Available online at www.sciencedirect.com

ScienceDirect

Coordination Chemistry Reviews 252 (2008) 1798–1818

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Sigmatropic and haptotropic rearrangements in organometallic chemistry

Ilya D. Gridnev *

Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-I3-28, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Received 18 September 2007; accepted 16 October 2007

Contents

Abstract

This review describes two kinds of fluxionality in organometallic compounds: rearrangements proceeding via breaking and reformation of either σ-(sigmatropic rearrangements) or π-bonds (haptotropic rearrangements).

Keywords: Fluxionality; Sigmatropic rearrangements; Haptotropic rearrangements; Dynamic NMR; Organometallic complexes; Sigmatropic shifts

1. Introduction

The ability of organometallic compounds to undergo intramolecular rearrangements involving cleavage of some chemical bonds and formation of others was an exciting discovery made more than 50 years ago already [1,2]. It became still more fascinating 10 years later with the availability of variable temperature NMR experiments that proved the validity of the initial assumptions [3]. Since then a large number of structurally non-rigid organometallic compounds have been prepared, and their fluxional properties have been studied in detail, mainly by means of NMR spectroscopy.

There were several approaches to the classification of the different types of fluxionality in organometallic compounds. We

---

* Tel.: +81 3 5734 3723; fax: +81 3 5734 3723.
E-mail address: gridnev.i.aa@m.titech.ac.jp.

0010-8545/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2007.10.021

will accept the most general division into sigmatropic (cleavage and formation of σ-bonds) and haptotropic (cleavage and formation of π-bonds) rearrangements. In addition, dyotropic rearrangements in which both types of metallotropic migrations occur simultaneously will be discussed.

The area has been frequently and extensively reviewed [4–12]. Hence, instead of trying to cover all literature comprehensively, we will give a brief overview of the results highlighted already in previous reviews, and then concentrate on the most recent achievements in this field.

2. Sigmatropic rearrangements

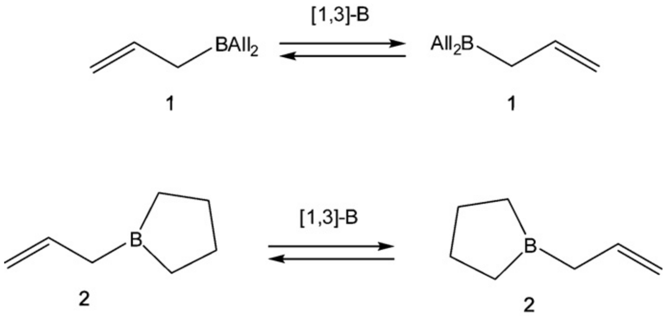
2.1. Sigmatropic rearrangements in linear organometallic compounds

Many σ-allylic derivatives of metals are fluxional in solution. However, most of the rearrangements responsible for this fluxionality are intermolecular. Thus, the intermolecular character of the allylic rearrangements in the derivatives of aluminium, [13] cadmium, [14] and zinc [15,16] has been proved experimentally. A mixed mechanism with the predominance of the intermolecular one has been initially proposed for diallylmercury [17]. However, it was later shown that an intermolecular rearrangement takes place in allylmercury derivatives that occurs only in the presence of Lewis acids [18]. The same is true for allylstannanes [19–21]. Facile intramolecular rearrangements are known for allylmagnesium compounds; however, in this case the interpretation of the experimental data is difficult due to ionisation and Schlenk equilibria [22,23]. The activation barriers of the sigmatropic migrations in allylsilanes [24,25] and allylgermanes [26] are higher than 120 kJ/mol.

Allylboranes exhibit a truly intramolecular allylic rearrangement in a temperature range appropriate for extensive NMR studies. This rearrangement is facilitated by the easily accessible 2p-AO of the boron atom which plays a pivotal role in the formation of the transition state of the borotropic migration. Facile intramolecular [1,3]-B shifts in allylic type triorganoboranes result in a reversible migration of dialkylboryl groups along the conjugated polyolefinic chain. This opens the possibility of constructing molecules with sophisticated, but predictable dynamic properties and provides an approach to structures accessible only with difficulty by conventional synthesis.

2.1.1. [1,3]-B shifts in linear organoboranes of the allylic type

It was found in 1965 that the ^{1}H NMR spectrum of triallylborane **1** is temperature-dependent [27]. At temperatures below −40 °C, **1** gives an A_2BX_2 spectrum. Increasing the temperature leads to the broadening of the signals of the CH_2B and $CH_2=$groups, and at 90 °C (60 MHz) the spectrum pattern is AX_4. These spectral changes are independent of the concentration of **1**, and testify therefore for the reversible intramolecular migrations of the diallylboryl group from the position 1 to the position 3 of the allylic moiety. Very similar dynamic effects were observed in the ^{1}H NMR spectra of 1-allylborolene **2** (Scheme 1) [28].

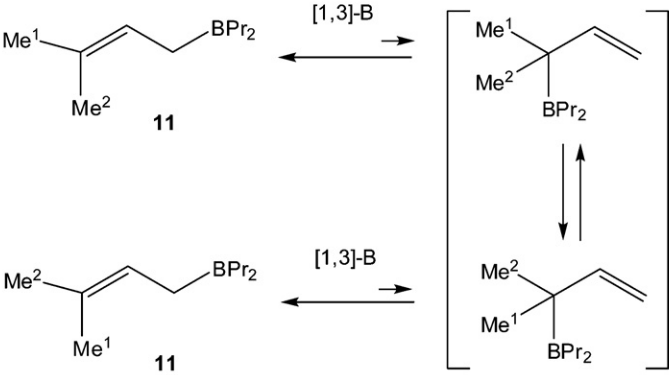


Scheme 1. Degenerate [1,3]-B shift in allylboranes.

During the following decades a considerable number of fluxional allylboranes have been studied. The data on the activation parameters of the [1,3]-B shifts in linear allylboranes are collected in Table 1. The rearrangements in Table 1 are organized by way of their appearance in the NMR spectra in the following way.

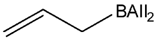
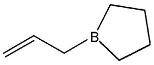
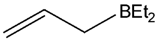
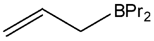
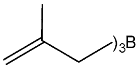
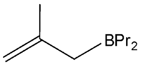
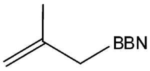
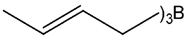
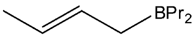
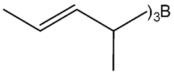
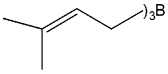
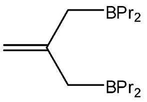
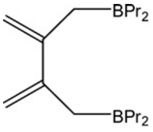
(1) The simplest case is the degenerate rearrangement, *e.g.* in triallylborane **1** (Scheme 1). Such a rearrangement results in averaging the exchanging signals in the NMR spectra producing a characteristic line-shape dependence in the ^{1}H and ^{13}C NMR spectra. True values of activation parameters can be derived either from line-shape analysis or by 2D EXSY spectroscopy.
(2) Several consecutive [1,3]-B migrations can result in a formally degenerate rearrangement (compound **11**, Scheme 2). The barriers of the degenerate transformations can be measured similarly to those for the direct degenerate rearrangements. However, in this case one can only obtain effective activation parameters for the overall reaction occurring in two- or several steps.
(3) Interconversion of isomers can proceed via several steps via unobservable, relatively unstable allylic isomers (*e.g.* Scheme 3). The effective rate constants for such interconversions (compounds **8**, **9**) are uniformly higher than those for direct 1,3-B shifts.

For all rearrangements summarized in Table 1, the intramolecular mechanism has been proved experimentally [34]. The rearrangement takes place only in boranes, with a 2p-AO



Scheme 2. Multi-step degenerate rearrangement in borane **11**.

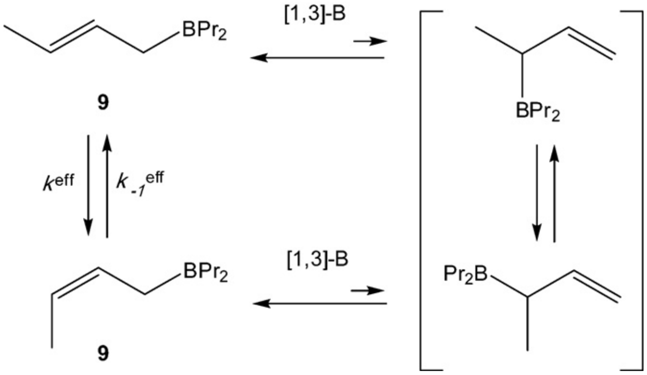
Table 1
Activation parameters for the [1,3]-B shifts in simple allylboranes

Compound	Type of rearrangement[a]	E_A (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1}) (T)	Reference
 **1**	**1**	42		[28]
			61.2 (312)	[29]
			61.9 (298)	[30]
 **2**	**1**	63		[28]
 **3**	**1**	49		[31]
 **4**	**1**		66.1 (298)	[30]
 **5**	**1**		61.5 (311)	[29]
			62.3 (298)	[30]
 **6**	**1**		64.0 (298)	[30]
 **7**	**1**		47.8 (303)	[32]
 **8**	**3**		80.0 (353)[b]	[33]
			72.8 (298)[c]	[30]
 **9**	**3**		70.3 (298)[d]	[30]
 **10**	**1**		54.7 (298)	[30]
 **11**	**2**		96.0 (425)	[31]
			77.5 (298)	[30]
 **12**	**1**		54.3 (298)	[30]
 **13**	**1**		74.5 (298)	[30]

Notes: [a]See text for explanations; [b]$\Delta G^{\circ}_{353} = 2.95$ kJ/mol; [c]$\Delta G^{\circ}_{298} = 1.81$ kJ/mol; [d]$\Delta G^{\circ}_{298} = 1.01$ kJ/mol.

of boron remaining unoccupied: in amino-complexes of allylic boranes the [1,3]-B shift does not proceed. The analysis of the relative values of activation parameters of allylic rearrangements indicates also that the appropriate configuration of the boron atom is important for the ease of rearrangement. Thus, in a series of simple allylboranes **1**–**7**, the free activation energies of the [1,3]-B migration lie within the narrow range of 60–66 kJ/mol when the substituents on boron are alkyls or allyls (compounds **1**, **3**, **4**, **5**, and **6**). Incorporation of the boron atom into a five-membered heterocycle significantly retards the rearrangement (compound **2**). On the other hand, for compound **7**, which contains a boron atom incorporated into BBN bicycle, the barrier for the [1,3]-B shifts is notably lower compared to its alkyl(allyl)-substituted analogs (compounds **5** and **6**).

Introduction of a methyl substituent into the position 2 of the allylic moiety does not affect significantly the barriers of the 1,3-B shifts (compare compounds **1** and **5**; **4** and **6**). The substitution of the position 2 with functional groups (compounds **12**, **13**) changes the activation barriers of allylic rearrangement notably. It was suggested that the [1,3]-B shift in **12** is facilitated by the participation of the 2p-AO of the second boron atom in the formation of the transition state [30]. The opposite effect for borane **13** is probably due to the decrease of electron density on the double bond due to the conjugation in the butadiene fragment. Quantum chemical calculations [35] prove the importance of the boron 2p-AO for the realization of the sigmatropic migrations in allylboranes.



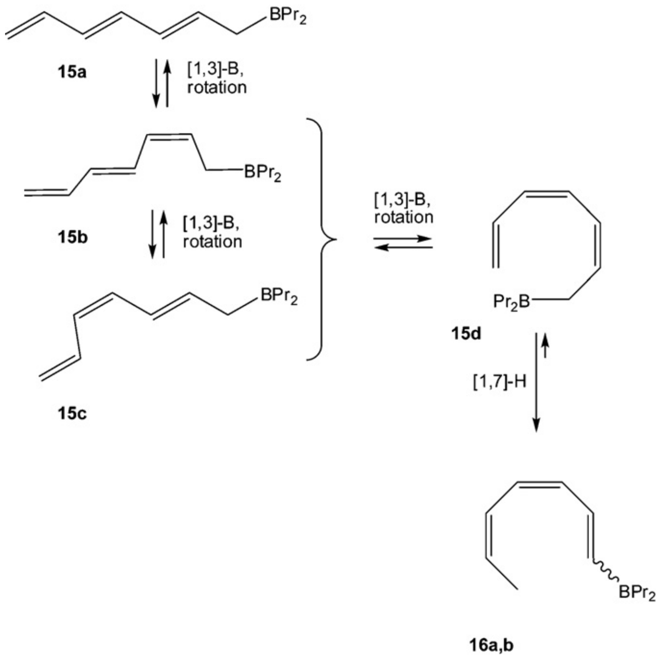
Scheme 3. Interconversion of isomers via consecutive [1,3]-B shifts.

A reversible dependence of the line-shape on the temperature was observed in the ^{13}C NMR spectrum of pentadienyl(dipropyl)borane **14** over the temperature range 300–395 K. The exact nature of the rearrangements taking place in this compound was determined by the line shape analysis and 2D EXSY NMR experiments [36].

The fastest dynamic process in **14** is the degenerate rearrangement in *E*-isomer **14a**. It proceeds through two consecutive 1,3-B shifts via unstable allylic isomer **14c** (Scheme 4). The lower rate of the sigmatropic 1,3-B migrations in the *Z*-isomer **14b** compared to **14a** is probably due to the greater bulkiness of the *cis*-allylic substituent.

An estimation of the effective barriers $\Delta G^{\neq}_{\mathrm{EE}}$, $\Delta G^{\neq}_{\mathrm{EZ}}$, and $\Delta G^{\neq}_{\mathrm{ZZ}}$ made by line-shape analysis of the ^{13}C NMR spectra afforded the following values:

- $\Delta G_{\mathrm{EZ}}(366) = 3.5 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$;
- $\Delta G^{\neq}_{\mathrm{EE}}(366) = 82.3 \pm 0.9\,\mathrm{kJ\,mol^{-1}}$;
- $\Delta G^{\neq}_{\mathrm{EZ}}(366) = 85.5 \pm 0.9\,\mathrm{kJ\,mol^{-1}}$;
- $\Delta G^{\neq}_{\mathrm{ZZ}}(366) = 91.5 \pm 0.9\,\mathrm{kJ\,mol^{-1}}$.



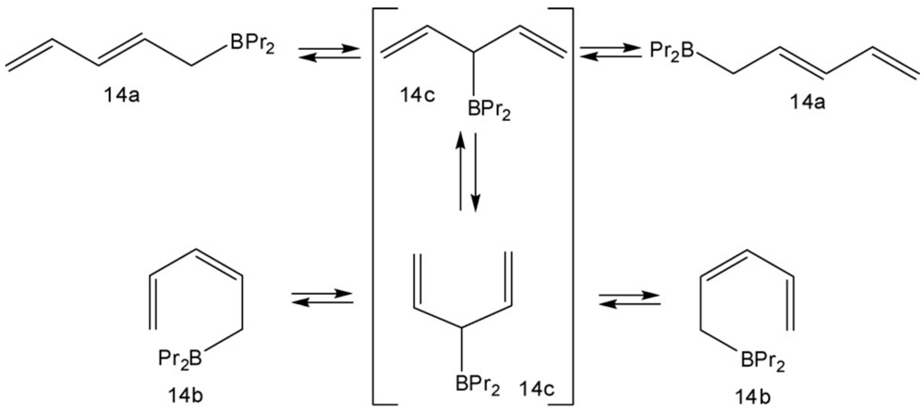
Scheme 5. Sigmatropic [1,3]-B shifts in **15a–d** facilitate [1,7]-H shift in **15d**.

