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Catalysis by metal complexes in organoaluminium synthesis

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ABSTRACT. In this review a summary is given of studies conducted both within and outside the Soviet Union on the synthesis and conversions of organoaluminium compounds (OACs) in the presence of metal complexes as catalysts. The following reactions have been examined: catalytic hydro-, carbo- and cyclo-alumination of unsaturated compounds, cross-coupling and conjugate addition of OACs to enones, and certain other conversions of OACs in the presence of metal complexes as catalysts.

The bibliography includes 211 references.

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I. Introduction

In contrast with organomagnesium compounds, which have been widely used in organic synthesis since their discovery by Grignard, organoaluminium compounds (OACs) were almost unknown up to the 1950s. Since then, in spite of their cheapness and the availability of simple derivatives, they have been used mainly as components in catalytic systems for oligo- and poly-merisation of olefins.

In recent years the position has changed as many OACs have been elevated to a position of importance in organic synthesis and laboratory practise, in spite of the fairly high risks associated with their handling. Thus, *i*-Bu_2AlH is now one of the most widely used reducing agents in organic synthesis; the effective use of OACs as selective alkylating agents also deserves a special mention.

The new opportunities for using OACs in organic synthesis are now more and more associated with catalysis by metal complexes. Their selectivity has led to the discovery of many hitherto unknown reactions of practical value, and the mild conditions under which they can be conducted have minimised handling risks. Some reactions uncharacteristic of OACs have also led to the preparation of novel reagents considered previously as 'exotic'. During the last 10–15 years, a significant growth in publications in this area has been recorded.

In this review there is a survey of the results obtained by using homogeneous metal complexes as catalysts in the synthesis of varied OACs and their subsequent reactions; information has been excluded on the use of OACs as components of catalytic systems for the oligo- and poly-merisation of unsaturated compounds.

II. Hydroalumination

Hydroalumination of unsaturated compounds is one of the most characteristic reactions of OACs and frequently applied[1]. It is more than 25 years ago that the first experiments in hydroalumination with complex metal catalysts were undertaken with a view to broadening the scope of the reaction.[2,3] Since then, a large number of publications and patents have appeared in which many transition metals have been proposed as hydroalumination catalysts. However, as a result of exhaustive studies in this area by Ashby et al.[4–6], it has been established that both hydrometallation and hydrogenation of the unsaturation can take place in the presence of low-valent transition metal complexes, the latter course arising by hydride transfer from the medium. Thus, at the present time, any report on catalytic hydrometallation is greeted with much scepticism if there is no supporting evidence over and above analytical data on the products of hydrolysis of the reaction mass. It is our opinion that, nowadays, only titanium and zirconium compounds are 'beyond reproach' as hydroalumination catalysts. However, in this review there will be an examination of several interesting conversions in the presence of other transition metal complexes where the formation of OACs has been reliably confirmed.

1. Hydroalumination of acetylenes

Hydroalumination of disubstituted acetylenes is relatively facile, and can be achieved under fairly mild conditions with the aid of *i*-Bu_3Al or *i*-Bu_2AlH in the absence of any catalyst; however, it is not possible to avoid unwanted side reactions or subsequent conversions of the formed vinylalanes.[1,7]

A catalytic amount of $Ni(acac)_2$ enhances the reaction of OACs with 4-octyne, phenylpropyne and certain other disubstituted acetylenes at 25 °C.[8] At the same time, titanium or zirconium complexes have no effect on this reaction.[9,10]

However, in the presence of Cp_2TiCl_2, complexes of *i*-Bu_3Al with organomagnesium compounds (*i*-BuMgBr, EtMgBr) hydroaluminate the majority of disubstituted acetylenes readily under mild conditions, thereby avoiding unwanted reactions.[9–11]

$$R^1C{\equiv}CR^2 + n\ i\text{-}Bu_3Al.RMgBr \xrightarrow[0-20\ ^\circ C,\ 20\ min]{Cp_2TiCl_2(2\%),\ Et_2O}$$

$$\rightarrow \underset{95-98\%}{\overset{M}{\underset{R^1}{|}}\!=\!\underset{R^2}{|}} \xrightarrow{D_2O} \underset{100\%\ (Z\text{-isomer})}{\overset{D}{\underset{R^1}{|}}\!=\!\underset{R^2}{|}}$$

R^1, R^2 = Alk, Ar, OR^3, $SiMe_3$; $n = 3-10$;

M = organomagnesium or organoaluminium compound.

The stereoselectivity with this reagent is as high as that with 9-borabicyclo[3.3.1]nonane, and there is no difference in regioselectivity for the hydrometallation of unsymmetrically disubstituted acetylenes.

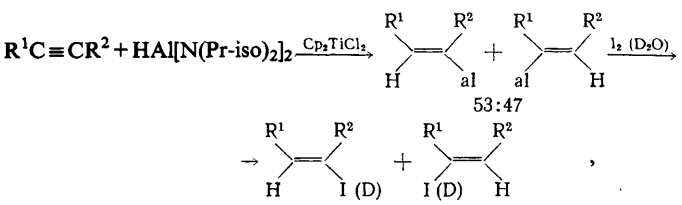
In the carboalumination of monosubstituted acetylenes with triethyl- and tripropyl-aluminium,[12-13] there is little mention of catalytic hydroalumination as a side reaction, and no indication on the possibility of achieving selective hydroalumination.

There are numerous examples of hydroalumination of acetylenes with a variety of complex hydrides. For this purpose, Ashby[14] recommended the novel bis(dialkylamino)alanes, being prepared in quantitative yield by interaction of aluminium with *sec*-amines under hydrogen pressure:

$$Al + H_2 + 2\,R_2NH \xrightarrow[\text{benzene}]{140\ ^\circ C,\ \sim 140\ atm\ H_2} HAl(NR_2)_2, \quad 100\,\%$$

R = Pr, Bu, Am.

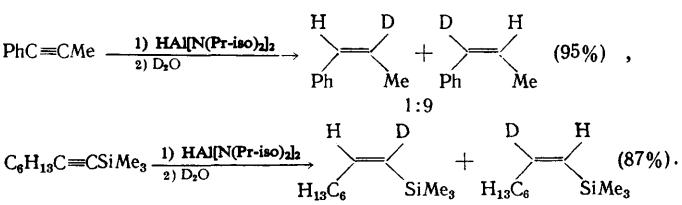
In the presence of 5 mol% Cp_2TiCl_2, these hydrides readily add to mono- and di-substituted acetylenes in benzene (in which they are very soluble) at 0 °C to room temperature.[15] The conversion of the acetylenes is nearly quantitative. (*Z*)-Alkenylalanes (90–96%) are the main products, the corresponding (*E*)-isomers being formed in no more 1–4% yield.



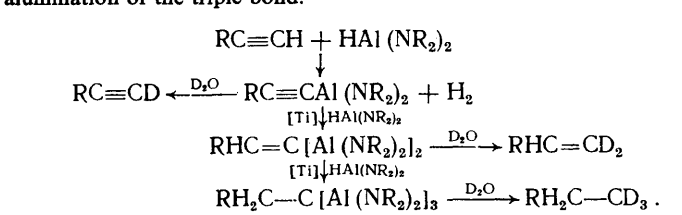
R^1 = Me, R^2 = n-Pr, al – organoaluminium compound.

Subsequent treatment with D_2O led to 96–97% incorporation of deuterium into the derived alkenes. The corresponding alkanes are formed simultaneously in up to 10% yield[16].

