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Mechanisms of reactions of organoaluminium compounds with alkenes and alkynes catalyzed by Zr complexes

L V Parfenova, L M Khalilov, U M Dzhemilev

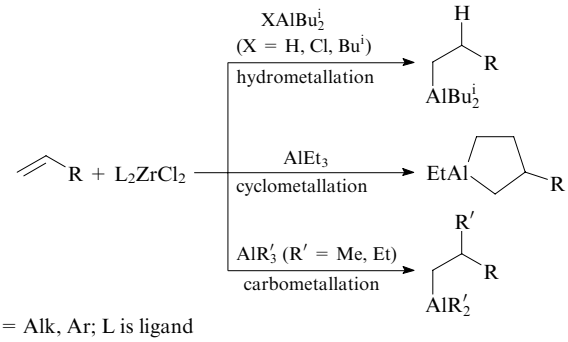
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Abstract. The results of studies dealing with mechanisms of hydro-, carbo- and cycloalumination of alkenes and alkynes catalyzed by zirconium complexes are generalized and systematized for the first time. Data about the structures of intermediates responsible for the formation of the target compounds are presented and the available data on the effect of the structure of organoaluminium compounds and the electronic and steric factors determining the catalytic activity of metal complexes in these reactions are considered in detail. Much attention is paid to studies of the influence of reaction conditions on the chemo-, regio- and stereoselectivity of the Zr-containing complex catalysts. The bibliography includes 217 references.

I. Introduction

The use of transition metal complexes in the organoaluminium chemistry led to the development of new chemo-, regio- and stetreoselective methods for the formation of carbon – hydrogen, carbon – carbon and metal – carbon bonds *via* the formation of organometallic compounds of new classes. Among transition metal complexes, Ti and Zr compounds have found wide use in laboratory practice and in industry due to their relatively low cost and broad range of reactions performed with compounds of these metals, which is not the case for many known and described metal complex catalysts. The best known reactions that proceed in bimetallic systems based on organoaluminium compounds (OAC) and Ti or Zr complexes are the Ziegler – Natta polymerization, di- and oligomerization and reactions giving low-molecular-mass products, *viz*., hydro-, carbo- and cyclometallation of unsaturated compounds.[1 – 18]



R = Alk, Ar; L is ligand

For the development of new catalysts and prediction of their properties, design of catalytic systems with allowance for electronic and steric features of the reactants and the nature of the solvent and temperature and the development of efficient methods for control of the reactions, it is necessary to know the detailed mechanisms of these transformations. The modern experimental and theoretical methods for investigation of reaction mechanisms are able to answer these questions to a larger or smaller extent. Among the experimental methods used to study homogeneous catalytic reactions involving metal complexes, special mention should be made of dynamic NMR spectroscopy as the most informative method, which allows direct monitoring of the reactions. The greatest progress along this line was achieved in the studies of catalytic systems consisting of OAC and zirconium π-complexes. This is due to several reasons. First, a broad range of reactions can be accomplished using these systems, starting from hydro-, carbo- and cyclometallation and ending with polymerization of unsaturated compounds. Second, these systems are convenient for investigations, as π-ligands bonded to zirconium function as a sort of magnetic probes reflecting the electronic state of the transition metal atom. In addition, the reaction times also proved convenient for observation, as well as the absence of paramagnetic species, which, for

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example, in the case of titanium complexes, preclude the monitoring of the genesis of intermediate complexes of 'living' catalytic systems due to pronounced signal broadening in the NMR spectra.

Experimental investigations of the reactions of OAC with alkenes catalyzed by Zr complexes are extensively performed by known research groups.[1–20] The reviews on this subject published previously focus primarily on the synthetic potential of Zr–Al bimetallic catalytic systems, but do not give critical analysis of the mechanisms of formation and action of the catalytically active sites in these reactions. The views on the mechanisms of hydro-, carbo- and cyclometallation of alkenes and alkynes catalyzed by titanium group metal complexes formed gradually following accumulation of knowledge on the dependence of reaction chemo- and stereoselectivities on the nature of the reactants and conditions and knowledge on the structures of possible intermediates. Therefore, we considered it pertinent to describe more fully the chronology of the research along this line and to discuss the ideas of the mechanisms of these reactions, despite the fact that the most significant results were obtained in the last 15 years.

Thus, the purpose of this review is to survey and describe systematically data on the structures of intermediate complexes involved in the formation of products of hydro-, carbo- and cyclometallation of alkenes and alkynes and on the effects of the electronic and steric factors, the structure of the ligand environment and reaction conditions on the selectivity of Zr catalysts.

II. Mechanism of alkene and alkyne hydroalumination with organoaluminium compounds catalyzed by zirconium π-complexes

The thermal hydroalumination of alkenes discovered more than 50 years ago is widely used both in the laboratory practice and in industry. The use of metal complex catalysts allowed performing this reaction under mild conditions with high regio- and stereoselectivities.[21,22]

The mechanism of catalytic hydroalumination of alkenes has been discussed in a number of publications where zirconium hydride complexes were assumed as key intermediates. The following scheme for alkene hydroalumination with lithium aluminium hydride catalyzed by $ZrCl_4$ was proposed:[23]

$$LiAlH_4 + ZrCl_4 \longrightarrow L_nZrH$$

$$L_nZrH + CH_2{=}CHR \longrightarrow L_nZrCH_2CH_2R$$

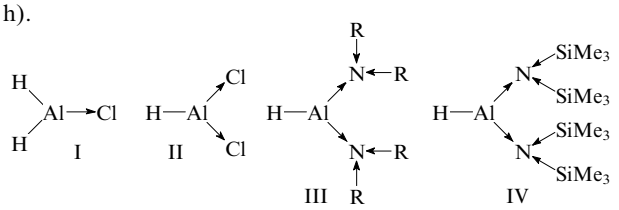
$$L_nZrCH_2CH_2R + LiAlH_4 \longrightarrow L_nZrH + al{-}CH_2CH_2R$$

$$al = \frac{1}{4}(LiAl)$$

The first step gives rise to transition metal hydride formed upon ligand exchange; then this species coordinates alkene to give an alkyl or alkenyl derivative. In the last step, OAC is formed and the Zr hydride is recovered as a result of transfer of the alkyl (or alkenyl) fragment from Zr to Al. A similar mechanism was proposed for $ZrCl_4$- or $HfCl_4$-catalyzed hydroalumination of linear and cyclic alkenes with diisobutyl aluminium hydride.[24] A study of the reactivities of various aluminium hydride derivatives in $TiCl_4$-catalyzed alkene hydroalumination[25] showed that they can be arranged in the following order of decreasing activity:

$$LiAlH_4 > AlH_3 > AlH_2Cl > HAlCl_2$$

It is believed that the decrease in the reaction rate is caused by the ability of the Cl atom to withdraw the electron density, resulting in strengthening of the H–Al bond, *i.e.*, this bond becomes less reactive than that in AlH_3.[26] If the Al-containing molecule has two Cl atoms, their effect becomes more pronounced due to the synergistic effect, and this sharply reduces the reaction rate. The different reactivities of type $HAl(NR_2)_2$ and $HAlCl_2$ compounds in the hydroalumination were also interpreted based on electronegativity.[26] Nitrogen and chlorine atoms have equal electronegativity (3.0) but the nitrogen atom is bonded to an alkyl carbon atom and is affected by it. The H–Al bond becomes weaker and, hence, more reactive. Therefore, hydroalumination with compound $HAl(NR_2)_2$ is much faster (15 min) than the same reaction with $HAlCl_2$ (6 h).

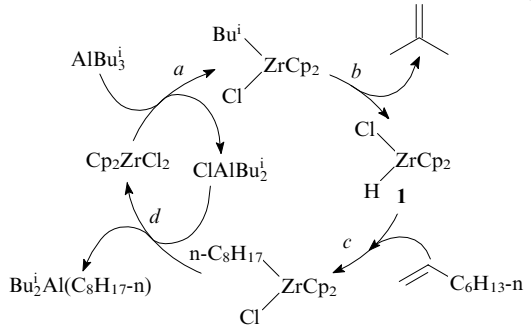


The reactivity changes as follows: AlH_3 > I > II and II < III < IV (the arrows mark the direction of the inductive effect).

According to the mechanism proposed for the hydroalumination of alkenes, dienes and alkynes with aluminium hydride catalyzed by transition metal halides (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn),[26,27] the first step is exchange reaction between the metal halide and aluminium hydride to give the transition metal hydride; this is the key intermediate of hydroalumination. The reducing properties of the transition metal hydride are due to the overlap of the free d orbital of the metal ion and the π-orbital of the C=C bond of the substrate. According to this assumption, Cu^{I} (d^{10}) and Zn^{II} (d^{10}) having no vacant d orbital cannot interact with the alkene. The half-filled d shell of Mn^{II} (d^5) should also decrease the hydrometallating ability. Indeed, catalysts based on Cu, Zn and Mn were much less active than Ti, Co or Ni compounds. Then the transition metal hydride coordinates the unsaturated substrate to give the π-complex. The next step comprises the metal hydride addition to the substrate to give the alkyl derivative. Under the assumption that the alkene or diene activation should be induced by d^0 metal complexes, the equilibrium should be shifted from the unsaturated π-complex to the d^0 metal alkyl. At the next step, the alkyl derivative of the transition metal is transmetallated by aluminium hydride to give alkyl aluminium compound and metal hydride, thus closing the catalytic cycle.

Negishi *et al.*[28,29] proposed a mechanism of alkene hydroalumination by $AlBu^i_3$ catalyzed by Cp_2ZrCl_2 (Cp = η^5-C_5H_5) (Scheme 1), which includes the alkylation of the initial form of the catalyst (*a*); elimination of isobutylene upon β-hydride transfer (*b*); hydrozirconation of the alkene (*c*); transmetallation of the zirconium intermediates with $ClAlBu^i_2$ (*d*) giving rise to the target higher alkylalanes.

Scheme 1



Zirconocene hydrochloride (**1**) was proposed as the key intermediate coordinating the alkene. As shown by Schwartz and co-workers,[15,30–33] this intermediate readily reduces unsaturated compounds.

Uranium salts (UCl_3 and UCl_4) were also proposed as catalysts for hydroalumination of alkenes by $LiAlH_4$.[34] The key intermediate proposed for these reactions is the hydride complex $U(AlH_4)_3$ with the U–H–Al bridge, which hydrometallates alkenes to give the intermediate compound $U(AlH_4)_2(AlH_3CH_2CH_2R)$. The hydrometallation reaction involves preliminary coordination of alkene to uranium followed by insertion of the unsaturated compound into the Al–H bond.

However, the above-considered mechanisms and structures of intermediates are hypothetical, because these intermediates and complexes involved in hydroalumination have not been isolated and identified. More recently, we studied in considerable detail[35–39] the mechanism of catalytic hydroalumination of α-alkenes with $XAlBu^i_2$ (X = H, Cl, Bu^i) by dynamic NMR spectroscopy and by independent synthesis of some intermediates formed in these reactions. It was shown (Scheme 2) that hydroalumination is a multistep process involving both successive and competitive reactions. In all three systems (Cp_2ZrCl_2–$ClAlBu^i_2$, Cp_2ZrCl_2–$HAlBu^i_2$ and Cp_2ZrCl_2–$AlBu^i_3$), mixed Zr,Al hydride complexes are initially formed, only the complex $[Cp_2ZrH_2 \cdot ClAlBu^i_2]_2$ (**2a**) among them being the active form of the catalyst that hydroaluminates alkenes to give alkyl zirconocene chlorides **3** and alkylalanes **4**.

Subsequently, Parfenova *et al.*[40] developed a kinetic model of the reaction that accounted for the low stability of intermediate **2a** and different activities of OAC in the catalytic hydroalumination. It was shown[40] that the rate of the catalytic reaction is determined by the ratio of the rates of competing steps, namely, the transition of active complex **2a** to low-activity intermediate **5** and the reaction of active complex **2a** with the alkene.

Studies of the structure of Zr,Al hydride complexes, their activity and the mechanism of action in the reactions with alkenes, as well as the effect of the π-ligand environment and the nature of OAC on the catalytic hydroalumination of alkenes,[41,42] extended the views on the structure of the catalytic active site of this reaction, in particular, it was proposed that the monomeric complex $[Cp_2ZrH_2 \cdot ClAlBu^i_2]$ (**6**) rather than dimer **2a** is the active form of the catalyst.

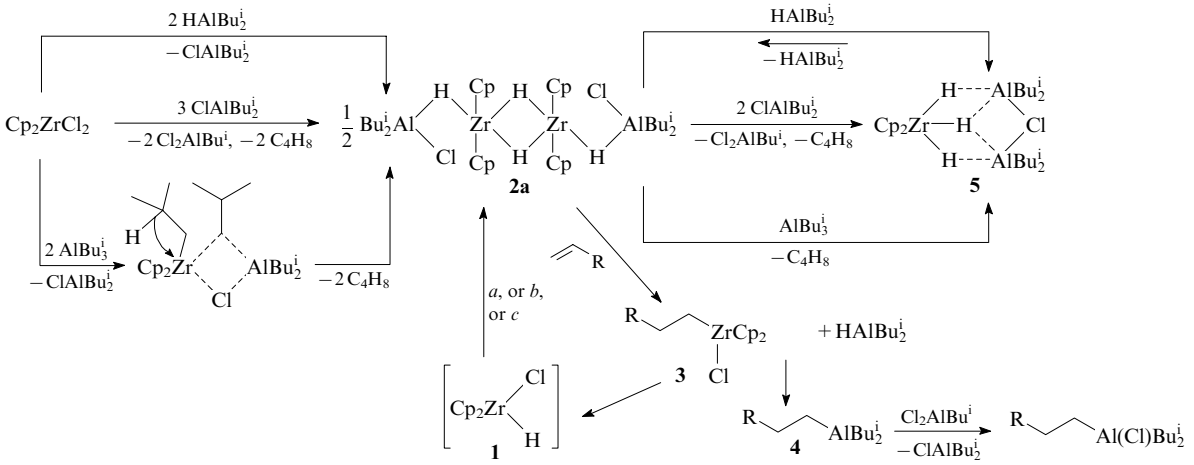
Subsequently, quantum chemical modelling of the mechanism of this reaction[43] substantially supplemented the experimental scheme proposed previously (Scheme 3).

The thermodynamically probable pathway of the reaction between Cp_2ZrCl_2 and $HAlBu^i_2$ includes the formation of the bridged complex $[Cp_2ZrCl_2 \cdot HAlBu^i_2]$ (**7**), which dissociates to give Cp_2ZrHCl. The subsequent coordination of $HAlBu^i_2$ affords the intermediate $[Cp_2ZrH_2 \cdot ClAlBu^i_2]$ (**6**), which forms dimer **2a**. The possible alternative pathways to trihydride complex **5**, which is inactive in alkene hydroalumination, have been considered. It was shown that complex **5** can be converted to several Zr,Al hydride complexes of various compositions (*e.g.*, complexes **8a**, **9** and **10**). It was suggested that complexes **1**, **5**, **6** and **9** directly participate in the hydroalumination of alkenes.

Thus, hydroalumination of alkenes on treatment with $XAlBu^i_2$ (X = H, Cl, Bu^i) catalyzed by Zr π-complexes was found to be a complex multistep process comprising successive and competitive steps. The steps give intermediate Zr,Al hydride complexes of various structures, their reactivities depending on the presence of a free Zr–H bond.

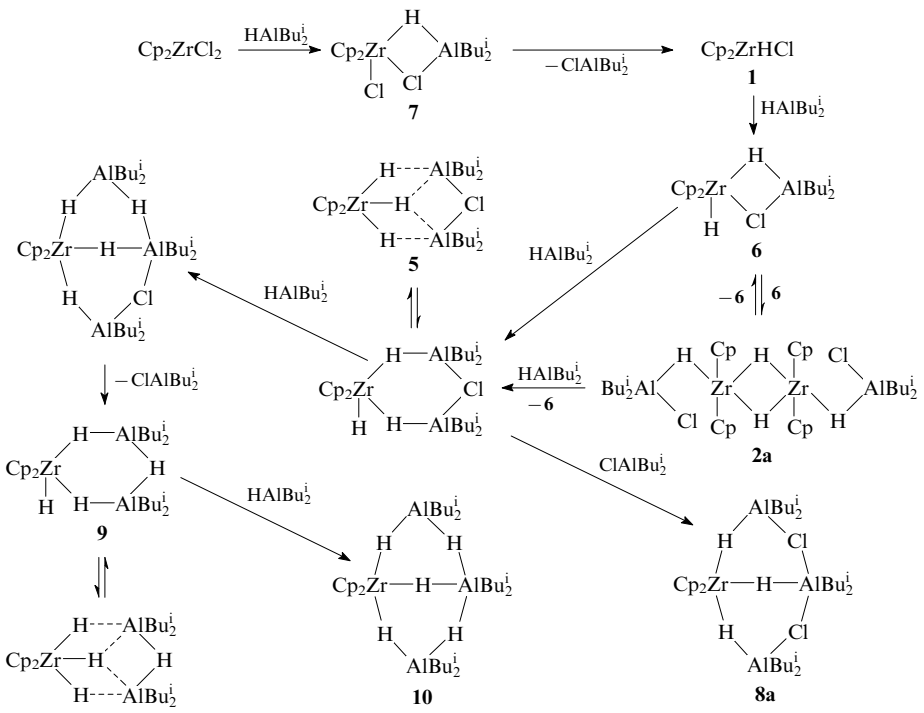
These complexes are based on zirconocene hydrides[44–66] the structure and composition of which are mainly determined by spatial characteristics of the π-ligand. It was noted that solid Cp_2ZrH_2 and Cp_2ZrHCl are poly-

Scheme 2



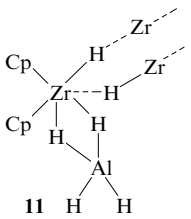
R = n-C$_n$H$_{2n+1}$ (n = 5–8); (*a*) $HAlBu^i_2$; (*b*) $ClAlBu^i_2$ (–Cp_2ZrCl_2); (*c*) $AlBu^i_3$ (–C_4H_8)

Scheme 3

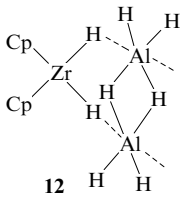


meric. In hydrocarbon solvents, the dimer $[Cp_2ZrH_2]_2$ existing in equilibrium with the monomer was also detected.[53] It was found[62] that complexes with bulky ligands, for example, Cp*(η^5-$C_5H_3Bu^t_2$-1,3)ZrH_2 (Cp* = η^5-C_5Me_5), Cp*(η^5-$C_5H_2Me_3$-1,2,4)ZrH_2, (η^5-$C_5H_3Bu^t_2$-1,3)$_2ZrH_2$, Cp*(η^5-C_5HMe_4)ZrH_2 and $Cp^*_2ZrH_2$ are monomeric; the complexes with less bulky ligands, $[Cp^*CpZrH_2]_2$, [Cp*(η^5-$C_5H_4Bu^t$)$ZrH_2]_2$, [Cp*(THI)$ZrH_2]_2$ (THI is 4,5,6,7-tetrahydroindenyl) and [(η^5-$C_5H_3Pr^i_2$-1,3)$ZrH_2]_2$, are most often dimeric in solution, whereas Cp*(η^5-$C_5H_3Pr^i_2$-1,3)ZrH_2 and (η^5-$C_5HMe_4)_2ZrH_2$ form an equilibrium mixture of monomers and dimers, their ratio depending on the temperature and concentration.

