of 4-bromo- or 4-methyl-substituted complexes, IHP started at temperatures above 130 °C). At 100 °C, the replacement of the fluoranthene ligand by C_6D_6 in the course of η^6,η^6-IHR was not observed. This replacement was achieved only at 130 °C. After 10 h, the ligand : $C_6D_6Cr(CO)_3$ ratio reached 1 : 1 and the replacement of fluoranthene by C_6D_6 was completed in 30 h (data from ^{1}H and ^{2}H NMR spectroscopy and TLC).

In isomeric fluoranthene complexes, η^6,η^6-IHR were observed in melts for the first times, *i.e.*, the rearrangements proceed in the absence of solvating interactions with solvent molecules, which can lead to elimination of the tricarbonylchromium group from the ligand. Thus when melted in a tube at 154 °C, the complex **38** was completely converted into the isomer **37**, which was established by TLC and NMR spectroscopy. This fact is yet further evidence of the intramolecular character of η^6,η^6-IHR in tricarbonylchromium complexes of polycyclic aromatic compounds.

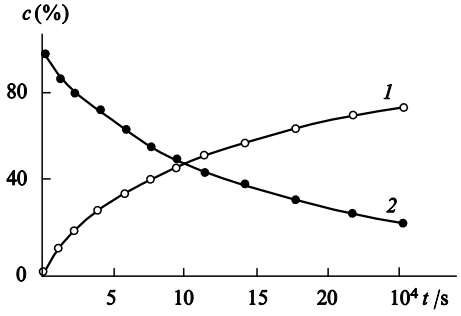


Figure 4. Kinetic curves for changes in the concentration (c) of the complexes **37** (*1*) and **38** (*2*) in the course of IHR.

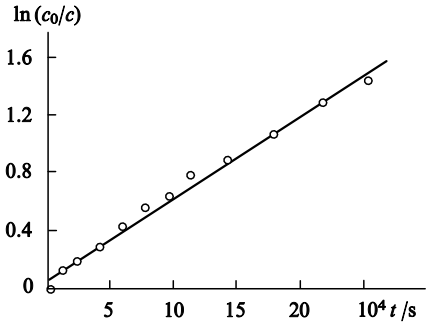
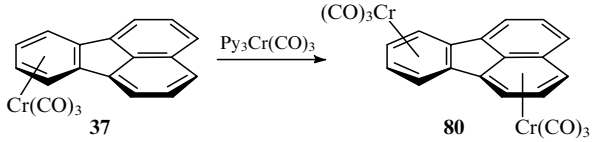


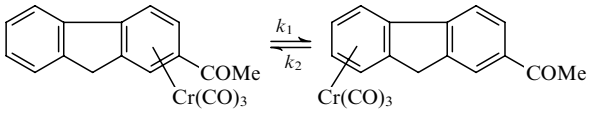
Figure 5. Kinetic first-order dependence for irreversible IHR **38** ⇌ **37** at 90 °C;
c_0 and c (%) are the initial concentration of the complex **38** and the concentration at time t, respectively.

The rearrangements in fluoranthene complexes proceed substantially more readily than those in biphenyl derivatives for two reasons. First, the ligands in the complexes **37** and **38** are planar (according to the X-ray diffraction data). Second, the difference in thermodynamic stability of the complexes **37** and **38** is substantially larger than that in the case of analogous biphenyl pairs.

The Öfele reaction of the complex **37** with an excess of $Py_3Cr(CO)_3$ afforded a binuclear fluoranthene complex (**80**) in 70% yield. The complex **80** has, apparently, a *trans*-structure. It should be noted that the complex **38** did not react with $Py_3Cr(CO)_3$ under the same conditions.



Recently, η^6,η^6-IHR in tricarbonylchromium complexes of 2-acetylfluorene, which is a planar analogue of biphenyl, have been studied by ^{1}H NMR spectroscopy (deuteriotoluene, 120 °C).[138]



Under these conditions, the intramolecular inter-ring haptotropic rearrangement was accompanied by the replacement of the fluorenyl ligands by deuteriotoluene ($k_{sub} = 0.19 \times 10^{-5}$ s^{-1}). According to the kinetic and thermodynamic data [$k_1 = 0.18 \times 10^{-5}$ s^{-1}, $k_2 = 0.024 \times 10^{-5}$ s^{-1}, $\Delta G^{\neq} = 33.5$ kcal mol^{-1}], the η^6,η^6-rearrangements in these complexes proceed much more rapidly than those in biphenyl complexes because the ligand in the former complexes (as in the complexes **37** and **38**) is planar.