High regioselectivity is recorded only for the hydrometallation of 1-phenylprop-1-yne and 1-(trimethylsilyl)oct-1-yne:



For monosubstituted alkynes, deuterolysis of the products of hydroalumination affords, principally, a mixture of alkenes and alkanes in approximately equal amount with varying levels of D-incorporation; this confirms the complex nature of the metallation, and notably the aspect of mono- and di-hydroalumination of the triple bond.[16]



Hydroalumination of disubstituted acetylenes with other complex hydrides ($LiAlH_4$, $LiAlH_2[N(Pr\text{-}i)_2]_2$, $NaAlH_2(NEt_2)_2$, $NaAlH_2[N(Pr\text{-}i)_2]_2$, $LiAlMe_3H$) in the presence of Cp_2TiCl_2 or other titanium reagents proceeds in much the same way, the only difference being that stereoselectivity is higher (in some cases up to 100%) than with bis(dialkylamino)alanes and that side reactions are less.[5,6,16-19]

Mono- and di-phenyl-substituted acetylenes undergo hydroalumination non-selectivity, a significant amount of (*E*)-alkenylalanes being formed.[19]

2. Hydroalumination of olefins

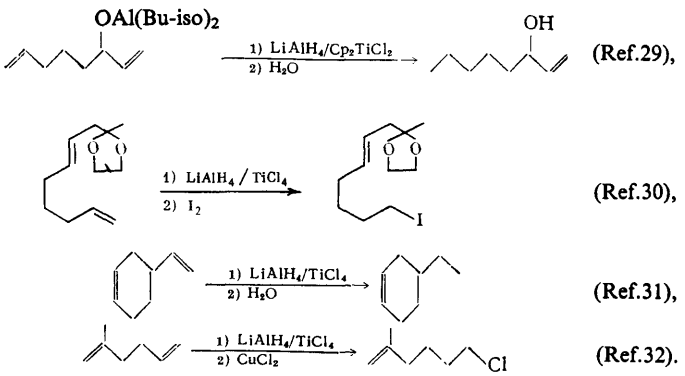
Catalytic hydroalumination of olefins is widely used in organic synthesis for a variety of purposes: for selective reduction of double bonds or their functionalisation, as well as for the preparation of higher OACs of defined structure for subsequent conversions.[20] Almost all of the readily available aluminium hydrides and simple alkylalanes have been used as hydroaluminating agents. For such purposes, $LiAlH_4$ has been most frequently used. Since Sato discovered that titanium and zirconium compounds may be used as catalysts for hydroalumination of olefins under mild conditions,[21,22] this reaction has found widespread application.

A variety of titanium complexes, among which those immobilised on inorganic[23] or polymeric[23,24] supports, is currently available for catalysed hydroalumination. The preliminary report[25] on the successful application of V and Cr salts as catalysts has not been subsequently confirmed. Recently, there was a communication[26] on the use of exotic catalysts, such as uranium salts (UCl_3 and UCl_4), for the hydroalumination of C_2–C_8 α-olefins. Zirconium complexes are no less effective than titanium complexes as catalysts; they are used preferably for the hydroalumination of allylic alcohols and ethers[27] since deoxygenation of these substrates takes place in the presence of titanium complexes.

It is reported[7,23,28] that reaction proceeds via intermediate formation of titanium or zirconium hydride complexes, which initially hydrometallate the olefin and are regenerated by subsequent transmetallation of the formed transition metal alkyl derivatives.

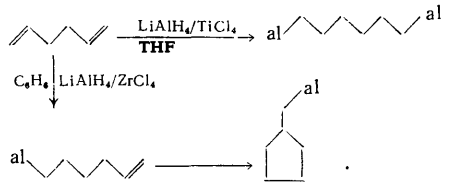
$$LiAlH_4 + ML_m \rightarrow L_nM{-}H,$$
$$L_nM{-}H + CH_2{=}CH{-}R \rightarrow L_nMCH_2{-}CH_2{-}R,$$
$$L_nMCH_2{-}CH_2{-}R + LiAlH_4 \rightarrow L_nM{-}H + al{-}CH_2{-}CH_2{-}R,$$
$$M = Ti, Zr;\ al = LiAl/4.$$

The relative reactivity of the alkenes in these reactions depends largely on steric factors. Disubstituted alkenes react far more slowly than monosubstituted alkenes, which in certain cases facilitates selective hydroalumination of the less substituted double bond:



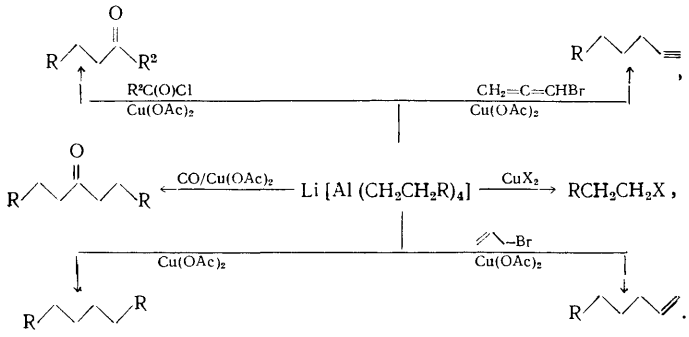
The course of the reaction with unconjugated α,ω-dienes, notably with 1,5-hexadiene, depends on the nature of the catalyst and the

reaction conditions. Thus, by using $TiCl_4$ in THF, 1,5-hexadiene was converted into acyclic bis-OACs; however, on replacement of THF by benzene, or of $TiCl_4$ by $ZrCl_4$, intramolecular cyclisation takes place:[9,15]



By catalytic hydroalumination a variety of highly reactive lithium tetralkylaluminates can be obtained, including derivatives with *O*- and *N*-functional groups.[27,30,33] Scheme 1 illustrates certain of their conversions in the presence of copper salts.[34–41]

Scheme 1



Such complex hydrides as $NaAlH_4$, $LiAlMe_3H$, $NaAlMe_3H$, and $NaAl(OCH_2CH_2OCH_3)_2H_2$ are no less active than $LiAlH_4$ in this respect.[6]

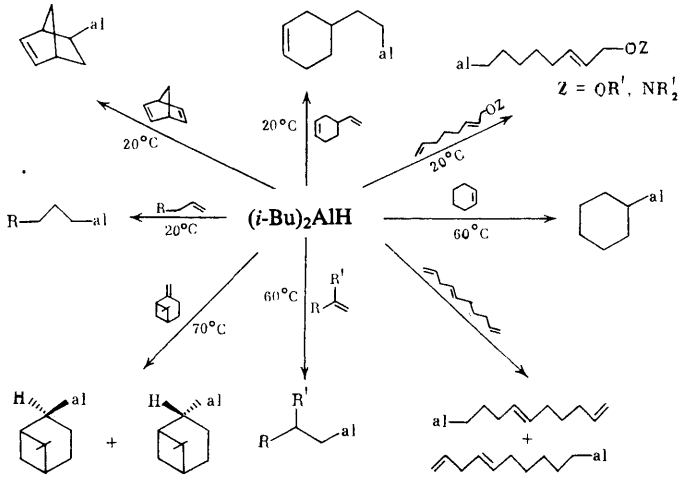
At the same time, other hydrides which Ashby studied, e.g. $HAl[N(Pr\text{-}i)_2]_2$, $HAl(NEt_2)_2$, $HAl[N(SiMe_3)_2]_2$, H_2AlCl, and $HAlCl_2$, displayed somewhat lower activity on hydroalumination of α-olefins in the presence of titanium complexes. As indicated above, the corresponding zirconium complexes exert almost no catalytic effect on the reaction.[4]

It has been reported that catalytic hydroalumination of conjugated dienes, e.g. isoprene, butadiene, and 1,3-hexadiene, can be achieved with $HAl[N(Pr\text{-}i)_2]_2$. However, selectivity in these reactions is not high.[4,23]

The more accessible and inexpensive alkylalanes may be used in place of complex hydrides for synthetically viable hydroaluminations. For hydroalumination of olefins with $(i\text{-}Bu)_2AlH$ under mild conditions, the most effective catalysts are zirconium salts;[42] with titanium catalysts, however, isomerisation and oligomerisation of the olefins are noted side reactions.