A large number of various Zr,Al-hydride complexes were obtained in reactions of zirconocene chlorides, hydrides and alkyl derivatives with OAC. Thus upon the reaction of Cp_2ZrHCl with $LiAlH_4$ taken in a 1 : 1 ratio at room temperature in THF, the complex $Cp_2Zr(H)AlH_4$ was detected.[45] The possible oligomeric structures (**11** and **12**) were proposed for this compound.



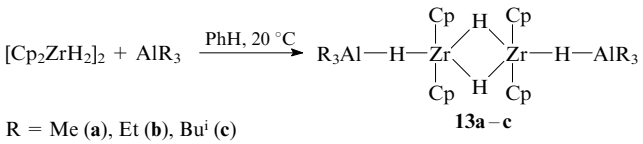
11



12

Subsequently, the same authors obtained complex **13a** by the reaction of $[Cp_2ZrH_2]$ with $AlMe_3$ in benzene at room temperature.[67] Complex **13b** of the same type was also detected in the reaction of Cp_2ZrMe_2 with $AlEt_3$.[68] However, the ^{1}H NMR data for complex **13b** obtained in this way contradict with the results of the former publication.[67]

In other studies,[35,36] NMR data for this complex were determined more thoroughly and a similar complex **13c** was prepared.

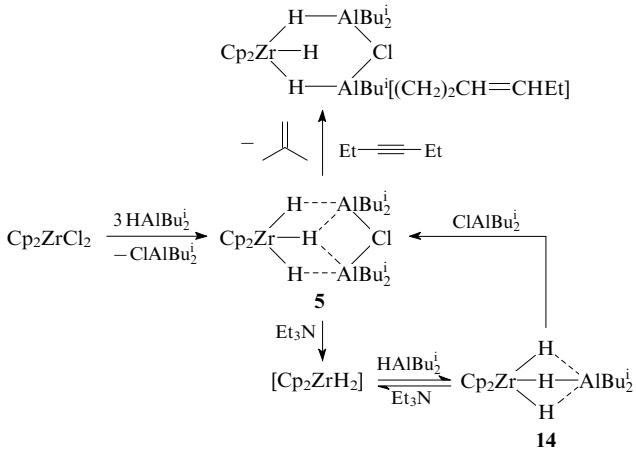


R = Me (**a**), Et (**b**), Bu^i (**c**)

13a–c

It was also shown[47] that the reaction of dialkyl aluminium hydride with Cp_2ZrX_2 (X = Cl, H, Alk) does not occur as a simple ligand exchange giving zirconocene hydrides but affords mixed bimetallic Zr,Al hydride complexes of various compositions. For instance, $[Cp_2ZrH_2]$ reacts with $HAlBu^i_2$ (3 : 2.8 molar ratio) in benzene at room temperature to give dark-blue-coloured thermally unstable complex **14** (Scheme 4).

Scheme 4



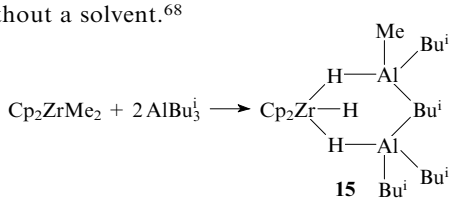
14

Complex **14** reacts with $ClAlBu^i_2$ to be completely converted to thermally stable trihydride complex **5**, which

can also be prepared by the reaction of Cp_2ZrCl_2 with $HAlBu^i_2$ in a 1 : 3 molar ratio.[47]

Trihydride complex **5** was tested in the hydroalumination of hex-3-yne at room temperature;[69] however, the products could not be identified. This reaction was accompanied by evolution of isobutylene; therefore, the authors proposed that alkyne reacts with the aluminium hydride moiety, resulting from β-hydride transfer and elimination of methylenealkane (see Scheme 4). According to Shoer and Schwartz,[70] complex **5** reduces carbonyl compounds to monohydric alcohols.

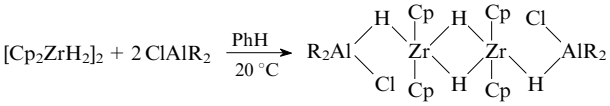
Complex **15**, whose structure is similar to the structure of **5**, was obtained in the reaction of Cp_2ZrMe_2 with $AlBu^i_3$ without a solvent.[68]



15

As the temperature increases to 50 °C, the signal of the hydride atoms in the NMR spectra of this complex is broadened, which may be indicative of fast exchange between them.

In a study of the mechanism of catalytic hydroalumination of alkenes with $XAlBu^i_2$ (X = H, Cl, Bu^i), we found a new Zr,Al complex **2a** (see Scheme 2), which can be obtained by the reaction of $[Cp_2ZrH_2]_2$ with $ClAlBu^i_2$ taken in a 1 : 2 ratio in benzene (or toluene) at 20 °C.[35–37] A similar reaction of zirconocene dihydride with $ClAlEt_2$ furnished complex **2b**.[37,41,42] The structures of complexes **2a**,**b** were confirmed by cryoscopy and NMR spectroscopy.



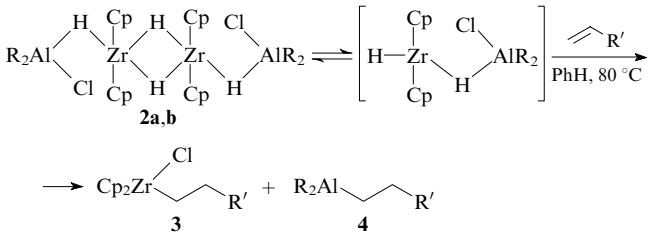
2a,**b**

R = Bu^i (**a**), Et (**b**)

For studying the effect of the nature of OAC on the reactivity of Zr,Al hydride complexes in the hydroalumination, compounds **2a**,**b**, **13b**,**c** and **14** were made to react with terminal alkenes in benzene at room temperature at different molar ratios of reactants. The lowest activity was found for complexes **13b**,**c**. Monitoring of hydrometallation of alkenes with these reagents directly in the NMR tube showed that at the molar ratio reagent : alkene = 1 : 2, the reaction gives alkylalanes **4** and alkyl hydride complexes **16** (Scheme 5). Apparently monomers **17** existing in equilibrium with dimers **13b**,**c** react with alkenes to give zirconocene alkyl hydrides **18**, which also exist in equilibrium with dimeric forms **16**.[71–73]

Analysis of the gaseous products of this reaction demonstrated evolution of ethane in experiments with $AlEt_3$ and formation of isobutane in the case of $AlBu^i_3$. Probably, the presence of an additional amount of the alkene accelerates the decomposition of the resulting zirconocene alkyl hydrides **18** to 'Cp_2Zr' and the corresponding alkanes RH[71,72] upon β-elimination. Complex **14** reacted with alkenes similarly to complexes **13b**,**c**.

The reactions of alkenes with complexes **2a**,**b** were found[41,42] to afford alkyl zirconocene chlorides **3** and alkylalanes **4** in a 1 : 1 molar ratio (^1H and ^{13}C NMR data).



2a,**b**

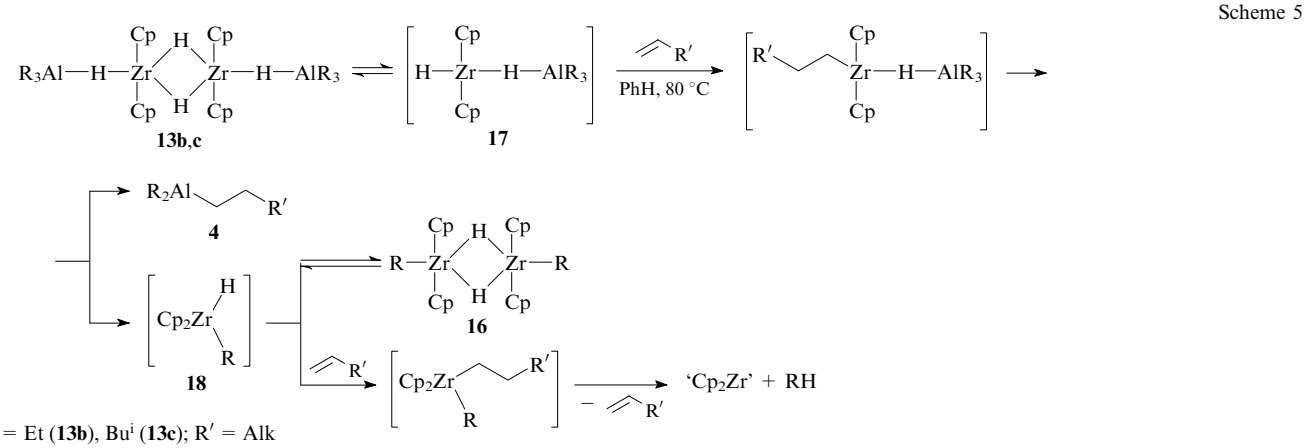
3 **4**

R = Bu^i (**a**), Et (**b**); R′ = Alk

Complexes **2a**,**b** are more reactive in hydrometallation than complexes **13b**,**c** and **14**. Probably, chlorine-containing OAC in Zr,Al hydride complexes accelerate the intramolecular exchange between bridging and terminal H atoms in the dimer $[Cp_2ZrH_2]_2$ in solution[53] to a higher extent than trialkylalanes and shift the equilibrium between the dimeric and monomeric forms. The shift of the equilibrium under the action of $ClAlR_2$ toward the monomer accelerates the alkene insertion into the Zr—H bond in chlorine-containing Zr,Al hydride complexes **2**. It was also shown that these complexes are more reactive than the Schwartz reagent **1**. The different reactivities may be caused by high solubility of the synthesized Zr,Al bimetallic complexes in the initial solvent and additional activation of zirconocene dihydride by the complexation with OAC.

Moreover, in the addition to bicyclic alkenes having a sterically hindered double bond, complexes **2** show a diastereoselectivity different from that of the Schwartz reagent

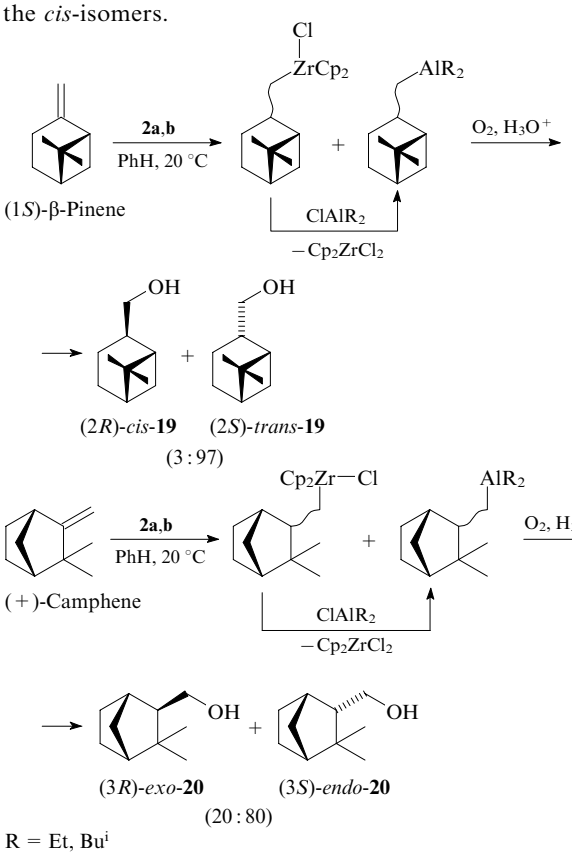
Scheme 5



13b,**c** **17** **4** **16** **18**

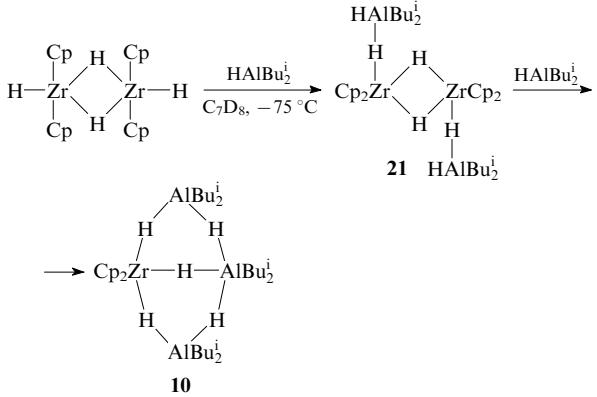
R = Et (**13b**), Bu^i (**13c**); R′ = Alk

or $HAlBu^i_2$.[41,42,74,75] For example, the hydrometallation of (1*S*)-β-pinene and (+)-camphene with complexes **2a**,**b** at room temperature proceeds with high stereoselectivity giving predominantly the thermodynamically more stable *trans*-isomers of products **19** and **20**, respectively, whereas the addition of Cp_2ZrHCl[76] or $HAlBu^i_2$ (Ref. 77) occurs from the least sterically hindered *trans*-side to give mainly the *cis*-isomers.



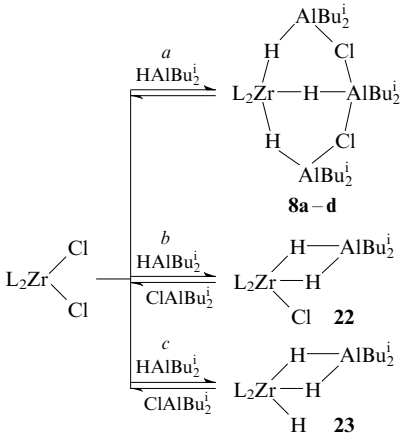
R = Et, Bu^i

A ^{1}H NMR study of the reaction of Cp_2ZrCl_2 with 3 equiv. of $HAlBu^i_2$ in toluene-d_8 showed the formation of complex **8a** (see Schemes 3 and 6), while complex **10** is formed in the reaction of 0.5 equiv. of $[Cp_2ZrH_2]_2$ with 3 equiv. of $HAlBu^i_2$ at −75 °C *via* intermediate complex **21**.[78] Previously, on the basis of NMR data and molecular mass measurements, structure **14** was proposed for complex **10**.[35,36,47]



Complexes **8b**–**d**, similar to **8a**, were obtained in the reaction of $(Bu^nC_5H_4)_2ZrCl_2$, $(1,2\text{-}Me_2C_5H_3)_2ZrCl_2$ or $(Me_3SiC_5H_4)_2ZrCl_2$ with $HAlBu^i_2$ in benzene or toluene at 25 °C (Scheme 6).[78]

Scheme 6



(*a*) L = Cp (**a**), $Bu^nC_5H_4$ (**b**), $1,2\text{-}Me_2C_5H_3$ (**c**), $Me_3SiC_5H_4$ (**d**);
(*b*) L = SBI, EBI, EBTHI, $Me_2C(C_5H_4)_2$, $Me_2Si(C_5H_4)_2$, *etc.*;
(*c*) L = $Me_2Si(2\text{-}Me_3Si\text{-}4\text{-}Bu^tC_5H_2)_2$, $Me_2Si(3\text{-}Bu^tC_5H_3)_2$

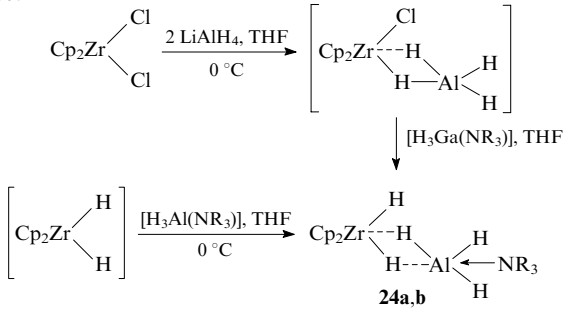
The reactions of *ansa*-complexes *rac*-$(SBI)ZrCl_2$ [SBI = $Me_2Si(Ind)_2$, Ind is inden-1-yl], *rac*-$(EBI)ZrCl_2$ [EBI = $1,2\text{-}(Ind)_2C_2H_4$], *rac*-$(EBTHI)ZrCl_2$ [EBTHI = $1,2\text{-}(H_4Ind)_2C_2H_4$)], $Me_2C(C_5H_4)_2ZrCl_2$, $Me_2Si(C_5H_4)_2$. $.ZrCl_2$, *rac*-$Me_2Si(2,4\text{-}Me_2C_5H_2)_2ZrCl_2$, $(Me_2Si)_2(C_5H_3)_2$. $.ZrCl_2$ and $(Me_2Si)_2(3,5\text{-}Pr^i_2C_5H)(C_5H_3)ZrCl_2$ with a 2–5-fold excess of $HAlBu^i_2$ in benzene or toluene give, according to NMR spectra, hydride complexes **22** containing a $[ZrH_2]$ group.[78,79] The presence of one broadened signal of hydride atoms was attributed to the existence of fast intermolecular exchange.