Heptatrienyl(dipropyl)borane **15** isomerizes at elevated temperatures producing a vinyl borane **16** via a [1,7]-H sigmatropic shift in the *Z*,*Z*-isomer **15d** (Scheme 5) [37]. The content of **15d** in the equilibrium mixture is only 1%. Nevertheless, due to reversible interconversions of **15a–d** taking place via 1,3-B shifts and intramolecular rotations, the 1,7-H shift proceeds until a new equilibrium is established. The equilibrium mixture at 373 K contains 92% of **16** (mixture of two isomers in a ratio 95:5) and 8% of **15** (mixture of 4 isomers **15a–d**). This phenomenon was used for the first synthesis of isomerically pure *Z*,*Z*-1,3,5-heptatriene by the reaction of **29** with acetic acid [38].

2.1.2. Sigmatropic rearrangements in other linear organometallic compounds

As we have mentioned already, intramolecular sigmatropic rearrangements are not characteristic for the allylic derivatives of metals except for those of boron. The suprafacial pathway for a [1,3]-sigmatropic shift requires inversion of the stereochemical configuration of the central atom that can be effectively achieved only because of the presence of the empty 2p-AO on the boron atom.

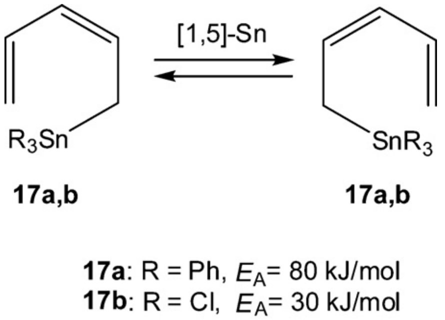
The orbital requirements for [1,5]-sigmatropic shifts are opposite, and one could expect to detect [1,5]-M migrations in 2,4-pentadienyl derivatives of metals. However, such observations are quite rare.



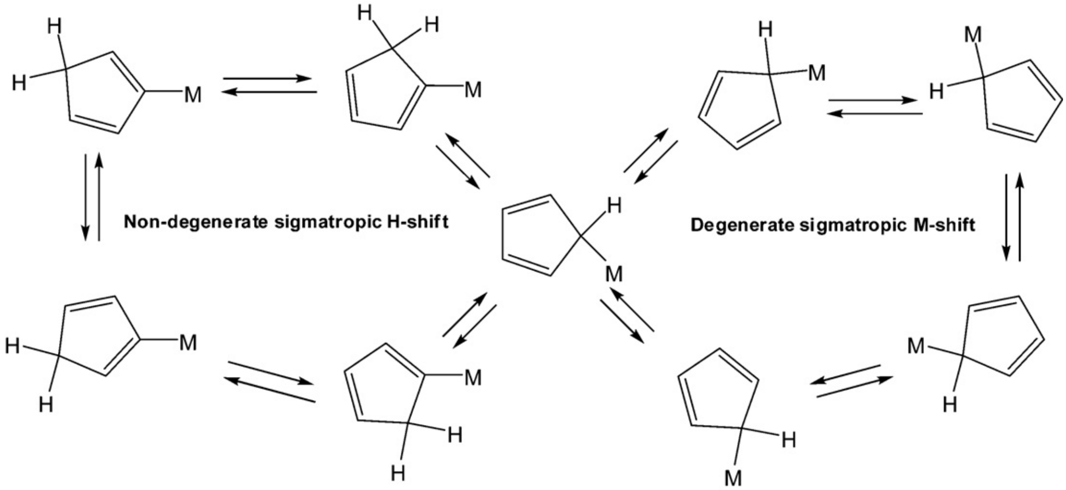
Scheme 4. Sigmatropic rearrangements in borane **14**.

The chemistry of pentadienylmetals is well studied [39,40]. The pentadienyl derivatives of alkali metals (Na, K, Rb, Cs) are ionic compounds. They are dynamic in solution due to the fast equilibria among *S*-, *W*-, and *U*-conformations of the pentadienyl anion [41–47]. The pentadienyl derivatives of lithium, [48,49] magnesium, [50] beryllium, [51] and zinc [51] demonstrate more complicated dynamic behavior including equilibria between ionic and σ-bound structures together with conformational equilibria in the anion.

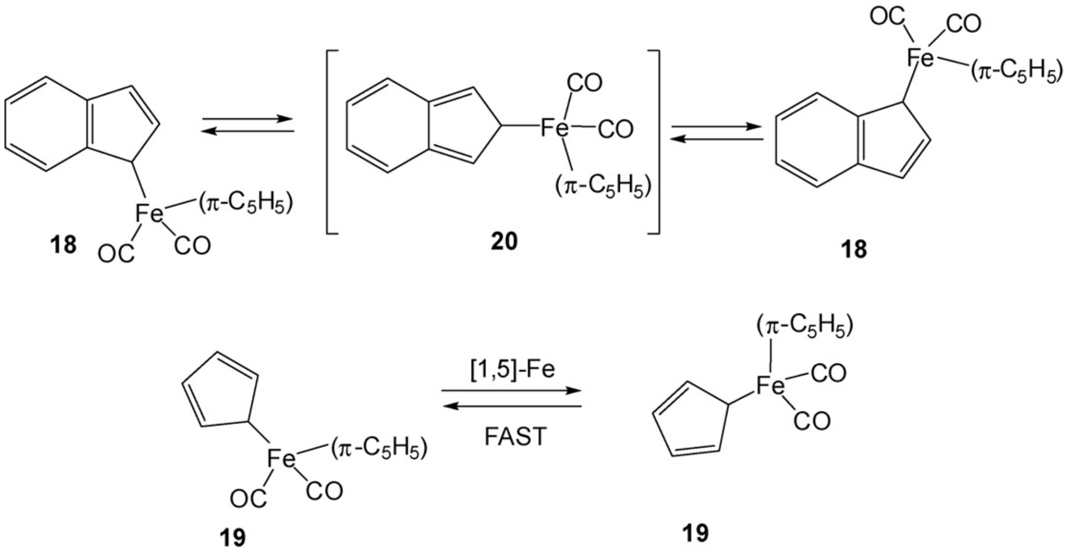
Pentadienyl(trimethyl)silane is non-fluxional [52]. On the other hand, *Z*-isomers of the pentadienyltin compounds **17a**,**b** exhibit sigmatropic [1,5]-Sn shifts (Scheme 6) [20,53]. The rearrangement in corresponding *E*-isomers does not take place at all. Comparing this situation with the dynamic behavior of the boron compound **14** (Scheme 4), one can clearly see the alternation of the metallotropic migration mechanisms that is in accord with the predictions of the molecular orbital theory. Noteworthy is the significant difference in the activation barriers of the [1,5]-Sn migrations in compounds **17a** and **17b** (Scheme 6); apparently changing the phenyl substituents on tin for the more electronegative chlorine atoms facilitates the sigmatropic migrations.



Scheme 6. Sigmatropic [1,5]-shift in the pentadienyl derivatives of tin.



Scheme 7. Sigmatropic rearrangements in η^1-cyclopentadienyl organometallic compounds [9].



Scheme 8. Sigmatropic migrations in indenyl and cyclopentadienyl derivatives **18** and **19**.

2.2. Sigmatropic rearrangements in cyclic organometallic compounds

2.2.1. Sigmatropic rearrangements in cyclopentadienyl and indenyl derivatives of metals

Numerous known organometallic derivatives of cyclopentadiene exhibit fast sigmatropic migrations of the organometallic group and/or sigmatropic hydrogen shifts. This was also historically the very first system where fluxionality has been found, and the regularities of the metallotropic migrations in various compounds of the type have been intensively studied for 30 years from 1960 to 1990. The results of these studies were thoroughly covered in the excellent review of Jutzi [9] and replenished in further reviews of the same author [8,54,55]. Therefore, in the present account we will only shortly mention the main features of the sigmatropic migrations in organometallic derivatives of cyclopentadienes referring the reader to the previous reviews for details.

All sigmatropic rearrangements that can take place in a η^1-cyclopentadienyl derivative of metal are summarized in the Scheme 7. Depending on the relative values of the activation barriers for metallotropic migrations and sigmatropic [1,5]-H shifts, the dynamic behavior of a particular compound can result in complicated multi-component systems (especially when the cyclopentadienyl ring is non-symmetrically substituted) that were rarely fully analyzed. Nevertheless, many compounds have been investigated as the main components of these equilibria [9].

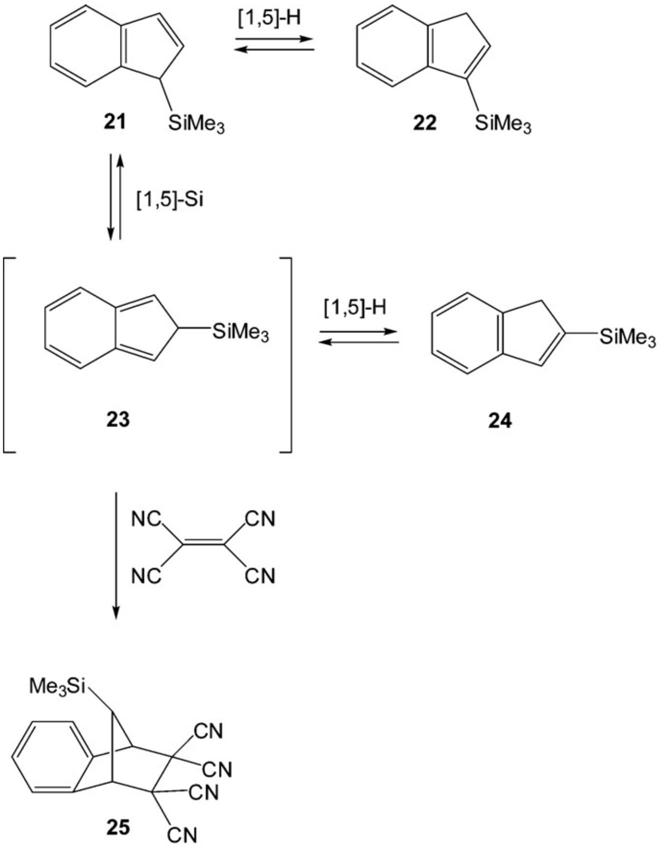
It is not easy to distinguish experimentally between two possible mechanisms of the metal migration, *viz.* [1-5]-M ([1,2]-M) and [1,3]-M shifts. All available data testifies that most probably [1,5]-M shifts occur in most of organometallic cyclopentadienes. However, neither conclusion is possible in cases when even at low temperatures only averaged signals are observed in the NMR spectra due to extremely fast metallotropic migrations.

The activation barriers of metallotropic migrations are lower for heavier metals. The substituent effects on the rates of sigmatropic migrations depend on the nature of the migrating atom. For example, whereas rather drastic substituent effects are characteristic for the cyclopentadienyl derivatives of group 13 (B, Al, Ga, In), only very small substituent effects have been documented for the cyclopentadienyl derivatives of group 14 (Si, Ge, Sn) [9].

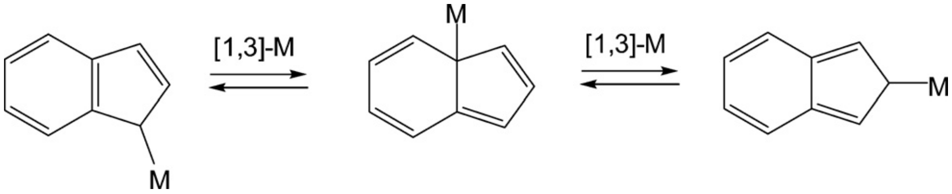
Sigmatropic migrations in the indenyl derivatives of metals were studied at the same time as their cyclopentadienyl analogs. The interest to the indenyl system arose after Cotton has reported in 1967 that the iron compound **18** is static at ambient temperature, [56] whereas in its cyclopentadienyl analog **19** only averaged signals are observed in the ambient temperature NMR spectrum due to the fast sigmatropic migrations of the $Fe(CO)_2(\pi\text{-}C_5H_5)$group [3] (although 30 years later [1,5]-Fe migrations in **18** have been detected by 2D EXSY and SST techniques, [57] they are evidently much slower than those in cyclopentadienyl compound **19**) (Scheme 8). This result has been interpreted as the argument in favor of sigmatropic [1,5]-Fe migrations in compound **19**. It was suggested that if the $Fe(CO)_2(\pi\text{-}C_5H_5)$ group could migrate in **19** via [1,3]-Fe sigmatropic shifts, one could expect equally fast migrations in **18**. On the other hand, [1,5]-Fe migrations in **18** require intermediacy of thermodynamically unstable compound **20** (that can be trapped by the reaction with an appropriate dienophile [57]), hence the high activation barrier for sigmatropic migrations in **18** can be explained [3].

This suggestion of Cotton was used in further studies of the dynamic behavior of σ-indenyl derivatives of mercury [58], silicon [59–64], tin [59,63–66] and germanium [63,64] for the discussion of the mechanism of metallotropic migrations in the indenyl derivatives of metals. Migration of the organometallic group from the position 1 to the position 3 was observed in all these compounds, but the activation barrier of the rearrangement was usually approximately 35 kJ/mol higher than in the corresponding cyclopentadienyl derivatives that is taken as an evidence in favor of [1,2]-M migrations [63]. The same argumentation has frequently been used in a series of reviews [11,67,68] and in numerous publications [56,69–78]. We would like to note, however, that this approach neglects the electronic effects of the phenyl ring on the activation parameters of metallotropic rearrangements.

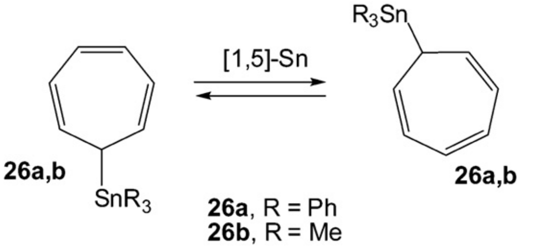
Larrabee was the first to show that the intermediates of the type **20** really exist, when he found that the [1,5]-H shift in 1-trimethylsilylindene **21** yields at 150 °C not only expected 3-isomer **22**, but also 2-trimethylsilylindene **24** that evidently forms via the intermediacy of **23** (Scheme 9) [58]. Ashe III showed also that **23** can be trapped in a reaction with a dienophile, such as tetracyanoethylene [62]. Trapping of simi-



Scheme 9. Trapping of the intermediate **23**.