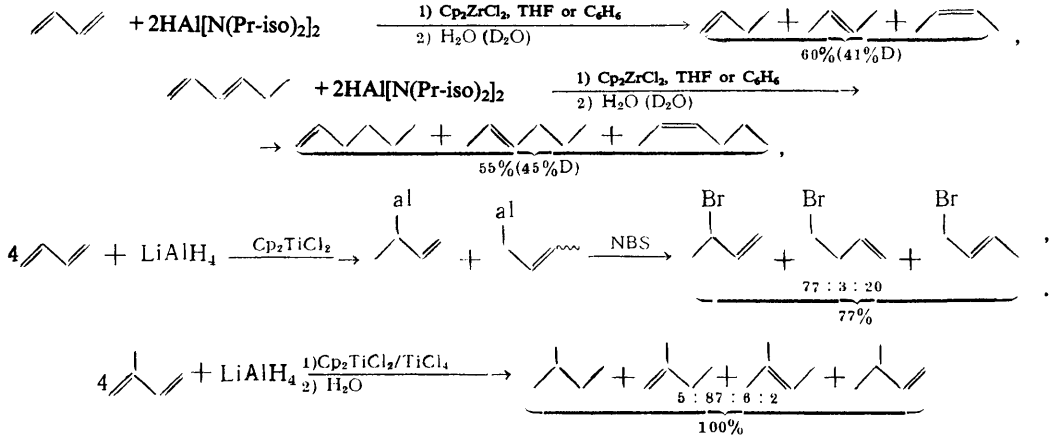
Thus, hydroalumination of α-olefins and norbornene derivatives with $(i\text{-}Bu)_2AlH$ can be effected almost quantitatively in the presence of $ZrCl_4$ at 20 °C during 3–6 h; the same reaction with α,β- and β,β′-disubstituted olefin requires a higher temperature (*ca.* 60 °C), thereby facilitating selective hydroalumination of polyene hydrocarbons possessing double bonds with different degrees of unsaturation (Scheme 2).[43–46]

Scheme 2



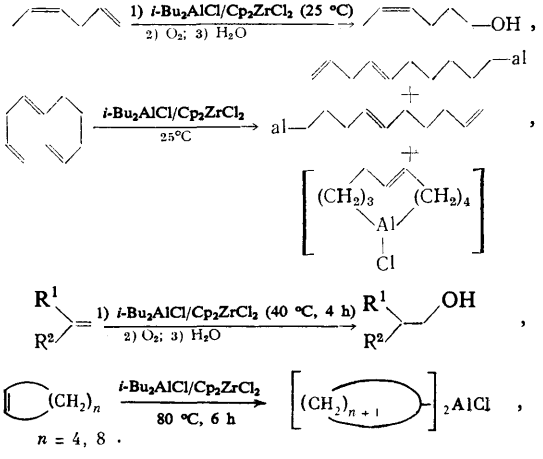
Chlorozirconium alkoxides have proved to be the most effective catalysts for hydroalumination of cyclic olefins.[44] The rate of hydroalumination of cyclic olefins depends on the ring size and decreases in the order: $C_5 > C_6 > C_7 > C_{12} > C_8$.

$i\text{-}Bu_3Al$ and $i\text{-}Bu_2AlCl$ are effective for the hydroalumination of a variety of olefins in the presence of a catalytic amount of Cp_2ZrCl_2.[47–50] $i\text{-}Bu_3Al$ adds to α-olefins even at 0–20 °C, which permits the synthesis of higher OACs under mild conditions; these include derivatives with functional groups (OH, SPh, Br) [47].

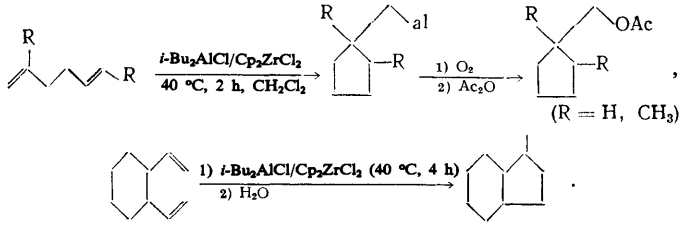


The interaction of *i*-Bu_3Al with cyclic olefins takes place at > 80 °C, although it is not possible to introduce more than two of the three isobutyl groups.[50]

Catalytic hydroalumination with *i*-Bu_2AlCl affords higher dialkylaluminium chlorides which cannot be obtained by classical routes, i.e. by non-catalytic hydroalumination.[48,50,51] For this reaction a general rule has been established: for hydroalumination with *i*-Bu_2AlH, α-olefins react most readily (at 25 °C), the disubstituted unsaturation in linear olefins reacts at 40 °C, and cyclic olefins only participate in reaction at 80 °C and above.

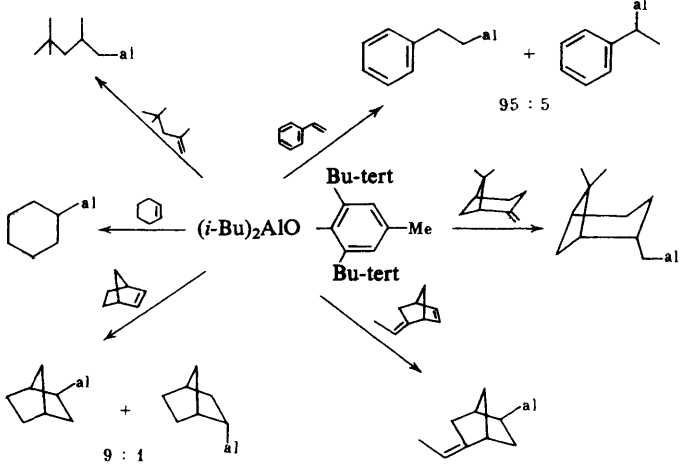


The interaction of 1,5-dienes with *i*-Bu_2AlCl under these same conditions leads to the formation of cyclic products:

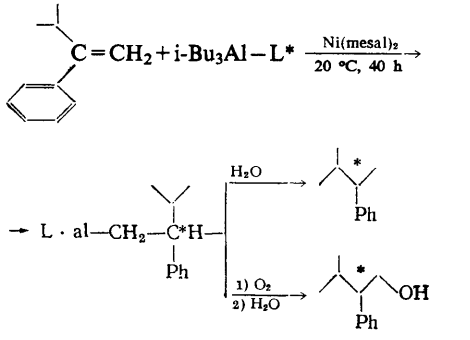


The organoaluminium monoaroxide obtained by interaction of *i*-Bu_2AlH with 2,6-di-tert-butyl-4-methylphenol regioselectively hydroaluminates mono- and di-substituted olefins (among which certain norbornene derivatives) at > 140 °C in xylene in the presence of *i*-Bu_2AlH/Cp_2ZrCl_2 as catalyst (Scheme 3).[52]

Scheme 3

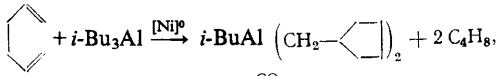


The asymmetric hydroalumination of prochiral alkenes with complexes of the type *i*-Bu_3Al-L^* (where L^* is an optically active amine, such as (–)-N,N-dimenthylmethylamine) is catalysed by $Ni(mesal)_2$ (where mesal is methyl salicylate):



Hydrolysis or oxidation of the formed alane yields the corresponding optically active hydrocarbon or alcohol with a maximum optical yield of 27% [53] and 67% [54], respectively. The possibility of regenerating the chiral base affords this method real potential in synthetic chemistry.

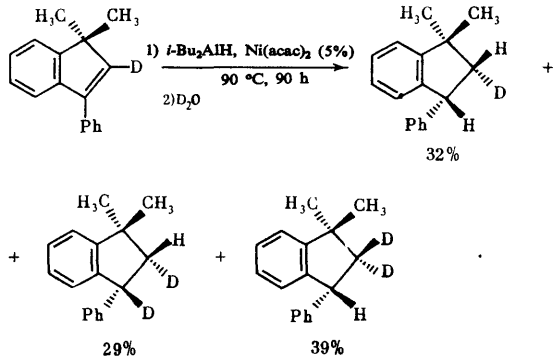
The use of zero-valent nickel complexes as catalysts for the hydroalumination of α-olefins with *i*-Bu_3Al permits the removal of the nickel catalyst as volatile $Ni(CO)_4$ at the end of the reaction; the higher OACs thus obtained do not contain catalytic impurities.[54]



$$[Ni]_0 \xrightarrow{CO} Ni(CO)_4,$$

$$[Ni]^0 = (C_2H_4)_3Ni,\ (COD)_2Ni,\ (PhCH{=}CHPh)_3Ni.$$

A recent systematic study of the mechanism of nickel-catalysed hydroalumination has revealed that there are general features in common with a mechanism involving hydride transfer. Experimental data confirms the fact that there are catalytically active intermediates, most notably bimetallic nickel-aluminium hydrides[55].