Considerably different products of the reaction of L_2ZrCl_2 with $HAlBu^i_2$ were found in the case of *tert*-butyl-substituted complexes, namely, *rac*-$Me_2Si(2\text{-}Me_3Si\text{-}4\text{-}Bu^tC_5H_2)_2$. $.ZrCl_2$ and *meso*-$Me_2Si(3\text{-}Bu^tC_5H_3)_2ZrCl_2$. In these experiments, trihydride complexes **23** were obtained. The fact that bridged zirconocene dichloride complexes with bulky β-substituents in the Cp rings reacted with $HAlBu^i_2$ to give trihydride clusters instead of chloro dihydride complexes was attributed to the steric repulsion between the Cl ligands and β-Bu^t substituents. This repulsion can be overcome by replacing the rather long Zr–Cl bond (2.45 Å) by shorter Zr–H bond (1.95 Å).

Thus, all zirconium complexes with π-ligands not bonded to each other react with $HAlBu^i_2$ to give tetranuclear trihydride clusters **8**. Most of the studied *ansa*-complexes produce chloro dihydride complexes **22**, whereas sterically more crowded complexes with β-Bu^t substituents yield trihydride complexes **23**. The researchers cited attributed this finding to different degrees of freedom for the rotation of cyclopentadienyl ligands; more mobile ligands give rise to larger complexes (compounds **8**).

Interesting results on the synthesis of Zr,Al hydride complexes were reported by Khan *et al.*[80] The authors proposed two methods for the synthesis of the complexes $[Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(NR_3)]$ (**24a**,**b**) the structure of which was established by X-ray diffraction and NMR and IR spectroscopy. The first method is the reaction of Cp_2ZrCl_2 with an excess of $LiAlH_4$ in THF at 0 °C followed by treatment of the reaction mixture with $[H_3GaNR_3]$ (NR_3 is quinuclidine, NMe_3). Colourless complexes **24** were isolated from the light pink solution in 50% yield. According to the authors, the pink colour was due to the presence of reduced

Zr^{3+} compounds as minor products. Probably, gallium hydride serves as not only the source of amine but also the source of hydride atoms, which replace Cl in the initial Cp_2ZrCl_2. When $[H_3AlNR_3]$ is used, the second step occurs much more slowly than in the case of the corresponding gallane. If only amine is used in this reaction, complex **24** is not formed in the second step. Another method for the preparation of complexes **24** is the reaction of $[Cp_2ZrH_2]$ with $[H_3AlNR_3]$ in THF. In this case, a significant difference is more intense pink colour of the reaction mixture, while the isolated product is colourless, as in the previous case.

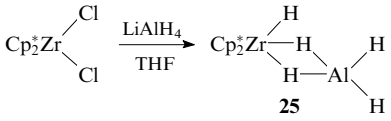


24a,b

$NR_3 = C_7H_{13}N$ (**a**), NMe_3 (**b**)

The ^1H NMR spectra of complexes **24a,b** recorded in THF-d_8 exhibited signals of only tertiary amines and Cp ligands. The absence of signals for hydride atoms was attributed to the occurrence of fast hydride exchange or equilibrium between $[Cp_2ZrH_2]$, $[H_3AlNR_3]$ and complexes **24a,b** in solution.

It was found that the reaction of $Cp^*_2ZrCl_2$ with $LiAlH_4$ in a 1:2 molar ratio in THF at room temperature also produces a bimetallic complex, $Cp^*_2ZrH(\mu^2\text{-}H_2AlH_2)$ (**25**),[61] similar to complexes **24**.

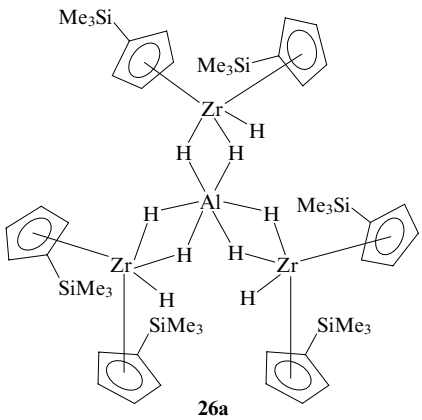


25

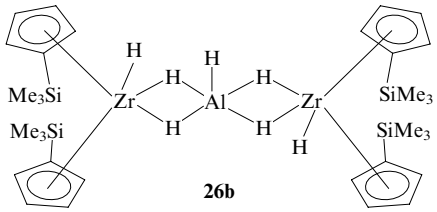
Broadening of NMR signals for the hydride atoms at room temperature attests to the existence of an exchange process. With temperature decrease, the signals narrowed down; however, heating of the sample did not induce coalescence of signals up to decomposition of the complex. An X-ray diffraction study shows that in the crystalline state, complex **25** forms dimers with Al–H–Al bridges.

Meanwhile, the reaction of 1 equiv. of Cp'_2ZrCl_2 ($Cp' = Me_3SiC_5H_4$) with 2 equiv. of $LiAlH_4$ in Et_2O at room temperature affords compound **26**; according to X-ray diffraction data,[81] this product crystallizes from solution in two forms: $[Cp'_2Zr(H)(\mu\text{-}H)_2]_3Al$ (**26a**) or $[Cp'_2Zr(H)(\mu\text{-}H)_2]_2AlH$ (**26b**).[81] Structures of this type were also obtained for Ti^{III} (Refs 82–84).

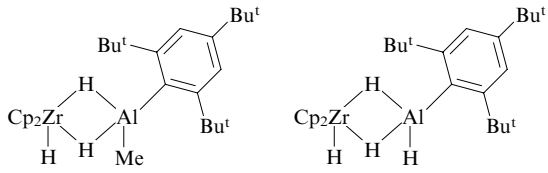
The use of aluminium hydride with the bulky substituent Mes* $(Mes^*AlH)_2$ ($Mes^* = 2,4,6\text{-}Bu^t_3C_6H_2$) for the reaction with Cp_2ZrMe_2 in hexane or benzene affords the binuclear cluster $Cp_2Zr(H)(\mu^2\text{-}H)_2Al(Me)Mes^*$ (**27**) with a smaller size compared to compound **26**. The complex $Cp_2Zr(H).(\mu^2\text{-}H)_2Al(H)Mes^*$ (**28**) with a similar structure was obtained from Cp_2ZrHCl and $[Mes^*AlH_3Li(THF)_2]_2$ in toluene at 0 °C.[85] According to X-ray diffraction, NMR and IR data, the methyl group in complex **27** migrates from the Zr to Al atom, which are linked by two hydride bridges.



26a



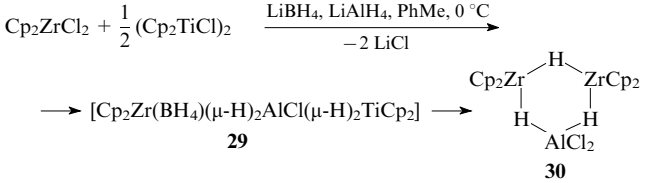
26b



27 **28**

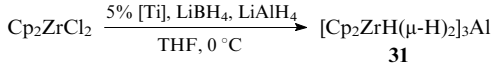
Note that complex **28** reacts very slowly with diphenylacetylene. Heating of a stoichiometric mixture of reactants for 20 h at 70–80 °C afforded a dark-red solution. Unfortunately, the reaction products were not isolated or identified.[85]

An attempt was made[86] to synthesize trinuclear heterometallic complexes $Cp_2Zr(X')(\mu\text{-}H)_2Al(X)(\mu\text{-}H)_2TiCp_2$ (X, X′ = Cl, H, BH_4). It was assumed that these complexes containing transition metal atoms in different oxidation states (Ti^{3+} and Zr^{4+}) may have unique structural and catalytic properties. It was found that complex **29** is unstable, its decomposition being accompanied by the reduction of Zr^{4+} to Zr^{3+} to give $[Cp_2Zr(\mu\text{-}H)]_2(\mu\text{-}H)AlCl_2$ (**30**).



29 **30**

It was shown that after mixing of the reactants, reduction of Zr^{4+} in complex **29** starts even at room temperature. At 40 °C, the reaction ends after 2–3 h to give complex **30** as red needle-like crystals. The reaction of Cp_2ZrCl_2 with $LiAlH_4$ and $LiBH_4$ (0.9:2:1) in the presence of 5 mol.% Cp_2TiCl_2 in THF at 0 °C yields complex **31**, similar to **26a**, in which the oxidation state of Zr atoms is +4.



31

Subsequently, the yield of complex **30** was increased by introducing a catalytic amount of $CoBr_2$ in the reaction of Cp_2ZrCl_2 with $LiAlH_4$ (Ref. 87).

The foregoing leads to the conclusion that the Zr,Al hydride complexes are Zr—H—Zr- and Zr—H—Al-bridged structures based as a rule on a zirconocene hydride moiety. This moiety, in turn, may be a self-associated structure if its formation is not prevented by steric restrictions caused by bulky π-ligands. The energy of cleavage of these bridging bonds or the ability of the complex to have initially a free Zr—H bond are the factors determining the reactivity of Zr,Al hydride complexes in the hydroalumination of alkenes.

III. Mechanisms of carbo- and cycloalumination of alkenes and alkynes by organoaluminium compounds catalyzed by zirconium π-complexes

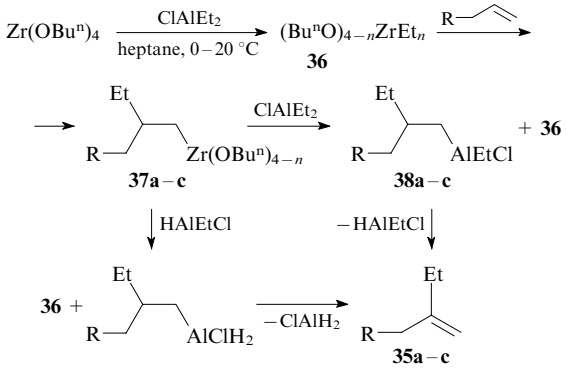
The thermal carboalumination of alkenes and alkynes occurs under drastic conditions and is accompanied by side hydro- and dehydroalumination reactions. In the presence of metal complex catalysts, carboalumination can be carried out under milder conditions with high regio- and stereoselectivity.[1,4,8–12]

The first attempts to study the mechanism of catalytic carboalumination were made by Van Horn and Negishi.[88] During a study of Cp_2ZrCl_2-catalyzed reactions of alkynes with $AlMe_3$, the authors suggested that alkyl zirconocene derivatives are formed as intermediates in this reaction. More recently, the bipolar bimetallic complex $MeZrCp_2-Cl^+-Al^-Me_2Cl$ (**32**), which is a 16-electron Lewis superacid, was postulated[11,12,89–91] as the active site (Scheme 7). It is formed *via* intermediates **33a** and **34a**.

As noted by the researchers cited, this reaction mainly follows the carbozirconation mechanism, although an alternative direct carboalumination step cannot be ruled out.

As an early example of direct oxidative β-ethylation of alkenes, consider the reaction of $ClAlEt_2$ with alk-1-enes (1 : 2 molar ratio) catalyzed by $Zr(OBu^n)_4$ under mild conditions (0–20 °C), resulting in β-ethyl-substituted alkenes **35a–c** (Scheme 8).[92] It was suggested that the ethyl group is introduced into the β-position of alk-1-enes as a result of 1,2-carbozirconation of alkenes by Zr alkyl complexes **36** stabilized by aluminium chloride and subsequent transmetallation of intermediates **37a–c** and dehydroalumination of intermediates **38a–c** and **39a–c**.

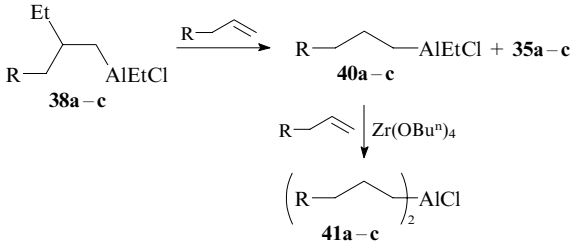
Scheme 8



R = Pr^n (**a**), n-C_5H_{11} (**b**), n-C_7H_{15} (**c**); $n = 1–4$

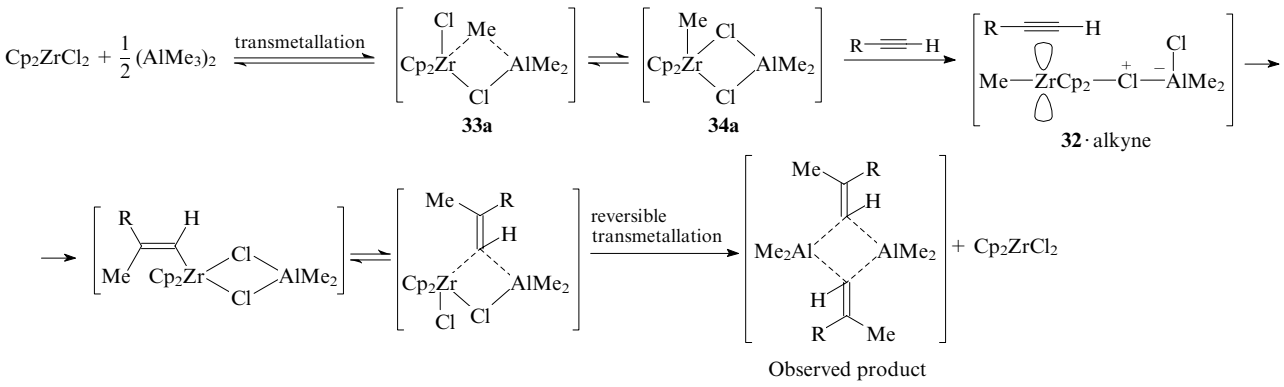
Subsequently, it was found[93] that apart from 3-methylidenealkanes **35a–c**, the reaction gives alkyl ethyl aluminium chlorides **40a–c** (or dialkyl aluminium chlorides **41a–c**) in equal ratios. Therefore, the proposed scheme was somewhat altered. According to Scheme 9, 2-ethylalkyl ethyl aluminium chlorides **38a–c** formed upon transmetallation of organozirconium compounds **37a–c** react with excess of alk-1-ene to be converted to **35a–c** and **40a–c**. The participation of the latter in the alkylation of Zr complexes and transmetallation in the presence of alk-1-ene affords 1,1′-disubstituted alkenes **35a–c** and OAC **41a–c**.

Scheme 9

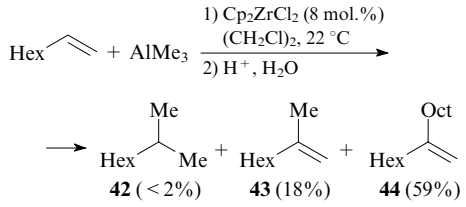


It was found[93] that Cp_2ZrCl_2 and $Zr(acac)_4$ (acac is acetylacetonate) are inactive in β-alkylation of alk-1-enes. In the presence of catalysts $ZrCl_4$, $(py)_2ZrCl_2$ (py is pyridine), $TiCl_4$ or $Ti(OBu^n)_4$, transalkylation of $ClAlEt_2$ with the products of ethylation and dimerization of the starting alkenes takes place. The catalytic activity of the tested transition metal complexes decreases in the series Ti > Zr > Hf.

Scheme 7

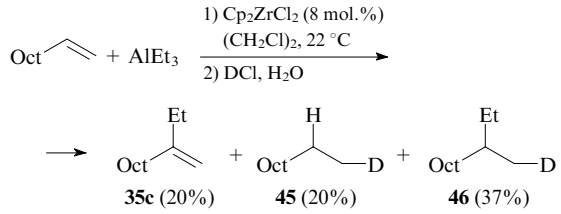


It was found that the reaction of $AlMe_3$ and oct-1-ene taken in a 1 : 1 ratio carried out in the presence of Cp_2ZrCl_2 (8 mol.%) in 1,2-dichloroethane at 22 °C does not give the desired **42** but instead yields 2-methylalkene **43** and dimerization product **44**.[94]



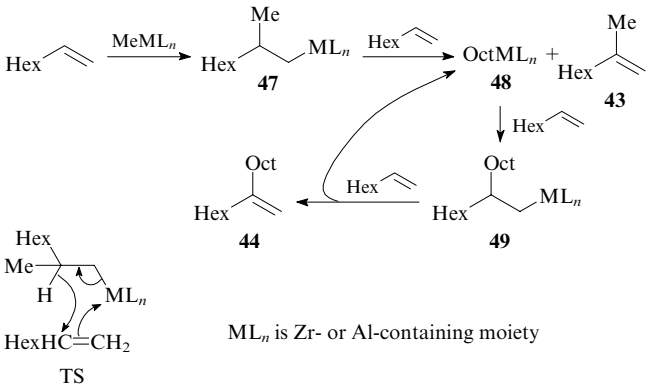
Hex = n-C_6H_{13}, Oct = n-C_8H_{17}

Transformations of the same type were found in the Cp_2ZrCl_2-catalyzed reaction of dec-1-ene with $AlEt_3$ under the same conditions.[95] Apart from methylidenealkane **35c**, the products of alkene hydro- (**45**) and carboalumination (**46**) were identified.



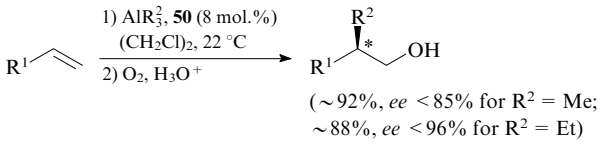
The initially formed (2-methyloctyl)aluminium or (2-methyloctyl)zirconium derivatives **47** react with alkene presumably *via* a six-centre transition state TS, giving rise to 2-methyloct-1-ene (**43**) and hydrometallation product **48**. The latter carbometallates the alkene to give compound **49**, which again hydrometallates the alkene to give methylidenealkane **44**, thus closing the catalytic cycle (Scheme 10).

