Russian Chemical Reviews **69** (2) 121 – 135 (2000) © 2000 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2000v069n02ABEH000519

Metal complex catalysis in the synthesis of organoaluminium compounds

U M Dzhemilev, A G Ibragimov

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Abstract. The published data on the synthesis of organoaluminium compounds involving metal complex catalysts are generalised and systematised. Hydro-, carbo- and cycloalumination reactions of alkenes, conjugated dienes and alkynes catalysed by Ti and Zr complexes are considered in detail. The use of organoaluminium reagents in organic synthesis and novel reactions involving these compounds are discussed. The bibliography includes 240 references.

I. Introduction

About 40 years have passed since the discovery by Ziegler *et al.*[1] of a direct method for the synthesis of trialkylalanes based on the reaction of alkenes with activated aluminium and hydrogen. In this period, organoaluminium compounds (OAC) have become indispensable tools in practical synthetic and organometallic chemistry.

Fundamental studies into the chemistry of OAC carried out in the 1960's[2–8] have formed the basis for the development of industrial methods for their synthesis. Special mention should be made of the investigations carried out by prominent Soviet specialists Zakharkin,[9,10] Zhigach[11,12] and Korneev[13,14] who have developed and industrialised a wide range of practically important OAC including co-catalysts for polymerisation and oligomerisation of alkenes and dienes.[15]

The manufacture of OAC has considerably stimulated the interest of investigators in these compounds as promising reagents for fine organic and organometallic synthesis. The most important fields of their application include thermal hydroalumination of alkenes, dienes and alkynes; reduction of carbonyl compounds, esters and nitriles; synthesis of higher OAC and selective functionalisation of unsaturated compounds. The results of these studies are summarised in numerous reviews and monographs (see, *e.g.*, Refs 16 – 20).

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Received 11 March 1999
Uspekhi Khimii **69** (2) 134 – 149 (2000); translated by R L Birnova

Studies by Tolstikov *et al.* (see Refs 18 and 19) deserve special mention, since they generalise the data on OAC as efficient reagents for organic synthesis. Thus the recently published monograph by Kouchin and Tolstikov[19] provides a systematic description of the published data concerning the synthesis and conversions of OAC since 1970; however, more recent studies carried out in the last decade have not been cited in this book. Meanwhile, the fact that modern studies into the chemistry of OAC widely employ metal complex catalysis has made it possible not only to alter the strategy of organoaluminium synthesis but also to develop chemo-, regio- and stereoselective synthetic procedures for obtaining novel classes of OAC under mild conditions; these methods compete favourably with traditional approaches which utilise elevated pressures and temperatures.

The most efficient and widely employed catalysts for the reactions with OAC include Ti and Zr complexes and, in a lesser degree, Hf-, Co-, Ni-, V- and rare-earth element-containing compounds.

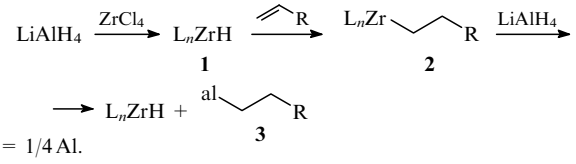
About ten years have passed since the publication of the reviews[16,17] dealing with the application of metal complex catalysts based on Ti and Zr complexes in the synthesis and transformations of OAC. Numerous publications appeared in this decade and they were devoted to non-traditional catalytic methods for the synthesis of OAC. The present review summarises the most important published data on the application of metal complex catalysts in the synthesis of OAC by catalytic hydro-, carbo- and cyclo-metallation of alkenes, dienes and alkynes using the simplest alkylaluminium compounds and aluminium hydrides and systematises the data on the synthetic conversions of OAC in the presence of transition metal complexes.

II. Catalytic hydroalumination of alkenes

Thermal hydroalumination of mono-, di-and trisubstituted alkenes with OAC containing an Al – H bond is still one of the most popular methods for the synthesis of higher OAC.[18–20] Unfortunately, this method suffers from a number of disadvantages which considerably restrict its application, *viz.*, hydroalumination has to be carried out at elevated temperatures (70 – 150 °C); moreover, this reaction is not suitable for all types of alkenes, since the presence of functional groups strongly complicates the results of reactions.

The reaction of $LiAlH_4$ with α-alkenes in the presence of Ti and Zr complexes is one of the first examples of catalytic hydro-

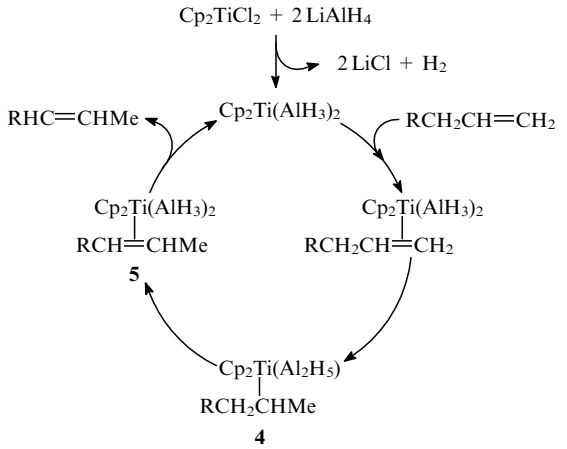
alumination under mild conditions (0–20 °C).[21] This novel procedure allows the synthesis of lithium tetraalkylalanates in 60% to 100% yields. Sato *et al.*[21] who studied the mechanism of catalytic hydroalumination of alkenes with $LiAlH_4$ in the presence of Zr complexes suggested that this reaction generates active hydride zirconium complexes **1**, which hydrozirconate alkenes with the formation of alkylzirconium complexes **2**. Transalkylation of the latter with $LiAlH_4$ gives lithium tetraalkylalanates **3**.



al = 1/4 Al.

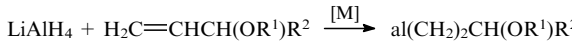
Using hydroalumination of hex-1-ene with lithium aluminium hydride as an example, it was shown [22] that $TiCl_4$, VCl_4, Cp_2TiCl_2 and Cp_2ZrCl_2 manifest high catalytic activity comparable with that of $ZrCl_4$. In the case of VCl_4 and Cp_2TiCl_2, hydroalumination products were formed together with hex-2-ene resulting from isomerisation of the original hex-1-ene. The isomerisation of terminal alkenes in the presence of Cp_2TiCl_2 is shown in Scheme 1. The coordination of the central atom of the catalyst with an alkene results in the corresponding alkyltitanium σ-complex **4** in which the transfer of the hydride ion is accompanied by the formation of a complex **5** in the presence of an excess of the α-alkene. Decomposition of the complex **5** yields a mixture of stereoisomeric hex-2-enes.[23]

Scheme 1



In their reactivities in the hydroalumination reaction, aluminium hydrides and alkenes can be arranged in the following orders: [24] $LiAlH_4 > AlH_3 > AlH_2Cl > AlHCl_2$; $RCH=CH_2 > R_2C=CH_2 > RCH=CHR$.

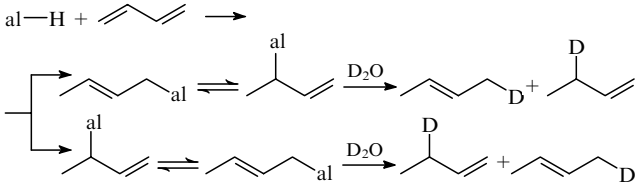
Co, Ni and Fe chlorides,[25,26] Cr [27] and U [28] salts and transition metal complexes immobilised on inorganic [29] or polymeric supports [29,30] can be used as catalysts in hydroalumination reactions. In contrast with thermal hydroalumination, catalytic hydroalumination in the presence of Zr and Ti complexes can also be performed in the presence of such functionally substituted alkenes as allylic alcohols and ethers.[31–33]



R^1, R^2 = Alk, Ph; al = 1/4 Al.

Subsequent one-pot conversions of lithium tetraalkylalanates are of considerable practical interest. Thus cross-coupling of lithium tetraalkylalanates formed *in situ* with allyl halides in the presence of copper salts [CuBr, CuI, CuCN, $CuCl_2$, $Cu(OAc)_2$] yields alkenes which are three carbon atoms longer than the starting compounds;[34] the CuCl-catalysed reaction with propargyl bromide yields terminal allenes in high yields.[35] This reaction is one of the simplest and most convenient procedures for one-step conversion of alkenes into the corresponding allenes. Later, cross-coupling was successfully extended to allenyl bromide,[36] carboxylic acid halides,[37] acrolein [38] and methyl vinyl ketone.[38,39] Catalytic hydroalumination with $LiAlH_4$ and subsequent functionalisation of the alkylalanes formed makes it possible to convert the starting alkenes into the corresponding organic halides,[40] acetates [41] or organoboron compounds [42] in one step.

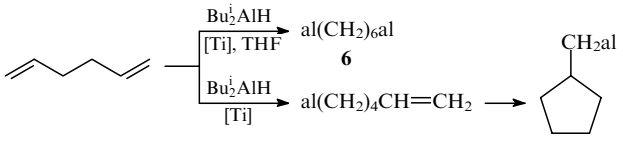
Unlike reactions with terminal alkenes, hydroalumination of 1,3-dienes with $LiAlH_4$ or $NaAlH_4$ in the presence of catalysts, such as Cp_2TiCl_2 or $TiCl_4$ occurs less selectively and affords 1,2-, 1,4- and 3,4-addition products.[43,44]



al = 1/4 Al.

Along with complex aluminium hydrides, readily available alkylaluminium hydrides are also used for catalytic hydroalumination of alkenes. In the example of hydroalumination of a mixture of isomeric decenes with Bu^i_2AlH in the presence of catalytic amounts of $Ti(OBu)_4$, it was established that the terminal double bond enters into the reaction 154 times faster than the *cis*-disubstituted bond and 241 times faster than the *trans*-disubstituted bond.[45]

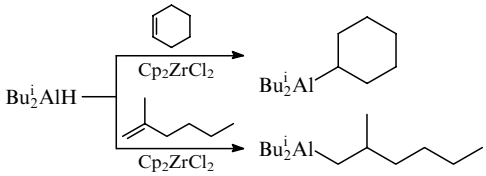
Hydroalumination of hexa-1,5-dienes with Bu^i_2AlH has a number of specific features. In the presence of $Ti(OBu)_4$ as a catalyst (1.5 mol.%) [46] and without it [5] hydroalumination occurs, which is followed by intramolecular cyclisation. However, when the reaction is carried out in solvents containing electron-donor atoms (N, O, S, P), no cyclisation takes place and the α,ω-dialuminium compound **6** is formed instead.[46] These data suggest that in the course of hydroalumination the starting hydrometallating reagent readily forms donor-acceptor complexes with the solvent owing to the lone electron pair of the heteroatom, which prevents the intramolecular cyclisation.