As a rule a significant amount of saturated products is formed in addition to OACs.

III. Carbo- and cyclo-alumination

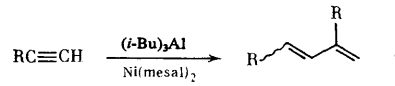
Stereo- and regio-selective single-step addition (i.e. monocarbometallation) of organometallic compounds to olefins and acetylenes is extremely important in synthetic planning since it leads to the

simultaneous formation of a metal–carbon and carbon–carbon bond. Although various metals are known to participate in the carbometallation of multiple bonds, only zirconium-catalysed carboalumination and cuprate synthesis by the Normant procedure permits the desired addition with high regio- and stereo-selectivity.

1. Carboalumination of acetylenes

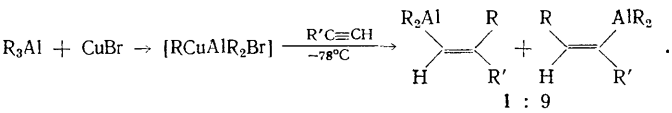
Non-catalytic carboalumination of mono- and di-substituted acetylenes is rarely applied in synthetic chemistry because of the low selectivity[7]. However, the number of transition metals which have been used as catalysts for this reaction is extremely large.

Attempts at selective carbometallation of monosubstituted acetylenes in the presence of Ni and Mn have proved to be effectively negative. Thus, treatment of mono-substituted acetylenes with i-Bu_3Al in the presence of $Ni(mesal)_2$ led to the formation of dimers:



Under the same conditions enynes gave a more complex mixture containing a small amount of product derived by hydro- and carbometallation, in addition to di- and tri-mers.[56–59]

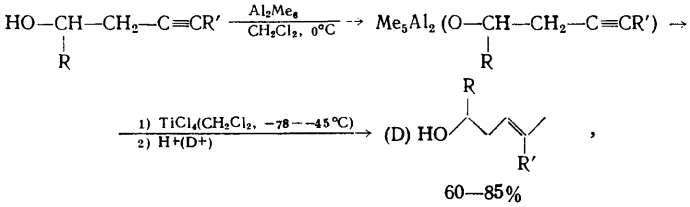
Carboalumination of 1-alkynes with trialkylalanes in the presence of $Cu(acac)_2$ and Ph_3P (Al : Cu : P = 2 : 1 : 1) is accompanied by their polymerisation, which leads to a reduction in the yield of desired product. High yields (up to 80%) and ⩾90% selectivity were found only by interaction of 1-alkynes with bimetallic aluminocuprate reagents, $R_3Al-CuBr$.[60,61]



1 : 9

Disubstituted acetylenes, propargyl and homopropargyl alcohol, as well as ether derivatives thereof, were shown to be inactive under these reaction conditions.

More promising results were obtained by using titanium-containing catalysts which in certain cases lead to high regio- and stereo-selectivity. However, this reaction also has a number of limitations. The best results are obtained for the carbometallation of the relatively accessible homopropargyl alcohols on treatment with Me_3Al in the presence of $TiCl_4$.[62,63]

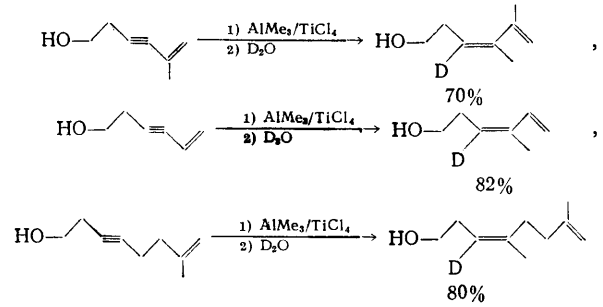


60—85%

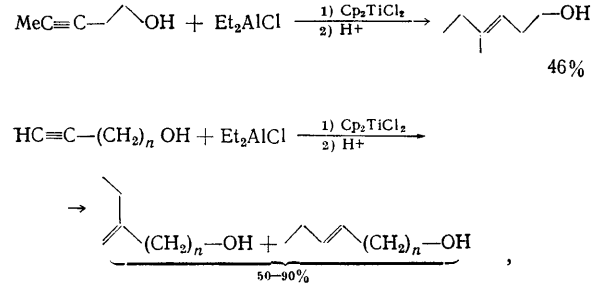
R = H, Me, Et, Ph; R′ = H, Me, Et, n-Pr, i-Pr, n-Bu, n-Am, Ph.

All the homopropargyl alcohols shown in the above scheme are selectively methylated at the triply-bonded carbon atom which is furthest from the OH-group.

In the case of 5-en-3-yn-1-ols, reaction affords (3Z)-4-methylalka-3,5-dien-1-ols in high yield and with complete selectivity; here also the methyl group is exclusively on the C_4 atom.[64]



By replacement of Me_3Al by Et_2AlCl or $EtAlCl_2$, the level of regioselectivity is the same only in the case of disubstituted alkynes[65,66], the stereoselectivity remaining unchanged.

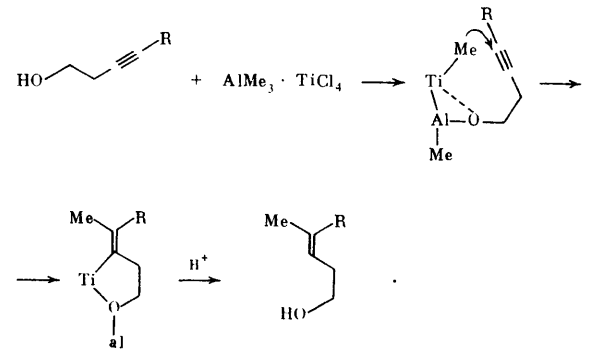


$n = 2-4$.

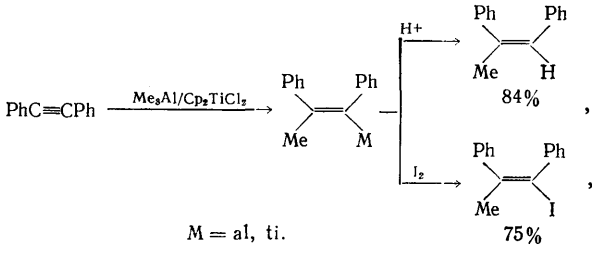
In this case Cp_2TiCl_2 has proved to be the best catalyst on conducting the reaction at 0 °C in methylene chloride during 4–6 h.

Evidently, reaction takes place via carbotitanation followed by transalkylation, although in isolated cases[66] it can be achieved easily in the presence of a catalytic amount (*ca.* 10 mol%) of the titanium reagent. However, as a rule, in order to obtain suitable yields, an equimolar amount of $TiCl_4$ or Cp_2TiCl_2 (relative to the starting alkyne) and twice the amount of OAC is required. According to certain authors,[67] the effective catalysts are four-valent titanium compounds which require activation by reduction to the three-valent state.

The regio- and stereo-selectivity of the reaction is determined by intramolecular formation of cyclic alkynyloxymetallic intermediates which are not disposed to β-hydride elimination or any other side reaction[62].

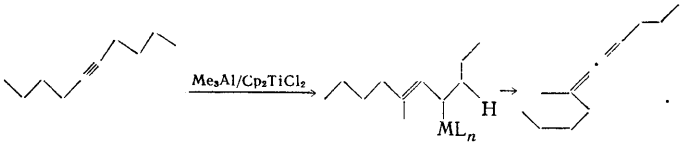


On the other hand, carboalumination of mono- and di-substituted alkynes which do not possess a hydroxyl group proceeds, as a rule, with low selectivity. Diphenylacetylene is an exception since it is readily carboaluminated under mild conditions with Me_3Al/Cp_2TiCl_2. The obtained OAC is converted on hydrolysis to (*Z*)-1,2-diphenylpropene (84%), while treatment with iodine affords 1-iodo-1,2-diphenylpropene (75%).[68]



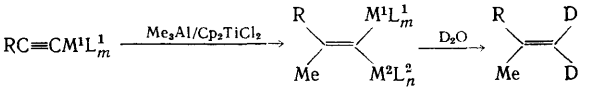
M = al, ti.