Scheme 10

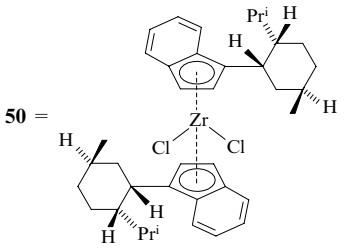


ML_n is Zr- or Al-containing moiety

It turned out that only using Zr complexes with bulky π-ligands having planar chirality [for example, (S_p,S_p)-$(NMI)_2ZrCl_2$ (NMI is η^5-{[(1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]inden-1-yl} (**50**)[96]] in chlorine-containing solvents, it is possible to perform the alkene carboalumination with high chemo- and stereoselectivities.[94, 95]



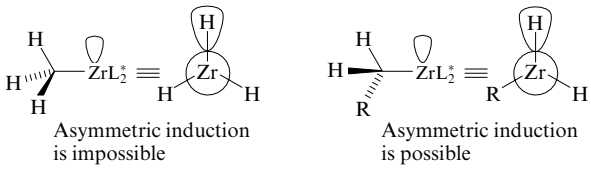
R^1 = n-C_6H_{13}, Bu^i, cyclo-C_6H_{11}, Bn, Ph, *etc.*;



Considering the proposed reaction mechanism, it was suggested that the yield of carbometallation products should increase as a result of retardation of the β-hydride transfer in the six-centre transition state TS (see Scheme 10). Apparently, the bulky π-ligands in the Zr complex prevent this six-centre interaction.

Moreover, the observed high enantioselectivity of the carbometallation may be interpreted only from the standpoint of direct addition of the Zr–R bond to the alkene where the substrate coordination is controlled by the spatial arrangement of ligands. The active sites of the reaction may be represented by both the [L_2ZrMe^+] cation formed upon dissociation of the corresponding Zr,Al complex and the proper Zr,Al complex in which the Zr–C bond is activated by the addition of OAC, as is postulated for Ziegler–Natta processes (Scheme 11).[97]

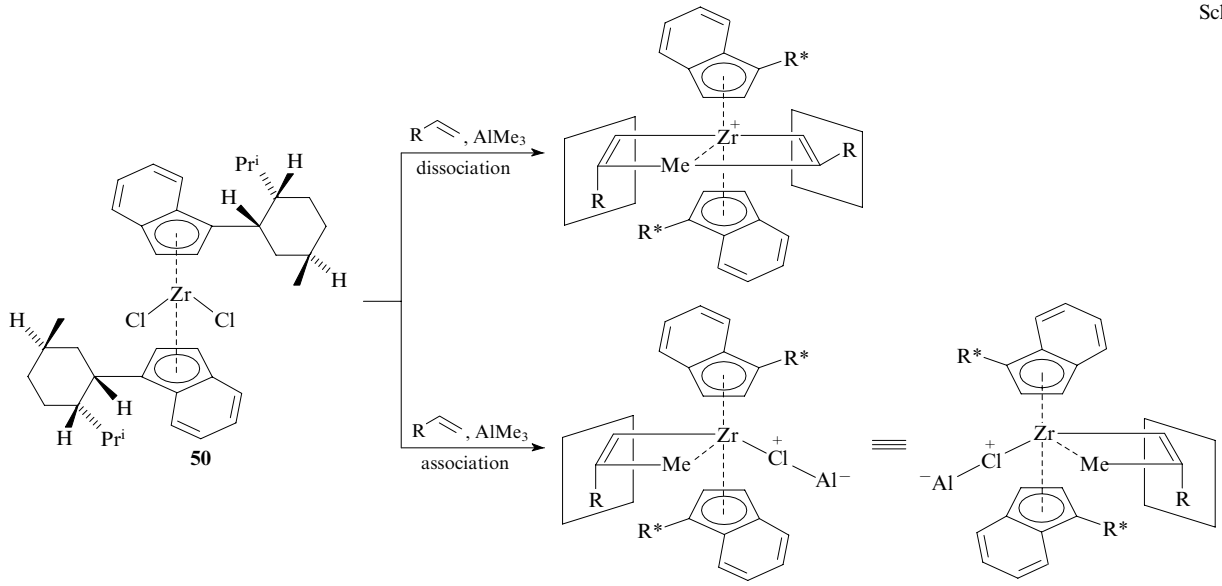
It was noted[94, 95] that the reaction with AlR_3 (R = Me, Et) predominantly gives products with *R*-configuration of the chiral centre in the β-position; in the case of $AlEt_3$, the enantiomeric excess in the product of carboalumination of alkenes increases. The enhanced enantioselectivity in the case of ethylalumination as compared with methylalumination was explained[11] by the effect of chiral neomenthyl ligands: α-agostic interaction may be responsible for the secondary stereoinduction in the case of ethyl or bulkier alkyl groups.



Later it was found[98] that the replacement of $AlMe_3$ by $AlEt_3$ in the reaction with terminal alkenes catalyzed by complex **50** changes the absolute configuration of the β-chiral centre from *R* to *S* in the carboalumination products. Also, the use of hydrocarbon solvents instead of chlorinated solvents in the ethylalumination was found to considerably decrease the enantioselectivity.

For interpreting the observed effects of the nature of OAC and the reaction conditions, we proposed the following hypothesis. The stereoselectivity of catalyst **50** and other complexes of this type may be due to the dependence of the conformational mobility of ligands on the solvent and the temperature.[96, 99] The conformational mobility is related to the possibility of rotation of π-ligands relative to one

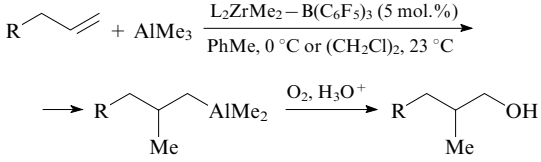
Scheme 11



another around the Zr centre. Consequently, a mixture of C_1- and C_2-symmetric complexes is formed in the solution. Probably, the interaction of the Zr complex with OAC under appropriate conditions (solvent, temperature) leads to stabilization of the particular rotamer of Zr,Al complex **51** (Scheme 12, for simplicity, the designations of the Zr atom and the indene double bonds in the intermediates are omitted).

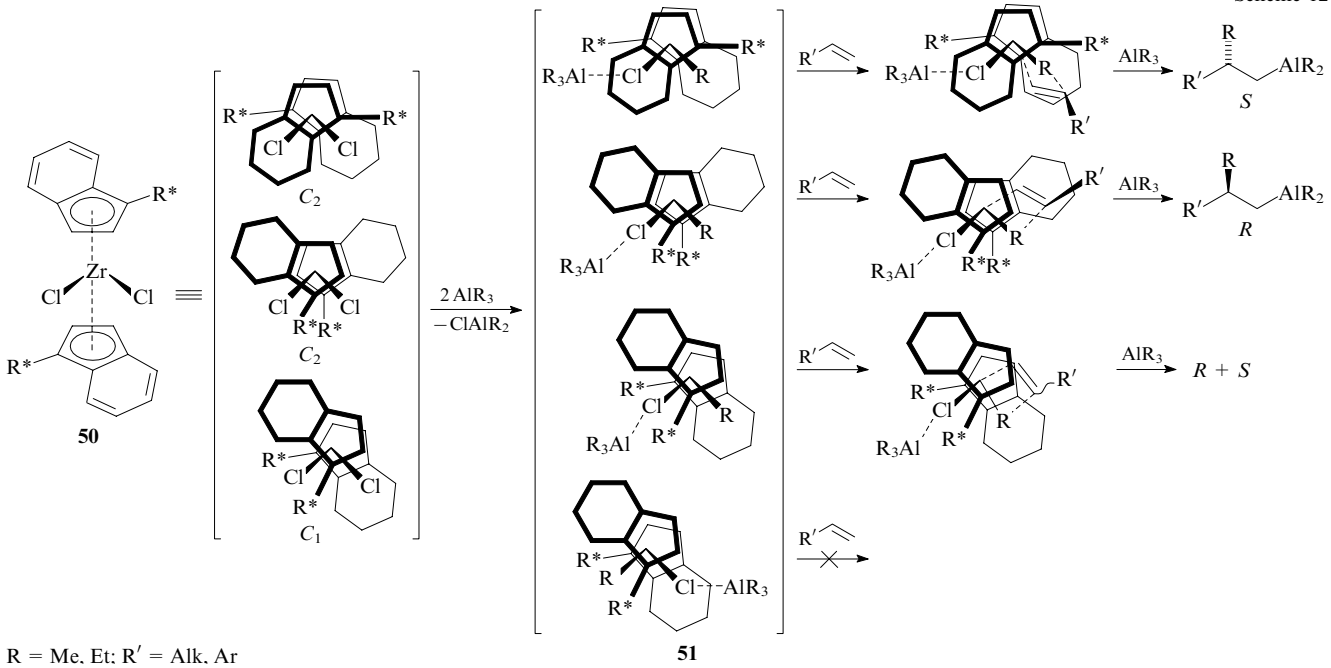
Thus, the dependence of the enantioselectivity of the carboalumination on the nature of the OAC and the conditions is apparently caused by the change in the composition of the rotamers of Zr,Al intermediates.

The use of co-catalysts, boron or aluminium compounds, in the carboalumination made it possible to increase the activities and selectivities of metallocene complexes not only in polymerization [100] but also in carboalumination of alkenes. This is not surprising, as carbometallation can be treated as an early stage of the polymerization process. For instance, the carboalumination of terminal alkenes with $AlMe_3$ occurs selectively when the two-component catalyst $(Cp^*_2ZrMe_2)-B(C_6F_5)_3$ is used (toluene, 0 °C). The yield of the carboalumination product within 12 h is 75%.[101] Then the rate of alkene conversion in the reaction with $AlMe_3$ was studied for a number of catalysts, $Cp^*_2ZrMe_2$, (EBTHI)$ZrMe_2$ and $(NMI)_2ZrMe_2$, in dichloroethane and toluene.[102]



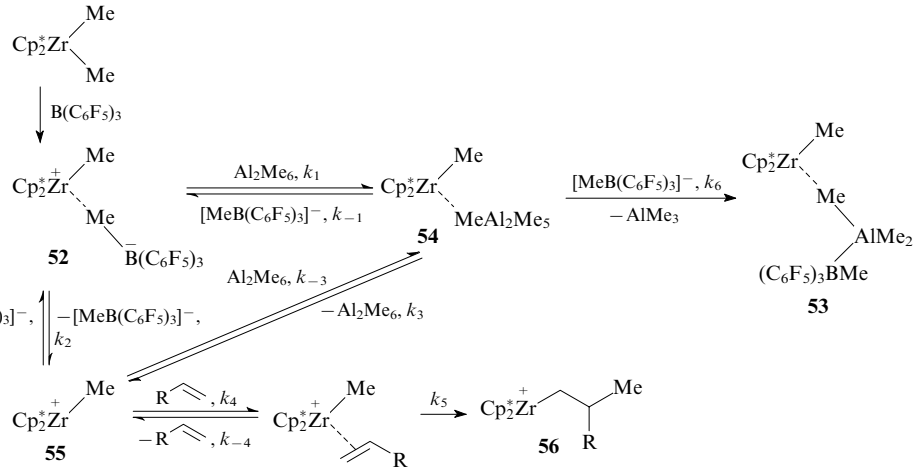
L = Cp*, NMI, *etc.*; R = Alk

Scheme 12



R = Me, Et; R′ = Alk, Ar

Scheme 13



R = Alk

It was noted that the activities and selectivities of the catalytic systems for the carboalumination of alkenes depend appreciably on the catalyst and solvent natures. The highest rate of transformation of allylbenzene into the carbometallation products was observed in the case of the catalysts $Cp^*_2ZrMe_2$ and $(NMI)_2ZrMe_2$ and the lowest rate was observed in the case of $(EBTHI)ZrMe_2$. In toluene, metallocenes were inefficient for carboalumination except for $Cp^*_2ZrMe_2$ (in most cases, oligomers and polymers were formed), and the rate and the selectivity of this reaction were much higher in chlorinated solvents. On the basis of the obtained data, a probable mechanism of alkene carboalumination by $AlMe_3$ in the presence of the $Cp^*_2ZrMe_2-B(C_6F_5)_3$ catalytic system was proposed[102] (Scheme 13).

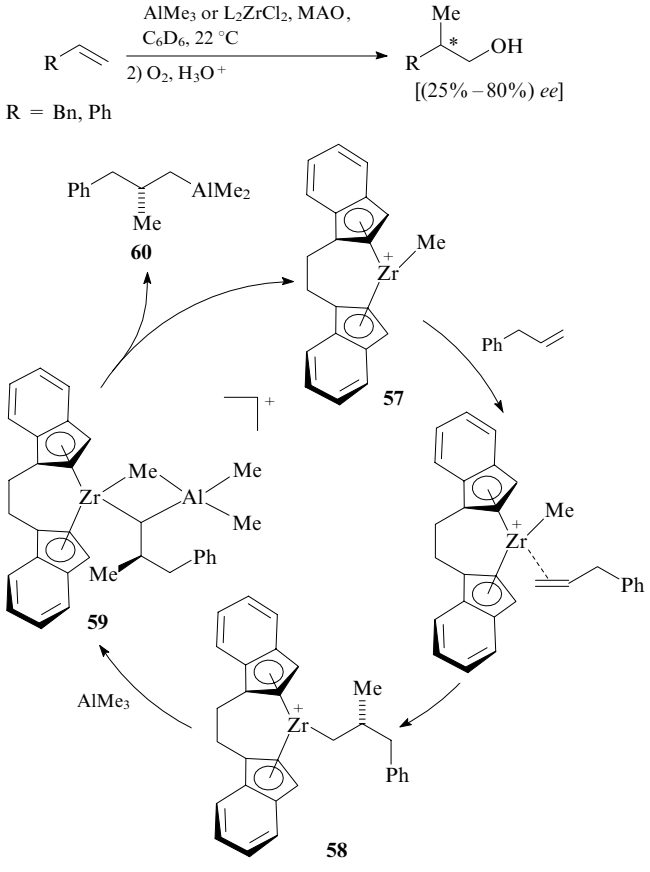
The ^1H and ^{13}C NMR studies showed that treatment of dimethylzirconocene with tris(pentafluorophenyl)borane produces ion pair **52**, which is slowly converted to complex **53** in the presence of $AlMe_3$. The rate of transformation of ion pair **52** to product **53** is much lower than the rate of alkene conversion and the contribution of the equilibrium concentration of complex **53** to the overall reaction rate is insignificant. Although complex **54** was not observed by spectroscopy, it was considered as a kinetically significant intermediate. The loss of a ligand in ion pair **52** or in intermediate **54** results in reactive cation **55**.[103–107] The rate-limiting coordination of alkene by this cation is accompanied by fast alkyl group transfer to give zirconium alkyl cation **56**.

The transformation of the zirconocene cations obtained from $(NMI)_2ZrMe_2$ and $Cp^*_2ZrMe_2$ into the stable inactive complexes **53** occurs more slowly than in the case of the catalyst $(EBTHI)ZrMe_2$ even when $AlMe_3$ is present in a large excess; therefore, the carbometallating activity of these catalysts is retained. The high carbometallation rate in a more polar solvent such as dichloroethane may be a consequence of weaker interaction between the methyl zirconocene cation and trimethylaluminium in intermediate **54** and easier ion exchange in polar solvents (better ion separation in the cation-active intermediates). Weakening of the coordination of borate anion or trimethylaluminium facilitates the coordination of alkene, thus ensuring high rate of substrate insertion.

On the basis of the study of the reactions of $AlMe_3$ with sterically hindered alkenes (allylbenzene and styrene) in the presence of (*S*,*S*)-*ansa*-zirconocenes, (*S*,*S*)-$(EBI)ZrCl_2$, (*S*,*S*)-$(SBI)ZrCl_2$, (*S*,*S*)-$Me_2Si(3\text{-}MeInd)_2ZrCl_2$ and (*S*,*S*)-$Me_2Si(DMInd)_2ZrCl_2$ (DMInd is 4,7-dimethylinden-1-yl) activated by $[Ph_3C][B(C_6F_5)_4]$ or methylalumoxane (MAO), a methylalumination mechanism was proposed, which is presented in Scheme 14.[108, 109]

According to this mechanism, in the presence of $[Ph_3C][B(C_6F_5)_4]$ or MAO, the initial complex is converted to the activated state, cationic complex **57**. The subsequent alkene coordination and insertion furnish new zirconium alkyl cation **58**. The association of the $AlMe_3$ molecule with cation **58** results in the formation of the heterobimetallic complex **59**, which undergoes alkyl exchange and dissociation to give the target OAC **60**.[109]

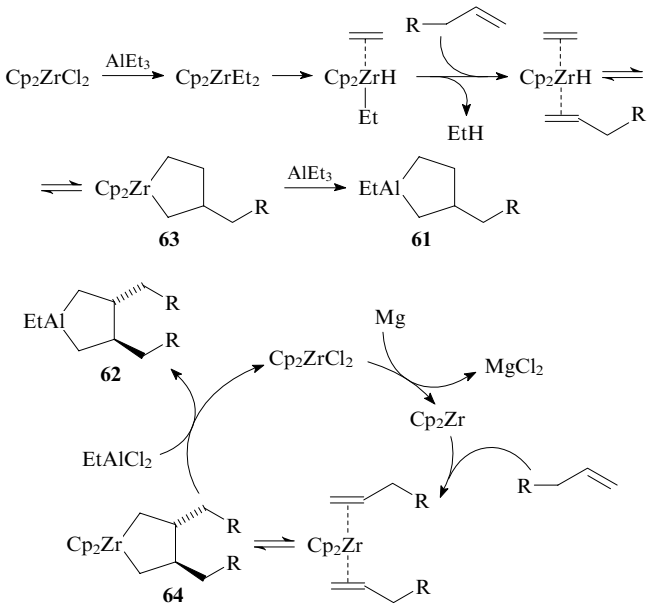
Scheme 14



R = Bn, Ph

As opposed to the above results, Dzhemilev *et al.*[1,3,5,6,110,111] found for the first time that Cp_2ZrCl_2-catalyzed reactions of $AlEt_3$ or $EtAlCl_2$ with alkenes and alkynes in non-polar solvents (benzene, toluene, hexane) afford previously unknown 3-mono- (**61**) and *trans*-3,4-disubstituted (**62**) aluminacyclopentanes with high regio- and stereoselectivity as well as the corresponding aluminacyclopentenes (Scheme 15).