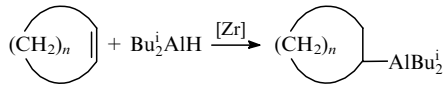
[Ti] = $Ti(OBu)_4$, al = 1/3 Al.

Commercially available diisobutylaluminium hydride can be used as an efficient hydroaluminating reagent for linear and cyclic mono-, di- and trienes including those containing functional groups. Zirconium complexes proved to be the most active catalysts in these reactions.[16,47] Thus Bu^i_2AlH hydroaluminates α-, α,β-disubstituted and cyclic alkenes in high yields in the presence of $ZrCl_4$ even at ~20 °C (3–6 h).[48] The use of titanium-containing catalysts results in the formation of side products as a result of isomerisation of the original alkenes.[23] This reaction virtually does not occur in the absence of the catalysts.

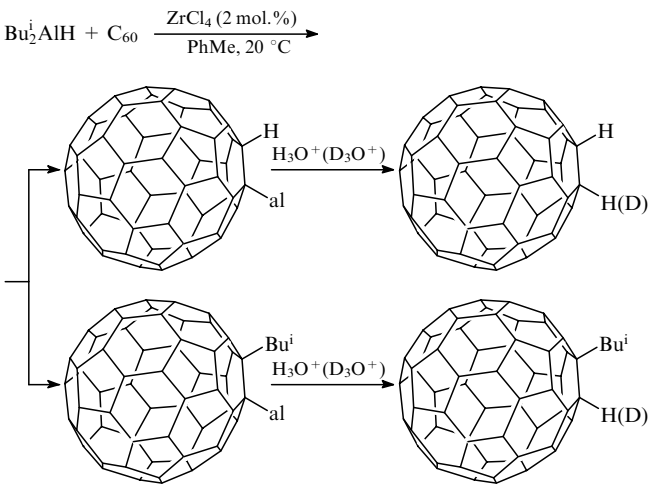
An analysis of the literature data on hydrozirconation of alkenes [49] prompts a conclusion that hydroalumination yields reactive zirconium hydride intermediates able to hydrozirconate alkenes; further transmetallation of alkyl and cycloalkyl zirconium complexes results in higher OAC.[48]



Studies by Tolstikov *et al.*[50] have shown that zirconium chloroalkoxides $(RO)_nZrCl_{4-n}$ are more reactive catalysts of the hydroalumination reaction than $ZrCl_4$ or $Zr(OBu)_4$. Therefore, a mixture of $ZrCl_4$ with Bu^nOH, MeOH, EtOH and Pr^nOH is used to obtain a reactive catalyst. The rate of cycloalkene hydroalumination depends on the ring size and decreases in the following order: $C_5 > C_6 > C_7 > C_{12} > C_8$.

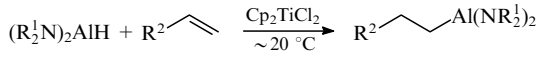


Hydroalumination of the C_{60} fullerene with Bu^i_2AlH in the presence of $ZrCl_4$ or $(RO)_nZrCl_{4-n}$ at ~20 °C {C_{60} : [Al] = 1 : (100–300), 24 h, toluene} was carried out by Ibragimov *et al.*[51,52] Data from hydrolysis and deuteriolysis of fullerene-containing OAC suggest that these reaction conditions favour the formation of both hydro- and carboalumination products (total yield ~90%).

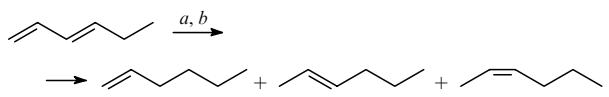


al = 1/3 Al.

Bis(dialkylamino)alanes manifest high reactivity in hydroalumination of alkenes, however, only in the presence of Cp_2TiCl_2.[53,54] These compounds hydroaluminate α-alkenes, methylidenealkanes and aliphatic disubstituted alkenes in practically quantitative yields. Cycloalkenes are less reactive in this reaction. Tri- and tetrasubstituted alkenes cannot be involved in this reaction.

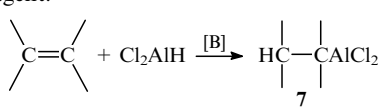


The advantage of bis(dialkylamino)alanes over dialkylalanes is in the feasibility to use them for catalytic hydroalumination of conjugated dienes; however, the selectivity of these reactions is rather low as in the case of complex hydrides.[55,56]



(*a*) $(Pr^i_2N)_2AlH$, Cp_2TiCl_2, THF, 12 h, 20 °C; (*b*) H_2O (55%).

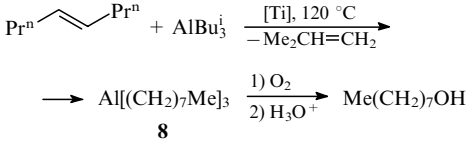
Dichloroalane which reacts with alkenes in the presence of boron derivatives to give the corresponding higher alkyldichloroaluminium compounds **7**, is used as a reactive hydroaluminating reagent.[57–60]



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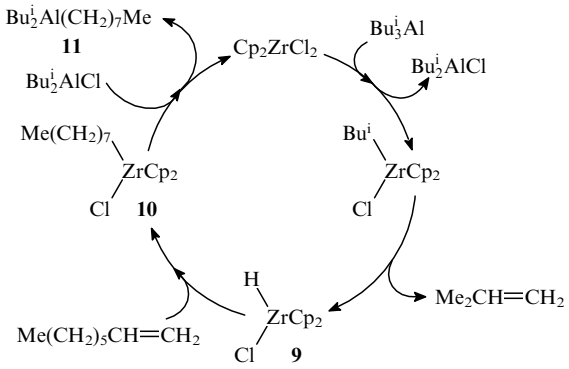
[B] = $PhB(OH)_2$, $B(OH)_3$, Et_3B, $B(OMe)_3$, 9-borabicyclo[3.3.1]-nonane (9-BNN), BF_3OEt_2.

Hydroalumination of disubstituted alkenes with Bu^i_3Al in the presence of Ti^{4+} or Zr^{4+} salts at 110–120 °C gives predominantly OAC **8**.[61] Apparently, the catalyst induces the isomerisation of the disubstituted double bond in the original alkenes into the terminal bond which is much more readily hydroaluminated with Bu^i_3Al.

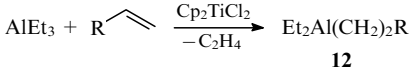


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The yield of reaction products in hydroalumination of alkenes with Bu^i_3Al strongly depends on the nature of the catalyst. Thus in the presence of catalytic amounts of Cp_2ZrCl_2, higher trialkylalanes can be synthesised from terminal alkenes and $AlBu^i_3$ in high yields (0 °C, 6 h).[62] This reaction does not take place in the absence of the catalyst. Such a high reactivity of Bu^i_3Al in the presence of Cp_2ZrCl_2 can be attributed to the formation of zirconium hydrides **9**,[63,64] which hydrometallate alkenes at low temperatures to give the complex **10**. Subsequent transmetallation of alkyzirconium complexes results in alkylalanes **11**.

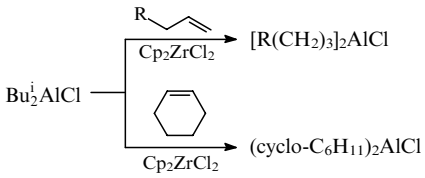


Hydroalumination of terminal alkenes with yet another hydroaluminating reagent, *viz.*, $AlEt_3$ in the presence of Cp_2TiCl_2, follows a similar path and yields alkyl(diethyl)alanes **12**.[65]

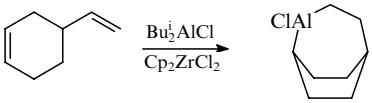


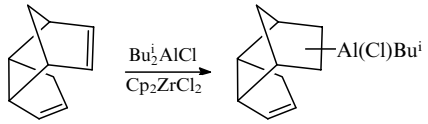
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Higher dialkylaluminium chlorides cannot be synthesised by thermal transalkylation with Bu^i_2AlCl; therefore, the use of Bu^i_2AlCl for Cp_2ZrCl_2-catalysed hydroalumination of alkenes[66] which gives nearly quantitative yields should be regarded as a significant breakthrough.

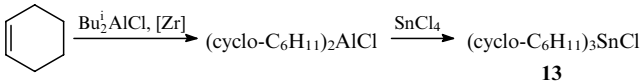


This reaction involves non-conjugated di- and trialkenes (including cyclic and functionally substituted ones).[67] Hydroalumination of norbornenes with Bu^i_2AlCl is stereoselective and affords the corresponding cycloalkylhalogenoalanes.[68] The reactions involving 4-vinylcyclohexene and dicyclopentadiene result in bi- and tri-cyclic halogenoalanes.



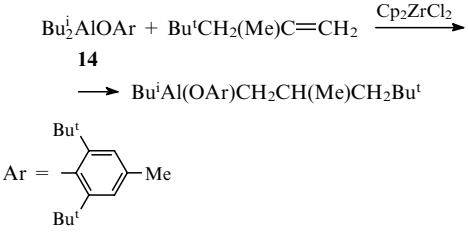


The Cp_2ZrCl_2-catalysed hydroalumination of cyclohexene with Bu^i_2AlCl was successfully employed to obtain tricyclohexyltin chloride (**13**).[69]



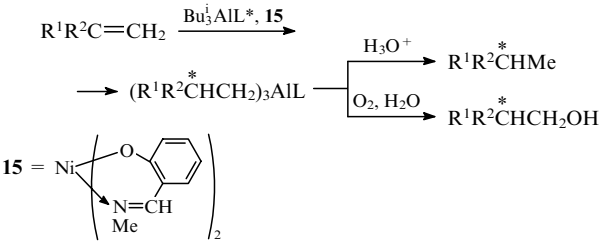
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(2,6-Di-*tert*-butyl-4-methylphenoxy)diisobutylaluminium (**14**) was recommended for use as a regio- and stereoselective reagent for hydroalumination of alkenes and carbonyl compounds in the presence of a two-component catalyst, Cp_2ZrCl_2–aluminium hydride (1:1).[70]



Because of the low reactivity of reagent **14**, hydroalumination should be performed at high temperature (145 °C); however, the presence of a bulky aryloxy substituent ensures high regioselectivity of this reaction.