Scheme 10. Possible intermediates available via [1,3]-M shift.



Scheme 11. [1,5]-Sn Shift in cycloheptatrienyltin derivatives.

lar intermediates in the reactions with dienophiles has also been applied in further research [63,79].

It should be noted, however, that despite the common opinion, the trapping of the intermediates like **20** or **23**, although being quite interesting and instructive observation, does not provide an unequivocal proof of the [1,5]-sigmatropic shift, since generally speaking their generation via two consecutive [1,3]-shifts is conceivable (Scheme 10).

This consideration suggests that probably the best arguments in favor of [1,3]- or [1,5]-sigmatropic migrations in indenyl (and cyclopentadienyl) organometallic derivatives are orbital requirements. Thus, the dynamic behavior of 1-indenyl(diethyl)borane was interpreted as [1,3]-B shift by analogy with other allylboranes.[80] On the other hand, studies of the interconversion of various isomers for the compounds of the types $R_2Si(C_9H_7)_2$ [76,81,82] and $RSi(C_9H_7)_3$ [79] have shown that all dynamic processes observed in these indenyl derivatives can be explained by consecutive [1,5]-Si shifts.

2.2.2. *Sigmatropic rearrangements in cycloheptatrienyl and cyclononatetraenyl derivatives of metals*

Cycloheptatrienyl and cyclononatetraenyl rings give more possibilities for an organometallic group to migrate in various fashions that was used for the experimental probing of the orbital symmetry principles. Thus, in 1971 Larabee reported facile [1,5]-Sn sigmatropic shifts in triphenylcycloheptatrienyl tin **26a** [83]. This observation was later confirmed twice [84,85]; the same mechanism was recently found for trimethylcycloheptatrienyl tin **26b** (Scheme 11) [86]. These results clearly demonstrate the importance of orbital control in sigmatropic migrations, since the tin moiety migrates selectively to the most remote position in the ring.

On the other hand, in cycloheptatrienyl(dipropyl)borane **27** the dipropylboryl group migrates reversibly to the nearest position that formally corresponds to a [1,7]-B sigmatropic shift [86]. Different migration mechanisms are also observed in the cyclononatetraenyl derivatives of boron and tin (Table 2). In the cyclononatetraenyl ring the organotin group migrates most rapidly to the nearest position (that formally corresponds to a [1,9]-Sn shift in compound **28**), whereas the fastest rearrangement in the organoboron compound **29** is the [1,3]-B shift.

The data on the sigmatropic rearrangements in the compounds **26**–**29** (Table 2) show clear alternation in the mechanism of fastest sigmatropic migrations for boron and tin: [1,3] and [1,7] shifts are observed for boron compounds, whereas the corresponding tin derivatives only show [1,5] and [1,9] migrations. Taking into account the symmetry of the bonding orbitals for boron and tin, the sigmatropic shifts with inversion (Möbius type transition state) for boron and with retention (Hückel type transition state) for tin agree nicely with the qualitative predictions of molecular orbital theory [86,87].

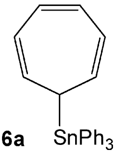
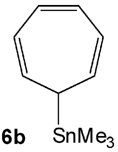
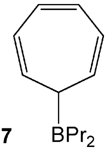
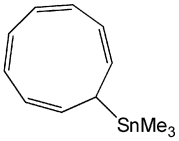
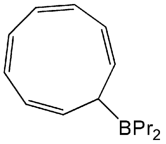
Furthermore, the selectivity *among allowed processes* may be rationalized using the least motion principle. The [1,7]-B shifts in **27** (migration to the nearest position of cycloheptatriene) proceed faster than the [1,3]-B shifts in the same compounds; the orbitally allowed [1,7]-B migration in cyclononatetraenyl boron is strongly energetically disfavored compared to [1,3]-B shifts, for which the small distance between the reaction termini allows the formation for flat homo-aromatic transition structures [30,86,87].

Nevertheless, the barriers for sigmatropic shifts in cyclic polyolefins are not controlled directly by the distance of the migration termini. Thus, the [1,7]-B shift (migration to the adjacent position) in cycloheptatrienylborane **27** is about 30 kJ/mol higher in energy than the [1,3]-B shift in cyclononatetraenylborane **29** (Table 2). Moreover, despite the different nature of the migrating groups, the rearrangement barriers for the cycloheptatrienyl boron and tin compounds **26a**, **26b**, and **27** as well as for the cyclononatetraenes **28** and **29** are rather similar. Hence, the energetics of sigmatropic migrations are mainly determined by the properties of the carbocycle rather than by the nature of the migrating group.

The most probable reason for the faster rearrangements in the cyclononatetraenyl ring is its higher conformational flexibility. Thus, a computational analysis of the sigmatropic migrations in **29** showed that the experimentally observed [1,3]-B migrations occur only in *endo*-conformer, whereas for the *exo*-conformer only a non-degenerate [1,2]-B migration is possible that leads to the formation of mono-*trans* isomer (Scheme 12) [89]. The latter process has a relatively high activation barrier and cannot be observed directly. Nevertheless, **29a**-mono-*trans* is a key intermediate of irreversible rearrangements occurring in **29** at ambient temperature (see Section 2.2.3) [90].

The cycloheptatrienyl derivatives of ruthenium [91], and rhenium [92], exhibit sigmatropic migrations of the corresponding

Table 2
Experimental data on boron and tin sigmatropic migrations in cyclic conjugated molecules

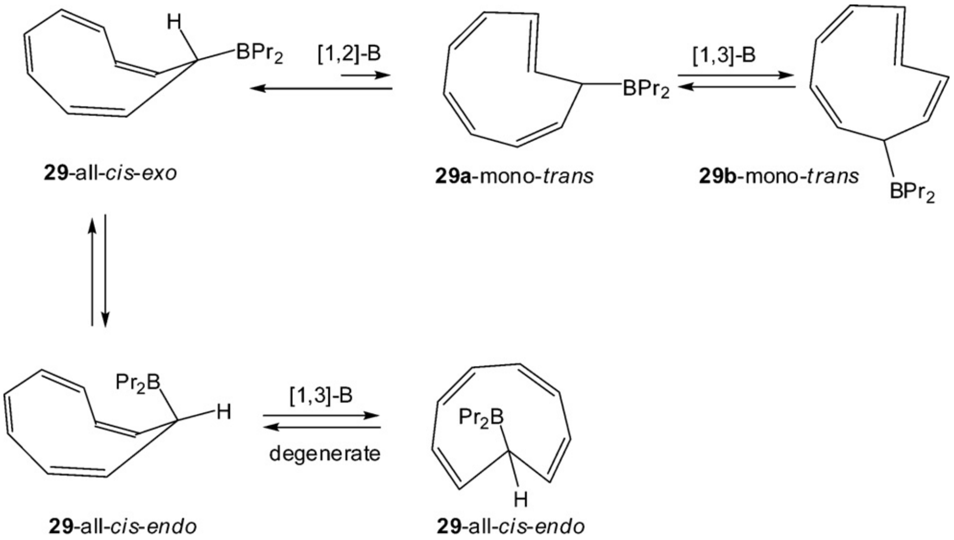
Compound	Type of rearrangement	$\Delta G(T)$ (kJ mol^{-1})	E_A (kJ mol^{-1})	Reference
 **26a**	[1,5] Sn	64.8 ± 0.5		[85]
 **26b**	[1,5] Sn	75.2 ± 0.2 (298)	65.4 ± 0.3	[85]
 **27**	[1,7] B[a]	77.0[b]		[85]
 **28**	[1,9] Sn[a]	38.0 ± 0.4 (173)	25.2 ± 2.5[c]	[87]
 **29**	[1,3] B[a]	36.8 ± 0.4 (195)	26.1 ± 2.2[d]	[88]

[a] The fastest rearrangement.

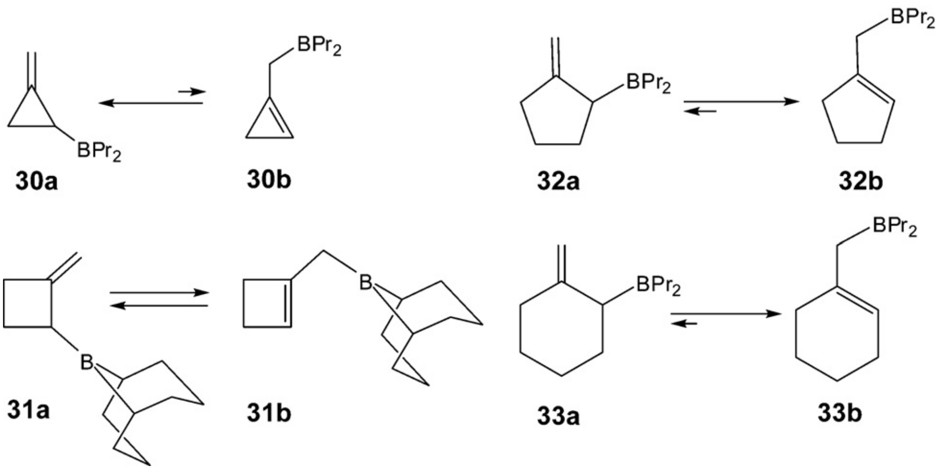
[b] Computed value (B3LYP/6-311 + G*//B3LYP/6-31G* + ZPVE, Ref. [14]).

[c] Computed value (B3LYP/6-311G*(3-21G* on Sn)//B3LYP/6-31G* (3-21G* on Sn) = 26.4 kJ/mol.

[d] Computed value (B3LYP/6-311 + G*//B3LYP/6-31G*) = 25.1 kJ/mol.



Scheme 12. Sigmatropic migrations of the dipropylboryl group in compound **29**.



Scheme 13. [1,3]-Sigmatropic boron shifts in compounds **30**–**33**.

organoelement group in the nearest position, *i.e.* they demonstrate the same selectivity as the boron derivative **27**. Qualitative orbital considerations would probably suggest that they must rather behave similarly to tin [6], but apparently the orbital control is less important for the transition metal derivatives, and so migration to the nearest position of the cycloheptatriene ring prevails.

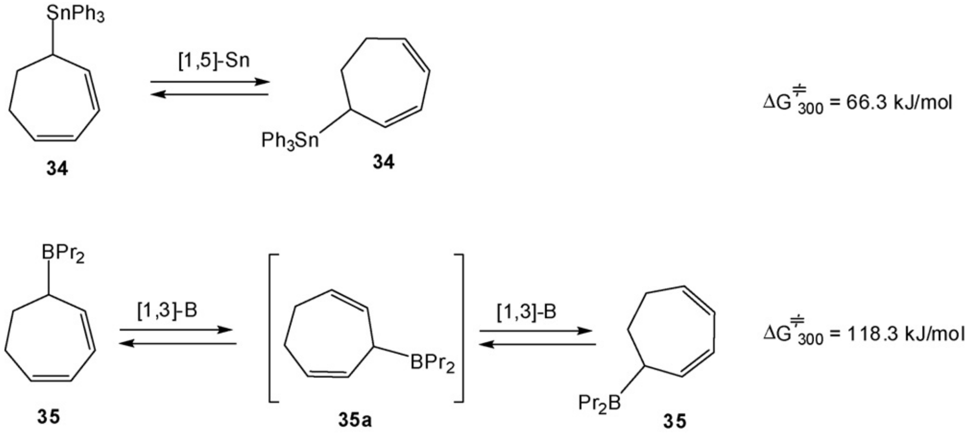
2.2.3. Sigmatropic rearrangements in other cyclic derivatives of metals

In most cases sigmatropic migrations are observed as degenerate rearrangements in symmetric molecules. If there is no molecular symmetry in the organometallic derivative, then sigmatropic rearrangements lead to the rapid establishment of thermodynamic equilibrium that usually is strongly shifted in favor of the most stable isomer. In such cases it becomes impossible to observe the rearrangement directly. This point is well illustrated by a series of organoboron compounds **30**–**33** (Scheme 13).

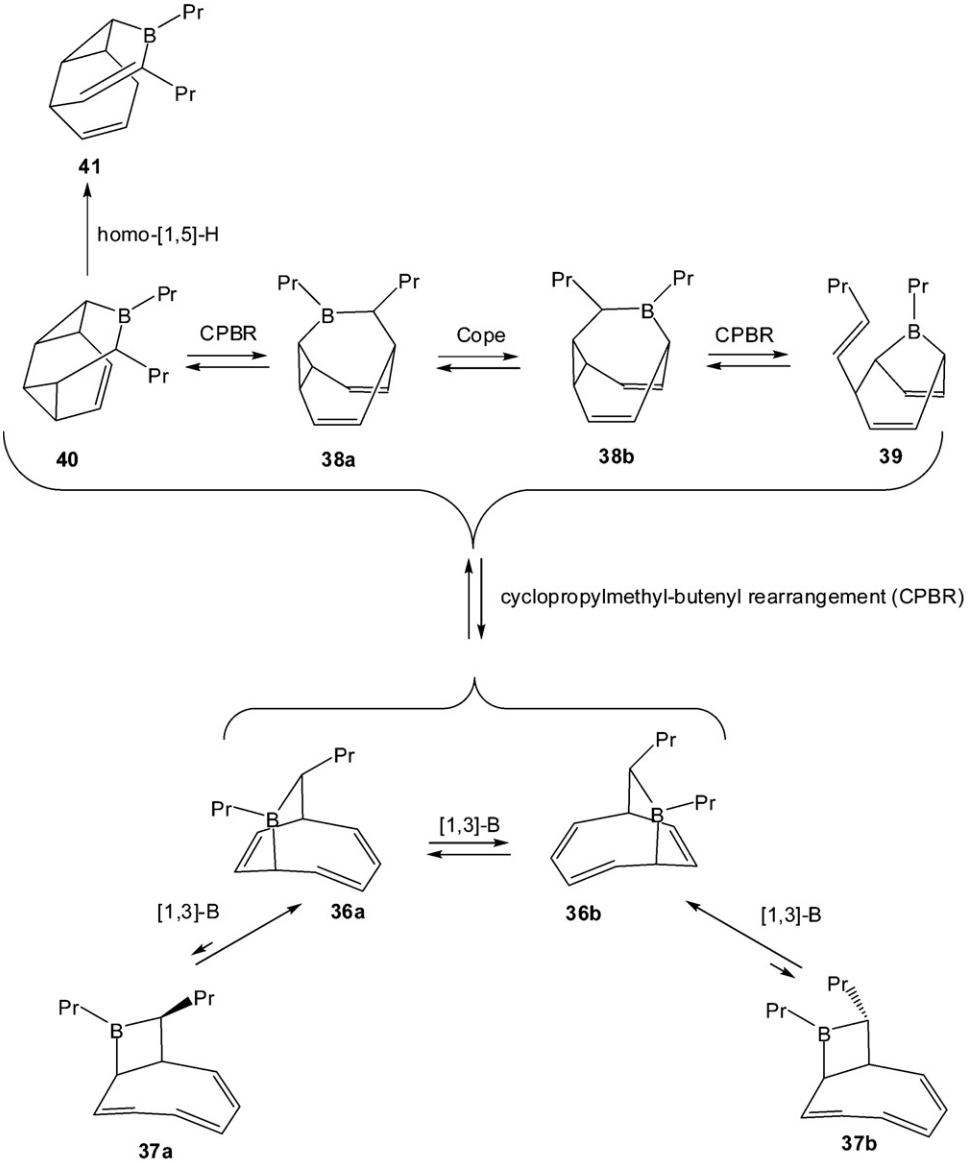
Whereas, in the case of cyclopropenyl derivative **30** only the methylenecyclopropane form **30a** was observed in solution [93], in the compounds **32** and **33** only cyclopentenylmethyl and cyclohexenylmethyl isomers **32b** and **33b** were detected [94]. The compound **31** with a four-membered ring is apparently an intermediate case; it is a rare example of similar stabilities of two tautomeric forms **31a** and **31b**. The rapid equilibrium was studied in detail by NMR [95].