At the same time, reaction of dialkyl-substituted alkynes, e.g. 5-decyne, affords predominantly allenes:[68]



The yield of the products derived by carbometallation of monoalkyl-substituted acetylenes does not exceed 30%; unidentified oligomeric products are formed in the main.

For acetylenes functionalized at one of the unsaturated C-atoms by heteroatomic substituents (ZnCl, BR'_2, AlR'_2), the most selective system for carbometallation is Me_3Al/Cp_2TiCl_2.

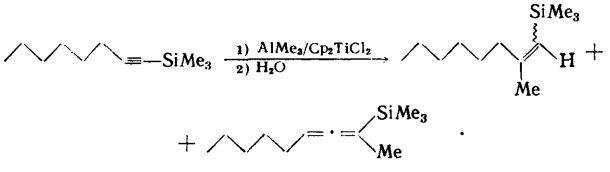


$M^1L^1_m$ = ZnCl, BR'_2, AlR'_2;

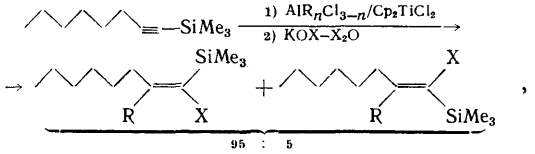
$M^2L^2_n$ = Al- and (or) Ti-containing group.

The heterobimetallic intermediates thus formed are converted on deuterolysis to 1,1-dideuterio-2-methylalkenes in 75–85% yield.[12]

In the case of carbometallation of 1-trimethylsilyl-1-alkynes, the yield and composition of the product is largely dependent on the reaction conditions and on the subsequent treatment of the intermediate alkenyl complexes. Thus, a mixture of vinyl- and allenyl-silanes was obtained in approximately 80% yield by carbometallation of 1-trimethylsilyl-1-octyne with trimethylaluminium.



Higher selectivity can be achieved by using halogen-containing alanes. In view of the marked increase in rate of the key step, the formation of side-products is kept to a minimum.[69]

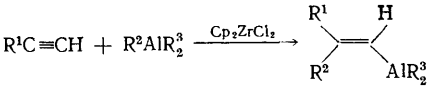


R = Me, Et; X = H, D.

The decomposition of the carbometallation product with aqueous KOH (or KOD in D_2O) is a critical stage which determines the reproducibility of the results; if an equimolar amount of triethylamine or another Lewis base is added before decomposition, then non-deuteriated isomeric vinylsilanes are formed, the *trans*-isomer predominating.[70] This effect is explained by the destabilising effect of the Lewis base on the intermediate alkenylaluminium complexes, which facilitates their protonolysis by the reaction medium.[71,72]

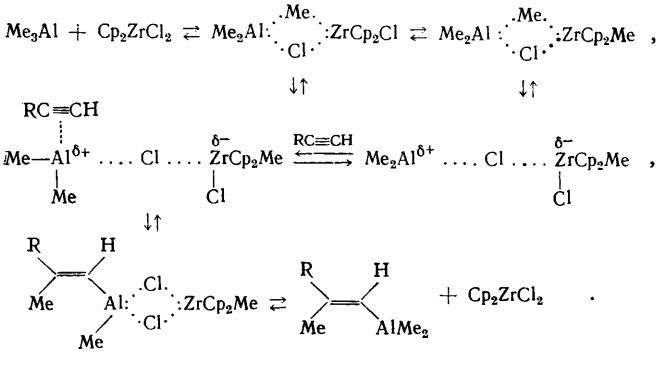
The problems normally associated with catalytic carboalumination of acetylenes have been overcome most effectively by using zirconium-containing catalysts. Discovered in 1978 by Negishi and Van Horn[69], the zirconium-mediated route has been studied in detail and found a place in synthetic organic chemistry for selective carboalumination of acetylenes; it is especially useful for the selective formation of isoprenoid residues, which are constituents of a large number of natural products. Because various aspects of this reaction have been discussed repeatedly in previous reviews,[12,72–77] only the fundamental characteristics of the reaction will be briefly touched on here.

As a rule the interaction of mono- or di-substituted acetylenes with alkylalanes affords the corresponding *cis*-adducts (*ca.* 98% stereochemical purity) in approaching quantitative yields.

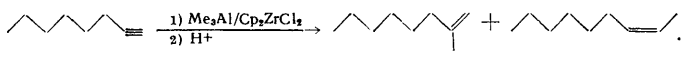


Reaction with trimethylalane is the most selective and that most often used; normally it is carried out in the presence of a catalytic amount (10 mol%) of Cp_2ZrCl_2. However, in certain cases, an equimolar amount of Cp_2ZrCl_2 and Me_3Al can be used to maximise the yield of desired product.

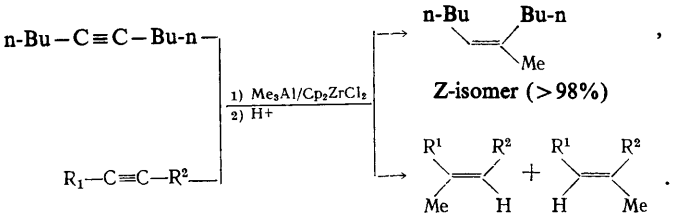
The mechanism of the reaction still requires clarification; however, current data would suggest that, in contrast with the corresponding titanium-catalysed process, it involves a direct interaction of the aluminium–carbon bond with the acetylene group.



Reaction of mono-substituted acetylenes with Me_3Al is not only stereoselective, but also regioselective.[79,80] Thus, 1-octyne, after appropriate treatment and hydrolysis, was converted into a 95:2 mixture of 2-methyl-1-octene and 2-nonene in a total yield of 97%:

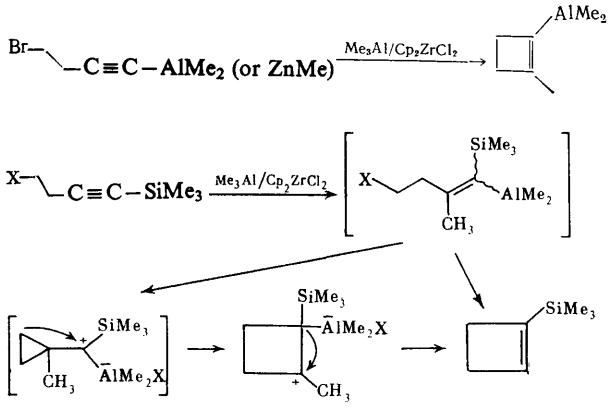


Symmetrically di-substituted acetylenes react with Me_3Al with the same stereoselectivity;[73] however for unsymmetrical substrates regioselectivity depends on the nature of the substituents.[12,78]

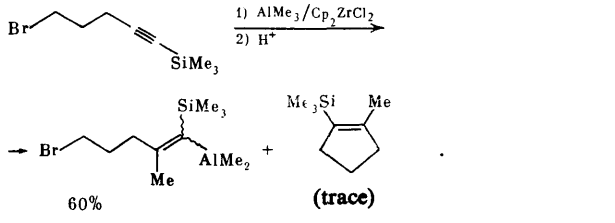


The overall yield is 89%. As well as alkyl groups, the alkyne component can contain such substituents as alkenyl, aryl, halogens, OH, OR′, SPh, and $OSiR'_3$; alkadiynes are also reactive, but only one of the two multiple bonds is affected, even in the presence of an excess of $AlMe_3$.[81,82]

ω-Halogen-substituted acetylenes with trimethylsilyl, dialkylaluminium, or alkylzinc groups on the terminal carbon of the unsaturation are exceptions to the rule; here, functionalised cyclobutenes are formed instead of the expected adducts.[83,84]