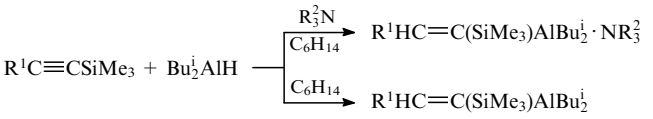
It was shown [71, 72] that the exchange reaction between optically active solvates ($L^* \cdot Bu^i_3Al$) and disubstituted terminal alkenes in the presence of a nickel(II)–*N*-methylsalicylidenamine complex **15** gives optically active trialkylalanes; their further oxidation or hydrolysis results in optically active alcohols or hydrocarbons. (−)-*N,N*-Dimethylmenthylamine, (+)-(*S,S*)-2,3-dimethoxy-1,4-bis(*N,N*-dimethylamino)butane, (+)-*N,N*-dimethylbornylamine, (+)-(*R*)-*N,N*-dimethyl-1-phenylethylamine, *etc*. were used as chiral ligands which form solvates with $AlBu^i_3$.[71, 72]



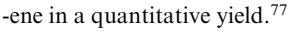
Hydroalumination of oxabicycloalkenes with Bu^i_2AlH can be carried out in the presence of $Ni(COD)_2$ (COD is cyclooctadiene) or its derivatives with phosphines;[73] the regio- and enantioselectivity of this reaction largely depend on the ligand environment of the central atom of the catalyst.

III. Catalytic hydroalumination of alkynes

Non-catalysed hydroalumination of disubstituted acetylenes can be achieved by using Bu^i_2AlH, Et_2AlH or Bu^i_3Al under sufficiently mild conditions but is characterised by low selectivity, since the vinylalanes formed in this reaction undergo further transformations.[20] Hydrolysis of vinylalanes results in 1,2-disubstituted alkenes with a *Z*- or an *E*-configuration depending on the nature of the starting hydroaluminating reagent,[74] the structure of the alkyne [75] and the solvent.[76]

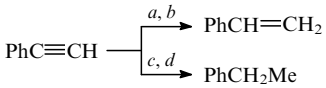


In the presence of transition metal complexes, hydroalumination of alkynes sometimes occurs with higher selectivity and in higher yields. For example, the reaction of oct-1-yne with Bu^i_2AlH in the presence of stoichiometric amounts of methylcuprate (1.25 h, 20 °C) and subsequent hydrolysis of the reaction mixture give oct-1-ene in a quantitative yield.[77]



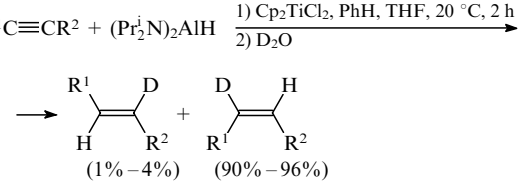
(*a*) Bu^i_2AlH, MeMgBr, CuCl, LiCl, THF; (*b*) H_2O (100%).

Hydroalumination of monosubstituted acetylenes normally yields a mixture of alkenes and alkanes, since mono- and dihydroalumination of the triple bond occur simultaneously. Selective mono- or dihydroalumination of alkynes can be carried out in the presence of Fe or Ni salts.[26]



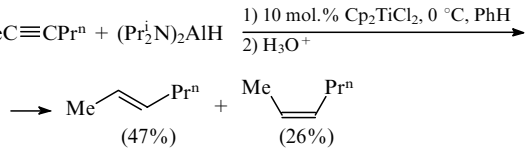
(*a*) $LiAlH_4$, $FeCl_2$, ~20 °C, 24 h; (*b*) H_2O (94%);
(*c*) $LiAlH_4$, $NiCl_2$, ~20 °C, 24 h ; (*d*) H_2O (99%).

Hydroalumination of mono- and disubstituted acetylenes with $LiAlH_4$ in the presence of $TiCl_4$ or Cp_2TiCl_2 can be carried out with high selectivity. Thus the reaction of oct-4-yne or hex-2-yne with hydride aluminium complexes [$LiAlH_4$, $NaAlH_4$, $LiAlMe_3H$, $NaAlMe_3H$, $NaAl(OCH_2CH_2OMe)_2H_2$] in the presence of catalytic amounts of Cp_2TiCl_2 in THF yields alkenylalanes after 2 h at 20 °C; hydrolysis of the latter results in *cis*-oct-4-ene and *cis*-hex-2-ene, respectively (yields ~100%).[78] Aminoalanes can also be used for hydroalumination of alkynes.[53] In this case, hydroalumination of disubstituted acetylenes occurs with high selectivity and under milder conditions than that of terminal alkynes. Thus in the presence of 5 mol.% of Cp_2TiCl_2, the reaction of methylphenylacetylene with $(PrN)_2AlH$ gives alkenylalanes in a total yield of >95%.[54] The reaction of aminoalanes with disubstituted acetylenes predominantly occurs as the *cis*-addition, which makes it possible to use this method for the synthesis of *Z*-alkenes.



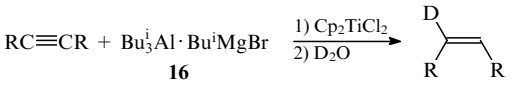
R^1 = Me: R^2 = Bu^n, n-C_6H_{13}, Ph; R^1 = R^2 = Ph.

The composition of the reaction mixture depends on temperature, solvent and reaction time. Thus hydroalumination of hex-2-yne with $(PrN)_2AlH$ in benzene at 0 °C yields a mixture of alkenylalanes with *trans*- and *cis*-configurations of the substituents. Their hydrolysis yields a mixture of isomeric hex-2-enes.[54]

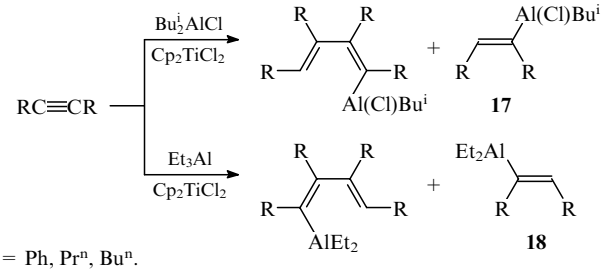


The aluminium-magnesium reagent **16** (Bu^i_3Al–Bu^iMgBr) [79] the efficiency of which is comparable with that of 9-BBN was

recommended for stereoselective hydrometallation of disubstituted acetylenes. This method is especially efficient in the conversions of disubstituted acetylenes into *Z*-alkenes. In the presence of 2 mol.% Cp_2TiCl_2, the reaction with an excess of this reagent (3–10 equiv.) occurs at 20 °C and is completed within 20 min. *Z*-Alkenes are formed in 95%–98% yields and with ~98%–100% selectivity.

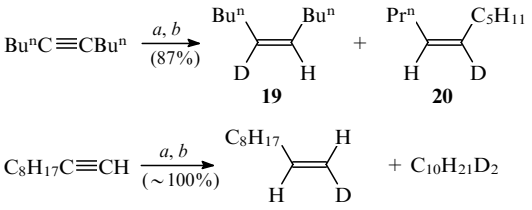


The recently synthesised reagents $Bu^i_2AlCl-Cp_2TiCl_2$ and $Et_3Al-Cp_2TiCl_2$, designed for selective hydroalumination of disubstituted acetylenes into the corresponding unsaturated OAC **17** and **18** the stereoselectivity of which is close to 100%, deserve special attention.[80–82] Hydrolysis of OAC **17** and **18** results in *Z*-alkenes. Depending on the structure of the original alkynes and reaction conditions, 5% to 30% of alkadienylalanes are formed together with alkenylalanes. The structure of the unsaturated OAC **17** and **18** has been established by spectral methods.[83]



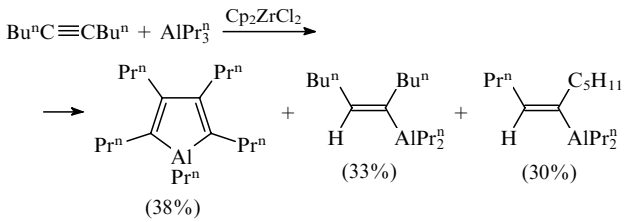
R = Ph, Pr^n, Bu^n.

Hydroalumination of disubstituted acetylenes with Bu^i_3Al in the presence of catalytic amounts of Cp_2ZrCl_2 is accompanied by the formation of isomeric alkenylalanes, their hydrolysis affords alkenes **19** and **20** (~1:1).[84,85] Under analogous conditions, terminal alkynes yield a mixture (~1:1) of mono- and 1,1-dialuminium compounds in practically quantitative yields.[84]



(*a*) Bu^i_3Al, Cp_2ZrCl_2; (*b*) D_2O.

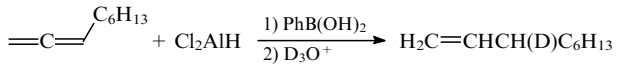
In contrast with hydroalumination with $Et_3Al-Cp_2TiCl_2$,[81] the reaction of disubstituted acetylenes with Pr^n_3Al in the presence of Cp_2ZrCl_2 occurs less selectively and gives a mixture of isomeric alkenylalanes (total yield 63%) and alumacyclopentadiene (38%).[84]



It should be noted that selective hydroalumination of terminal alkynes with trialkylalanes R_3Al [R = Et, Bu^i, $EtCH(Me)CH_2$] does not take place if Fe or Ni complexes substituted titanium- or zirconium-containing catalysts. In this case, the alkenylalanes formed undergo further conversions; subsequent hydrolysis results in a complex mixture of alkenes, 1,3-dienes and trialkyl-substituted benzenes.[86,87]

Hydroalumination of mono- and disubstituted acetylenes has found wide application in synthetic organic chemistry, particularly in the synthesis of practically valuable trisubstituted alkenes,[76] substituted 1,3-dienes,[88] alk-1-en-3-ynes,[89] alkenylsilanes and alkenyl sulfones,[90,91] 1-alkyl-2-halogenocyclopropanes,[92] *Z*-alkenes,[93] *etc*.