Cycloheptadienyl derivatives of tin **34** [85] and boron **35** [96] are fluxional (Scheme 14). Experimentally, migration of organometallic group from position 1 to position 5 is observed in both cases. However, apparently a [1,5]-Sn shift takes place in compound **34** [85], whereas a sequence of two [1,3]-B shifts occurs in compound **35** similarly to the analogous rearrangement in *Z*-pentadienyl(dipropyl)borane **14b** (see Section 2.1.1) [97]. This conclusion follows from comparing the activation parameters of the corresponding rearrangements: the barrier of borotropic migration in **35** is almost twice as high as the barrier of the stannotropic rearrangement in **34**, although in cycloheptatrienyl derivatives of boron and tin these barriers were very close in value (see Table 2).

Two isomeric boranes **36a**,**b** (Scheme 15) interconvert via fast [1,3]-B shifts ($\Delta G^{\neq}_{298} = 52.2 \pm 0.1$ kJ/mol); this equilibrium was studied in detail by NMR [98]. However, the dynamic behavior of this boron compound is much more complex. Thus, it was shown that another allylic isomer **37** is the direct precursor of **36** in the series of rearrangements starting from the



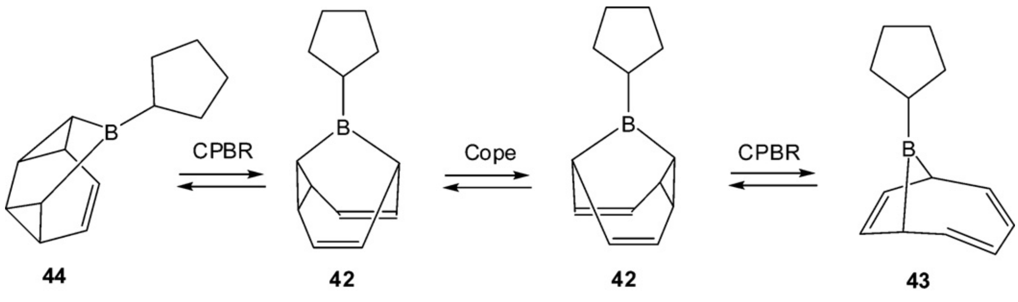
Scheme 14. Sigmatropic rearrangements in cyclohaptadienyl derivatives of tin and boron.



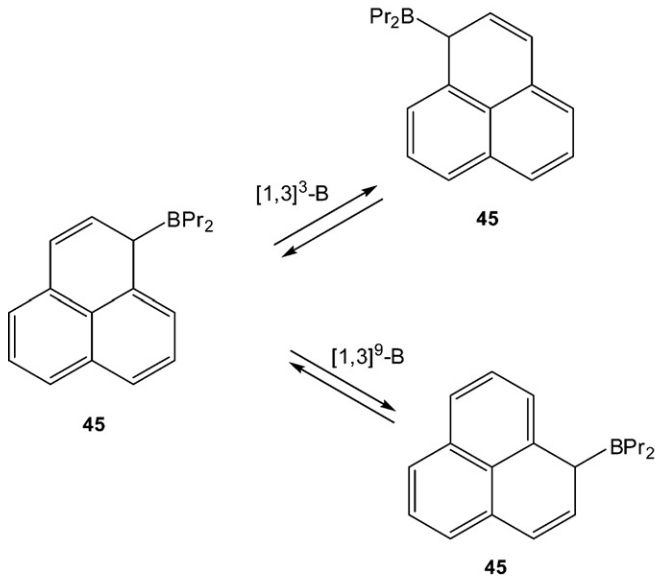
Scheme 15. Plethora of rearrangements in the bicyclic borane **36**.

cyclononatetraenyl(dipropyl)borane **29**. Moreover, **36** must be in fast equilibrium with borabullvallene **38** and its skeletal isomers **39** and **40**, since **38** is trapped selectively in the reaction of **36** with methanol, **39** is trapped selectively in the reaction of **36** with acetone, and **40** is a precursor of the tricyclic borane **41** that is the final product of thermal rearrangements starting from **29**. Thus, presence of the boron atom in a polyunsaturated cyclic molecule leads to appearance of a multitude of dynamic properties.

A similar abundance of intramolecular dynamics was found in borabarbarallane **42** (Scheme 16) [99]. Only compound **42** (fluxional due to degenerate Cope rearrangement) can be



Scheme 16. Sigmatropic rearrangements in compound **42**.



Scheme 17. Two different [1,3]-B shifts in compound **45**.

detected in solution by NMR [99,100], however, its minor tautomers **43** and **44** were trapped selectively in the reactions of **42** with acetone and methanol, respectively [99].

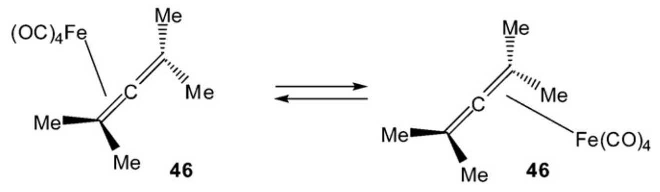
Cyclooctatetraenyl derivative of boron exhibits only fluctuation of double bonds typical for all cyclooctatetraenes. Sigmatropic migrations of boron do not occur in this compound because the empty 2p-AO of boron atom is blocked when it is located in a vinylic position [101].

Both possible [1,3]-B shifts take place in phenalenyl(dipropyl)borane **45** (Scheme 17) [102]. Rearrangement to position 9 occurs faster ($\Delta G^{\neq}_{298} = 63.6$ kJ/mol) than the migration to position 3 due to the more favorable geometry of the corresponding allylic fragment. Any of the two [1,3]-B shifts separately is spatially fixed to one allylic or benzylic fragment of **45**, respectively. However, the combination of both results in the possibility for the di-*n*-propylboryl group to migrate around the whole molecule [102].

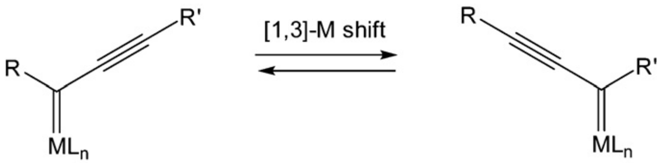
3. Haptotropic rearrangements

3.1. Haptotropic rearrangements in linear organometallic compounds

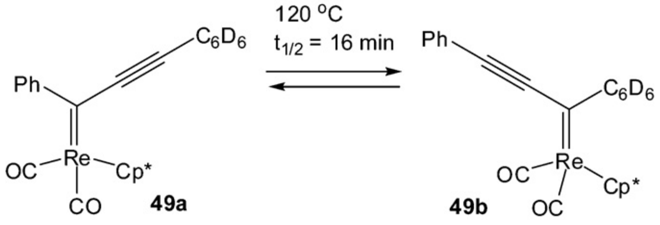
In 1967, Pettit reported that $Fe(CO)_3$ complex of tetramethylallene (**46**) is fluxional exhibiting intramolecular slippage of the irontetracarbonyl group between two double bonds of the allene moiety with low activation barrier (Scheme 18) [103].



Scheme 18. Haptotropic rearrangement in iron complex of tetramethylallene.



Scheme 20. [1,3]-M shift in alkynyl carbene metal complexes.



Scheme 21. Direct observation of [1,3]-Re haptotropic shift.

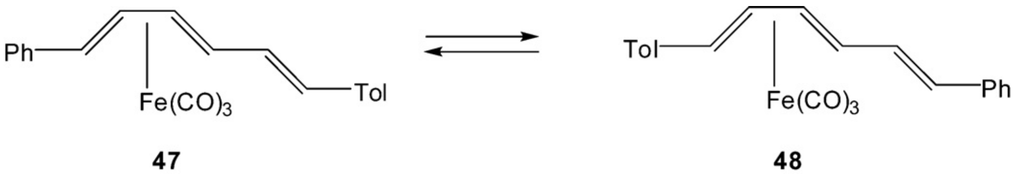
Similar rearrangements were later reported for platinum complexes of allenes [104,105].

In 1977, Rosenblum et al. made a systematic study of haptotropic migrations in cationic η^5-$C_5H_5Fe(CO)_2$ complexes of allenes with different orders of methyl substitution [106]. The rearrangement was shown to proceed via concerted [1,2]-shift of the η^5-$C_5H_5Fe(CO)_2$ moiety, since no racemization occurred when chiral allene complex was used.

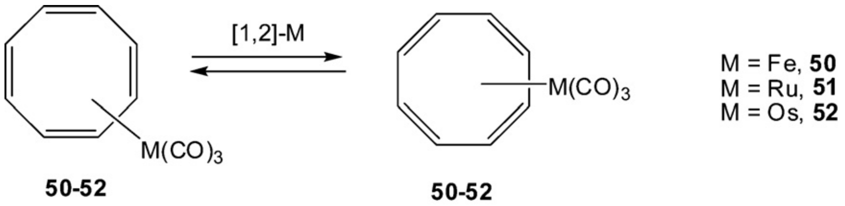
Haptotropic migration of the irontricarbonyl group was reported for the η^4-$Fe(CO)_3$ complexes of polyenes (*e.g.* Scheme 19) [107,108].

Another type of haptotropic migration, [1,3]-metal shift in alkynyl carbene metal complexes (Scheme 20), was postulated in 1993 as a process presumably occurring in the catalytic cycle [109].

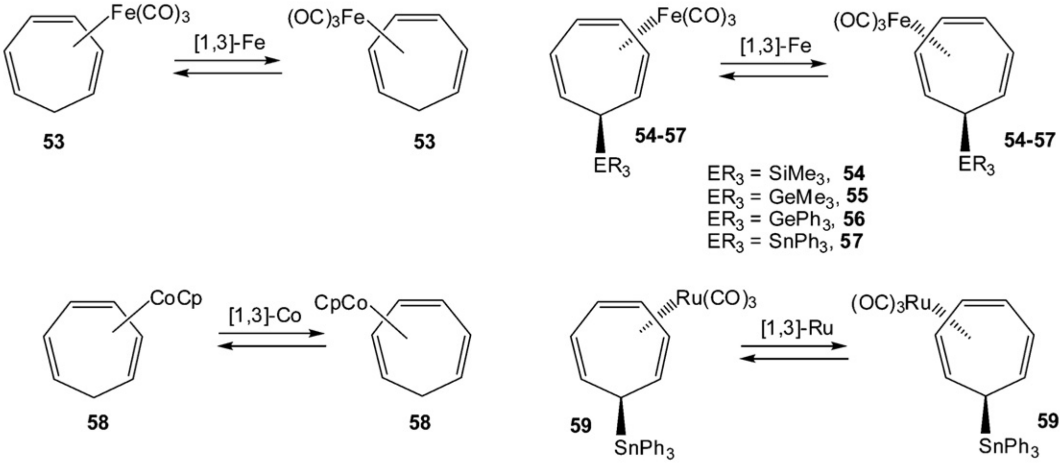
This mechanistic suggestion proved to be useful for designing and understanding catalytic cycles of various cyclization reactions involving catalysis with Ti [110], Cr, Mo, W [111] and Ru [112]. The [1,3]-Re shift was directly observed for deuterium-labeled alkynylcarbene complex **49** (Scheme 21) [113]. It was suggested that in fact this rearrangement can be mediated by traces of an η^1,η^2-dirhenium complex, since the coordination of an additional $[Cp(CO)_2Mn]$ fragment to



Scheme 19. Migration of $Fe(CO)_3$ moiety in polyenes.



Scheme 22. Haptotropic shifts in organometallic derivatives of cyclooctatetraene.



Scheme 23. [1,3]-M haptotropic shifts in cycloheptatrienyl complexes.

the alkyne linkage of an alkynylcarbene complex of the type $Cp(CO)_2Mn=C(R')C\equiv CR''$ yielded a highly fluxional molecule ($E_A = 38.9$ kJ/mol) with exchanging [η^1-carbene] and [η^2-alkyne] moieties [114]. The [1,1.5]-Re shift (motion of $Re(CO)_2Cp^*$ group to the adjacent triple bond yielding free carbene species) is also believed to be a key stage in the experimentally observed dimerization of Re complexes analogous to **49** [115].

3.2. Haptotropic rearrangements in cyclic organometallic compounds

3.2.1. Intra-ring haptotropic rearrangements

Experimental determination of the mode of metallotropic migrations in cyclooctatetraene derivatives of iron (**50**), ruthenium (**51**), and osmium (**52**) was one of the most challenging problems in the early stages of the studies of metallotropic rearrangements [11]. The careful and extensive analysis of the experimental and computed line-shapes of low-temperature NMR spectra suggested that the most probable mechanism of the fast metallotropic migrations were consecutive and random [1,2]-M shifts (Scheme 22) [11,115]. However, the technical limitations of those days, and inevitably qualitative character of the conclusions, did not allow one to be completely certain in the uniqueness of the [1,2]-M migration mechanism, since the kinetic estimations were unreliable. A recent study of osmium compound **52** unequivocally confirmed the mechanism of [1,2]-Os shifts ($E_A = 24.8$ kJ/mol) by 2D EXSY experiments [116]. DFT analysis showed that metallotropic migration occurs via a non-flat symmetric transition state (the computed activation barrier was 27.4 kJ/mol) in which the Os atom has only three strong bonds with carbon atoms of the cyclooctatetraene ring (Fig. 1) [116].

On the other hand, η^6-$M(CO)_3$ cyclooctatetraene complexes of chromium, molybdenum and tungsten mainly demonstrate that [1,3]-M shifts are considerably slower than [1,2]-M shifts in the compounds **50**–**52** [117].