Scheme 15



It can be said without exaggeration that the discovery of catalytic cycloalumination of unsaturated compounds and the subsequent extension of this reaction to other main group elements (Mg, Zn, In, B) laid the foundation of the development of a new research area: the chemistry of metallacycles derived from main group metals.

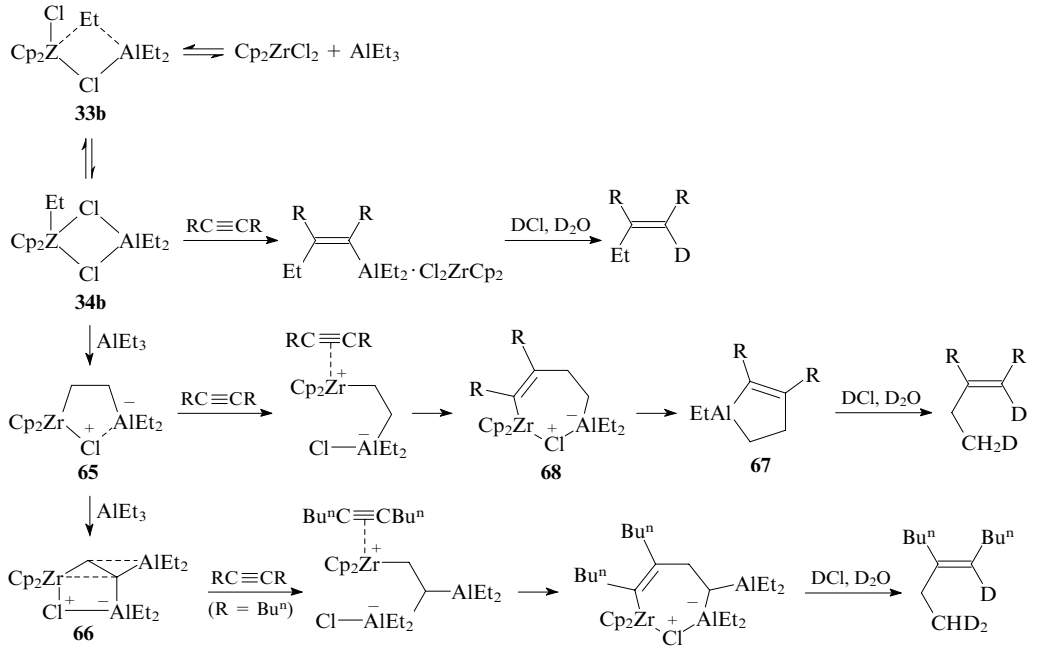
At an early stage of this research, on the basis of the structures of cyclic organozirconium compounds,[112–117] a mechanism of alkene cycloalumination was proposed, in which zirconacyclopentanes **63** and **64** or zirconacyclopentene were considered as the key intermediates; these compounds are transmetallated into the corresponding cyclic organoaluminium compounds **61** and **62** with direct replacement of the transition metal atom by a main group element (see Scheme 15).

The first attempt of experimental elucidation of the mechanism of this reaction was made[118] for the Cp_2ZrCl_2-catalyzed cycloalumination of alkynes after the pioneering publications of Dzemilev *et al.*[110,111] Having conducted unsuccessful experiments on zirconacyclopentene transmetallation with triethylaluminium, Negishi *et al.*[118] arrived at the conclusion that cyclic zirconium structures cannot be involved in cyclometallation. Thus, considering the results of studies of the ethylmagnesation of monosubstituted alkenes (Dzhemilev reaction)[119] and the data on the reaction of Cp_2ZrCl_2 with $AlEt_3$ (Refs 120–122) and resorting to the data on the mechanism of alkyne carboalumination in the $Cp_2ZrCl_2-AlMe_3$ system,[88–91] Negishi *et al.*[118] proposed the mechanism of alkyne carbo- and cycloalumination with triethylaluminium in the presence of Cp_2ZrCl_2 shown in Scheme 16.[118]

By analogy with Scheme 7, the dipolar bimetallic complex **34b** was proposed as the active intermediate of carboalumination, whereas the cycloalumination pathway was dictated by five-membered intermediates **65** and **66**. The reaction of the latter with alkyne, resulting in aluminacyclopentenes **67** goes through the formation of intermediate seven-membered cyclic complexes **68** and **69** the structure of which is similar to the structure of previously observed compounds $Cp_2Zr(\mu\text{-}X)(\mu\text{-}CH_2CH{=}CHCH_2)AlR_2$ (X = H, Cl, I; R = Cl, Me, Et, Bu^i).[123,124]

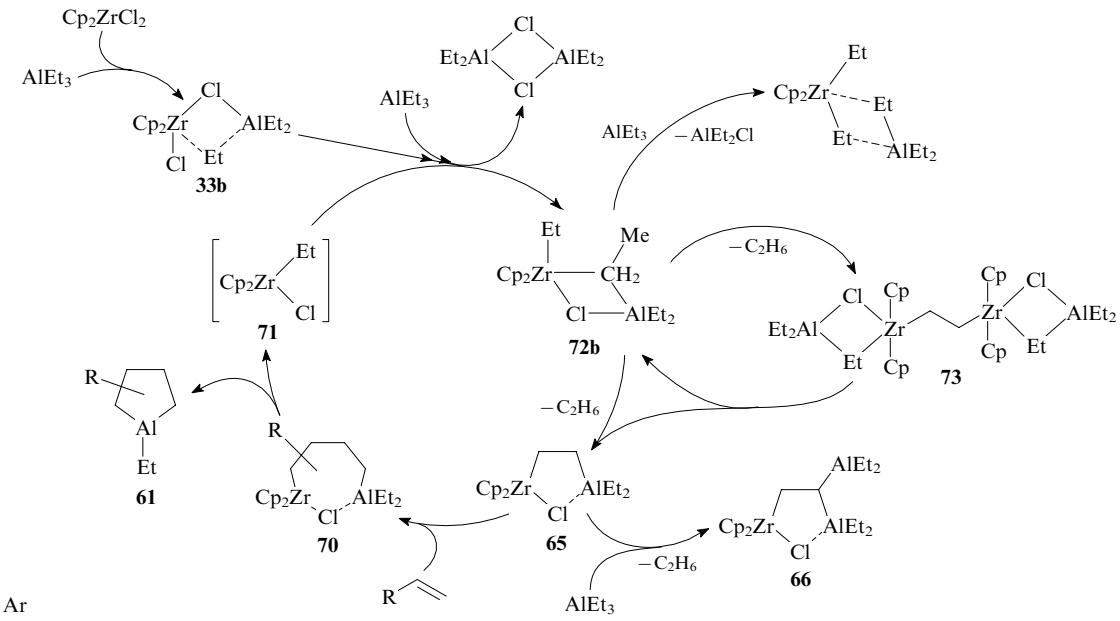
Our study of the mechanism of the cycloalumination of alkenes with $AlEt_3$ in the presence of Cp_2ZrCl_2 (Scheme 17) showed the formation of a large number of Zr,Al complexes,[120,121] where complex **65** being the key reaction intermediate.[125–128] This was also indicated by the estimated rate constants for particular steps.[129] The step of

Scheme 16



R = Alk, Ar

Scheme 17



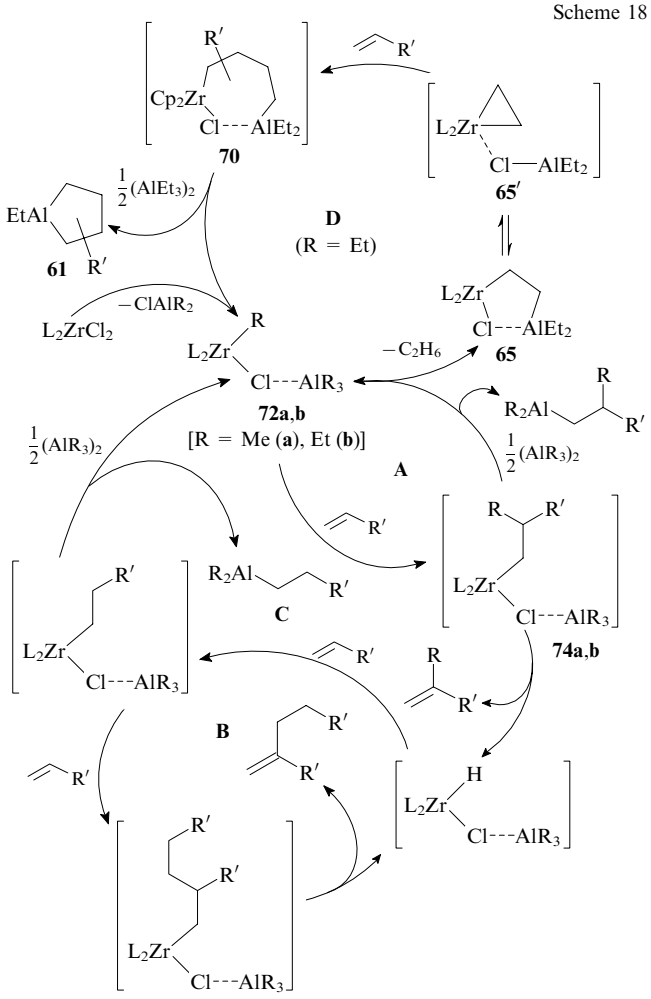
formation of five-membered complex **65** determines the rate of the whole cyclometallation process. An alkene molecule is inserted into this complex at the Zr−C bond with ring cleavage. This gives relatively unstable complex **70**, which is then converted to aluminacyclopentane **61** and ethyl zirconocene chloride **71**. The coordination of this species to a new $AlEt_3$ molecule results in the formation of active complex **72b** with closure of the catalytic cycle (see Scheme 17). The doubled complex **73** can arise as one of intermediates.

Based on studies of the effects of the OAC nature, catalyst structure and reaction conditions on the chemoselectivity of the reaction of alkenes with trialkylalanes catalyzed by the π-complexes L_2ZrCl_2 [L = Cp, η^5-C_5H_4Me, Cp*, η^5-C_9H_7 (indenyl), Flu (η^5-fluorenyl)][130–133] and considering the proposed[12,134,135] reaction mechanisms and experimental data on the ligand exchange between trialkylalanes and Zr π-complexes,[121,122,136] a reaction scheme was composed comprising catalytic cycles **A**−**D** with alkyl chloride complex **72** being the key intermediate (Scheme 18). The catalytic cycle of cyclometallation **D** is shown in more detail in Scheme 17.

The use of less electron-donating η^5-ligands in Zr complexes and chlorinated solvents results in a higher content of the catalyst active form **72**[131] and hence in acceleration of all steps, leading to a higher conversion of the alkene. The introduction of bulky substituents into the ligand,[94,95,98] together with the use of chlorinated solvents, probably retards the β-CH-activation in complexes **72** and **74** to a larger extent, and consequently the yield of carbometallation products increases. In the reaction with $AlEt_3$, the nature of the π-ligand contained in the catalyst has a weaker effect on the chemoselectivity than in the case of $AlMe_3$. Also, it was found that the β-hydride transfer in complex **72b** is accelerated in hydrocarbon solvents,[131] and, hence, the rate of formation of five-membered bimetallic intermediate **65** responsible for the cyclometallation pathway increases, resulting in higher yields of aluminacyclopentanes **61**.

Thus, carbo- and cyclometallation of alkenes and alkynes with OAC catalyzed by Zr π-complexes, as well as hydroalumination, are complex multistep processes involving numerous intermediate Zr,Al complexes (see Schemes 17 and 18). It was shown that the reaction chemoselectivity and rate are determined to a large extent by the composition and structure of the catalyst and the natures of the OAC and the solvent. In the mechanisms proposed above, the formation of the catalytically active sites is

Scheme 18



preceded by the steps of ligand exchange between the initial form of the catalyst and OAC, β-CH activation and alkene coordination on the catalytically active sites. These processes are discussed in detail in the following Sections.

1. Ligand exchange in the reactions of zirconocenes with organoaluminium compounds

a. Alkylation of zirconium π-complexes with organoaluminium compounds

It is knowin that in the formation of active sites in the Ziegler–Natta systems, a key step is the reaction of transition metal salts or compounds with a co-catalyst where alkyl, alkenyl or aryl σ-ligands migrate from a main group element atom to a transition metal atom. Well-known methods of the preparation of alkyl(aryl)-substituted zirconocenes[48,50,88,89,91,118,120,121,136–169] include reactions of L_2ZrCl_2 with organolithium and -aluminium compounds and with Grignard reagents.

In has been noted[140] that it is very difficult to control the degree of substitution in such systems (in particular, it is difficult to stop after monosubstitution), because there is probability of disproportionation of the monoalkyl chloride to dichloro and dialkyl derivatives. In a ^{1}H NMR study of the equilibrium between Cp_2ZrR_2, Cp_2ZrX_2 and Cp_2ZrRX in THF, the half-lives of the complexes ($\tau_{1/2}$) and the equilibrium constant (K_{eq}) of this reaction were determined.[142]

$$Cp_2ZrX_2 + Cp_2ZrR_2 \rightleftharpoons 2\,Cp_2ZrRX \qquad (1)$$

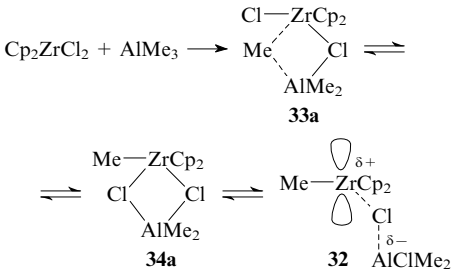
R = Me, Ph; X = F, Cl, Br, I

In terms of the exchange rate, ligands were arranged in the following order: F, I > Cl, Br and Me ≫ Ph. The origin of this order of exchange rates of halide ligands was not discussed in the study cited, and the lower activity of Cp_2ZrPh_2 in ligand exchange as compared with Cp_2ZrMe_2 was attributed to higher strength of the Zr–Ph bond compared with the Zr–Me bond.[143] Note that some authors actually consider the fluoride ion to be the best leaving σ-ligand, which accounts for the higher activity of fluorinated zirconocenes in the polymerization.[65,170–173] It is of interest that the exchange rates for analogous titanium complexes[144] depend to a lesser extent on the ligand nature than in the case of zirconium complexes.

Among other factors that affect the degree of replacement of chlorine atoms in zirconocenes, the size of alkyl σ-ligands should also be noted. For example, by alkylation of metallocene dichlorides using $LiCH_2Ph$, dialkyl derivatives were obtained, while this reaction with $LiCH(SiMe_3)_2$ yielded alkyl metallocene chlorides.[145] The different behaviour of these reagents in this reaction is probably related to steric factors. Because of its large bulk, the $CH(SiMe_3)_2$ group can replace only one chlorine atom. The second chlorine atom can be replaced by a less bulky group such as Bu^n but not Bu^t or $N(SiMe_3)_2$. More recently, various mono- and dialkyl derivatives of Ti, Zr and Hf cyclopentadienyl complexes were studied.[147,149,166] It was also shown in the mentioned studies that an increase in the size of the alkyl ligand entails a decrease in the degree of alkylation of metallocenes.

The use of $AlMe_3$ instead of MeLi as the alkylating agent at the molar ratio $Cp_2ZrCl_2 : AlMe_3 = 1:1$ affords only dimethyl derivative, some of Cp_2ZrCl_2 remaining unreacted.[141] Subsequently, in an attempt to determine the structure of intermediates of alkyne methylalumination, it was noted[88] that the structure of the product formed in the reaction of Cp_2ZrCl_2 with $AlMe_3$ in dichloroethane could not be determined unambiguously; however, a ^{1}H NMR study demonstrated the existence of fast alkyl exchange between the starting Zr complex and trialkylalane to give alkyl zirconocene $Cp_2ZrMeCl$.