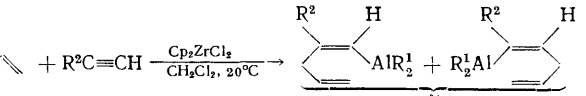
According to one report,[85] a π-type cyclisation is operative, in which the alkenyl fragment plays the role of nucleophile. The primary role of the σ-donor groups ($SiMe_3$, $AlMe_2$, ZnR) is to increase the nucleophilicity of the alkene. 5-Bromo-1-trimethylsilylalkynes are the least disposed to cyclisation, the principal products of reaction being acyclic.[85]



Unfortunately, the high (not less than 95%) regioselectivity associated with 'methylalumination' of terminal acetylenes falls to 75–85% on replacing the Me_3Al by other trialkylalanes.[12]

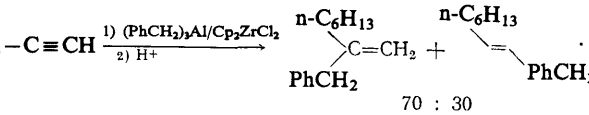
In addition to this, catalytic hydroalumination is a serious complication with those alkylalanes which are inclined to undergo β-hydride elimination. However, such hydroalumination can be successfully suppressed by using such reagent/catalyst combinations as $R_2AlCl-Cp_2ZrCl_2$ and $R_3Al-Cp_2Zr(R')Cl$.[12,86]

On account of the reduced regioselectivity, carboalumination with $AlEt_3$, $AlPr_3$ and other simple trialkylalanes has little synthetic value. The reactions of allyl- and benzyl-alanes with mono- and di-substituted acetylenes are no exception to this generalisation.[87,88]



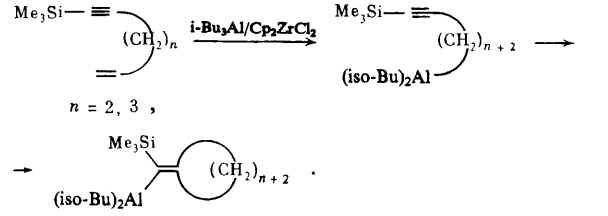
Here, stereoselectivity is almost 100%, but high regioselectivity is found only in the case of phenyl-substituted acetylenes. Reaction is impeded if a Me_3Si group is situated on the triple bond and in the presence of more than one equivalent of an ethereal solvent. Dimethyl- and diisobutyl-allylalanes have both been used as allylating agents; however in the latter case simultaneous hydroalumination may take place with the participation of the isobutyl group. Allylaluminium sesquibromide was shown to be inactive.

By comparison with allylalanes, benzylalanes are less active; reaction of $(PhCH_2)_3Al$ with 1-octyne takes place only at elevated temperatures (from 60 °C), affording a mixture of regioisomers in 90% total yield after 48 h.

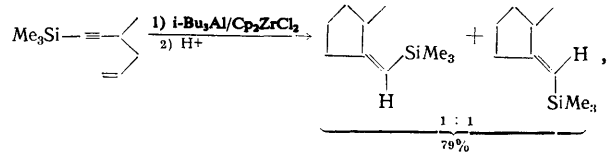


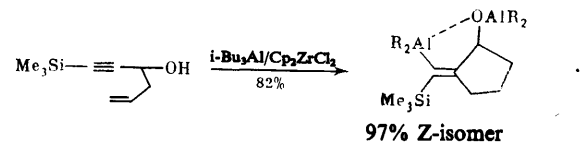
By replacing $(PhCH_2)_3Al$ with $(PhCH_2)_2AlMe$, products are formed via both benzyl- and methyl-alumination in approximately equal proportion, but $i\text{-}Bu_2AlCH_2Ph$ reacts only by cleavage of the isobutyl group.

Finally, as one further example of zirconium-catalysed carboalumination, the intramolecular variant leads to the formation of exocyclic alkenylalanes. In this case, the carbometallating agent is regenerated *in situ* as a result of interaction of $i\text{-}Bu_3Al$ with the double bond of the starting enyne.[88,89]



In almost all examples, reaction is non-stereoselective.

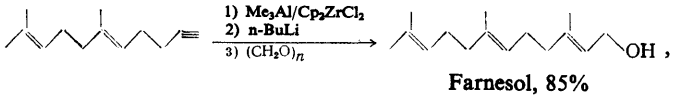




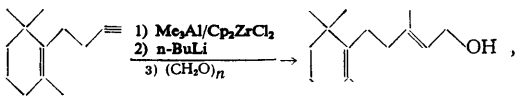
97% Z-isomer

In all of the above-mentioned examples of Cp_2ZrCl_2-catalysed carbometallation of terminal acetylenes with Me_3Al, the most useful synthetic aspect is the generation of key intermediates with high stereo- and regio-selectivity, as well as the high reactivity of the formed vinylalanes. The latter can be readily converted into other metallo-derivatives, e. g. boron, zirconium and mercury analogues, as well as into halogeno- or deuterium-containing hydrocarbons and compounds containing a variety of functional groups.[76]

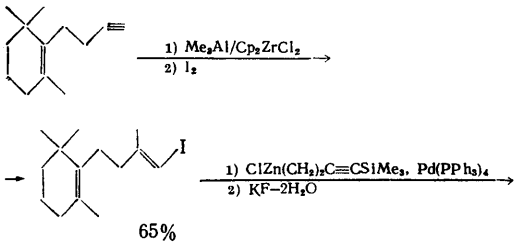
The reaction has been used in the synthesis of an entire series of natural and biologically active compounds containing an isoprenoid residue, e. g. farnesol, geraniol. monocyclofarnesol, ocimene, α-farnesene (see p. 1167), vitamin A, mokupalide, brassinolide, dendrolasin, milbemycin, verrucarin, zoapatanol and others.[75,76,90–102]

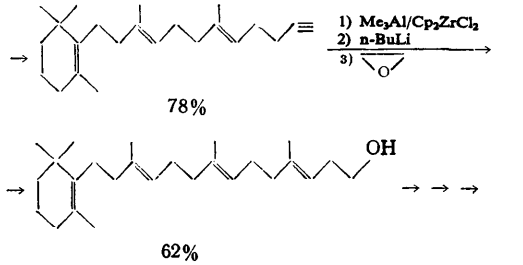


Farnesol, 85%

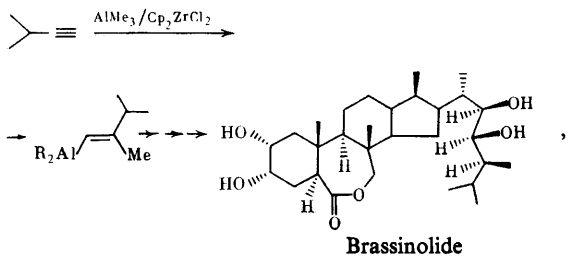


Monocyclofarnesol, 71%

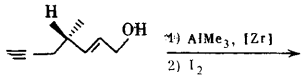


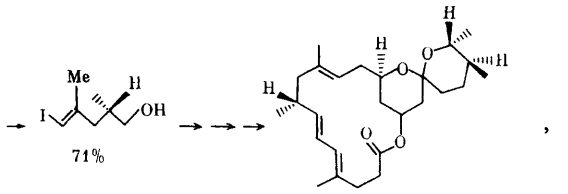


Mokupalide 50%

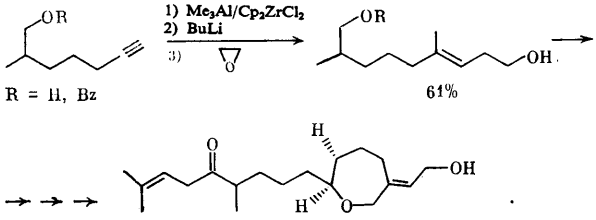


Brassinolide





Milbemycin

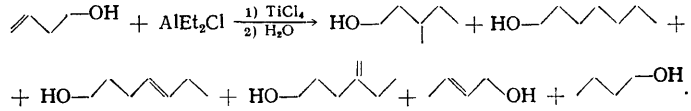


Zoapatanol

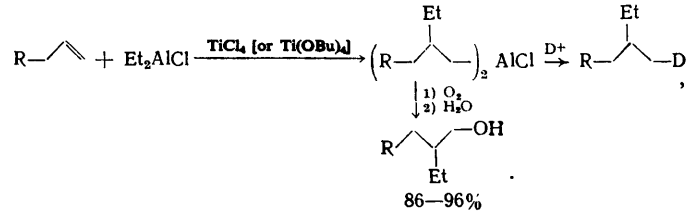
No doubt the more widespread application if this reaction has been restricted by the difficulties associated with handling concentrated solutions of trimethylaluminium.