Hydroalumination of allenes (both thermal with Bu^i_2AlH,[94] and that with the use of $LiAlH_4$ in THF in the presence of catalytic amounts of Ti or Zr complexes, *e.g.*, Cp_2TiCl_2, $TiCl_4$, $TiCl_3$, $ZrCl_4$ or Cp_2ZrCl_2) is non-selective.[95] This reaction may be highly regioselective with the use of $HAlCl_2$ in the presence of catalytic amounts of organoboranes.[95,96]



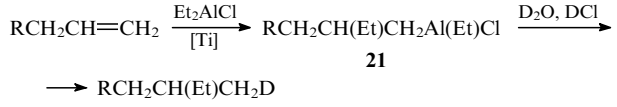
Thus in the majority of cases, stereoselective hydroalumination of alkynes and allenes occurs under mild conditions. Hydrolysis of the resulting higher alkenylalanes affords *Z*-alkenes in high yields.

IV. Carboalumination of alkenes catalysed by titanium and zirconium complexes

Catalytic carboalumination of unsaturated compounds gives an access to novel types of higher OAC. It is known[97] that carboalumination of terminal alkenes in the absence of catalysts usually occurs under drastic conditions and is accompanied by side reactions of hydro- and dehydroalumination. In the presence of metal complex catalysts, carboalumination proceeds under milder conditions and with higher selectivity.

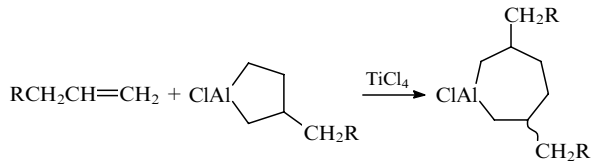
The first examples of catalytic carboalumination of alkenes aimed at the synthesis of higher dialkylhalogenoalanes were described in 1979.[98] This method is based on a consecutive insertion of ethylene at the Al–C bond in the presence of low-valent Ti complexes. This reaction results in the formation of higher OAC (dialkylaluminium chlorides) with the number of carbon atoms from 4 to 30.

The reaction of terminal alkenes with Et_2AlCl in the presence of 0.3 mol.%–3.0 mol.% $Ti(OBu)_4$ or $TiCl_4$ was studied by Dzhemilev *et al.*[99] It was found that Et_2AlCl carboaluminates alkenes even at ~20 °C; this reaction proceeds with high regioselectivity and affords the corresponding higher dialkylaluminium chlorides **21** in high yields.

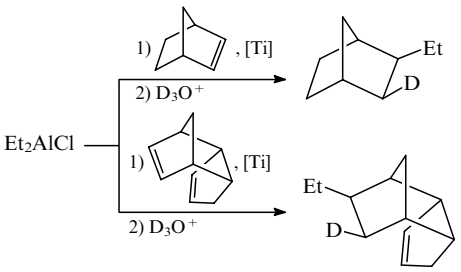


This reaction is of general character and is successfully employed in the synthesis of OAC and in directed synthesis of natural compounds.[99–101]

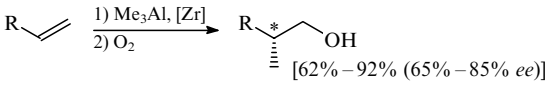
Carboalumination of terminal alkenes with 3-alkyl-1-chloroalumacyclopentanes was used to obtain other cyclic OAC, *e.g.*, 1-chloro-3,6-disubstituted alumacycloheptanes.[102]



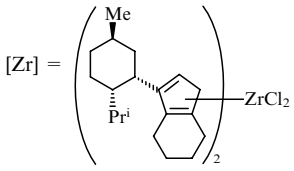
Dialkylhalogenoalanes, such as Et_2AlCl and Me_2AlCl, carboaluminate substituted norbornenes in the presence of catalytic amounts of Ti complexes [Cp_2TiCl_2, $Ti(acac)_2Cl_2$, $TiCl_4$] with high stereoselectivity; subsequent hydrolysis results in alkylated norbornanes.[103,104]



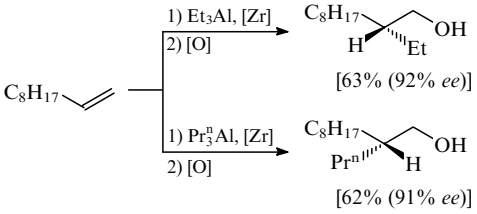
Carboalumination of terminal alkenes with Me_3Al in the presence of chiral derivatives of zirconocene, *e.g.*, bis(1-neomenthylindenyl)zirconium dichloride, bis(1-neo-isomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride, *etc.* with subsequent oxidation of alanes is used in a highly enantioselective synthesis of optically active alcohols.[105]



R = C_6H_{13}, Pr^iCH_2, Ph, $PhCH_2$, $HO(CH_2)_4$, $Et_2N(CH_2)_3$;

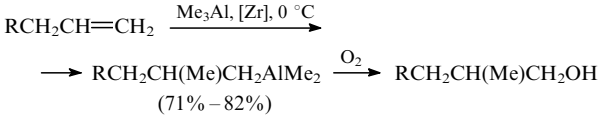


The direction of the reaction of trialkylalanes with alkenes depends on the solvent used. Thus carboalumination in 1,1-dichloroethane proceeds with high enantioselectivity in the presence of catalytic amounts of chiral zirconium catalysts.[106]



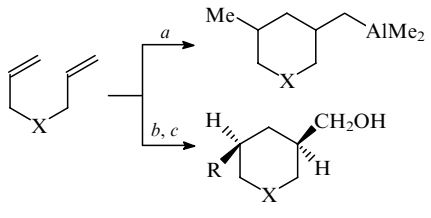
[Zr], bis(1-neomenthylindenyl)zirconium dichloride.

Carboalumination of terminal alkenes with Me_3Al is selective when a two-component catalyst $Cp_2^*ZrMe_2-B(C_6F_5)_3$ ($Cp^* = \eta^5$-C_5Me_5) (toluene, 0 °C, ~3 h) is used.[107]



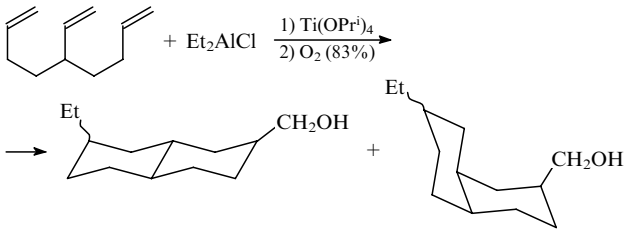
R = $H_2C{=}C(Me)(CH_2)_2$, $Me(CH_2)_2$.

In contrast with terminal alkenes, hexa-1,5-diene, hepta-1,6-diene, octa-1,7-diene and their N-, O- and Si-containing derivatives react with trialkylalanes[107] or dialkylhalogenoalanes[108] in the presence of Zr- or Ti-containing complex catalysts to give, as a rule, cycloalkylmethylalanes or their heterocyclic analogues.

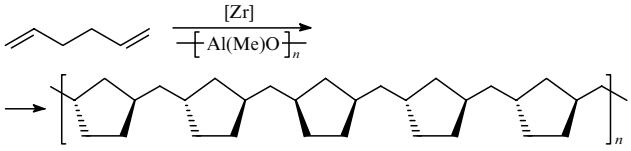


(*a*) Me_3Al, $Cp_2^*ZrMe_2$, $B(C_6F_5)_3$, 0 °C; $Cp^* = \eta^5$-C_5Me_5; X = $(CH_2)_n$, R_2Si, PhN, $CHOSiR_3$ (51%–88%); (*b*) R_2AlCl, $Ti(OPr^i)_4$; R = Et, Pr^n, Bu^i; X = CH_2; (*c*) [O].

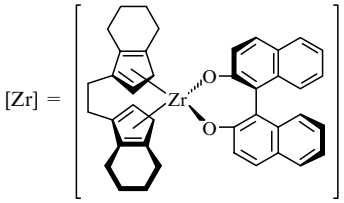
Negishi *et al.*[108] carried out cascade carboalumination of 5-vinylnona-1,8-diene in the presence of Et_2AlCl and $Ti(OPr^i)_4$ as a catalyst.



Catalytic carboalumination of non-conjugated dienes in the presence of Zr, Cp_2ZrX_2 or $Cp_2^*ZrX_2$ complexes (X = Cl, Me; $Cp^* = \eta^5$-C_5Me_5) and methylalumoxane $-[Al(Me)O]_n-$ was used for diastereo- and enantioselective cyclopolymerisation of hexa-1,5-diene. The diastereoselectivity of this reaction depends on the original catalyst. Catalysis with Cp_2ZrMe_2 at −78 °C results in a polymer *trans*-**22** (yield 91%), whereas in the case of $Cp_2^*ZrCl_2$ the yield of *trans*-**22** is 14% at −25 °C.[109] Cyclopolymerisation of hexa-1,5-diene in the presence of a chiral zirconium catalyst, (+)-(*S*)-**23**, and methylalumoxane gives the chiral polymer (−)-**22** {*trans*-isomer (68%), [α] = −49.3°}.[110,111]

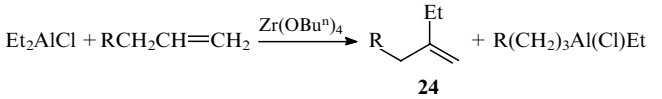


(−)-**22**



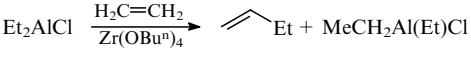
(+)-(*S*)-**23**

In the presence of $Zr(OBu)_4$, terminal alkenes are alkylated with Et_2AlCl into position 2; alkenes **24** are formed in one step and with high selectivity.[112]