Therefore, IHR in tricarbonylchromium complexes with different polycyclic aromatic ligands have been studied in sufficient detail. The kinetic and thermodynamic parameters of these rearrangements, which depend on the structure of the ligand and the nature of the substituents, are summarised in Table 8. The

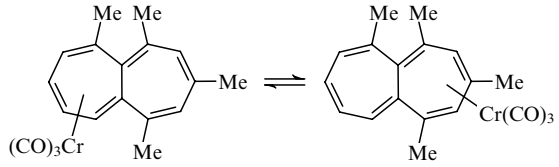
Table 8. Kinetic and thermodynamic data for η^6,η^6-IHP in tricarbonylchromium complexes with polycyclic ligands.

Ligand	T/K	K_{eq}	$10^5 k_1$ [a] /s^{-1}	$\Delta G^{\neq}$ /kcal mol^{-1}	E_a [b] /kcal mol^{-1}
2-Methylnaphthalene	358	2.09	3.02	28.5	26.9
Methylacenaphthene [c]	363	1.13	1.00	29.7	27.5–26.8
Fluoranthene	363	(see [d])	0.73	30.0	27.8–28.1
Methylacenaphthylene	363	1.18	2.29	29.1	26.9–25.5
1-Deuteriobiphenylene	393	1.00	4.79	31.0	28.6–27.8
4-Deuteriobiphenyl	447	1.00	6.42	35.1	32.4–31.5
4-Bromobiphenyl	447	(see [d])	5.13	35.3	32.6–31.72
2-Bromobiphenyl	447	(see [d])	2.23	36.04	32.5–33.4

[a] The rate constant k_1 defines the rate of migration of the tricarbonylchromium group between the substituted and unsubstituted rings. [b] The value was calculated taking into account average $\Delta S^{\neq}$. [c] Data for the *exo*-complexes. [d] Irreversible IHR.

data on IHR in complexes of other transition metals with polyaromatic ligands are scarce. Nevertheless, these data indicate that the rates of rearrangements depend substantially on the nature of transition metal and the ligand environment.

In conclusion, note that the first example of η^6,η^6-IHR in fused nonplanar polycycles, *viz*., in tricarbonylchromium complexes of substituted heptalene, which occur under rather drastic conditions, has been reported recently.[139]



6. Theoretical approach to studies of inter-ring haptotropic rearrangements in transition metal complexes with polycyclic aromatic ligands

During the progress of experimental investigations of IHR it became evident that further advances in studies of these processes could not be achieved without application of quantum-chemical methods. At present, *ab initio* high-level quantum-chemical calculations for heteroorganic and organometallic compounds are complicated. The restricted Hartree–Fock–Roothaan method with the use of small basis sets is well suited to studies of organic molecules. However, this method is inefficient in investigations of organometallic compounds. In the latter cases, it is necessary to perform calculations using larger basis sets with polarisation functions taking into account electronic correlations and relativistic corrections. As a result, theoretical studies were generally performed using semiempirical methods for calculating the structures and properties of organometallic compounds and only qualitative results were obtained. Recently, the application of the DFT method has opened prospects for obtaining reliable quantitative data.

Theoretical studies of the mechanisms and the major regularities of IHR in different systems were surveyed in a review.[140] The pioneering investigations in this field were carried out by Albright *et al*.[47]

7. Studies of the mechanism of η^6,η^6-haptotropic rearrangements in naphthalenechromium tricarbonyls by the density functional method

Recently, it has been demonstrated that time-saving calculations by the DFT method can give high-quality data competitive with the results of *ab initio* high-level quantum-chemical calculations.[141] The fact that the kinetic parameters of IHP in naphthalene complexes are weakly sensitive to the effect of the substituents in the ligand is somewhat unexpected (see Table 6) because the effects of the substituents are pronounced in the majority of other metallotropic rearrangements. Detailed investigations of the mechanism of the rearrangements by the DFT method provided reasonable explanations for this fact. Calculations were carried out with the use of the most-time-saving program with extended basis sets.[141] The results reproduced adequately the geometric parameters of tricarbonyl(η^6-naphthalene)chromium (**4**) determined by X-ray diffraction analysis,[85] including such details as the differences between the Cr–C(1) and Cr–C(2) bond lengths and between the Cr–C(4a) and Cr–C(8a) bond lengths (see the note in Table 9).

The results of calculations are given in Tables 9 and 10. These results agree qualitatively with the results obtained in another study.[47] In particular, migration of the $Cr(CO)_3$ group from one ring to another along the shortest path through the midpoint of the C(4a)–C(8a) bond is forbidden in the case of the basis states **A** and **B**.

Table 9. Comparison of the calculated geometric parameters of the model molecules with the experimental data.