2. Carboalumination of α-olefins

A significantly fewer number of publications have been devoted to the catalytic carboalumination of olefins. Thus, in contrast with homopropargyl alcohols,[63,67] homoallylic analogues are carboaluminated with very low selectivity on reaction with trialkylalanes or dialkylaluminium halides in the presence of titanium reagents ($TiCl_4$, $TiCl_2(acac)_2$, Cp_2TiCl_2).[63,67,103–105] Because of associated hydrometallation, hydrogenation, isomerisation and β-hydride elimination (in varying proportions), the yield of the regioisomeric mixture of OACs does not exceed 10–30%.

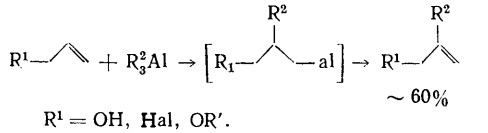


There are references to the selective carboalumination of α-olefins (C_6 to C_{12}) with diethylaluminium chloride in the presence of small amounts (0.5 to 3 mol%) of $TiCl_4$ or $Ti(OBu)_4$ at 20 °C in toluene over the course of 3 h.[106,107]



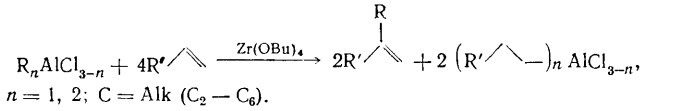
86—96%

Carboalumination of α-olefins with trialkylalanes in the presence of a stoichiometric amount of Cp_2TiCl_2 leads predominantly to the formation of products derived by β-hydride elimination, in addition to high molecular weight oligomers.[108]



R^1 = OH, Hal, OR'.

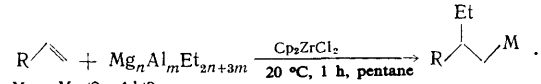
In the presence of a catalytic amount of $Zr(OBu)_4$, the analogous reaction with halogenalanes proceeds far more selectively, affording, in varying yield, products derived by β-alkylation of the starting olefins, in addition to the corresponding higher di-*n*-alkylaluminium halides.[51,109–112]



n = 1, 2; C = Alk (C_2 — C_6).

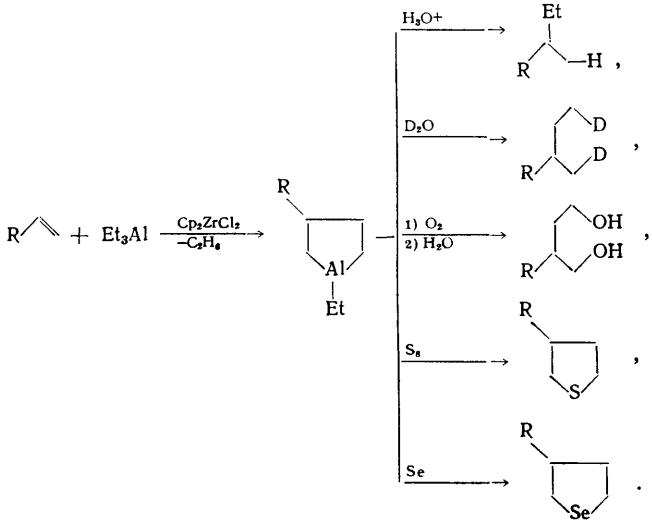
It is not possible to interrupt the process at the stage of carbometallation, even by varying reaction conditions and the proportion of starting materials; evidently, all stages proceed in one and the same catalytic matrix. The best yields were obtained by using dialkylaluminium halides, the activity of which was somewhat reduced with increase in the size of the hydrocarbon radical.[109] α-Olefins have been used as the unsaturated substrate; these may contain aryl substituents (but not OR or OH), as well as disubstituted double bonds. The latter do not react with alkylaluminium halides, but may undergo isomerisation.

It has been shown that, contrary to earlier reports,[51,97,111] triethylaluminium selectively carboaluminates α-olefins under the action of zirconium-containing catalysts, but only as complexes with Et_2Mg[106]



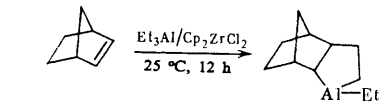
M = Mg/2, Al/3.

By interaction of an excess of Et_3Al with olefins in the presence of a catalytic amount of Cp_2ZrCl_2, β-substituted aluminacyclopentanes are formed along with evolved ethane; carboalumination does not take place under these conditions:[112,113]

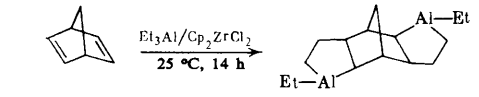


The described reaction is the first example of a catalytic cyclometallation. Although analogous catalytic reactions of organomagnesium and -lithium compounds are known,[116–118] this reaction type is normally found only in transition metal chemistry (as the non-catalytic variant).[114,115] The formation of intermediate zirconacyclopentane complexes has been proposed as the key step in the above reaction.[119–120]

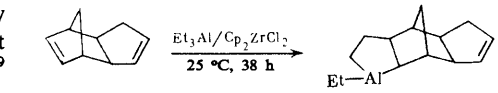
Not only α-olefins (including those with aryl and alkenyl substituents[121]) but also norbornene and some of its derivatives[122–124] may participate in the reaction with Et_3Al.



80 - 98% (Ref.122)



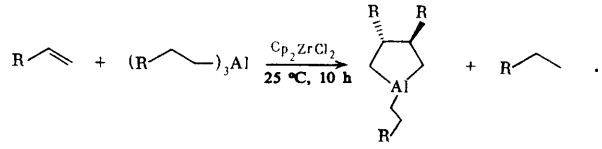
93% (Ref.123)



70 - 92% (Ref.124)

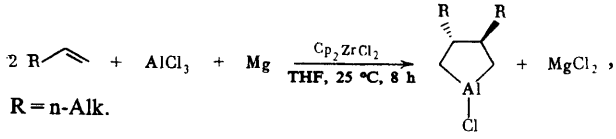
It is interesting to note that, on cyclometallation of norbornadiene, there is no formation of nortricyclene derivatives as observed with catalytic carbomagnesation[125] and hydroalumination.[46]

On replacement of $AlEt_3$ by higher trialkylalanes, their activity in the cyclometallation of α-olefins decreases.[126]



50 - 75%

1-Chloroaluminacyclopentanes are formed by interaction of 2 equivalents of the α-olefin with $AlCl_3$ in the presence of Mg-powder and a catalytic amount of Cp_2ZrCl_2:



R = n-Alk.

60 - 75%

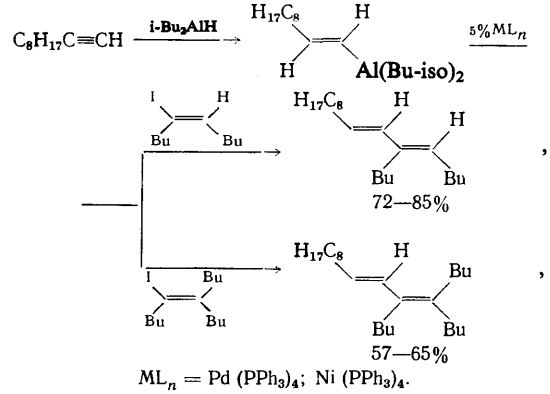
With the discovery of catalytic cyclometallation, there are wide possibilities for pursuing studies in a new field of organometallic chemistry: the chemistry of metallocycles of non-transition metals, the properties of which have, up to this time, remained almost unexplored. Thus, the obtained aluminacyclopentanes are extremely interesting synthetically, their reactivity differing from that of acyclic alkylalanes. In particular, they have proved to be suitable synthons

for the preparation of a variety of heterocyclic compounds,[127–131] and have found a use in natural product synthesis.[132–135] At the present time, much research is being performed on the reactions of alumina- and magnesia-cyclopentanes; some of their catalytic conversions will be examined below.