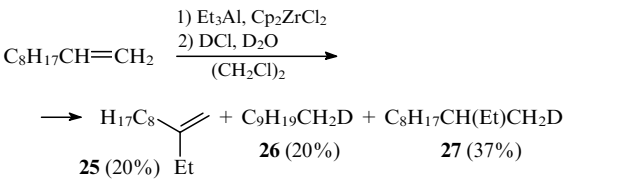


24

Ethylation of ethylene with Et_2AlCl in the presence of zirconium catalysts, *e.g.*, $Zr(OBu^n)_4$, $Zr(OR)_nCl_{4-n}$, served as the basis for the synthesis of but-1-ene.[113]



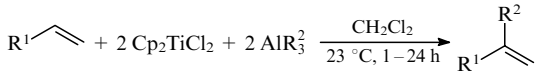
The reaction of dec-1-ene with $AlEt_3$ in the presence of Cp_2ZrCl_2 yields hydro- (**26**) and carboalumination (**27**) products as well as 1,1-dialkylethylenes **25**.[106]



25 (20%) **26** (20%) **27** (37%)

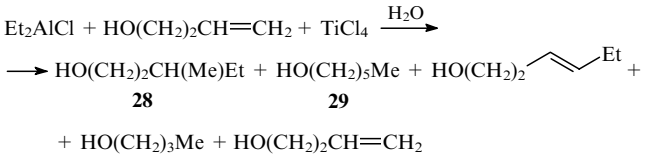
Reactions of trialkylalanes with terminal alkenes (including functionally substituted ones) in the presence of 2 equivalents of Cp_2TiCl_2 and trialkylaluminium in CH_2Cl_2 also result in 1,1-disubstituted alkenes. According to Barber *et al.*,[114] carboalumination of alkenes under these conditions affords trialkylalanes which contain hydrocarbon radicals with an *iso*-structure;

they undergo β-hydride elimination by titanium complexes to give the corresponding alkenes in sufficiently high yields (45% – 85%).

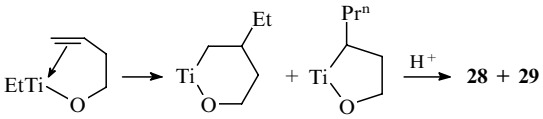


$R^1 = C_8H_{17}$, $MeCO_2(CH_2)_4$, $Br(CH_2)_4$, $NC(CH_2)_4$; R^2 = Me, Et, Bu^n.

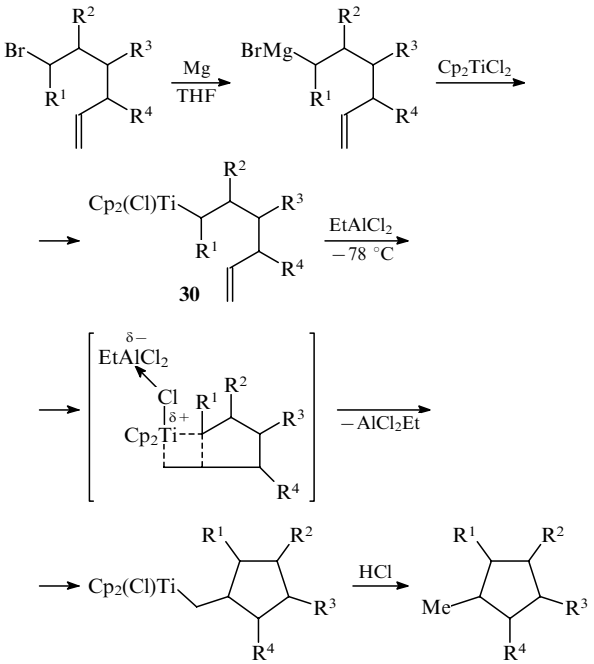
Homoallylic alcohols react with Et_2AlCl in a non-selective manner. This reaction can be accomplished only in the presence of stoichiometric amounts of Ti-containing compounds, *e.g.*, Cp_2TiCl_2, $TiCl_4$, $Ti(acac)_2Cl_2$.[114–117] Carbometallation results in two regioisomeric products (**28** and **29**) and is accompanied by side reactions, such as hydrometallation, hydrogenation, isomerisation and β-hydride elimination.



It is believed [114–117] that the reaction of Et_2AlCl with titanium compounds results in the formation of the corresponding ethyltitanium complexes which are active in further carbometallation of terminal alkenes. Subsequent hydrolysis affords isomeric alcohols **28** and **29**.



In a continuation of these studies, the reaction of intramolecular carbotitanation in the presence of $EtAlCl_2$ was further extended to the selective synthesis of substituted cyclopentanes from 1-bromohex-5-enes.[118–120] The role of $EtAlCl_2$ complexes consists in the activation of the intermediate titanium complex **30**.



Thus the carboalumination of alkenes with the simplest organoaluminium compounds catalysed by transition metal complexes permits simultaneous formation of C – C and Al – C bonds with high regio- and stereoselectivities. Further transformations of the organoaluminium compounds formed in the process make it possible to obtain alcohols, aldehydes, acids and other compounds.

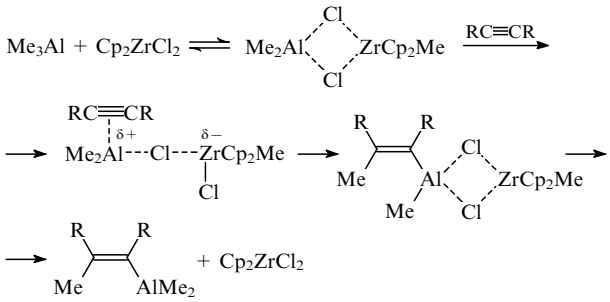
V. Carboalumination of alkynes catalysed by transition metal complexes

The reaction of gaseous acetylene with trialkylalanes occurs under mild conditions (40 – 60 °C) with high stereoselectivity and results in *Z*-alkenyldialkylalanes, this being one of the simplest examples of carboalumination of alkynes with OAC.[74] The features of this non-catalytic reaction and alkenylalane conversions are documented in a substantial body of literature (see, *e.g.*, Refs 18 – 20 and 121). Catalytic carboalumination of alkynes has been extensively generalised (*cf., e.g.*, Refs 17, 47, 122 – 125). The present review considers the synthesis of alkenylalanes by catalytic carboalumination of alkynes with trialkyl- and halogenoalkylalanes.

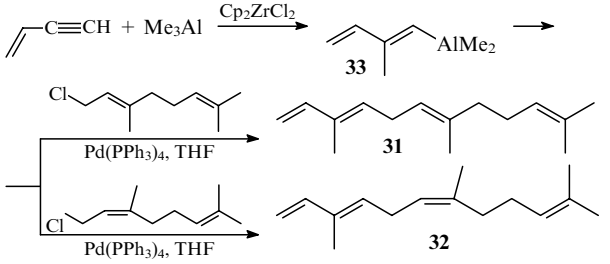
Carboalumination of mono- and disubstituted acetylenes is carried out in the presence of transition metal compounds derived from Fe,[86] Mn, Ni, Ti,[126–130] Zr [131] and Cu salts and complexes;[132–134] this reaction utilises trialkylalanes (Et_3Al, Bu^i_3Al, $[EtCH(Me)CH_2]_3Al$),[86] chlorodialkylalanes (Me_2AlCl,[135] Et_2AlCl,[131] Pr^n_2AlCl),[131] allyl-, benzylalanes [136] and alumocuprates [132–134] as carbometallating reagents. Such reactions are generally non-selective and yield a complex mixture of regioisomers.

A two-component system proposed by Negishi *et al.*[137–139] which contains $AlMe_3$ and catalytic amounts of Cp_2ZrCl_2 is one of the most efficient reagents for acetylene carbometallation presently available. Later, this system was modified by addition of H_2O.[140]

Yoshida and Negishi [141] have initially proposed that Cp_2ZrCl_2-catalysed carboalumination of alkynes involved methylation of Cp_2ZrCl_2 with trimethylaluminium to give $MeZrCp_2Cl$ and Me_2AlCl. Subsequent carbozirconation of the alkyne yields the corresponding alkenylzirconium derivatives; their transmetallation with Me_2AlCl results in alkenyldimethylalanes with simultaneous regeneration of the catalyst. The reaction mechanism included the existence of a reversible reaction where the methyl group or the methyl radical is transferred from the Al atom to the Zr atom as can be evidenced from the NMR data. However, further investigations [142, 143] showed that this reaction involves direct carboalumination of alkynes.

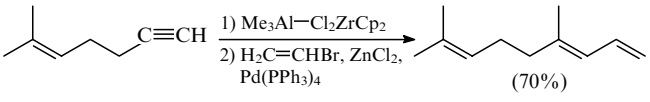


Carboalumination of alkynes resulted in a great number of practically important organoaluminium and organic compounds. Thus an elegant method was proposed for the synthesis of isoprene linear trimers **31** and **32** by stereo- and regiospecific cross-coupling of geranyl and neryl chlorides with alkadienylaluminium **33**.[144] The reagent **33** was synthesised by carboalumination of vinylacetylene with trimethylaluminium in the presence of catalytic amounts of Cp_2ZrCl_2.