The [1,3]-M mode of metallotropic migrations is observed in the complexes of cycloheptatriene. Thus, this mechanism of haptotropic rearrangement was found in η^4-cycloheptatrieneirontricarbonyl **53** and representative series of its analogs [118]. The [1,3]-Fe haptotropic migration in cycloheptatrienyl ring becomes more facile when it is sub-

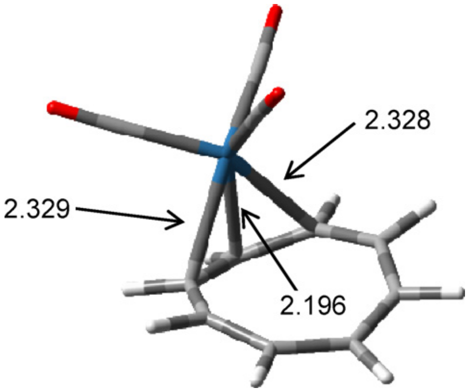


Fig. 1. Transition state for [1,2]-Os shift in **52** computed at B3LYP/SDD level of theory.

stituted with donor substituents in position 7 [118]. This is illustrated by the series of heterobimetallic complexes **54–57** [119] (Scheme 23): $\Delta G^{\neq}$ changes from 94 kJ/mol in **53** [118] to 72–75 kJ/mol in silicon and germanium derivatives **54–56** [119] and to 45 kJ/mol in the triphenyltin derivative **59** [120]. Similarly, [1,3]-M haptotropic shift was characterized in cycloheptatrienyl complexes of cobalt **58** [121] and ruthenium **60** [120].

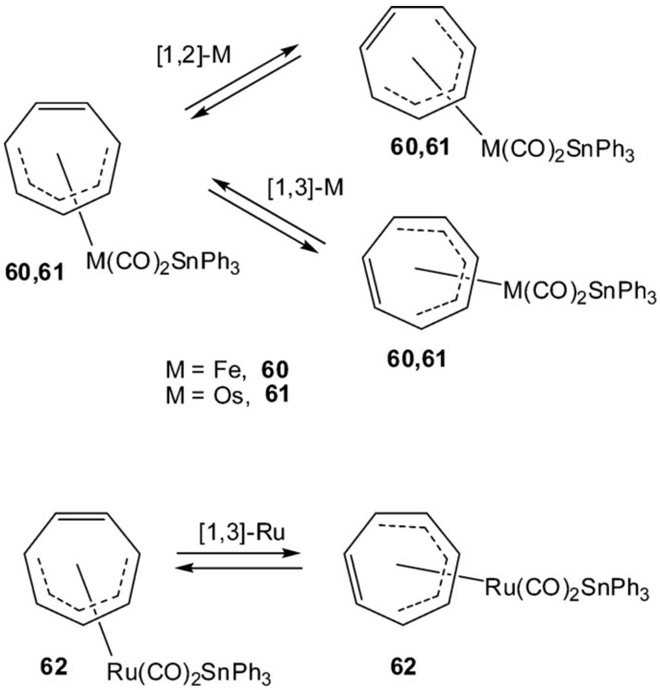
All known η^3- and η^5-organometallic derivatives of cycloheptatriene and cyclooctatetraene are fluxional. Early work based on the sophisticated line shape analysis invariably ascribed this fluxionality to [1,2]-Me shifts, and these data were reviewed by Mann in 1986 [122]. However, in more recent research applying magnetization transfer techniques mixed [1,2]-M and [1,3]-M shifts were detected for compounds **60** and **61**, whereas a pure [1,3]-Ru shift was observed in compound **62** (Scheme 24) [123].

3.2.2. Inter-ring haptotropic rearrangements

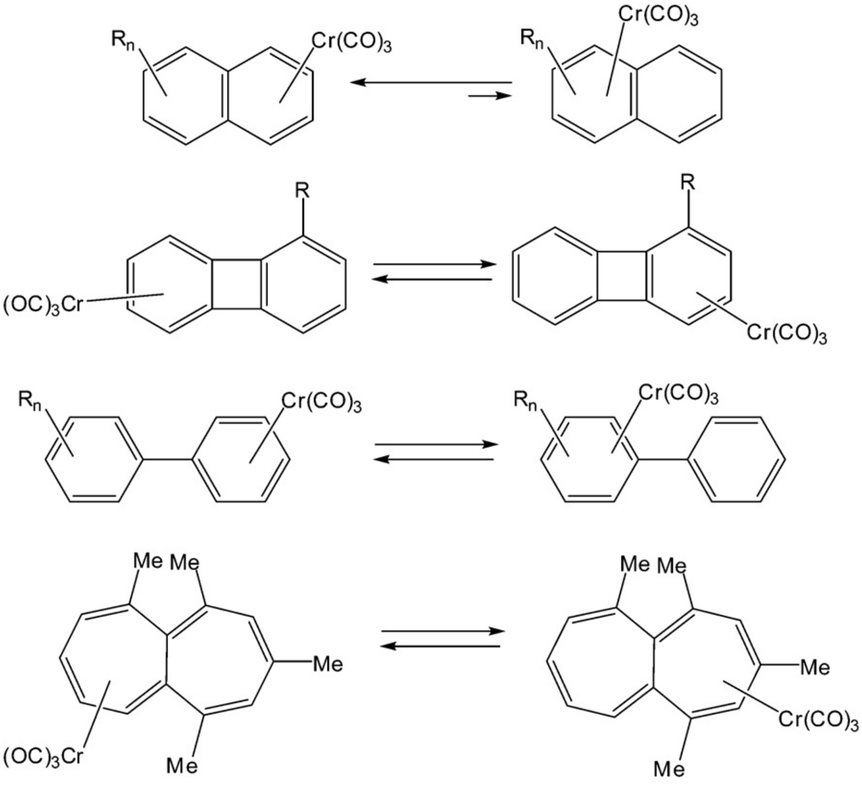
This is an extensively documented area covered recently in several reviews [4,5,7]; hence, we will briefly discuss the main trends in this chemistry and focus mainly on the reports published after 2004.

Metal complexes of non-symmetrically substituted aromatic hydrocarbons on heating undergo haptotropic migrations resulting in the equilibrium mixture of corresponding isomers (Scheme 25) [4,5,7].

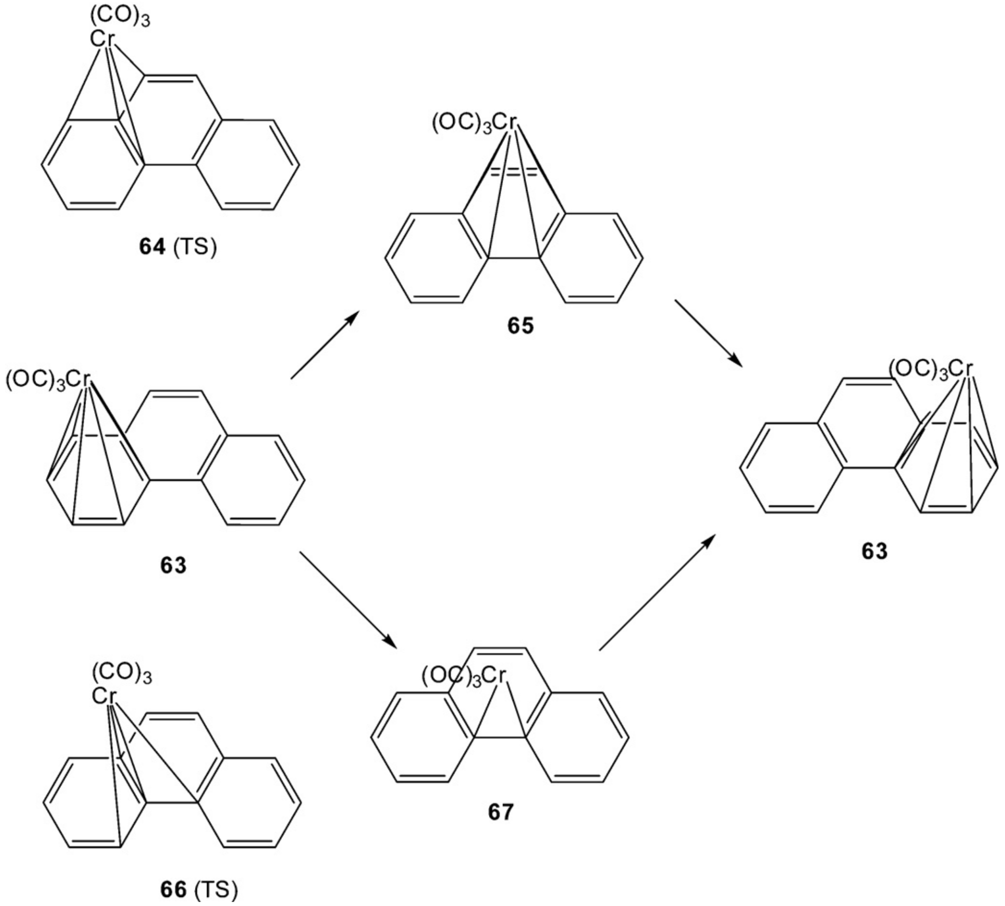
The rearrangement is not restricted to the adjacent aromatic rings of naphthalene, but occurs also in biphenyls, between remote aromatic rings or in fused non-planar polycycles (Scheme 25) [7]. Usually, the isomer having the chromiumtricarbonyl group in the less-substituted aromatic ring is more stable. Normal temperatures for the inter-ring haptotropic rearrangements are within 70–120 °C; the ease of the rear-



Scheme 24. η^5-Cycloheptatrienyl complexes exhibiting [1,3]-M migrations.



Scheme 25. Various types of inter-ring haptotropic rearrangements covered in the recent reviews [4,5,7].



Scheme 26. Mechanism of haptotropic migrations in **63** elucidated by DFT calculations.

rangement can be finely tuned by variation of the substituents [5,124]. Photochemical reaction is capable of bringing the equilibrium back to the less stable isomer, the combination of thermal and photochemical rearrangements has been discussed in terms of possible application for switchable devices [4,5]. The vast majority of the experimental results in this area were obtained for chromiumtricarbonyl complexes, however, inter-ring haptotropic rearrangements have also been described for Ni [125,126], Mn [127–130], Fe [129,131], Pd [132], Ir [133], hence the phenomenon itself is undoubtedly general.

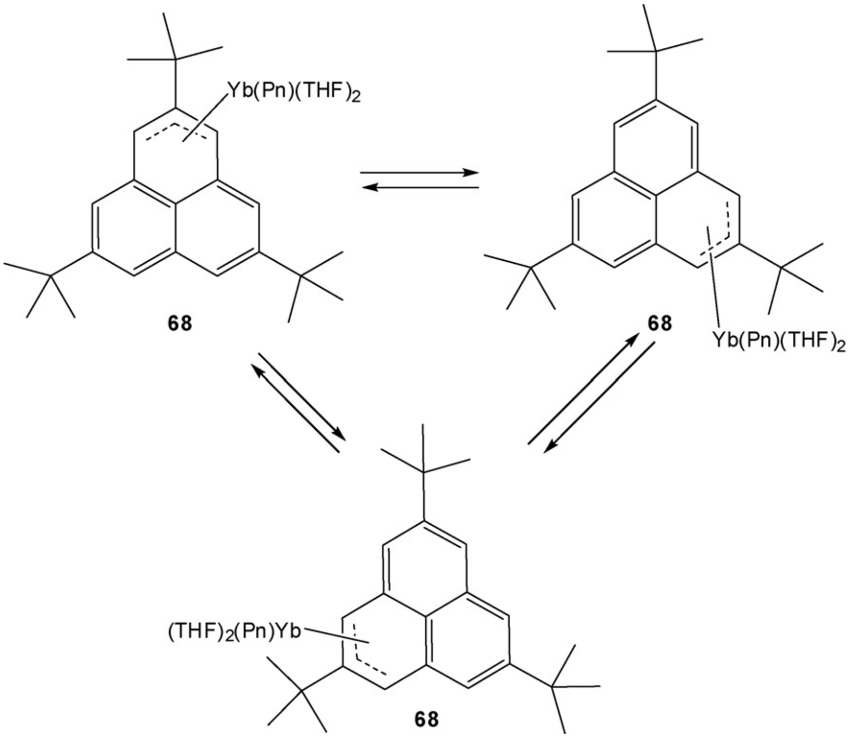
Recent theoretical studies of the $Cr(CO)_3$ group haptotropic migration in naphthalene [134] and phenanthrene [135,136] are available. Both studies corroborate the mechanism of haptotropic migration in which the chromiumtricarbonyl group does not follow the least motion principle, but rather proceeds along the ligand periphery with a η^4-trimethylenemethane complex as a transition state (*e.g.* **64** or **66** on Scheme 26 for the phenanthrene complex **63**) [135,136]. Two different pathways were found for **63** (Scheme 26), they are considered to be competitive and depending on the structure of substituents either one or the other can prevail [135,136].

On the other hand, in a theoretical study of the $Cr(CO)_3$ migration on (n,0) nanotube sidewalls the migrating group was found to take the shortest path to the adjacent ring, and in the transition state of the inter-ring rearrangement the chromiumtricarbonyl group resides directly over the C–C bond common to both cycles [137].

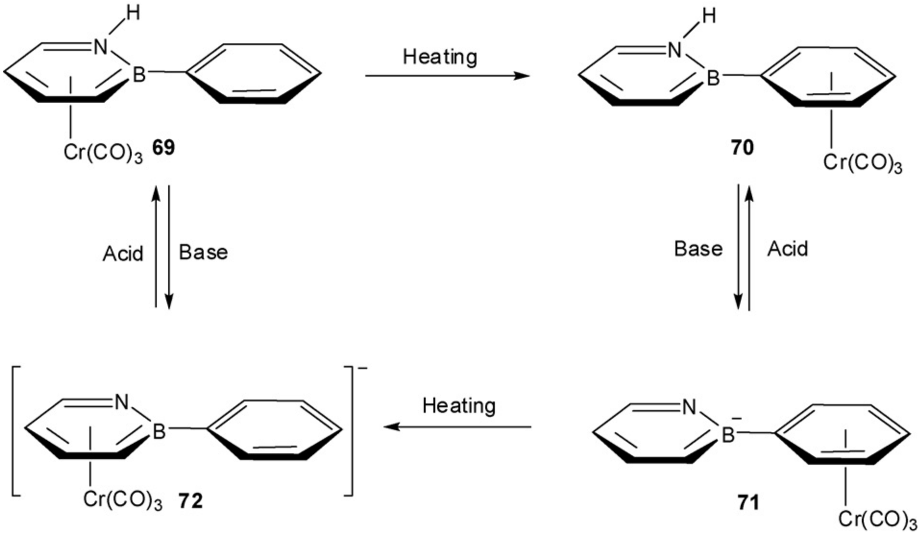
Recently, a highly fluxional η^3-phenalenyl complex of ytterbium was reported; degenerate inter-ring haptotropic migrations occur in compound **68** with a low activation barrier ($\Delta G^{\neq}$ lower than 40 kJ/mol; Scheme 27) [138]. This is much less than the 91 kJ/mol found previously for $[(\eta^3\text{-2,6,10-trimethylphenalenyl})Pd(tmeda)]PF_6$ [132]. The low activation barrier in the case of **68** is believed to indicate ionic binding in lanthanoid complexes [138].