The systems Me_mAlCl_{3-m}–$Me_nCl_{2-n}ZrCp_2$ ($m = 1-3$, $n = 0-2$) in 1,2-dichloroethane were studied by NMR in the −50 to 80 °C temperature range.[89,91] Unfortunately, the authours did not assign the NMR data to the structures of bimetallic complexes formed in these systems. All four systems exhibited carbometallating properties; however, the highest product yields were observed for the systems $Cp_2ZrCl_2-AlMe_3$ and $Cp_2ZrMeCl-AlMe_3$. A study of the reaction of Cp_2ZrCl_2 with $AlPr^n_3$ (1 : 1) in 1,2-dichloroethane demonstrated the formation of Cp_2ZrPr^nCl (⩽60%), and unreacted Cp_2ZrCl_2 also remained in the system (40%–45%). It was shown that no alkyl–chloride intermolecular exchange occurs in the system Cp_2ZrCl_2–$ClAlR_2$ (R = Me, Pr^n). It was noted[118] that the systems $ClAlMe_2-Cp_2ZrCl_2$ and $ClAlEt_2-Cp_2ZrCl_2$ exhibit no carbometallating properties in hexane. In view of the obtained experimental data, the authors assumed that the following bimetallic complexes are formed in the system $Cp_2ZrCl_2-AlMe_3$ (see also Scheme 7):



A more detailed study of the ligand exchange in the discussed systems was carried out by dynamic NMR spectroscopy.[136] On mixing Cp_2ZrCl_2 with Al_2Me_6 in a 1 : 1 ratio in benzene-d_6, the authors observed the formation of the monomethylated complex $Cp_2ZrMeCl$, which has long been in equilibrium with Cp_2ZrCl_2. The interconversion rate of Cp_2ZrCl_2 and $Cp_2ZrMeCl$ was found to be 2–3 s^{-1} at 30 °C. The complete transformation of Cp_2ZrCl_2 into $Cp_2ZrMeCl$ is attained by using a 20-fold excess of Al_2Me_6. A further increase in the OAC concentration does not result in the formation of the dimethyl derivative Cp_2ZrMe_2. The authors suppose that partial association of Cp_2ZrCl_2 and $Cp_2ZrMeCl$ with $AlMe_3$ or $ClAlMe_2$ may take place, because the ^{1}H and ^{13}C NMR spectra show a downfield shift of the Cp signals. However, if the association does occur, the exchange between Cp_2ZrCl_2 and $Cp_2ZrMeCl$ becomes impossible. Due to the lack of adequate information about the equilibrium processes, the following equation was chosen as the basic postulate:

$$Cp_2ZrCl_2 + Al_2Me_6 \rightleftharpoons Cp_2ZrMeCl + Al_2Me_5Cl \qquad (2)$$

The equilibrium constant for this reaction was determined from the equation

$$K_{eq} = \frac{[Cp_2ZrRCl][Al_2R_5Cl]}{[Cp_2ZrCl_2][Al_2R_6]} = \frac{Q}{I(1+1/Q)-1},$$

where

$$Q = \frac{[Cp_2ZrRCl]}{[Cp_2ZrCl_2]},$$

$$I = \frac{[Al_2R_6]_0}{[Cp_2ZrCl_2]_0}.$$

At $I = 1-15$, the equilibrium constant $K_{eq} = 0.49 \pm 0.008$, and at $I = 20$, $K_{eq} = 0.74 \pm 0.06$.[136] Thus, an increase in the excess of OAC, which is a Lewis acid, promotes the formation of a strong Lewis base, $Cp_2ZrMeCl$.

Thus, the alkyl exchange was studied for various trialkylalanes ($AlEt_3$ and $AlBu^i_3$) and zirconium complexes [Cp_2ZrCl_2, $(C_5H_4Me)_2ZrCl_2$, $(1,3\text{-}Me_2C_5H_3)_2ZrCl_2$, $(1,2,3\text{-}Me_3C_5H_2)_2ZrCl_2$, $(C_5HMe_4)_2ZrCl_2$, $Cp^*_2ZrCl_2$, $(C_5H_4Bu^t)_2ZrCl_2$, $(C_5H_4SiMe_3)_2ZrCl_2$, $Me_2Si(C_5H_4)_2.ZrCl_2$, $Me_4C_2(C_5H_4)_2ZrCl_2$, (BCDI)$(C_5H_4)_2ZrCl_2$ (BCDI is bicyclohexane-1,1′-diyl], *rac*-(SBI)$ZrCl_2$, *rac*-(EBI)$ZrCl_2$, $Me_2Si(2\text{-}Me_2NC_9H_5)_2ZrCl_2$, $Me_2C(Flu)(C_5H_4)ZrCl_2$]. It was found that the reaction of Cp_2ZrCl_2 with $AlEt_3$ proceeds 10 times faster ($K_{eq} \approx 5$) than with $AlMe_3$. For Al : Zr = 2 : 1 or 4 : 1, ethane evolution was observed, and various zirconocene derivatives formed. In the case of $AlBu^i_3$, decomposition of reaction products occurs even at the ratio Al : Zr = 1 : 1. The increase in the rate of the alkyl exchange following an increase in the size of the alkyl substituent in OAC was ascribed to lower stability of the ethyl-bridged $AlEt_3$ dimer as compared with the $AlMe_3$ dimer and to higher energy of the formation of the product of the reaction with zirconocene chloride, Al_2Et_5Cl, which also has a bridging Cl atom. Indeed, a study of alkyl exchange in the trialkylalane dimers showed[174] that an increase in the size of alkyl groups in trialkylalanes accelerates the alkyl exchange by increasing the fraction of the monomeric form the stability of which increases with increase in the bulk of the alkyl substituent. Unlike trialkylalanes, no intramolecular exchange occurs in alkyl aluminium halides owing to the formation of halogen-bridged dimeric structures.[175]

In the publication cited above,[136] it was shown that the lowest K_{eq} values (~ 0.005) correspond to the cyclopentadienyl derivatives with a large number of methyl substituents in the π-ligand, and the highest values (~ 1) are characteristic of Zr complexes with indenyl ligands linked by Me_2Si moieties. These results were interpreted as being due to the change in the electron density on the Zr atom. As the number of methyl substituents in the Cp ring increases, the electron density on the Zr atom increases and, hence, K_{eq}, decreases. This is consistent with data on the electronic properties of various zirconocenes obtained by X-ray photoelectron spectroscopy.[176, 177] Thus, Beck and Brintzinger[136] propose using K_{eq} as a measure of the electron density on Zr, although they do not rule out a contribution of the steric factor to the constant. The obtained data also attest to a relatively low electron density on the Zr atom in indenyl *ansa*-complexes. This observation is consistent with the general trend according to which indenyl ligands are less electron-donating than cyclopentadienyl ligands due to higher tendency to η^3-coordination.[178, 179]

An X-ray photoelectron spectroscopy study of the electronic properties of zirconocene derivatives demonstrated[180] that consecutive replacement of chlorine atoms in the Cp_2ZrCl_2 complex by methyl groups results in a substantial increase in the electron density on the Zr atom. In a study of unsymmetrically substituted ruthenocenes, π-ligands were arranged in the order of decreasing electron-donating properties: Flu > Cp* > Ind > Cp.[181]

However, subsequently it was found[137] that K_{eq} depends on the initial concentrations of Cp_2ZrCl_2 and Al_2Me_6, which may be due to the formation of adducts [$Cp_2ZrMeCl \cdot ClAlMe_2$]. Therefore, the authors of the cited paper investigated other equilibria in the presence of catalytic amounts of MAO:

$$L_2ZrCl_2 + Cp_2ZrClMe \rightleftharpoons L_2ZrClMe + Cp_2ZrCl_2 \quad (3)$$

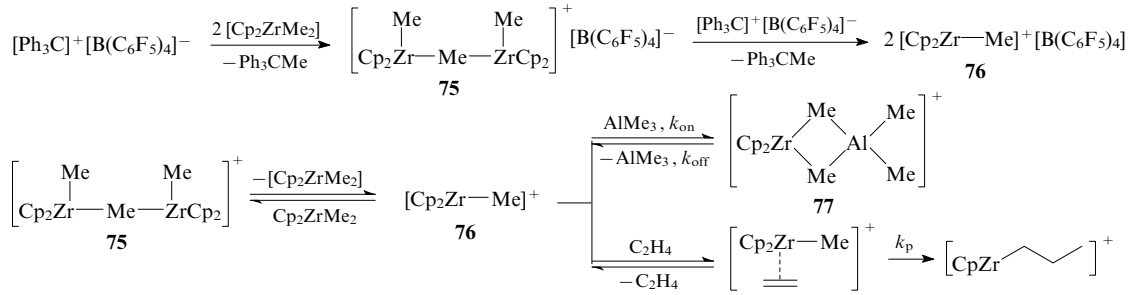
L = Cp*, 1,3-$Me_2C_5H_3$, $(Me_3Si)_2C_5H_3$, $Me_3SiC_5H_4$, MeC_5H_4, Ind;
L_2 = $Me_2Si(C_5H_4)_2$, $Me_2Si(2\text{-}MeInd)_2$, SBI, *etc.*

The free energy of the exchange (ΔG°_{exc}) determined for equilibrium (3) was in good agreement with the values ΔG°_{exc} calculated previously for equilibrium (2). Thus, the thermal effect related to the formation of the less polar Zr–C bond after cleavage of the more polar Zr–Cl bond is most sensitive to changes in the electron density on the metal atom, which in turn is determined by the nature of the π-ligand occurring in the complex.

During a ^1H and ^{13}C NMR study of the structures of complexes formed in the reaction of L_2ZrCl_2 and AlR_3 (L = Cp, Cp*; R = Me, Bu^i, Oct^i), the complexes [$L_2ZrRCl \cdot AlR_3$] occurring in a mixture with the unreacted starting L_2ZrCl_2 were detected[159] (these results were confirmed in other works[35, 36] for the system L_2ZrCl_2 + $AlBu^i_3$). It was shown[159] that an increase in the size of the alkyl substituent in OAC leads to higher content of the zirconocene alkyl complex, while the starting Cp_2ZrCl_2 is no longer detected. When the Cp ligand is replaced by Cp*, the alkylation rate decreases due to steric hindrance.

In this series of works, rather interesting results were obtained in a study of ionic-polymerization catalytic systems based on dimethyl zirconocene derivatives and organoboron compounds. It was found[182] that the reaction of Cp_2ZrMe_2 with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in CD_2Cl_2 at −60 °C affords binuclear complex **75** (Scheme 19) the stability of

Scheme 19



which depends on the content of $[Ph_3C]^+$ and the structure of the ligand. On heating, complex **75** is converted to monomeric cation **76**, which forms complex **77** in the presence of $AlMe_3$.

In this system, the active species is probably cation **76**. Thus, the observed decrease in the catalytic activity upon an increase in the dimethylzirconocene concentration may be caused by the shift of the equilibrium toward complex **75**. An excess of $AlMe_3$ is also undesirable, because in this case, the equilibrium shifts toward complex **77**, which is coordinatively saturated and has no vacant orbitals for binding the alkene.

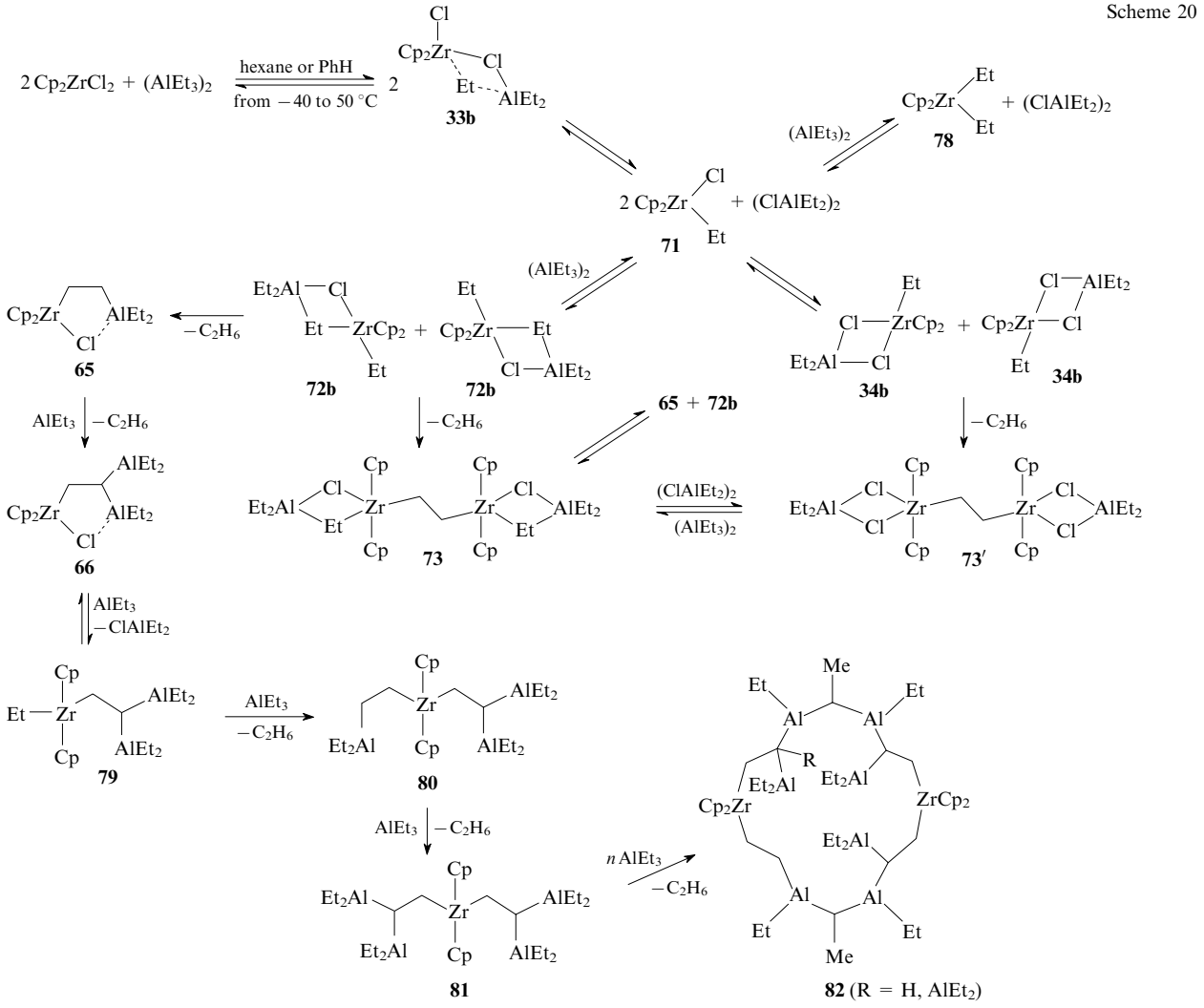
The 2D NMR experiments (2D EXSY method) carried out later confirmed [108] the existence of the exchange by methyl groups between complex **77** and free $AlMe_3$; however, no exchange took place between the bridging and the terminal methyl groups in complex **77** with either excess or deficit of $AlMe_3$. The exchange by methyl groups was also found in a mixture of $L_2Zr(^{13}CH_3)_2$ and $AlMe_3$.[107, 183] Presumably, this exchange occurs *via* the ion pair $[L_2ZrMe]^+[AlMe_4]^-$ (Refs 68 and 105). Here the zirconium complex functions as the methyl group donor and trimethylaluminium is the methyl group acceptor. Petros and Norton [108] made a similar assumption according to which the exchange should involve the formation of cation **76**, which coordinates the alkene. In an NMR experiment, the rate constant k_{off} was determined; this constant affects the carboalumination rate: the greater k_{off}, the higher the activity of the system (see Scheme 19).

The k_{off} value decreases in the series of ligands EBI > Cp > EBTHI, which is in agreement with the order of decreasing the electrophilicity of alkyl metallocene cation **76**. Indeed, the catalyst $(EBTHI)ZrMe_2$ was almost inactive in the reaction with alkenes, whereas $(EBI)ZrMe_2$ showed high activity.

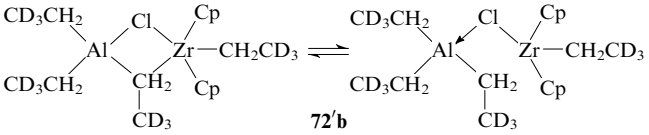
A great contribution to the study of the systems $Cp_2ZrCl_2 - AlEt_3$ was made by Kaminsky *et al.*[120, 121] They were able to show that ethyl zirconocene chloride (**71**) formed in this reaction, can be coordinated to a trialkylalane molecule in the presence of an excess of $AlEt_3$ to give rather stable four-membered bimetallic complex **72b** (Scheme 20).

On replacement of the H-form of trialkylalane by deuterated analogue, it was possible to follow the dynamic processes typical of complex **72b**. Thus in the ^1H NMR spectrum of the compound obtained in the reaction of $Cp_2ZrEtCl$ with $Al(CH_2CD_3)_3$ in toluene-d_8, the CH_2 signals of the reaction product were shifted downfield relative to those of pure $Al(CH_2CD_3)_3$. The authors also found a decrease in the temperature of coalescence of the resonance signals of the bridging and terminal ethyl groups at the aluminium atom in the system $Cp_2ZrEtCl - AlEt_3$ as com-

Scheme 20



pared with the dimer $(AlEt_3)_2$, which was attributed to the formation of complex **72b**. The retarded exchange is possible due to the existence of dynamic equilibrium



72′b

The formation of complex **72b** in the reaction of Cp_2ZrCl_2 with $AlEt_3$ was also supported in other works.[125–128] Kaminsky *et al.*[120,121] did not rule out the coordination of $Cp_2ZrEtCl$ to the $ClAlEt_2$ molecule formed in the first step. This should afford complex **34b**, which, however, was not isolated. Probably, this complex is unstable, because the reaction of zirconium chloroalkyl and chloroalkenyl complexes with $ClAlR_2$ or with $AlCl_3$ was shown[69] to result in immediate formation of Cp_2ZrCl_2 and dialkyl alkenyl aluminium derivative. Subsequently it was found[131] that the reaction of $ClAlEt_2$ with $Cp_2ZrEtCl$ rapidly affords Cp_2ZrCl_2 and $AlEt_3$ even at low temperature (−90 °C). In our study, it was found[35,36] that the reaction of $ClAlBu^i_2$ with Cp_2ZrRCl (R = Alk) in benzene proceeds at high rate to give Cp_2ZrCl_2 and alkylalane. Thus, complexes **33a**,**b** and **34a**,**b** are most likely unstable.

Apart from the alkyl zirconocene chloride derivatives formed in the reaction of Cp_2ZrCl_2 and $AlEt_3$, Kaminsky *et al.*[120,121] do not rule out the formation of diethyl zirconocene **78** upon the exchange reaction of $Cp_2ZrEtCl$ with a new $AlEt_3$ molecule (see Scheme 20); however, no evidence for its existence is given. Unlike unstable diethylzirconocene, diethyl hafnocene Cp_2HfEt_2 is a stable compound.[68,184–186]

The doubled intermediate **73** decomposes under certain conditions to give ring **65**, which undergoes a number of transformations to be converted to complexes **79**–**82**.

Thus, the reactions of zirconocene dichlorides with trialkylalanes give bimetallic Zr,Al alkyl complexes. The degree and rate of alkylation depend on both the steric and electronic factors of π-ligands contained in the zirconium complexes and the nature of the organoaluminium reagent, namely, on the fraction of the monomer in the monomer–dimer equilibrium.