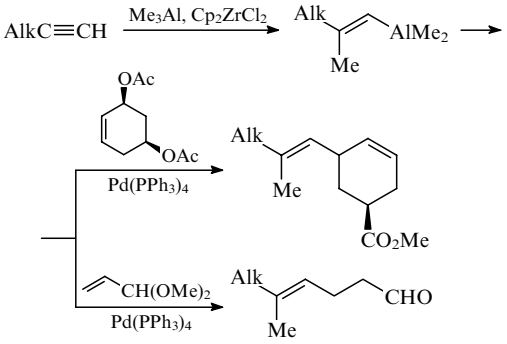


Catalytic carboalumination of terminal alkynes with $AlMe_3$ with subsequent functionalisation of the alkenylalanes formed was used for the synthesis of natural isoprenoids, *e.g.*, geraniol,[145] monocyclofarnesol [146] and farnesol.[147]

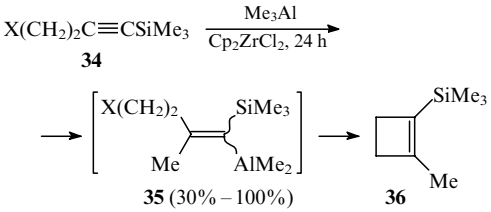
An efficient procedure has been developed for the synthesis of polyenic hydrocarbons of different structure (including those containing conjugated double bonds) using alkenylalanes and catalytic amounts of phosphine complexes of Ni or Pd.[148]



A similar approach was used in the synthesis of cyclic and acyclic functionally substituted unsaturated compounds.[149, 150]

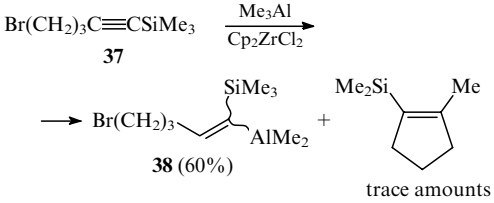


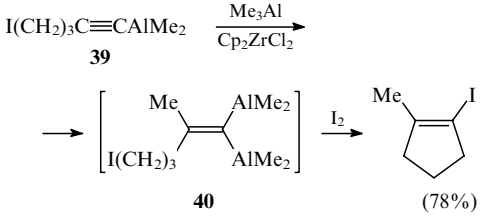
The ability of alkenylalanes to enter into the cross-coupling reactions with organic halides was used as the basis for a new method of synthesis of substituted cyclobutenes. Thus carboalumination of silylated alkynes **34** with trimethylaluminium under mild conditions yields alkenylalanes **35** containing a good leaving group X. Intramolecular cyclisation of the intermediates **35** results in 1-methyl-2-(trimethylsilyl)cyclobutene (**36**).[151]



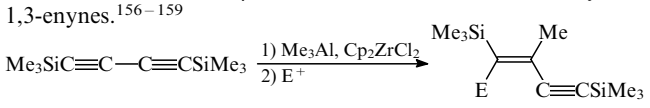
X = Cl, Br, I, OTs.

Carbometallation of ω-halogen-substituted 1-trimethylsilylalk-1-ynes or enynes with alkyl derivatives of Al, Zn or Li followed by intramolecular cyclisation of the organometallic compounds formed allows one to synthesise substituted cycloalkenes in high yields.[152–154] 5-Bromo-1-trimethylsilylpent-1-yne (**37**) is the least prone to intramolecular cyclisation; it generates alkenylalane **38** in 60% yield. The iodo-substituted alkynylalane **39** enters into the carboalumination reaction to give the dialuminium derivative **40**; treatment of the latter with I_2 gives iodo-substituted cyclopentene.[155]



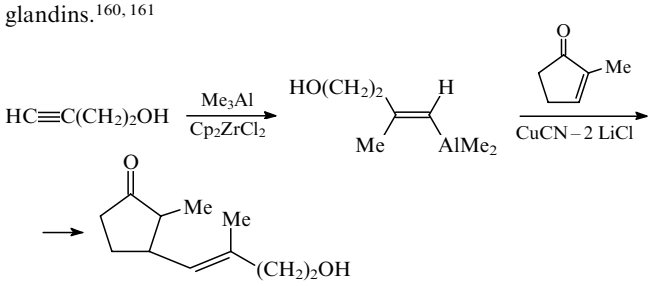


Cp_2ZrCl_2-Catalysed carboalumination of mono- and disubstituted acetylenes or 1,3-diynes is an example of an efficient regio- and stereoselective synthesis of trisubstituted alkenes, homoallylic alcohols, esters of α,β-unsaturated acid and 1,4-disilylated 1,3-enynes.[156–159]

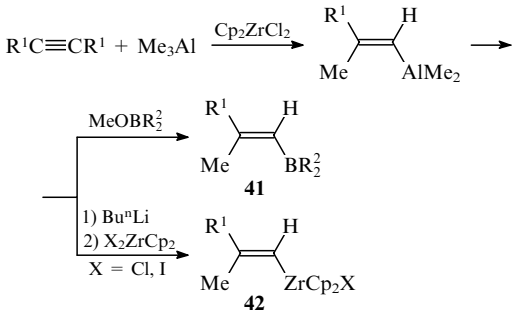


E = H (69%), D (60%), Br (56%), Cl (47%), Ac (44%).

Alkenylalanes obtained by carboalumination of alkynes are extremely useful for introducing alkenyl groups into the β-position of cyclic enones. This approach was used, for example, in the preparation of key compounds for the synthesis of prostaglandins.[160, 161]



Transmetallation of alkenylalanes with organoboron or organozirconium compounds occurs under mild conditions (25 °C, 1 h) and affords the corresponding alkenylboron- (**41**) or -organozirconium (**42**) compounds which can further be used in terpenoid syntheses.[162]

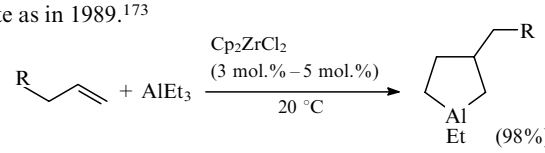


In recent years, catalytic carboalumination of alkynes has found wide application in the synthesis of natural and biologically active compounds, *e.g.,* brassinolide,[163] milbemycin,[164–166] zoapatanol,[167] macbecin fragments,[168] synthetic precursors of lophotoxin and pukalide,[169] mokupalide,[170] trichoverrol B,[171] verrucarin,[172] *etc.*

VI. Cycloalumination of alkenes in the presence of zirconium- and titanium-containing catalysts

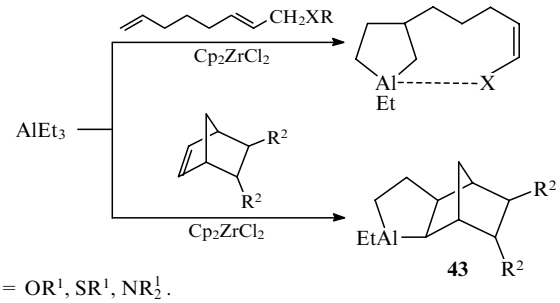
The methods developed in the late 1980's dealt mainly with the synthesis of alkyl-, cycloalkyl-, alkenyl- and vinylalanes. Data on the possibility of preparative synthesis of stable three- and five-membered OAC were practically absent in the literature. The first report on a regioselective synthesis of previously unknown five-

membered OAC (alumacyclopentanes, ACP) was published as late as in 1989.[173]



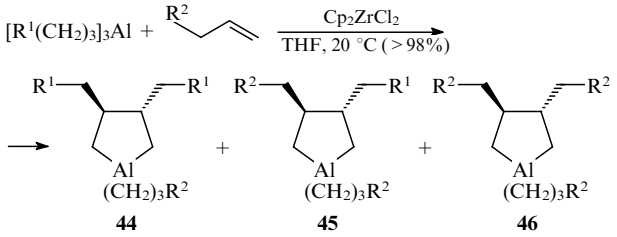
Later, it was found that this reaction is versatile and allows one to perform a one-step synthesis of five-membered OAC from $AlEt_3$ and terminal alkenes in nearly quantitative yields. This reaction was termed as 'catalytic cycloalumination of unsaturated compounds' [174–177] or 'cyclic carboalumination'.[84, 178]

O-, *N*- and *S*-containing alkenes and norbornenes also undergo cycloalumination to give the corresponding ACP.[179, 180] The cycloalumination of norbornenes is highly selective and results in the formation of five-membered metallocycles **43** having an *exo*-configuration.[179]

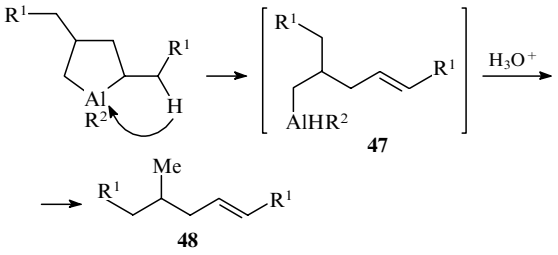


X = OR^1, SR^1, NR^1_2.

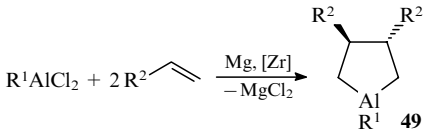
Substitution of higher OAC for $AlEt_3$ affords predominantly *trans*-3,4-disubstituted ACP **44**–**46**.[181]



This is accompanied by the formation of 2,4-dialkyl-substituted alumacyclopentanes (5%–12%); the latter undergo intramolecular β-hydride conversions into *E*-alkenylalanes **47** and, after hydrolysis, into *E*-alkenes **48**.[181]



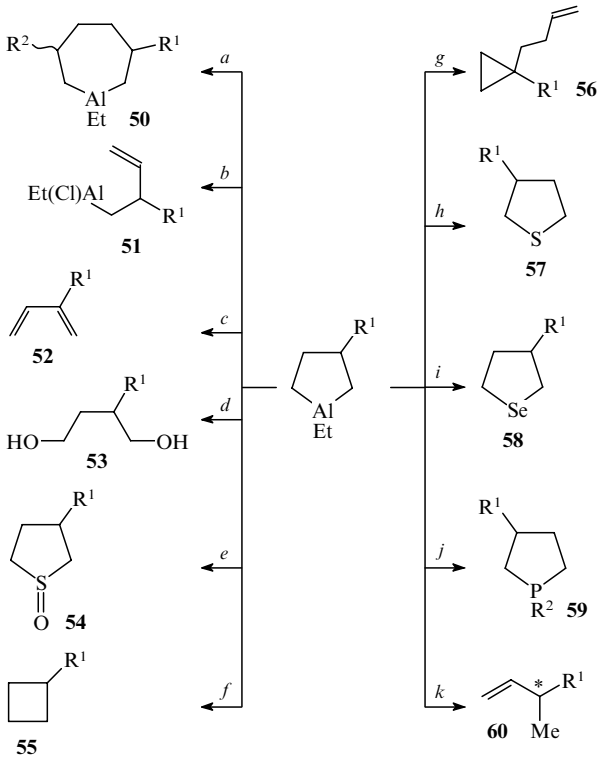
After substitution of dihalogenoalanes for higher trialkylalanes, the cycloalumination of terminal alkenes occurs more selectively and gives *trans*-3,4-dialkyl-substituted ACP. In contrast with previously developed procedures;[173, 179, 180] the reactive catalytic intermediate, *viz*., Cp_2Zr, is generated in these reactions by reduction of Cp_2ZrCl_2 in THF by Mg activated with $RAlCl_2$. This approach enables the synthesis of 1-alkyl-, 1-alkoxy-, 1-dialkylamino- and 1-halogeno-*trans*-3,4-dialkyl-substituted alumacyclopentanes **49** from α-alkenes, dihalogenoalanes and metallic magnesium (which is a halogenide ion acceptor) in the presence of catalytic amounts of Cp_2ZrCl_2 or $ZrCl_4$ (yields 70%–90%).[182–184] The structure of substituted alumacyclopentanes, the position of substituents and their configuration were established by spectral methods.[185, 186]



R^1 = Alk, RO, R_2N; R^2 = Alk(C_3–C_{20}); [Zr] = Cp_2ZrCl_2, $ZrCl_4$.