Heterocyclic biphenyl chromium complex **69** is a kinetic product of the reaction of 1,2-dihydro-2-phenyl-1,2-azaborine with $Cr(CO)_3(CH_3CN)_3$. However, it undergoes haptotropic rearrangement when heated to 140 °C yielding the more stable complex **70** with chromiumtricarbonyl group coordinated to the normal phenyl ring. Deprotonation switches the relative attractiveness of the rings for the $Cr(CO)_3$ group, and heating of the anionic complex **71** brings the chromiumtricarbonyl group back to the heterocycle (Scheme 28) [139,140].

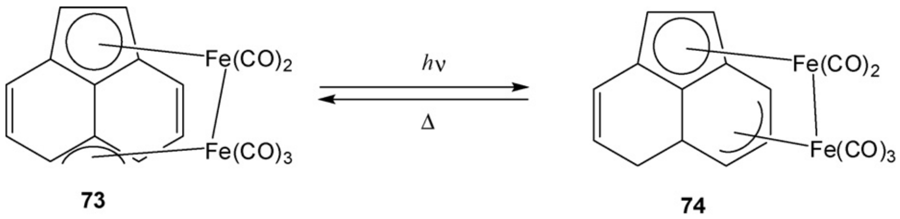
Another example of a switchable haptotropic rearrangement was recently reported for the binuclear diiron complexes **73** and **74** (as well as for their aceantylene analogs) [141]. Thermal reaction converts **74**–**73**, whereas the photochemical transformation is capable of recovering **74** (Scheme 29). Interestingly, the same rearrangements were detected in a solid state by



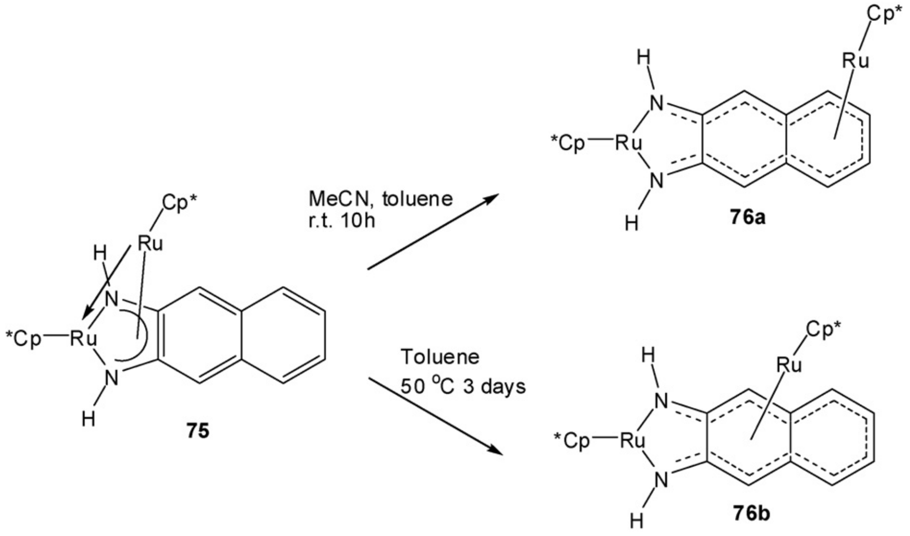
Scheme 27. Degenerate haptotropic rearrangement in **68** (Pn = η^3-2,6,10-tri-*tert*-butylphenalenyl).



Scheme 28. Switchable haptotropic rearrangements for the heterocyclic biphenyls **69**–**72**.



Scheme 29. Switchable interconversion of a diiron complex.



Scheme 30. Two different haptotropic rearrangements in complex **73**.

monitoring the process with IR in KBr pellet. The cycle is repeatable for over 10 times without the change in signal intensity [141].

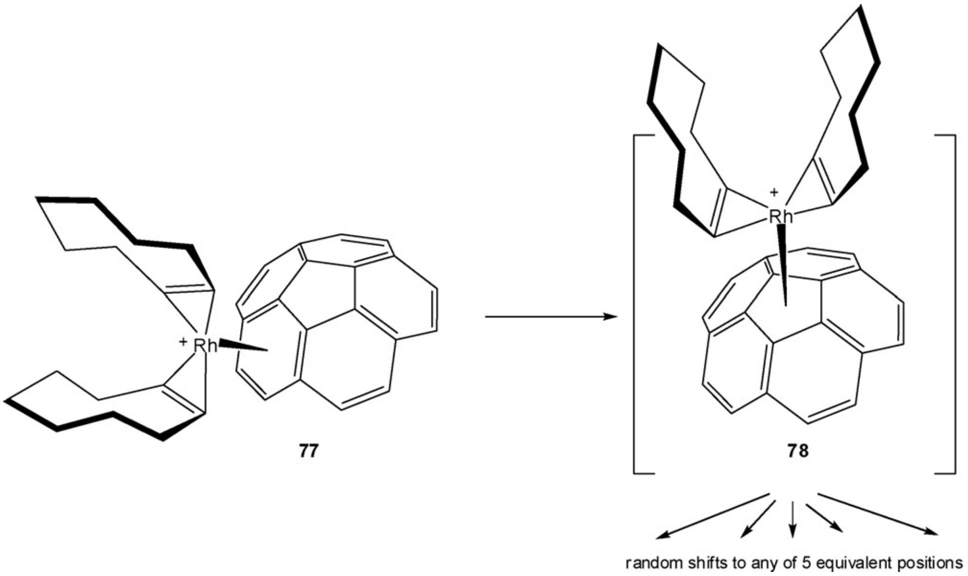
An interesting example of a solvent-assisted haptotropic rearrangement was recently reported for the amino-bridged diruthenium complex **75** [142]. Heating compound **75** in acetonitrile yields the rearrangement product **76a**, whereas isomerization in toluene affords another product **76b** (Scheme 30). Since **76a** and **76b** did not interconvert on prolonged heating, it was assumed that the isomerization in acetonitrile proceeds through the solvent-assisted intermediates [142].

The first example of a haptotropic rearrangement in corannulene was recently reported for the cationic bis-cyclooctene-η^6-corannulene complex of Rh **77** [143]. The 2D EXSY NMR experiments implicate the "hub" mechanism of fast migrations, in which the organometallic moiety migrates by walking over the central five-membered ring via the η^5-coordinated intermediate **78** rather than moving from one arene ring to the next (Scheme 31). One of the cyclooctene ligands can be easily replaced by PPr^i_3; the haptotropic rearrangement in the resulting complex is faster than in **77**. On the other hand, the iridium analog of **77** is not fluxional, presumably due to the shorter and stronger Ir–C bonds [143].

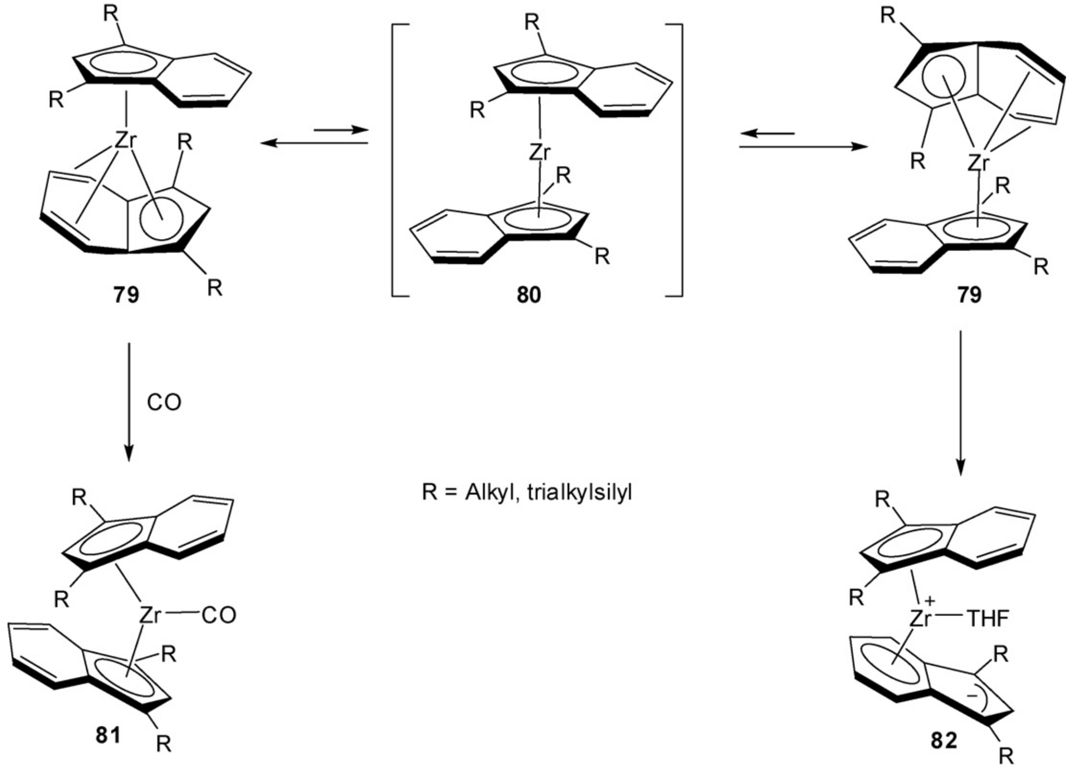
3.2.3. Mixed cases

There are examples of haptotropic migrations that are difficult to classify as intra- or inter-ring rearrangements.

First example is the famous case of beryllocene and its derivatives that are highly fluxional in solution presumably due to two independent processes: [1,5]-sigmatropic shifts of the Be(η^5-C_5H_5) unit around the periphery of the η^1-C_5H_5 ring and molecular inversion that interchanges the η^5- and η^1-rings [144]. However, to date these conclusions are based on X-ray structures of known berryllocenes and cannot be



Scheme 31. Haptotropic migrations in corannulene Rh complex **77**.



Scheme 32. Haptotropic rearrangements in bis(indenyl)zirconium complexes.

supported by direct NMR observation of the solution dynamics, since the rearrangements are invariably too fast. Recently, $Be(C_5Me_5)_2$, $Be(C_5Me_4H)_2$, and $Be(C_5Me_5)(C_5Me_4H)$ were prepared with hope that the rates of the rearrangements in these compounds would be lower, however this was not the case [145].

Similar in some respect is the degenerate rearrangement of bis(indenyl)zirconium sandwich complexes discovered recently by Chirik et al. [146–148]. In these compounds, one indenyl ligand is η^5-coordinated, whereas the second one acquires unusual η^9-coordination (Scheme 32). Thorough kinetic [147] and theoretical [147,149,150] studies suggest that the degenerate rearrangement occurs through the η^5,η^5-intermediate **78**. The coordination mode in compounds **77** can be shifted to the more normal η^5,η^5-hapticity by reacting them with CO, olefins or alkynes (*e.g.* **79**), whereas η^6,η^5-complexes can be obtained by additionally ligating Zr with a donating solvent or diphosphine ligand (*e.g.* **80**) [146–148].

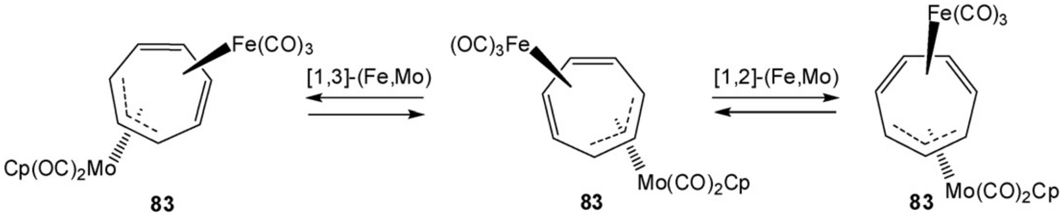
4. Dyotropic (diatropic, tandem) rearrangements of organometallic compounds

The term "dyotropic rearrangement" (from Greek word δυο—two) was introduced in 1972 by Reetz to describe the reactions with simultaneous (or apparently simultaneous) breaking and reformation of two σ-bonds [151,152]. It was later applied by the same author [153] and others [154] to describe the rearrangements of acetoxymethylsilanes to the corresponding silyl acetals. However, in recent years this term has not been frequently used, and is mainly applied in synthetic organic chemistry [155–157]. In organometallic chemistry similar phenomena are described as a "tandem metal shift" or "diatropic rearrangement" [120] (probably misspelled "dyotropic"). The reason for that confusion is probably the strict initial definition of Reetz who clearly stated that only breaking and reformation of two σ-bonds is qualified as "dyotropic rearrangement". The author of the present review feels that it could be expedient to extend this term for the rearrangements where the breaking and forming bonds are σ-,π- or π-,π-bonds. This would describe a class of organometallic rearrangements involving sophisticated simultaneous movement of several atoms.

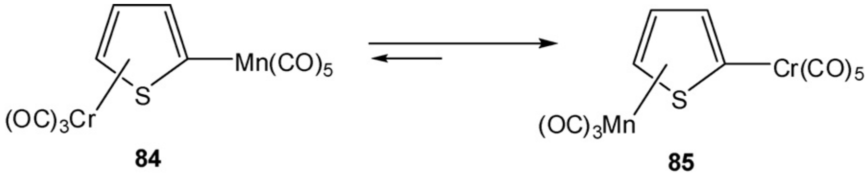
In 1969, Cotton and Reich reported the synthesis of complex **83** that was highly fluxional in solution (E_A 55 kJ/mol). Lineshape analysis allowed them to exclude all rearrangement pathways except [1,2]-shifts (probably with admixture of [1,3]-shifts) *of both metals simultaneously* [158]. Hence, this rearrangement (Scheme 33) can be qualified as π-,π-dyotropic rearrangement.

Apparently, the same type of rearrangement takes place in numerous known fluxional bi- and trimetallic derivatives of cycloheptatriene with a metal–metal bond [159–170]. Unfortunately, the topology of the rearrangements observed in these compounds has rarely been probed, and the regulations governing the selectivity and kinetics of these rearrangements are unknown so far.

An interesting example of a σ-,π-dyotropic rearrangement was reported in 1993 by Lotz et al. When crystals of complex **84** were dissolved in polar solvents such as acetone or THF, this compound spontaneously underwent a metal exchange process to afford the thermodynamically favored compound **85** without



Scheme 33. π-,π-Dyotropic rearrangement in complex **83**.



Scheme 34. Equilibrium between complexes **84** and **85**.