Bond	Calculated values /Å	Experimental values /Å	Deviation [a]
$Cr(CO)_6$ (see [b])			
Cr–C	1.908	1.924	−0.016
C–O	1.153	1.165	−0.012
(η^6-C_6H_6)$Cr(CO)_3$ (see [c])			
$Cr-C_{CO}$	1.846	1.863	−0.017
$Cr-C_{PhH}$	2.222	2.208	0.014
C–C	1.410, 1.426	1.417	0.001
(η^6-$C_{10}H_8$)$Cr(CO)_3$ (see [d])			
$Cr-C_{CO}$	1.847	1.815–1.830	0.025
Cr–C(1)	2.218	2.186, 2.214	0.018
Cr–C(2)	2.214	2.213, 2.214	0.001
Cr–C(4a)	2.336	2.306, 2.337	0.015
C(2)–C(3)	1.426	1.375	0.051
C(3)–C(4)	1.405	1.389, 1.383	0.019
C(4)–C(4a)	1.439	1.447, 1.404	0.014
C(4a)–C(8a)	1.442	1.439	0.003

Note. The atomic numbering scheme used for (η^6-$C_{10}H_8$)$Cr(CO)_3$ is shown in Scheme 1.

[a] The difference between the experimental and calculated values. [b] The experimental values were determined by electron diffraction study.[142] [c] The experimental values were determined by electron diffraction study.[143] [d] The experimental values were determined by X-ray diffraction analysis.[85]

Scheme 1

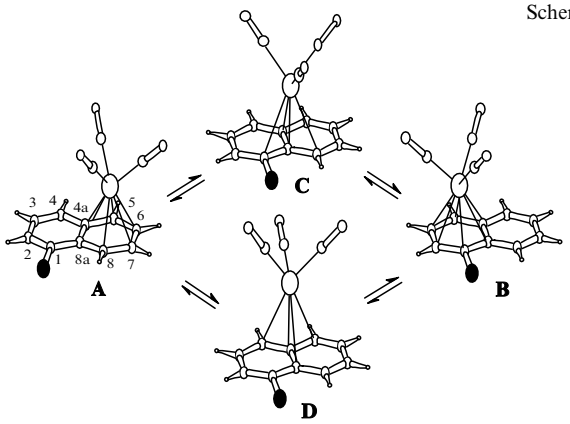


Table. 10. Relative energies of the isomeric complexes **A** and **B** and the transition states **C** and **D** (kcal mol^{-1}).

R	A	B	C	D
H	0	0	30.44	30.44
1-Cl	0	2.78	33.93	30.82
2-Cl	0	2.22	30.23	30.91
1-$SiMe_3$	−1.64	0	29.59	30.63
2-$SiMe_3$	−4.47	0	26.41	26.62
1-Me	0.52	0	32.18	30.38
2-Me	−0.19	0	28.86	29.92

The transition state for (η^6-$C_{10}H_8$)$Cr(CO)_3$ (**3**) has the structure of the trimethylenemethane complex with the symmetry C_{2v} in which the $Cr(CO)_3$ group is coordinated through the C(4), C(4a), C(5) and C(8a) atoms and is slightly shifted to the periphery of the ligand. The potential energy surface does not have a stationary point (a local minimum) corresponding to an inter-

mediate of the η^3-allylic type, which had been postulated in another study.[47]

For tricarbonylchromium complexes of substituted naphthalenes, the tricarbonylchromium group can migrate between the substituted and unsubstituted rings *via* two paths through the transition states **C** and **D**. The results of calculations reproduce adequately the relative stabilities of the isomers **A** and **B**, which differ by the position of the $Cr(CO)_3$ group in the unsymmetrically substituted naphthalene ligand. The presence of the substituent changes the energy of the transition state **C** in which this substituent is located in the immediate vicinity of the migrating group, whereas the energy of the transition state **D** changes only slightly (± 0.5 kcal mol^{-1}). Therefore, the existence of two reaction pathways one of which is virtually nondisturbed is, on the whole, responsible for the low sensitivity of the kinetic parameters of the rearrangement to the effects of the substituent in the ligand. Taking into account the assumptions made (the isolated-molecule approximation was used and the difference in the zero-point energy was ignored), the calculated activation barriers agree well with the experimental $\Delta G^{\neq}$ values.

IV. Conclusion

Essentially all known data on IHR in π-complexes of transition metals with fused polycyclic ligands are surveyed in the present review. Metallotropic rearrangements revealed in new complexes and elucidation of the general regularities of these rearrangements are of considerable importance because they gave impetus to the development of new synthetic procedures.

Presently, the general concepts of IHR are rather clearly stated. Further studies should be aimed at the more detailed theoretical description of these processes, in particular, it is necessary to have an idea of the structures of transition states in the course of IHR to perform the directed construction of new tautomeric systems. In this respect, calculations of the potential energy surfaces for the rearrangements with the use of more rigorous quantum-mechanical methods will be of paramount importance.

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