The incorporation of an alkene molecule into the Al–C bond of 3-alkyl-substituted ACP in the presence of Ti complexes is an efficient procedure for obtaining 1-ethyl-3,6-dialkyl-substituted alumacycloheptanes **50**.[102] The cleavage of the Al–C bond in ACP in the presence of nickel catalysts results in the unsaturated OAC **51**[187] or 2-alkyl-substituted 1,3-dienes **52** in quantitative yields (Scheme 2).[188]

Scheme 2



(*a*)  R^2, [Ti]; (*b*) , [Ni]; (*c*) , [Ni]; (*d*) O_2;

(*e*) $SOCl_2$; (*f*) , [Pd]; (*g*) , [Ni]; (*h*) S_8; (*i*) Se;

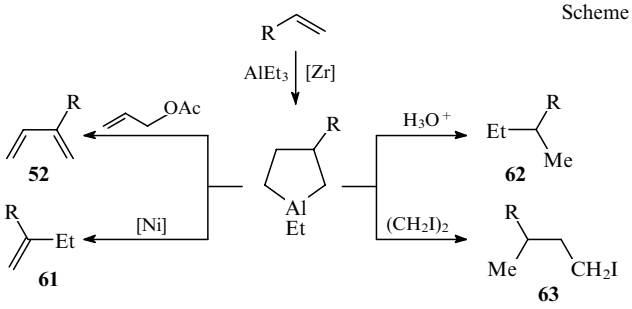
(*j*) R^2PCl_2; (*k*) Zr–L*.

ACP was used in the synthesis of different classes of compounds (see Scheme 2). They are active co-catalysts in co-telomerisation reactions as well as in one-pot conversions of α-alkenes into 1,4-butanediols **53**,[189] thiolane 1-oxides **54**,[190] cyclobutanes **55**,[191, 192] cyclopropanes **56**,[193] thiophanes **57**, selenophanes **58**,[194, 195] phospholanes **59**,[196] α,ω-dienes [197] and optically active hydrocarbons **60**.[198]

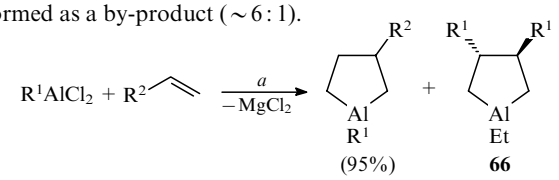
ACP were used as intermediates in preparative syntheses of 2-alkyl-substituted 1,3-dienes **52** (β-vinylation [188]), 1,1-dialkylethylenes **61** (reductive β-vinylation [187, 199]), branched hydrocarbons **62** (reductive β-ethylation [200]) and iodo-derivatives **63** (reductive β-iodoethylation [201]) from alkenes (Scheme 3).

The use of ACP offers a simple approach to the synthesis of linear *E*-isoprenoids **64** and **65** with a definite number of the C_5 fragments.[202] Alumacyclopentanes can be used in the synthesis of biologically active compounds, *e.g.,* pheromones of pine sawfly, German cockroach and mealworms *Tribolium confusum* and *Tribolium castaneum* (Scheme 4).[203–206]

Scheme 3

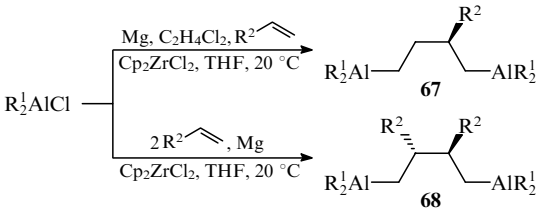


A method for the synthesis of 3-alkyl-substituted ACP from α-alkenes and $AlEt_3$ (see Refs 173, 179, 180) was recently modified through the application of more readily available and less pyrophoric reagents. This novel procedure is also based on the *in situ* generation of an active catalytic species, *viz*., Cp_2Zr, from Cp_2ZrCl_2 and simultaneous introduction of α-alkene and ethylene molecules, synthesised *in situ* from dichloroethane and metallic Mg, into the coordination sphere of the central atom of the catalyst.[207,208] The main product of this reaction is 3-alkyl-substituted ACP; 1-ethyl-*trans*-3,4-dialkyl-substituted ACP **66** is formed as a by-product (~6 : 1).



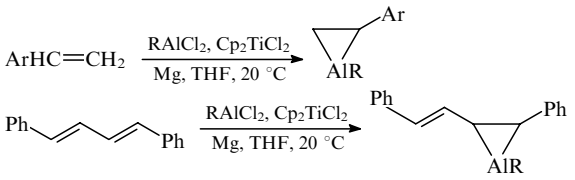
(*a*) Cp_2ZrCl_2, Mg, $C_2H_4Cl_2$, THF, 20 °C.

Substitution of R_2AlCl for $RAlCl_2$ gives substituted 1,4-dialuminiobutanes **67** and **68** which represent a novel class of acyclic OAC. This reaction was studied rather comprehensively for numerous α-alkenes and structurally different OAC.[209]

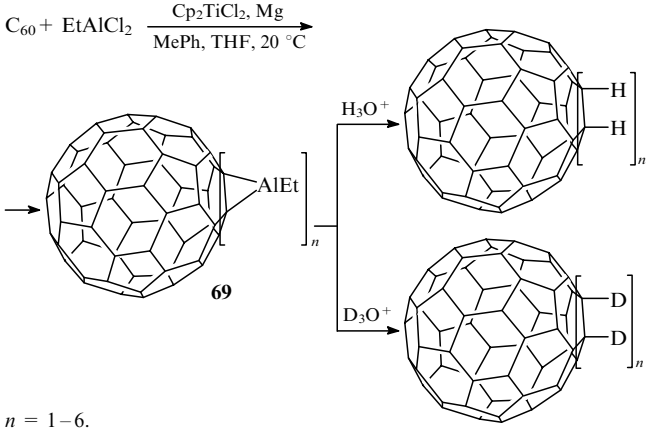


$R^1 = OR^3, NR^3_2, R^3S, Alk(C_3-C_{20})$.

In 1997, Dzhemilev *et al*. developed a method for the synthesis of a previously unknown class of metallacycles, *viz*., alumacyclopropanes. Cycloalumination of arylalkenes (styrene, *o*- and *p*-methylstyrene and 1,4-diphenylbuta-1,3-diene) with ethylaluminium dichloride in the presence of metallic magnesium as a chloride ion acceptor and Cp_2TiCl_2 yielded alumacyclopropanes (yields 80%).[210]

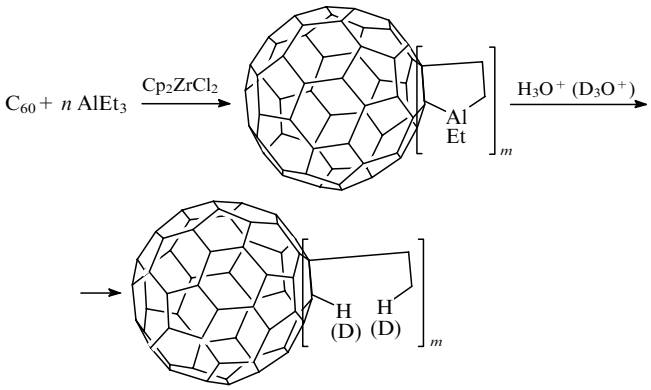


Treatment of the C_{60} fullerene with $EtAlCl_2$ in the presence of Cp_2TiCl_2 and Mg yielded the organometallic compounds **69** containing alumacyclopropane fragments.[207,211] Cycloalumination of C_{60} probably involves titanacyclopropane intermediates, $Cp_2Ti(\eta^2\text{-}C_{60})$;[212] transmetallation of the latter with $EtAlCl_2$ results in fullerenic alumacyclopropanes **69**.



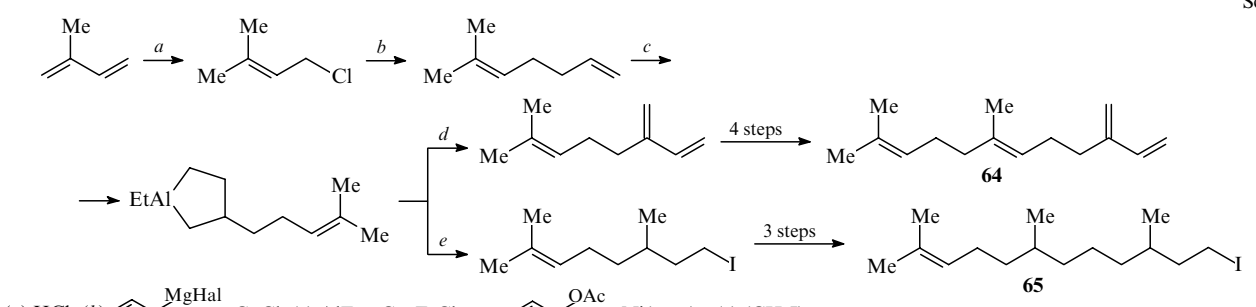
$n = 1-6$.

Cp_2ZrCl_2-Catalysed cycloalumination of the C_{60} fullerene with $AlEt_3$ recently carried out by Dzhemilev *et al*.[213,214] gave the organometallic derivatives of C_{60} containing alumacyclopentane fragments. Organometallic fullerene derivatives containing two alumacyclopentane fragments are formed in toluene (~22 °C, 36 h) at the C_{60} : $AlEt_3$ ratio of 1 : 30 (total yield ~80%). At the C_{60} : $AlEt_3$ ratio of 1 : 300, up to 12 alumacyclopentane fragments can be introduced into the C_{60} molecule.