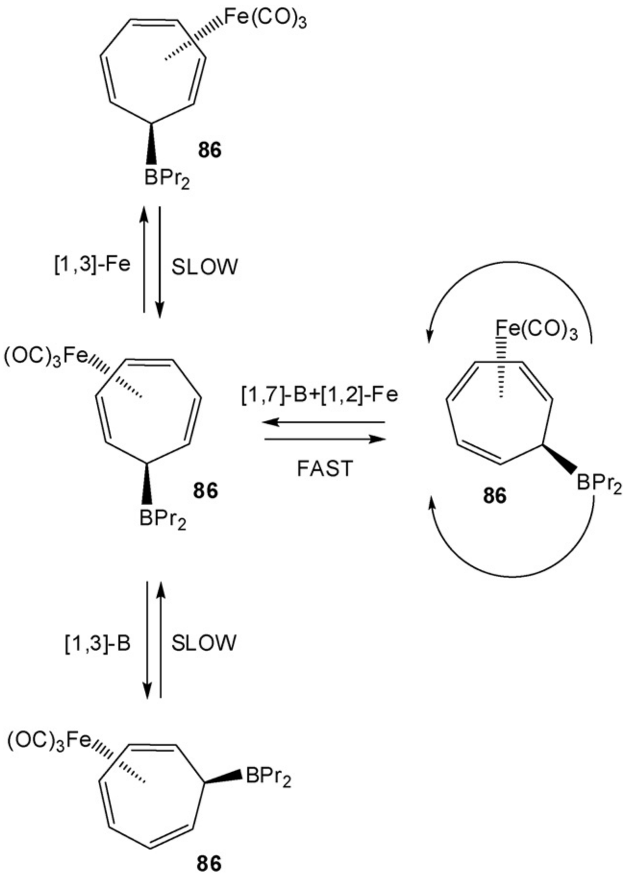
formation of any side products (Scheme 34) [171]. Equilibrium concentration in deuterioacetone (>85% of **85**) is achieved after 24 h at 30 °C. Note, however, that besides migration of two metals, two CO ligands must change their positions; hence, a stepwise process cannot be excluded.

A clear example of σ-,π-dyotropic rearrangement is [1,7]-B + [1,2]-Fe rearrangement in the irontricarbonyl complex of cycloheptatrienyl(dipropyl)borane **86** [172]. The lack of symmetry in the molecule of **86** makes possible to distinguish experimentally between 13 possible pathways of degenerate rearrangement in this compound. Three rearrangements were identified by 2D NMR EXSY experiments: a [1,3]-B shift, a [1,3]-Fe shift and a [1,7]-B + [1,2]-Fe rearrangement (Scheme 35). The dyotropic rearrangement is approximately 10 times faster than either of the simple sigmatropic and haptotropic shifts. Moreover, the rate of the dyotropic rearrangement in **86** is significantly higher than the [1,7]-B shift in cycloheptatrienyl(dipropyl)borane itself (see Table 2, compound **27**). Formally analyzing the movement of dipropylboryl and irontricarbonyl groups required for the accomplishment of the [1,7]-B + [1,2]-Fe shift, one can see that the two organometallic groups are moving towards each other around the cycloheptatrienyl cycle. Another [1,7]-B + [1,2]-Fe rearrangement possible for the system is not observed in **86** clearly indicating the presence of orbital control in dyotropic rearrangements.

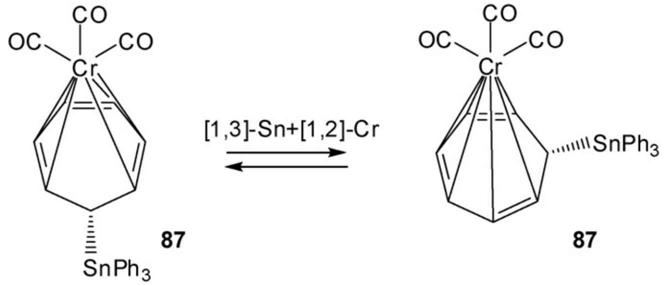
Migrations of boryl and stannyl groups follow alternative selection rules for sigmatropic migrations (see Section 2.2.2). Similarly, selection rules for dyotropic rearrangements with participation of these groups are different. Thus, in tin analogs of compound **86**, iron and ruthenium complexes **57** and **59** (see Scheme 23), simple [1,3]-M shift is the fastest observed rearrangement [120]. Slower dyotropic rearrangements were detected in both **57** and **59**. It was not possible to determine their exact nature, but it could be deduced from 2D EXSY NMR data that there is no selectivity in the direction of dyotropic rearrangements—triphenyltin group moved with equal probability in both possible directions [120].

In contrast to the η^1,η^4-complexes **57**, **59**, and **86** in which the presence of two organometallic groups accelerated intramolecular rearrangements, the facile [1,5]-Sn shift observed in triphenyl(cycloheptatrienyl)tin **26a** is completely stopped in η^6-coordinated complex **87**. Nevertheless, it was possible to detect a slow dyotropic rearrangement, *viz.* [1,3]-Sn + [1,2]-Cr shift (Scheme 36) [173].

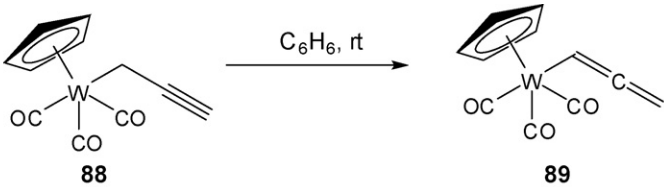
Rearrangement of propargylic tungsten complexes, *e.g.* **88** to allenyl complex **89** (Scheme 37) was interpreted as sigmatropic tungsten shift accompanied by [1,3]-H shift, in other words it



Scheme 35. Three independent fluxional processes in compound **86**.



Scheme 36. Dyotropic rearrangement in heterobimetallic complex **87**.



Scheme 37. Dyotropic rearrangement in propargylic tungsten complex **88**.

can be classified as a σ-,σ-[1,3]-(W, H) dyotropic migration [174,175].

Another example of a σ-,σ-dyotropic organometallic rearrangement is the palladium migration in polyaryl systems associated with the concominant shift of a hydrogen atom that has been found experimentally to be a pivotal step of several organic transformations mediated by palladium complexes [176].

5. Conclusions

The development of experimental and computational techniques has made possible detailed investigation of such sophisticated intramolecular processes as sigma- and haptotropic rearrangements in organometallic compounds. Although the fastest metallotropic migrations are comparable in their rates with conformational equilibria, unlike the latter they are strictly regulated electronically. The mode and rate of rearrangement can be finely tuned by appropriate choice of the organometallic group and the hydrocarbon (or heterocyclic skeleton). Hence, further research in this sophisticated but fruitful area can be expected to yield better knowledge of the regularities of chemical transformations, as well as contribute to the intelligent design of versatile molecular and supramolecular systems.

Acknowledgment

This work was financially supported by the Global COE Program of Tokyo Institute of Technology.

References

[1] G. Wilkinson, T.S. Piper, J. Inorg. Nucl. Chem. 2 (1956) 32.
[2] T.S. Piper, G. Wilkinson, J. Inorg. Nucl. Chem. 3 (1956) 104.
[3] M.J. Bennett Jr., F.A. Cotton, A. Davison, J.W. Faller, S.J. Lippard, S.M. Morehouse, J. Am. Chem. Soc. 88 (1966) 4371.
[4] K.H. Dotz, B. Wenzel, H.C. Jahr, Templ. Chem. I 248 (2004) 63.
[5] K.H. Dotz, H.C. Jahr, Chem. Rec. 4 (2004) 61.
[6] V.I. Minkin, I.E. Mikhailov, G.A. Dushenko, A. Zhunke, Russ. Chem. Rev. 72 (2003) 867.
[7] Y.F. Oprunenko, Russ. Chem. Rev. 69 (2000) 683.
[8] P. Jutzi, G. Reumann, J. Chem. Soc. Dalton Trans. (2000) 2237.
[9] P. Jutzi, Chem. Rev. 86 (1986) 983.
[10] C.W. Spangler, Chem. Rev. 76 (1976) 187.
[11] F.A. Cotton, Acc. Chem. Res. 1 (1968) 257.
[12] I.D. Gridnev, O.L. Tok, in: M. Gielen, R. Willem, B. Wrackmeyer (Eds.), Fluxional Organometallic and Coordination Compounds, Wiley, 2004, p. 41.
[13] H. Lehmkuhl, D. Reiner, J. Organomet. Chem. 33 (1970) C25.
[14] K.H. Thiele, J. Kohler, J. Organomet. Chem. 7 (1967) 365.
[15] K.H. Thiele, K. Zdumek, J. Organomet. Chem. 4 (1965) 10.
[16] E.G. Hoffmann, H. Nehl, H. Lemkuhl, K. Seevogel, W. Stempfle, Chem. Ber. 117 (1984) 1363.
[17] H.E. Ziegler, J.D. Roberts, J. Org. Chem. 34 (1969) 2826.
[18] P.D. Sleezer, S. Winstein, W.G. Young, J. Am. Chem. Soc. 94 (1972) 2515.
[19] D.J. Blears, S.S. Danyluk, S. Cawely, J. Organomet. Chem. 6 (1964) 284.
[20] M.J. Hails, B.E. Mann, C.M. Spencer, J. Chem. Soc., Dalton Trans. (1983) 729.
[21] Y. Naruta, Y. Nishigaichi, K. Maruyama, Tetrahedron 45 (1985) 1067.
[22] G. Wilke, B. Bogdanovic, P. Hardt, P. Heinbach, W. Keim, M. Kroener, W. Oberkirch, K. Tanaka, E. Stenrueke, D. Walter, H. Zimmermann, Angew. Chem. Int. Ed. Eng. 5 (1966).
[23] A. Hill, W.A. Boyd, H. Drsai, A. Darki, J. Organomet. Chem. 514 (1996) 1.
[24] H. Kwart, T. Slutsky, J. Am. Chem. Soc. 94 (1972) 2515.
[25] M. Takahashi, M. Kira, J. Am. Chem. Soc. 119 (1997) 1948.
[26] M. Kobayashi, M. Kobayashi, Chem. Lett. (1986) 385.
[27] B.M. Mikhailov, V.S. Bogdanov, G.V. Lagodzinskaya, V.F. Pozdnev, Russ. Chem. Bull. (1966) 386.
[28] V.S. Bogdanov, G.V. Lagodzinskaya, V.F. Pozdnev, B.M. Mikhailov, Russ. Chem. Bull. (1966) 944.
[29] B.M. Mikhailov, V.I. Smirnov, O.D. Smirnova, V.S. Bogdanov, Russ. Chem. Bull. (1975) 51.
[30] Y.N. Bubnov, M.E. Gurskii, I.D. Gridnev, A.V. Ignatenko, Y.A. Ustynyuk, V.I. Mstislavskii, J. Organomet. Chem. 424 (1992) 127.
[31] B.M. Mikhailov, Y.N. Bubnov, A.V. Tsyban, J. Organomet. Chem., 154 (1978) 113.
[32] G.W. Kramer, H.C. Brown, J. Organomet. Chem. 132 (1977) 9.
[33] V.S. Bogdanov, V.F. Pozdnev, Y.N. Bubnov, B.M. Mikhailov, Dokl. AN SSSR 193 (1970) 586.
[34] I.D. Gridnev, M.E. Gurskii, Y.N. Bubnov, in: G. Kabalka (Ed.), Current Topics in the Chemistry of Boron, R. Soc. Chem., Cambridge, 1994, p. 56.
[35] H. Jiao, P.v.R. Schleyer, Angew. Chem. 105 (1993) 1833.
[36] M.E. Gurskii, I.D. Gridnev, A.V. Geiderikh, A.V. Ignatenko, Y.N. Bubnov, V.I. Mstislavsky, Y.A. Ustynyuk, Organometallics 11 (1992) 4056.
[37] I.D. Gridnev, M.E. Gurskii, A.V. Ignatenko, Y.N. Bubnov, Yu.V. Il'ichev, Organometallics 12 (1993) 2487.
[38] M.E. Gurskii, I.D. Gridnev, Yu.V. Il'ichev, A.V. Ignatenko, Y.N. Bubnov, Angew. Chem., Int. Ed. Engl. 31 (1992) 781.
[39] H. Yasuda, A. Nakamura, J. Organomet. Chem. 285 (1985) 15.
[40] R.D. Ernst, Acc. Chem. Res. 18 (1985) 56.
[41] H. Yasuda, Y. Ohnuma, M. Yamauchi, H. Tani, A. Nakamura, Bull. Chem. Soc. Jpn. 52 (1979) 2036.
[42] H. Yasuda, M. Yamauchi, A. Nakamura, J. Organomet. Chem. 202 (1980) C1.
[43] H. Yasuda, M. Yamauchi, Y. Ohnuma, A. Nakamura, Bull. Chem. Soc. Jpn. 54 (1981) 1481.
[44] W. Oppolzer, S.C. Burford, F. Marazza, Helv. Chim. Acta 63 (1980) 555.
[45] D. Seyferth, K.R. Wursthorn, R.E. Mammarella, J. Org. Chem. 42 (1977) 3104.
[46] D. Seyferth, R.E. Mammarella, J. Organomet. Chem. 156 (1978) 299.
[47] R.B. Bates, S. Brenner, C.M. Cole, E.W. Davidson, G.D. Forsythe, D.A. McCombs, A.S. Roth, J. Am. Chem. Soc. 95 (1973) 926.