However, the ligand exchange step also arrives at equilibrium, *i.e.*, along with the forward reaction, the reverse reaction may occur in which the alkyl-substituted zirconocene reacts with alkyl aluminium chloride to be converted to the starting zirconocene dichloride. The transmetallation of Zr alkyl and alkenyl complexes with aluminium compounds is, most often, the final step of the reactions of OAC with alkenes catalyzed by transition metal complexes, although this is actually the same ligand exchange. Therefore, transmetallation is considered in the next Section.

b. Transmetallation of zirconium alkyl and alkenyl complexes in reactions with organoaluminium compounds

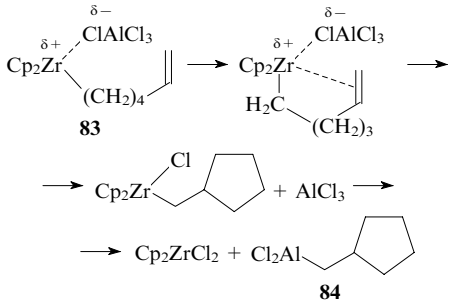
The first study of the transmetallation step, *i.e.*, the transfer of alkyl or alkenyl group from Cp_2ZrRCl to aluminium atom, was reported by Schwartz and Carr[187] in 1976 for the reaction of Cp_2ZrRCl with $AlCl_3$.

$$\underset{\mathbf{3}}{Cp_2ZrRCl} + AlCl_3 \xrightarrow[0\ ^\circ C,\ 10\ min]{CH_2Cl_2} Cp_2ZrCl_2 + RAlCl_2$$

R is alkyl or alkenyl

It was found[187] that the reaction of zirconium alkyl complexes **3** with $AlCl_3$ proceeds much more slowly than with the corresponding alkenyl derivatives of aluminium. In addition, zirconium alkyl complexes form only monoalkyl aluminium chloride $RAlCl_2$ with an excess of $AlCl_3$, while alkenyl complexes may afford both mono- and di- or trialkenylalanes depending on the Zr : Al ratio.

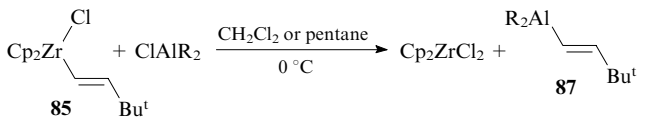
As a rule, the configuration of double bonds in the alkenyl residue does not change upon transmetallation. However, a study by low-temperature NMR spectroscopy (from −46 to 24 °C) carried out by the same researchers demonstrated that the reaction of $Cp_2Zr(Cl)[(CH_2)_4.CH{=}CH_2]$ (**83**) with $AlCl_3$ is accompanied by intramolecular cyclization of the alkenyl substituent, giving rise to cyclopentylmethyl aluminium dichloride (**84**).[69] Initially, $AlCl_3$ is coordinated to the organozirconium compound through chloride ligands, thus increasing the partial positive charge on the zirconium atom. This facilitates the coordination of a remote double bond to the transition metal atom.



83 **84**

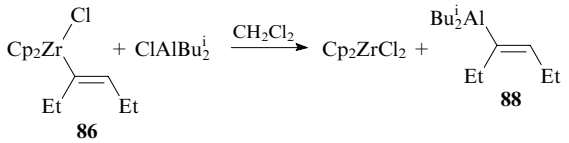
According to Carr and Schwartz,[188] cyclization of this type occurs at high temperatures with alkenylalanes containing a remote double bond in one of the alkenyl groups. A similar cyclization giving transmetallation products **84** might be also possible at low temperature due to the high electron density at the aluminium atom in the molecule of $[CH_2{=}CH(CH_2)_4]AlCl_2$ as compared with alane molecules, $[CH_2{=}CH(CH_2)_4]AlAlk_2$.

The zirconium alkenyl complexes **85** and **86** can also be transmetallated on treatment with dialkyl aluminium chlorides, resulting in the immediate formation of Cp_2ZrCl_2 and alkenylalanes **87** and **88**.[69]



85 **87**

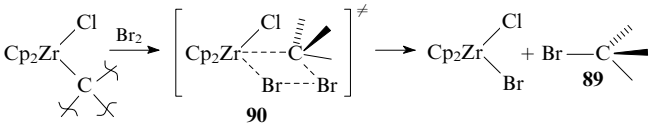
R = Me, Bu^i



86 **88**

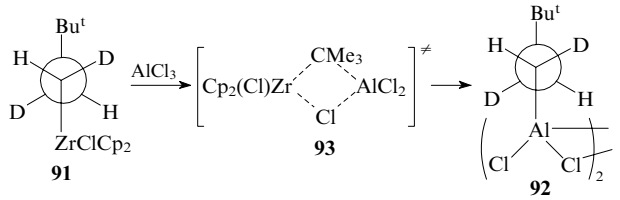
Carr and Schwartz[69] believe that the transfer of σ-bonded alkyl substituents from zirconium to aluminium is similar to bromination of alkyl(alkenyl) zirconocene

chloride, which follows the electrophilc cleavage mechanism. The alkyl halide **89** molecule is formed with retention of the configuration of substituents at the zirconium-bonded carbon atom, which is possible if the reaction goes through cyclic transition state **90**.[69]



The electrophilic reagent is initially coordinated to the Zr atom, lending an electron pair to a free low-lying orbital of the metal atom, which is favourable for a frontal attack on the Zr–C bond. The subsequent polarization of the coordinated electrophilic reagent results in bond cleavage and ring opening in the transition state.

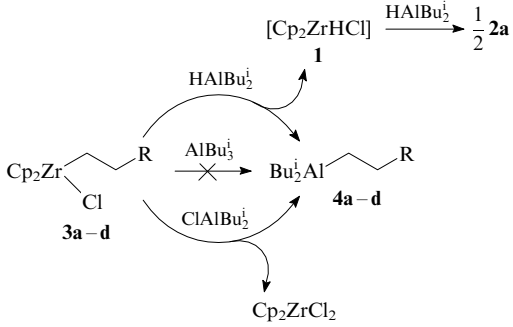
Study of transmetallation of deuterated organozirconium compound **91** by $AlCl_3$ showed that this reaction does indeed occur with retention of the configuration of substituents at the α carbon atom to give alkylalane **92**, which also supports the hypothesis on the possibility of transmetallation *via* a four-centre transition state **93** similar to the transition state **90** in the reaction with halogens.



Carr and Schwartz[187] present the following fact as evidence for the statement that transmetallation occurs *via* transition state **93**. It turned out that vinyl substituted OAC associated by means of bridging bonds involving sp^2-hybridized carbon atoms are more stable than alkyl analogues. Therefore, if transmetallation occurs *via* transition states similar to **93**, the transfer of alkenyl group from zirconium to aluminium should be faster than the transfer of alkyl group, which is in fact observed in experiments.[187]

For more detailed investigation of the transmetallation, the reactions of Cp_2ZrRCl with various OAC were studied in toluene at 22 °C[35,36] (Scheme 21).

Scheme 21

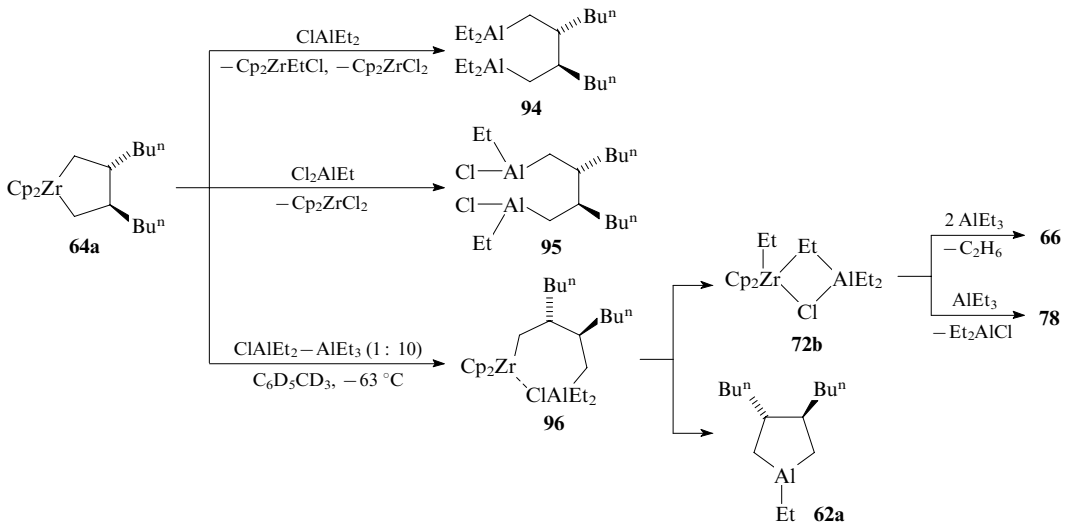


R = n-C_nH_{2n+1} [n = 5 (**a**), 6 (**b**), 7 (**c**), 8 (**d**)]

As it was found, Cp_2ZrRCl (**3a–d**) react with $HAlBu^i_2$ to give alkylalanes **4a–d** and complex **2a**. The latter is formed upon the fast reaction of Cp_2ZrHCl formed *in situ* with $HAlBu^i_2$. The reaction of complexes **3a–d** with $ClAlBu^i_2$ gives Cp_2ZrCl_2 and alkylalanes **4a–d**. Furthermore, $AlBu^i_3$ does not transmetallate compounds **3a–d**.

For elucidating the role of zirconacyclopentane intermediates in the cycloalumination of alkenes, a group of researchers[125,126,128] studied, using a model reaction, the reaction of *trans*-3,4-dibutylbis(η⁵-cyclopentadienyl)zirconacyclopentane (**64a**) prepared earlier[112] with OAC in toluene-d_8. It was shown that compound **64a** is not transformed under the action of $AlEt_3$. A similar result was obtained earlier for 2,3-dibutylbis(η⁵-cyclopentadienyl)zirconacyclopent-2-ene.[118] Dzhemilev and co-workers[125,128] succeeded in demonstrating that the reaction of $ClAlEt_2$ with zirconacyclopentane **64a** gives rise to a mixture of Cp_2ZrCl_2, $Cp_2ZrEtCl$ and 1,4-dialuminium derivative **94**. Ethyl aluminium dichloride rather slowly converts compound **64a** to Cp_2ZrCl_2 and chlortinated 1,4-dialuminium derivative **95**. Thus, the step of transmetallation of zirconacyclopentane into aluminacyclopentane cannot be accomplished by means of individual trialkylalanes or dialkyl aluminium halides (Scheme 22). Meanwhile, the joint use of both $AlEt_3$ and $ClAlEt_2$ (10 : 1) leads to transmetallation of zirconacyclopentane **64a** to aluminacyclopentane **62a**.

Scheme 22



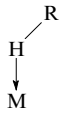
When this reaction is carried out at low temperature (−63 °C), it is possible to detect an intermediate, which was identified as structure **96** considering published data.[123,124] Complex **96** is fairly unstable being decomposed to give 3,4-disubstituted aluminacyclopentane **62a** and complex **72b**. The latter, in turn, is converted to complexes **66** and **78** (see Schemes 17 and 20).

Thus, the final step of transmetallation of zirconium alkyl or alkenyl complexes formed during the Zr π-complex-catalyzed reaction of alkenes or alkynes with OAC should apparently involve alkyl aluminium chlorides or hydrides, which are stronger Lewis acids than trialkylalanes.

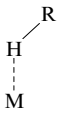
2. CH Activation processes in zirconium alkyl complexes

As a rule, transition metal alkyl complexes undergo activation and oxidative cleavage of the C−H bond to give a metal–hydrogen bond. The intramolecular coordination at C−H bonds resulting in the formation of M−H−C bridges is typical of most transition metals.[189] The arising bond is classified as a three-centre two-electron bond. This bond is formed either to complete the electron shell of the metal atom, which formally has 12–16 electrons, by the electron pair of the C−H bond to 18 electrons or to reduce the electron deficiency by 2 electrons. By now, transition metal complexes with M−H−C agostic bond have been characterized almost for all transition metals by structural methods in the solid phase or in solution.

The agostic and non-agostic M−H−C interactions are responsible for different structural and spectral characteristics.[190] For example, in the case of agostic interactions, the M−H distances are relatively short (1.8–2.3 Å) and the M−H−C angles are rather small (90–140°); non-agostic interactions tend to have longer M−H bonds (2.3–2.9 Å) and greater M−H−C angles (110–170°). In the ^{1}H NMR spectra, agostic interactions are responsible for a decrease in the corresponding spin−spin coupling constants $^1J_{CH}$ by 50–100 Hz. Moreover, the protons involved in agostic interactions are highly shielded, whereas in the case of non-agostic interactions the proton signals usually occur in lower field.



Agostic three-centre two-electron interaction

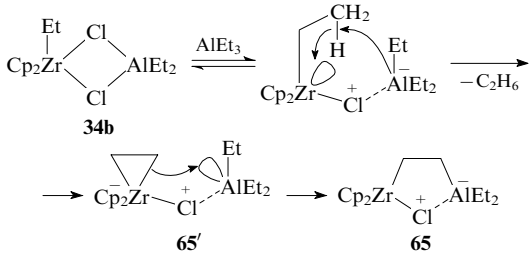


Non-agostic electrostatic interaction

In the case of zirconocene complexes, β-CH-activation processes are more typical.

As shown by Kaminsky *et al.*,[120–122] in the system $Cp_2ZrEtCl-AlEt_3$ upon temperature increase from −93 °C to 0 °C, Zr,Al alkyl complex **72b** is converted upon β-CH activation to complexes **65**, **73** and **73′** with ethane evolution (see Scheme 19). Complexes **73** and **73′** are poorly soluble in benzene; therefore, they precipitate when the reaction is carried out in concentrated solutions without excess of triethylaluminium. The formation of ethane and a compound with the $-ZrCH_2CH_2Zr-$ moiety in the reaction of Cp_2ZrCl_2 with $AlEt_3$ was established earlier.[191] The authors note that the system $Cp_2ZrCl_2-AlEt_3$ differs crucially from $Cp_2TiCl_2-AlEt_3$. In the latter system, Ti^{IV} is reduced to Ti^{III} and a mixture comprising ethane (50%), ethylene (45%) and C_4 hydrocarbons (5%) is evolved. A complex with an dizirconium ethylene moiety was synthesized in the reaction of Cp_2ZrMe_2 with $[Cp_2ZrEt.(CH_2{=}CH_2)]MgBr$ or EtMgBr and in the reaction of Cp_2ZrEt_2 with Cp_2ZrX_2 (X = Cl or Br).[192,193]

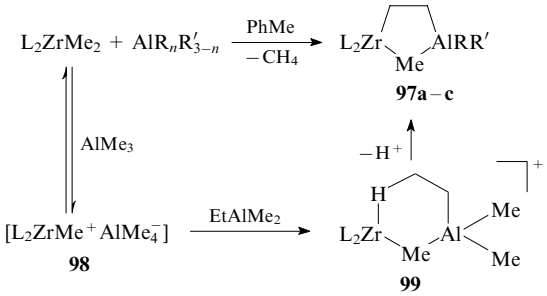
As the content of $AlEt_3$ increases, complexes **73** and **73′** can be destroyed to give complex **65**, which undergoes a second β-hydride transfer to be converted to complex **66** and then to complexes **79**–**82** (see Scheme 20).[120,121] It was noticed that these compounds reacted with terminal alkenes and 1,3-dienes in the presence of excess triethylaluminium but the products were not identified. The addition of water leads to the formation of alumoxanes, which are highly efficient homogeneous catalysts for polymerization of terminal alkenes and ethylene.[122] Negishi *et al.*[118] also noted that the formation of a five-membered bimetallic complex **65** requires β-H activation (see Scheme 16). The addition of an excess of Et_2AlCl to complex **33b** does not induce β-hydride transfer. The authors believe that the additional (second) equivalent of triethylaluminium replaces chlorodialkylalane in molecule **34b**, and complex **72b** thus formed undergoes bimetallic CH activation, which is possibly induced by β-agostic interaction in the EtZrCl moiety. An additional equivalent of $AlEt_3$ is needed to a higher extent than $ClAlEt_2$, as the latter forms relatively stable compound **34b**, which is less prone to form an open activated complex similar to structure **72b**. The formation of ring **65** occurs *via* zirconacyclopropane complex **65′** (see Refs 117, 184, 194–196).



It is of interest that reactions of these Zr, Ti or Hf metallacyclopropene complexes with OAC afford five-membered ethylidene bimetallic compounds with a planar four-coordinate carbon atom.[197–203]

Five-membered bimetallic complexes were also prepared[68] in the reaction of mixed aluminium trialkyls with dimethyl zirconocene (Scheme 23).