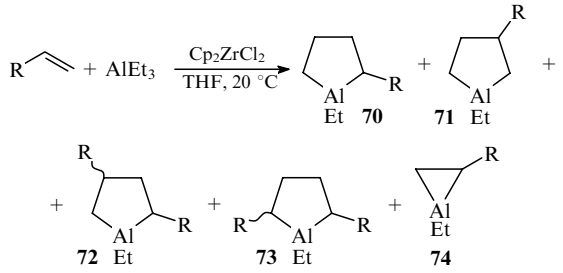
$n = 30, 300$; $m = 2-12$.

Scheme 4



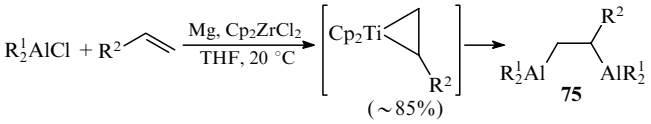
(*a*) HCl; (*b*) , CuCl; (*c*) $AlEt_3$, Cp_2ZrCl_2; (*d*) , $Ni(acac)_2$; (*e*) $(CH_2I)_2$.

In contrast with aliphatic alkenes, cycloalumination of terminal aryl-substituted alkenes with $AlEt_3$ in the presence of Cp_2ZrCl_2 occurs less selectively. Thus a mixture of mono- and disubstituted arylalumacyclopentanes and 2-aryl-1-ethylalumacyclopropane are formed in a total yield >90% (**70** : **71** : **72** : **73** : **74** ~ 50 : 25 : 15 : 3 : 7).[207, 215]



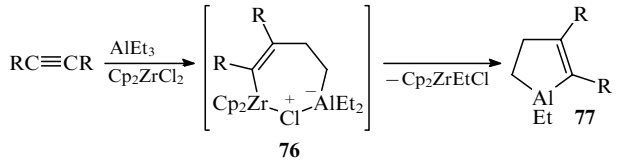
R = Ph, 2-MeC_6H_4, 4-MeC_6H_4.

The reaction of R_2AlCl with arylalkenes catalysed by Cp_2TiCl_2 was used in the synthesis of 1,2-dialuminiomethanes **75**.[215]



VII. Catalytic cycloalumination of alkynes

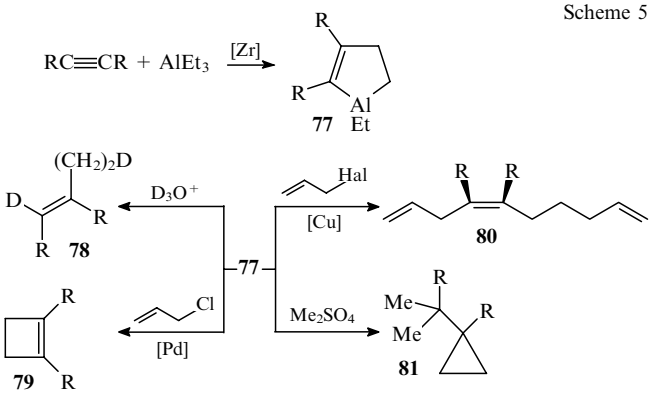
Simple procedures have been developed for the synthesis of unsaturated cyclic OAC from saturated three- and five-membered cyclic OAC in the presence of titanium- and zirconium-containing metal complex catalysts. Thus cycloalumination of disubstituted acetylenes with triethylaluminium in the presence of catalytic amounts of Cp_2ZrCl_2 gave 2,3-dialkyl(aryl)-substituted alumacyclopent-2-enes **77**.[216, 217] Carboalumination of disubstituted acetylenes in halogen-containing solvents yields acyclic alkenylalanes.[84] The nature of the solvent plays a crucial role in the formation of intermediate titanium- and zirconium-containing metallacycles **76**, the key intermediates in the synthesis of alumacyclopentenes **77**.[84, 218]



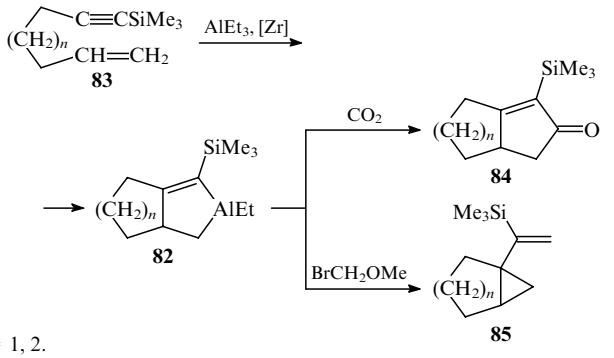
The structure of alumacyclopentenes **77** was established by spectral methods [217] and by their conversions. Thus hydrolysis of compounds **77** with D_2O gave trisubstituted alkenes **78** (Scheme 5).[217] Dealumination of OAC **77** in the presence of catalytic amounts of palladium phosphine complexes results in 1,2-disubstituted cyclobutenes **79**.[219] In the presence of an excess of dimethyl sulfate, compounds **77** are readily transformed into 1,1-dialkyl-substituted cyclopropanes **81**. Cross-coupling of OAC **77** with allyl halides results in 4,5-disubstituted 1,(4*Z*),9-decatrienes **80** (see Scheme 5).[220]

In 1998, Negishi *et al.*[178] carried out the synthesis of bicyclic alumacyclopentenes **82** by intramolecular cycloalumination of enynes **83** in the presence of catalytic amounts of Cp_2ZrCl_2.

Scheme 5

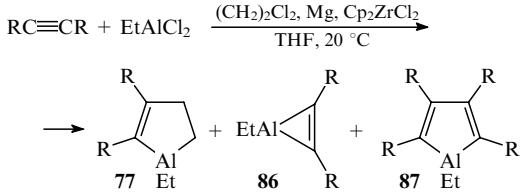


Subsequent treatment of OAC **82** with CO_2 or $BrCH_2OMe$ resulted in the corresponding cyclopentenones **84** and vinylcyclopropanes **85**.

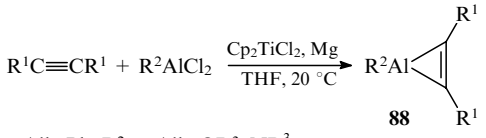


n = 1, 2.

A modified procedure for the synthesis of 1-ethyl-2,3-dialkyl-(aryl)alumacyclopent-2-enes **77** from disubstituted acetylenes and ethylene generated *in situ* from dichloroethane and activated metallic magnesium has been recently developed by Ramazanov *et al.*[221, 222] This reaction yields the corresponding alumacyclopropenes **86** and alumacyclopentadienes **87** as by-products (5% – 30%).



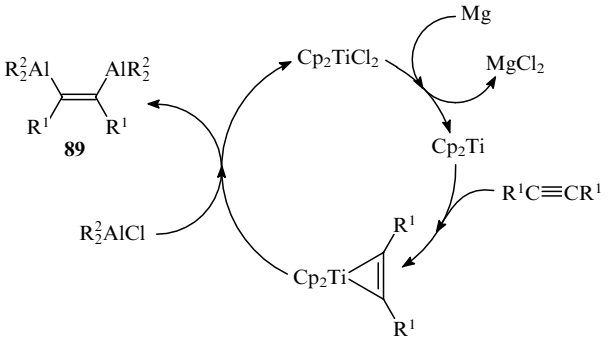
The synthesis of alumacyclopropenes **88** by cycloalumination of 1,2-disubstituted acetylenes using alkyldichloroalanes [223] in the presence of Ti complexes is one of the most substantial achievements in the synthesis of small alumacycles. Presumably, these reaction conditions favour the generation of titanacyclopropene intermediates,[224 – 235] their transmetallation with dihalogenoalanes results in the corresponding trisubstituted alumacyclopropenes **88**.[223, 236 – 238]



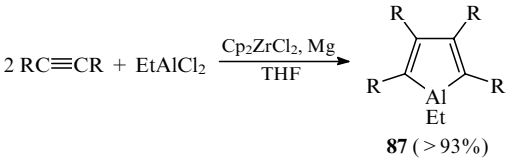
R^1 = Alk, Ph; R^2 = Alk, OR^3, NR^3_2.

In contrast with 1,2-disubstituted acetylenes, terminal alkynes react with $RAlCl_2$ in the presence of Ti complexes less selectively. This reaction yields alumacyclopentadienes **87** along with alumacyclopropenes **88**.

The synthesis of 1,2-dialuminioethylenes **89** by the reaction of 1,2-disubstituted acetylenes with R_2AlCl under the action of catalytic amounts of Cp_2TiCl_2 in the presence of a chloride ion acceptor (activated Mg) has been carried out by Dzhemilev *et al.*[239]



1-Ethyl-2,3,4,5-tetraalkyl-1-alumacyclopenta-2,4-dienes **87** were synthesised with high selectivity by cycloalumination of 1,2-dialkyl-substituted acetylenes using $EtAlCl_2$ in the presence of Cp_2ZrCl_2 (5 mol.%, ~23 °C, TTF).[221,240] The content of alumacyclopropenes in the reaction mixture does not exceed 5%–7%.



87 (>93%)

R = Alk(C_3–C_{10}).

VIII. Conclusion

In the past 10–15 years, organoaluminium compounds have gained popularity in the practice of synthetic organic and organometallic chemistry along with organomagnesium reagents.

The catalytic reactions of hydro-, carbo- and cycloalumination of alkenes, dienes and alkynes are carried out under mild conditions and yield OAC with high regio- and stereoselectivity. Thus OAC were used in the synthesis of the major classes of natural compounds, such as vitamins, antibiotics, alkaloids, steroids, carbohydrates, prostaglandins, isoprenoids, drugs, *etc*.

We are convinced that future syntheses will widely employ organoaluminium compounds and will be aimed at obtaining novel co-catalysts for oligomerisation and polymerisation reactions and efficient reagents for regio- and stereoselective reduction and alkylation of unsaturated compounds as well as at the development of non-traditional approaches to the design of organic and organometallic compounds and most advanced chemical technologies.

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