[48] M. Schlosser, G. Rauchschwalbe, J. Am. Chem. Soc. 100 (1978) 3258.
[49] H. Basshardt, M. Schlosser, Helv. Chim. Acta 63 (1980) 2393.
[50] H. Yasuda, M. Yamauchi, A. Nakamura, T. Sei, N. Kai, N. Yasuoka, N. Kasai, Bull. Chem. Soc. Jpn. 53 (1980) 1089.
[51] H. Yasuda, Y. Ohnuma, A. Nakamura, N. Kai, N. Yasuoka, N. Kasai, Bull. Chem. Soc. Jpn. 53 (1980).
[52] Y. Naruta, Y. Nishigaichi, K. Maruyama, J. Org. Chem. 56 (1991) 2011.
[53] Y. Naruta, Y. Nishigaichi, K. Maruyama, Tetrahedron 45 (1989) 1067.
[54] P. Jutzi, Pure Appl. Chem. 75 (2003) 483.
[55] P. Jutzi, N. Burford, Chem. Rev. 99 (1999) 969.
[56] F.A. Cotton, A. Musco, G. Yagupsky, J. Am. Chem. Soc. 89 (1967) 6136.
[57] M. Stradiotto, D.W. Hughes, A.D. Bain, M.A. Brook, M.J. McGlinchey, Organometallics 16 (1997) 5563.
[58] R.B. Larrabee, B.F. Dowden, Tetrahedron Lett. (1970) 915.
[59] A. Davidson, P.E. Rakita, J. Organomet. Chem. 23 (1970) 407.
[60] A. Davidson, P.E. Rakita, J. Organomet. Chem. 21 (1970) P55.
[61] P.e. Rakita, A. Davidson, Inorg. Chem. 8 (1969) 1164.
[62] A.J. Ashe III, Tetrahedron Lett. (1970) 2105.
[63] Y.-X. Chen, J.C. Raush, C.W. Chien, Organometallics 12 (1993) 4607.
[64] B.M. Mikhailov, T.K. Baryshnikova, V.S. Bogdanov, Zh. Obshch. Khim. 43 (1973) 1949.
[65] N.M. Sergeyev, Y.K. Grishin, Y.N. Luzikov, Y.A. Ustynyuk, J. Organomet. Chem. 38 (1972) C1.
[66] S.S. Rigby, H.K. Gupta, N.H. Werstiuk, A.D. Bain, M.J. McGlinchey, Polyhedron 14 (1995) 2787.
[67] F.A. Cotton, in: L.M. Jackman, F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resonance Spectroscopy, Academic, New York, 1975, p. 378.
[68] A.G. Anastassien, E. Reichmanis, A.E. Winston, Angew. Chem. 88 (1976) 382.
[69] C.H. Campbell, M.L.H. Green, J. Chem. Soc. A (1970) 1318.
[70] D.J. Ciapenelli, F.A. Cotton, L. Kruczynski, J. Organomet. Chem. 42 (1972) 159.
[71] P. West, M.C. Woodville, M.D. Raush, J. Am. Chem. Soc. 91 (1969) 5649.
[72] Y.N. Luzikov, N.M. Sergeyev, Y.A. Ustynyuk, J. Organomet. Chem. 65 (1974) 303.
[73] W. Kitching, B.F. Hegarty, D. Doddrell, J. Organomet. Chem. 21 (1970) 29.
[74] F.A. Cotton, D.L. Hunter, J.D. Jamerson, Inorg. Chim. Acta 15 (1975).
[75] C.P. Casey, J.M. O'Connor, Organometallics 4 (1985) 384.
[76] J.L. Atwood, A.D. McMaster, R.D. Rogers, S.R. Stobart, Organometallics 3 (1984) 1500.
[77] W.A. Herrmann, F.E. Kuhn, C.C. Romao, J. Organomet. Chem. 489 (1995) C56.
[78] S.S. Rigby, L. Girard, A.D. Bain, M.J. McGlinchey, Organometallics 14 (1995) 3798.
[79] R.J. Morris, P.L. Bock, J.M. Jefferis, D.M. Goedde, Polyhedron 16 (1997) 3699.
[80] I.D. Gridnev, A. Meller, Main Group Metal Chem. 21 (1998) 271.
[81] A.D. McMaster, S.R. Stobart, J. Am. Chem. Soc. 104 (1982) 2109.
[82] M. Stradiotto, S.S. Rigby, D.W. Hughes, M.A. Brook, A.D. Bain, M.J. McGlinchey, Organometallics 15 (1996) 5645.
[83] R.B. Larrabee, J. Am. Chem. Soc. 93 (1971) 1510.
[84] M.D. Curtis, R. Fink, J. Organomet. Chem. 38 (1972) 299.
[85] B.E. Mann, B.F. Taylor, N.A. Taylor, R. Woor, J. Organomet. Chem. 162 (1978) 137.
[86] I.D. Gridnev, O.L. Tok, N.A. Gridneva, Y.N. Bubnov, P.R. Schreiner, J. Am. Chem. Soc. 120 (1998) 1034.
[87] I.D. Gridnev, P.R. Schreiner, O.L. Tok, Y.N. Bubnov, Chem. Eur. J. 5 (1999) 2828.
[88] M.E. Gurskii, I.D. Gridnev, A.V. Buevich, Y.N. Bubnov, Organometallics 13 (1994) 4658.
[89] I.D. Gridnev, P.R. Schreiner, M.E. Gurskii, Y.N. Bubnov, A.O. Krasavin, V.I. Mstislavskii, Chem. Commun. (1998) 2507.
[90] I.D. Gridnev, M.E. Gurskii, A.V. Buevich, T.V. Potapova, Y.N. Bubnov, J. Org. Chem. 61 (1996) 3514.
[91] D.M. Heinekey, W.A.G. Graham, J. Am. Chem. Soc. 101 (1979) 6115.
[92] D.M. Heinekey, W.A.G. Graham, J. Am. Chem. Soc. 104 (1982) 915.
[93] Y.N. Bubnov, M.E. Gurskii, A.V. Ignatenko, Russ. Chem. Bull. 37 (1988) 1963.
[94] Y.N. Bubnov, L.I. Lavrinovich, Tetrahedron Lett. (1985) 4551.
[95] I.D. Gridnev, M.E. Gursky, Y.N. Bubnov, Organometallics 15 (1996) 3696.
[96] I.D. Gridnev, M.E. Gurskii, A.V. Geiderikh, Y.N. Bubnov, Mendel. Commun. (1996) 176.
[97] M.G. Hutchings, W.E. Paget, K. Smith, J. Chem. Res., Synop. (1983) 31.
[98] I.D. Gridnev, M.E. Gurskii, A.O. Krasavin, Y.N. Bubnov, Russ. Chem. Bull. 45 (1996) 2127.
[99] I.D. Gridnev, A. Meller, J. Org. Chem. 63 (1998) 3599.
[100] G.E. Herberich, H.W. Marx, S. Moss, P.v.R. Schleyer, T. Wagner, Chem. Eur. J. 2 (1996) 458.
[101] M.E. Gurskii, I.D. Gridnev, A.V. Buevich, T.V. Potapova, A.O. Krasavin, V.I. Mstislavskii, Y.N. Bubnov, Mendel. Commun. (1994) 223.
[102] O.L. Tok, I.D. Gridnev, E.M. Korobach, Y.N. Bubnov, Chem. Commun. (2000) 311.
[103] R. Ben-Shoshan, R. Pettit, J. Am. Chem. Soc. 89 (1967) 2231.
[104] K. Vrieze, H.C. Volger, M. Gronert, A.P. praat, J. Organomet. Chem. 16 (1969) 19.
[105] K. Vrieze, H.C. Volger, A.P. Praat, J. Organomet. Chem. 21 (1970) 467.
[106] B. Foxman, D. MArten, A. Rosan, S. Raghu, M. Rosenblum, J. Am. Chem. Soc. 99 (1977) 2160.
[107] H.W.J. Whitlock, Y.N. Chuah, J. Am. Chem. Soc. 87 (1965) 3605.
[108] H.W.J. Whitlock, C. Reich, W.D. Woessner, J. Am. Chem. Soc. 93 (1971) 2483.
[109] A. Padwa, D.J. Austin, Y. Gareau, J.M. Kassir, S.L. Xu, J. Am. Chem. Soc. 115 (1993) 2637.
[110] T. Takeda, M. Ozaki, S. Kuroi, A. Tsubouchi, J. Org. Chem. 70 (2005) 4233.
[111] J. Barluenga, R.B. de la Rúa, D. de Sáa, A. Ballesteros, M. Tomás, Angew. Chem., Int. Ed. 44 (2005) 4981.
[112] K. Ohe, M. Fujita, H. Matsumoto, Y. Tai, K. Miki, J. Am. Chem. Soc. 128 (2006) 9270.
[113] C.P. Casey, S. Kraft, M. Kavana, Organometallics 20 (2001) 3795.
[114] Y. Ortin, Y. Coppel, N. Lugan, R. Mathieu, M.J. McGlinchey, Chem. Commun. (2001) 1690.
[115] C.P. Casey, S. Kraft, D. Powell, J. Am. Chem. Soc. 124 (2001) 2584.
[116] I.D. Gridnev, N.U. Zhanpeisov, M.K.C. del Rosario, J. Phys. Chem. B 109 (2005) 12498.
[117] J.A. Gibson, B.E. Mann, J. Chem. Soc., Dalton Trans. (1979) 1021.
[118] K.J. Karel, T.A. Albright, M. Brookhart, Organometallics 1 (1982) 419.
[119] L.K.K. LiShinMan, J.G.A. Reuvers, J. Takats, G. Deganello, Organometallics 2 (1983) 28.
[120] I.D. Gridnev, M.K.C. del Rosario, Organometallics 24 (2005) 4519.
[121] R. Benn, K. Cibura, P. Hofman, K. Jonas, A. Rufinska, Organometallics 4 (1985) 2214.
[122] B.E. Mann, Chem. Soc. Rev. 15 (1986) 167.
[123] D.R. Muhandiram, G.Y. Kiel, G.H.M. Aarts, I.M. Saez, J.G.A. Reuvers, D.M. Heinekey, W.A.G. Graham, J. Takats, R.E.D. McClung, Organometallics 21 (2002) 2687.
[124] H.C. Jahr, M. Nieger, K.H. Dotz, Chem. Eur. J. 11 (2005) 5333.
[125] R. Benn, R. Mynott, I. Topalovic, F. Scott, Organometallics 8 (1989) 2299.
[126] A. Stanger, Organometallics 10 (1991) 2979.
[127] Y.A. Ustynyuk, O.I. Trifonova, Y.F. Oprunenko, V.I. Mstislavskiy, I.P. Gloriozov, N.A. Ustynyuk, Organometallics 9 (1990) 1707.
[128] M.E. Rerek, F. Basolo, Organometallics 3 (1984) 647.
[129] A. Decken, S.S. Rigby, L. Girard, A.D. Bain, M.J. McGlinchey, Organometallics 16 (1997) 1308.
[130] A. Decken, J.F. Britten, M.J. McGlinchey, J. Am. Chem. Soc. 115 (1993) 7275.
[131] N.A. Ustynyuk, N.A. Pomazanova, L.N. Novikova, D.N. Kravtsov, Y.A. Ustynyuk, Izv. Akad. Nauk SSSP, Ser. Khim. (1986) 1688.
[132] N. Nakasuji, M. Yamaguchi, I. Murata, J. Am. Chem. Soc. 108 (1986) 325.
[133] R.H. Crabtree, C.P. Parnell, Organometallics 3 (1984) 1727.

[134] I.P. Gloriozov, A.Y. Vasil'kov, Y.F. Oprunenko, Y.A. Ustynyuk, Russ. J. Phys. Chem. 78 (2004) 244.

[135] K.H. Dotz, J. Stendel, S. Muller, M. Nieger, S. Ketrat, M. Dolg, Organometallics 24 (2005) 3219.

[136] S. Ketrat, S. Müller, M. Dolg, J. Phys. Chem. A 111 (2007) 6094.

[137] F. Nunzi, F. Mercuri, F. De Angelis, A. Sgamellotti, N. Re, P. Giannozzi, J. Phys. Chem. B 108 (2004) 5243.

[138] D.J. Berg, J.L. Sun, B. Twamley, Chem. Commun. (2006) 4019.

[139] J. Pan, J.W. Kampf, A.J. Ashe, Organometallics 25 (2006) 197.

[140] J. Pan, J. Wang, M.M.B. Holl, J.W. Kampf, A.J. Ashe, Organometallics 25 (2006) 3463.

[141] S. Niibayashi, K. Matsubara, M. Haga, H. Nagashima, Organometallics 23 (2004) 635.

[142] S. Takemoto, S. Oshio, T. Shiromoto, H. Matsuzaka, Organometallics 24 (2005) 801.

[143] J.S. Siegel, K.K. Baldridge, A. Linden, R. Dorta, J. Am. Chem. Soc. 128 (2006) 10644.

[144] K.E. Nugent, J.K. Beatti, L.D. Field, J. Phys. Chem. 93 (1989).

[145] M.D. Conejo, R. Fernandez, E. Carmona, R.A. Andersen, E. Gutierrez-Puebla, M.A. Monge, Chem. Eur. J. 9 (2003) 4462.

[146] C.A. Bradley, E. Lobkovsky, P.J. Chirik, J. Am. Chem. Soc. 125 (2003) 8110.

[147] C.A. Bradley, I. Keresztes, E. Lobkovsky, V.G. Young, P.J. Chirik, J. Am. Chem. Soc. 126 (2004) 16937.

[148] C.A. Bradley, E. Lobkovsky, I. Keresztes, P.J. Chirik, J. Am. Chem. Soc. 127 (2005) 10291.

[149] L.F. Veiros, Organometallics 25 (2006) 2266.

[150] L.F. Veiros, Organometallics 25 (2006) 4698.

[151] M.T. Reetz, Angew. Chem., Int. Ed. 11 (1972) 129.

[152] M.T. Reetz, Angew. Chem., Int. Ed. 11 (1972) 130.

[153] M.T. Reetz, Adv. Organomet. Chem. 16 (1977) 33.

[154] J. Fässler, S. Bienz, Organometallics 13 (1994) 4704.

[155] S.E. Denmark, J.I. Montgomery, Angew. Chem., Int. Ed. 44 (2005) 3732.

[156] R. Fernández, M.A. Sierra, F.P. Cossío, Chem. Eur. J. 12 (2006) 6323.

[157] E. de Lemos, F.-H. Porée, A. Commercon, J.-F. Betzer, A. Pancrazi, J. Ardisson, Angew. Chem., Int. Ed. 46 (2007) 1917.

[158] F.A. Cotton, C. Reich, J. Am. Chem. Soc. 91 (1969) 847.

[159] M.J. Bennett, J.L. Pratt, K.A. Simpson, L.K.K. LiShingMan, J. Takats, J. Am. Chem. Soc. 98 (1976) 4810.

[160] A. Salzer, T. Egolf, W. von Philipsborn, Helv. Chim. Acta 65 (1982) 1145.

[161] R.G. Ball, F. Edelmann, G.-Y. Kiel, J. Takats, R. Drews, Organometallics 5 (1986) 829.

[162] F. Edelmann, J. Takats, J. Organomet. Chem. 344 (1988) 351.

[163] S.T. Astley, J. Takats, J. Organomet. Chem. 363 (1989) 167.

[164] W. Fu, R. McDonald, J. Takats, A.H. Bond, R.D. Rogers, Inorg. Chim. Acta 229 (1995) 307.

[165] M. Airoldi, T. Beringhelli, G. Deganello, G. Gennaro, M. Moret, F. Saiano, A. Sironi, Inorg. Chim. Acta 229 (1995) 461.

[166] M. Airoldi, G. Deganello, G. Gennaro, M. Moret, A. Sironi, J. Chem. Soc., Chem. Commun. (1992) 850.

[167] M. Airoldi, G. Deganello, G. Gennaro, M. Moret, A. Sironi, Organometallics 12 (1993) 3964.

[168] H. Wadepohl, W. Galm, H. Pritzkow, Angew. Chem., Int. Ed. 29 (1990) 686.

[169] H. Wadepohl, W. Galm, A.J. Wolf, J. Organomet. Chem. 452 (1993) 193.

[170] H. Wadepohl, W. Galm, H. Pritzkow, Organometallics 15 (1996) 570.

[171] T.A. Waldbach, P.H. van Rooyen, S. Lotz, Angew. Chem., Int. Ed. 32 (1993) 710.

[172] I.D. Gridnev, O.L. Tok, M.E. Gurskii, Y.N. Bubnov, Chem. Eur. J. 2 (1996) 1483.

[173] I.D. Gridnev, O.L. Tok, J. Am. Chem. Soc. 125 (2003) 14700.

[174] R.-S. Keng, Y.-C. Lin, Organometallics 9 (1990) 289.

[175] K.-W. Liang, G.-H. Lee, S.-M. Peng, R.-S. Liu, Organometallics 14 (1995) 2353.

[176] A.J. Mota, A. Dedieu, Organometallics 25 (2006) 3130.