Scheme 23

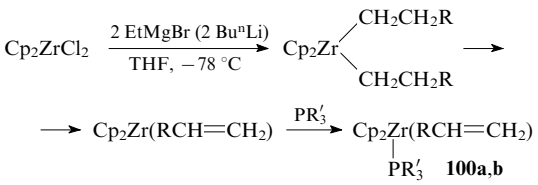


L = Cp or L$_2$ = $Me_2Si(C_5H_4)_2$; R = Me, R′ = Et; n = 0, 2;
97: R = R′ = Me (**a**), Et (**c**); R = Me, R′ = Et (**b**)

The reaction is accompanied by methane evolution. Complexes **97a**–**c** formed in the reaction are inactive with respect to ethylene in toluene solutions. The authors postu-

lated a mechanism according to which the first step of the reaction gives ion pair **98**. Then the electron-deficient carbon atom in L_2ZrMe^+ is solvated by trimethylaluminium to give $Zr-Me-Al$ and $Zr-H-CH_2-Al$ bridging bonds (complex **99**), as follows from mass-spectrometric investigations of this system in the gas phase. It is of interest that in structures like $[L_2ZrMe]^+[MeB(C_6F_5)_3]^-$, α-agostic interaction of hydrogen atoms of the methyl bridge with the transition metal atom occurs both in the solid state and in solution.[103, 104, 204] Apparently, in the presence of $EtAlMe_2$, agostic $Zr-H-CH_2-CH_2-Al$ interaction is possible.[68, 205] This interaction makes the agostic hydrogen atom more acidic; its subsequent elimination induced by $AlMe_3$ (or $AlMe_4^-$) affords metallacycle **97**. According to this scheme, complex **97** obtained from $Cp_2Zr(^{13}CH_3)_2$ had the ^{13}C label only in the $Zr-Me-Al$ bridging position. Thus, $AlMe_3$ may act as a Lewis acid (CH_3^- acceptor) and a Lewis base (H^+ acceptor). This type of behaviour of AlR_3 was observed by Grubbs and co-workers[206] in the reaction of Cp_2TiCl_2 with $AlMe_3$. A process similar to the above-described one occurs in MAO-activated catalytic systems. For example, in the reaction of alkyl metallocene with MAO, the α-hydride transfer and elimination of methane produce structures containing $Zr-CH_2-Al$ and $Zr-CH_2-Zr$ moieties, which are regarded catalytically inactive.[207, 208]

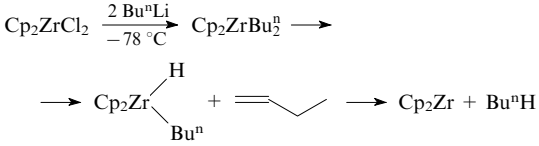
It was ascertained[184, 209] that Cp_2ZrEt_2 obtained in the reaction of Cp_2ZrCl_2 with 2–3 equiv. of EtMgBr in THF at −78°C is unstable and, upon β-CH activation, it is converted to zirconocenecyclopropane. The addition of substituted phosphines in the reaction mixture yields stable complexes **100a**,**b**. As shown previously by Alt *et al.*,[194] compound **100** is zirconacyclopropane, the phosphorus atom being located in the plane of the three-membered ring.



R = H (**a**), Et (**b**); PR'_3 = PMe_3, PMe_2Ph, $PMePh_2$

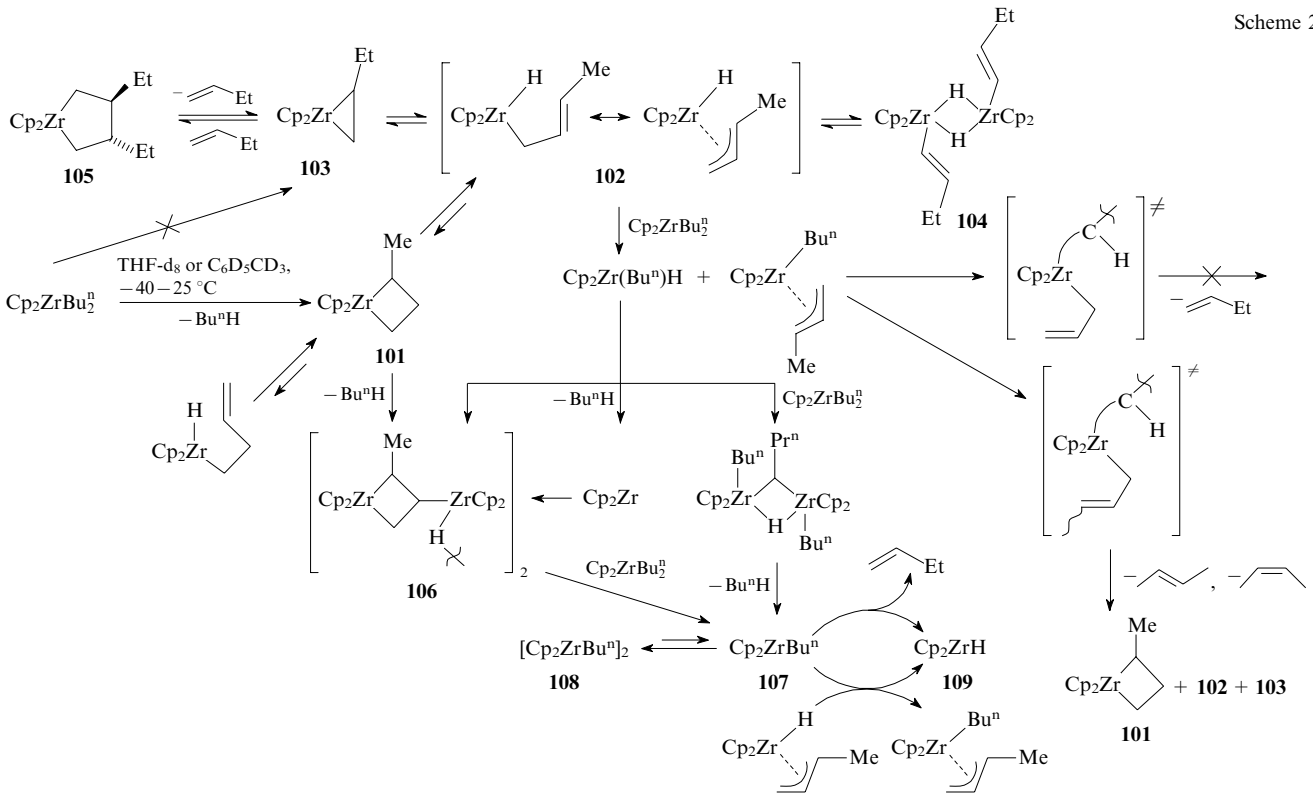
In the case of hafnium complexes, dialkyl derivatives were stable even at room temperature and gave alkene complexes similar to compounds **100a**,**b**.[184]

The use of butyllithium in this reaction results in the corresponding zirconocenebut-1-ene complexes **100b**, although previously it was supposed[162] that di-n-butyl zirconocene derivative decomposes to give '$ZrCp_2$' (this species was also considered as an intermediate in Scheme 15). This transformation is not accompanied by reductive elimination of n-octane (according to GLC). Cp_2ZrBu^nH formed upon β-elimination of but-1-ene from the complex $Cp_2ZrBu^n_2$, was considered as the most probable reaction intermediate



Ten years later, the system $Cp_2ZrCl_2-Bu^nLi$ was studied in detail by NMR spectroscopy.[169] It was found (Scheme 24) that $Cp_2ZrBu^n_2$ is unstable and decomposes to give butane as a result of γ-hydride transfer in the butyl

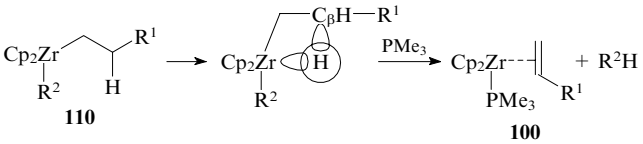
Scheme 24



group to give zirconacyclobutane **101**, which has not been observed experimentally but was postulated keeping in mind the observed reaction products. Complex **101** was converted to butenyl zirconocene hydride **102** from which zirconacyclopropane **103** and dimeric product **104** were formed. The subsequent thermolysis of the mixture furnished complexes **104**–**106**, which were stable for several days at room temperature.

In this scheme, the mechanism of formation of complex **105** remains obscure, because but-1-ene needed for this was not detected in the reaction mixture. The metal complex $Cp_2ZrBu^n_2$ can react with complex **102** through dimerization or ligand exchange steps. The subsequent reductive elimination of butane affords paramagnetic derivatives of zirconocene **107**–**109** with Zr oxidation state of +3 (Refs 169 and 210).

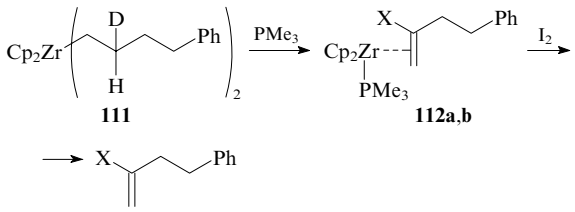
Negishi *et al.*[211] compared the rates of β-hydride transfer in alkyl groups of dialkylzirconocenes $Cp_2Zr(Me)R$ and $Cp_2Zr(Et)R$.



R^1 = Bu^n, Bu^i, Bu^t, Bn, *etc.*; R^2 = Me, Et

The β-hydride transfer rate was estimated by ^1H NMR monitoring of the transformation of complex **110** to **100** under the action of PMe_3, which functions as a stabilizer for complex **100**. For $Cp_2Zr(Me)R$, the β-hydride transfer rate decreased in the following order of R: Bu^s > Bu^t > Et > Bu^n > Bu^i. Thus, the reactivity of alkyl ligands as β-hydrogen donors correlates with the degree of substitution at the β-carbon atom and decreases in the sequence β-methyl > β-methylene > β-methine

The β-hydride transfer in complex **111** in the presence of PMe_3 furnished complexes **112a**,**b** in a 90% yield; the ratio of the complexes was determined for the iodinolysis products **113a**,**b**.



X = H (**a**), D (**b**)

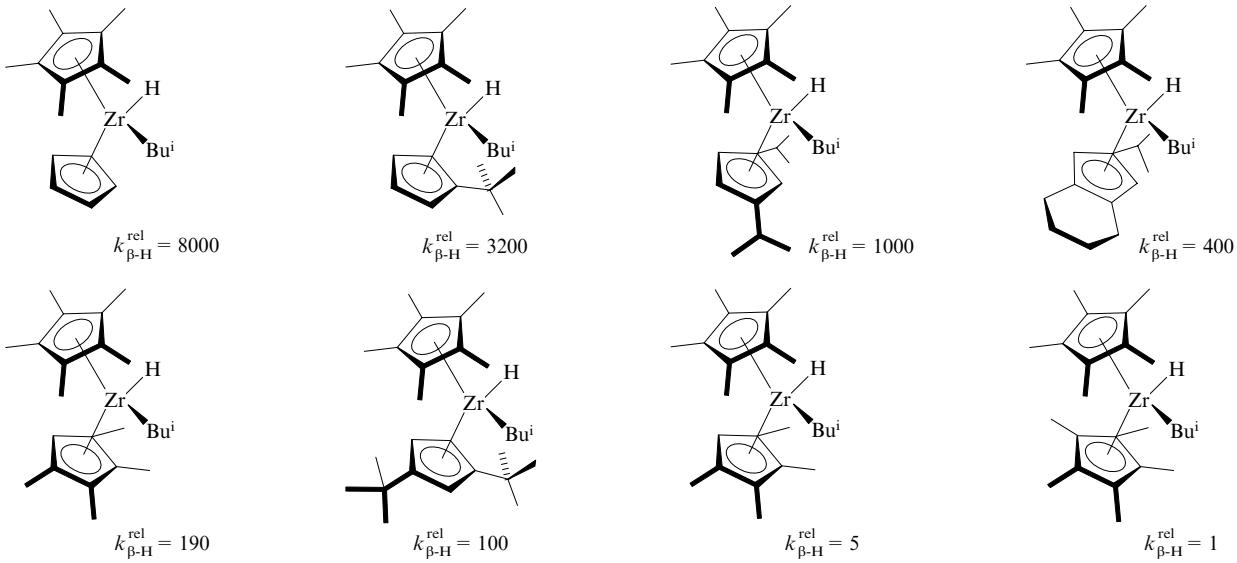
This result confirms the mechanism that implies β-agostic interaction of the $H-C_\beta$ bond with the Zr atom. It turned out that the stability of dialkyl zirconocenes increases with increase in the bulk of the π-ligand and the length of the alkyl substituent.[167]

The β-CH activation processes in alkyl zirconocene complexes were studied in detail.[168,212] The existence of fast reversible β-H transfer in the alkyl hydride complexes $(C_5H_{5-n}Me_n)(C_5H_{5-m}R_m)Zr(H)Bu^i$ (n = 4, 5; R = Me, Pr^i, Bu^t; m = 0–2, 4, 5) was demonstrated. An increase in the bulk of the π-ligand decreases the β-CH-activation rate (see below).

It was found[212] that in more substituted complexes, the steric factor predominates over the electronic factor, *i.e.*, the β-H-elimination rate in a normal alkyl group is higher than in an isoalkyl group ($k^{Bu^n}_{\beta-H}/k^{Bu^i}_{\beta-H} > 1$), whereas for less crowded complexes, the opposite is true: $k^{Bu^n}_{\beta-H}/k^{Bu^i}_{\beta-H} < 1$.

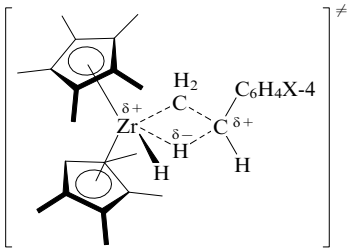
The β-CH-activation rate depends on the structure of the alkyl group in an ambiguous way. Indeed, an increase in the length of the hydrocarbon group may increase the β-H-elimination rate (R = $CH_2CH_2Bu^t$, $k^{rel}_{\beta-H}$ = 1; R = $(CH_2)_3Pr^i$, $k^{rel}_{\beta-H}$ = 12.1; R = $(CH_2)_3Me$, $k^{rel}_{\beta-H}$ = 12.4). The appearance of β-substituents also considerably accelerates this process (R = Bu^i, $k^{rel}_{\beta-H}$ = 62). The highest β-CH-activation rate was observed for the cyclopentyl substituent (R = cyclo-C_5H_9, $k^{rel}_{\beta-H}$ = 680).

The kinetic isotope effect (k_H/k_D) for the β-hydride transfer in isobutyl complexes $(C_5H_{5-n}R_n)_2Zr.(CH_2CXMe_2)L$ (X = H or D) amounts to ~4 and is classified as a primary isotope effect, which implies that the reaction goes through kinetically controlled cleavage of



the C—H(D) bond and the subsequent fast dissociation of the coordinated alkene. The isotope effect is higher than that for a number of other systems of this type, which may indicate that the transition state for less electrophilic neutral metallocene derivatives of group 4 elements is closer to the reaction products (greater degree of cleavage of the C—H bond).

Studies of the electronic contribution to the rate of the β-H transfer in a series of *para*-substituted phenethyl hydride complexes $Cp^*(\eta^5\text{-}C_5Me_4H)Zr(CH_2CH_2C_6H_4X\text{-}4)H$ (X = H, Me, OMe, CF_3) revealed a rather large negative Hammett reaction constant ($\rho = -1.80$), indicating a considerable development of a positive charge in the transition state:[212]



The nature of the second σ-ligand in the metallocene complex has a relatively greater influence on the rates of β-CH-activation and alkyl group isomerization.[168] As compared with alkyl hydride or methylalkyl complexes, in the chloro derivatives $Cp_2Zr(CH_2CHR_2)Cl$ (R = H, Me, Et), no β-H-elimination, alkene rotation or its repeated insertion took place, as was indicated by the absence of deuterium exchange in $Cp_2Zr(CH_2CDR_2)Cl$ or isotope rearrangement in $Cp_2Zr(^{13}CH_2Et)Cl$. The complex Cp_2ZrPr^nCl did not undergo exchange with $^{13}CH_2{=}CHMe$ either. The lack of β-CH-activation in the alkyl chloride complex $Cp_2Zr(CH_2C_6H_{11})Cl$ was once noted by Schwartz and coworkers.[72] Conversely, in the propylmethyl complex $Cp_2Zr(^{13}CH_2Et)Me$, the isotope rearrangement took place over a period of 3 h.[168] Since the methyl and chloride substituents are isosteric, the difference between the reactivities of the corresponding complexes may be caused by electronic properties, in particular, the π-electron-donating properties of the chloride ligand. The free electron pair of the chlorine atom may occupy the free non-bonding orbital of zirconocene, $1a_1$,[213] thus completing the outer shell of the transition metal atom to 18 electrons and ruling out the valence possibility of β-H-elimination.

It is of interest that unlike primary alkyl chloride complexes, internal acyclic and cyclic derivatives readily undergo β-CH-activation and isomerization.[30, 31, 168] For example, the complex Cp_2ZrBu^sCl is converted to Cp_2ZrBu^nCl over a period of several hours owing to β-H-elimination from the carbon atoms C(1) and C(3), which is also confirmed by experiments with deuterium-labelled compounds.

The agostic interactions play a considerable role in the processes of alkene insertion into catalytically active transition metal complexes in the polymerization. It was shown that α-agostic interactions in the transition state exert a substantial effect on the stereospecificity and the rate of alkene insertion at the alkene coordination step.[214] Meanwhile, β-agostic states were identified as stable structures in d^0-metal alkyl derivatives, which are most often inactive intermediates in alkene polymerization processes.[215–217]

IV. Conclusion

The information presented in the review clearly demonstrates that catalytic hydro-, carbo- and cycloalumination of alkenes and alkynes with organoaluminium compounds are complex multistep reactions involving a large number of intermediate bimetallic Zr,Al complexes. Organoaluminium compounds perform several functions, namely, they participate in exchange reactions in the early steps of interaction of the reactants giving rise to catalytically active sites, increase the Zr—H or Zr—C bond polarity in intermediates by forming Zr,Al complexes, which facilitates the alkene or alkyne insertion into these bonds. One more important role of OAC is transmetallation or transfer of the hydrogenated or alkylated group from the transition metal atom to the main group element and liberation of the reaction product from the coordination sphere of the catalytic complex as alkylalane, alkenylalane or aluminacarbocycle. The rates of ligand exchange, CH-activation and insertion of the unsaturated compound into the M—H or M—C bond is considerably affected by the steric and electronic structures of the catalysts, the zirconocene complex, which in turn depend on the π-ligand nature and, to a lesser extent, on the reaction conditions (temperature, solvent, reactant ratio). As a result, the pathway of the catalytic reaction of OAC with alkenes and alkynes is dictated by combination of several factors that determine the structure and reactivity of key intermediates.

We hope that in the near future, research along this line will bring the understanding of the mechanism of action of the Ziegler–Natta catalysts and, hence, it will become possible not only to forecast the catalytic activities of existing or known catalysts but also to create effective catalytic systems with specified properties.

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