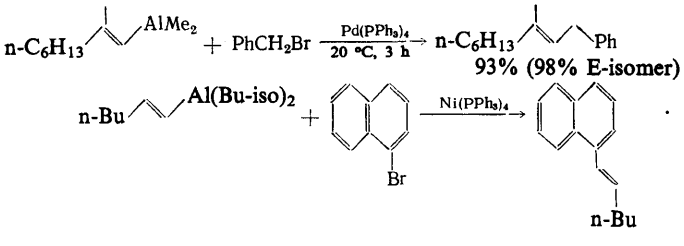
IV. Catalytic cross-coupling with organoaluminium compounds

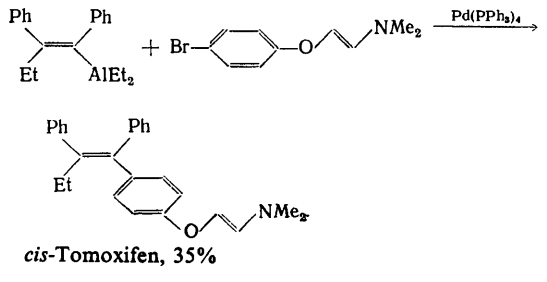
Discovered less than twenty years ago, catalytic cross-coupling is now one of the most generally applicable and far-reaching methods of forming the carbon–carbon bond from organometallic compounds. Among organoaluminium compounds which participate in cross-coupling, alkyl- and vinyl-alanes are most frequently used. This is, in part, because of their availability (via the above-described hydro- and carbo-metallation) and, in part, because of their ability to react selectively with a variety of electrophiles in the presence of a catalytic amount of transition metal complexes, notably Ni, Pd or Cu complexes.

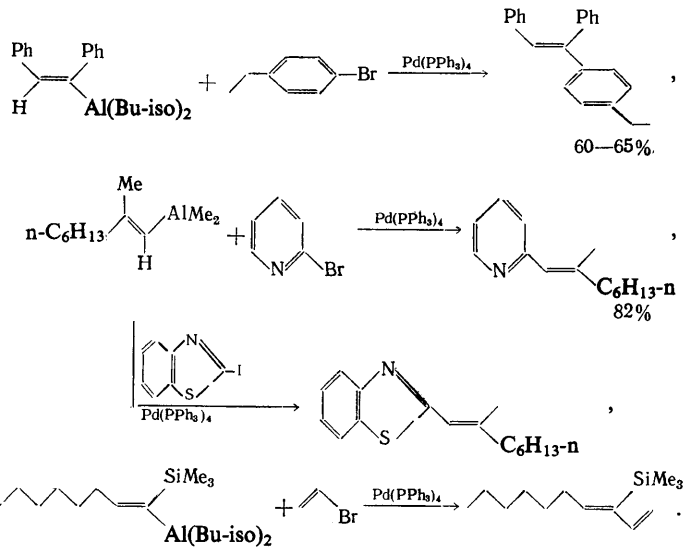
Negishi et al.[136,137] have developed an excellent method of preparing conjugated dienes and arylalkenes of defined configuration via Ni- or Pd-catalysed coupling of vinylalanes with alkenyl, aryl or benzyl halides. The method has been applied to the synthesis of a number of biologically active compounds or synthons for their preparation.[138–142]



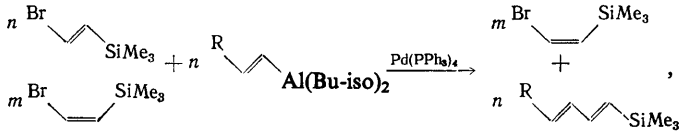
ML_n = Pd $(PPh_3)_4$; Ni $(PPh_3)_4$.





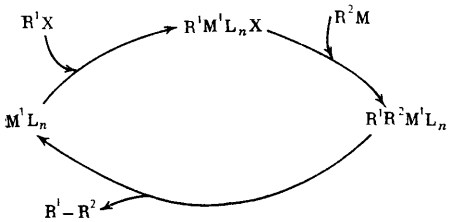


In all variants of the above cross-coupling, almost 100% stereospecificity results by using Pd-catalysts; however, there is some loss of stereoselectivity in the synthesis of conjugated dienes with Ni-complexes. Cross-coupling of (*E*)-1-alkenylalanes with a stereoisomeric mixture of (2-bromovinyl)trimethylsilanes proceeds stereoselectively in the presence of $Pd(PPh_3)_4$ (in THF–hexane at 40 °C for 16 h) with the formation of 4-alkyl-substituted (1*E*, 3*E*)-1-tri-methylsilyl-1,3-dienes, the stereo-purity of which exceeds 99%.[143]

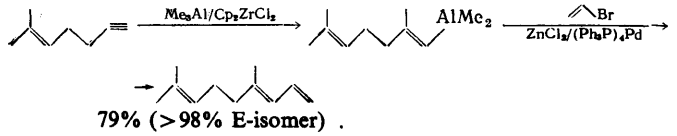


R = tert-Bu, n-C_5H_{11} , 74% (R = n-C_5H_{11}) , 84% (R = tert-Bu) .

According to a specifically mechanistic study, it was established that cross-coupling proceeds through an initial oxidative addition of a Pd(0)-complex, followed by a rate-determining transmetallation with participation of an organopalladium(II) complex, and rapid decomposition of the diorganopalladium complex formed to give the cross-coupling product.[144]

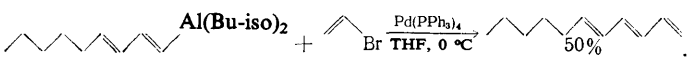


For cross-coupling of sterically hindered vinylalanes (notably those obtained by Zr-catalysed carboalumination) with vinyl halides it is necessary to use the bimetallic catalyst, $Pd(PPh_3)_4/ZnCl_2$.[145]

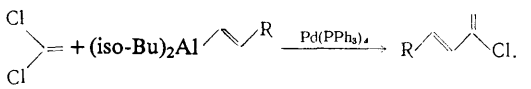


79% (>98% E-isomer) .

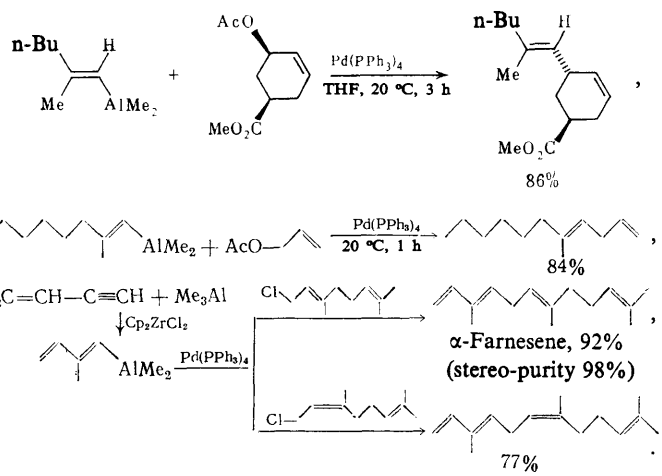
Without $ZnCl_2$ the yield remains below 1%. Dienylalanes may also undergo cross-coupling, although the products are obtained in high yield without $ZnCl_2$.[146]



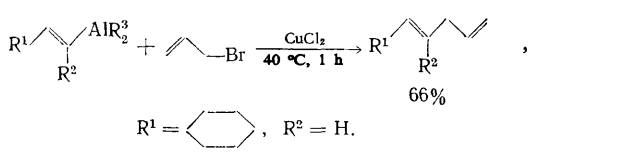
In the case of 1,1-dihalogenoalkenes, it is possible to replace selectively one of the chlorine atoms.[147]



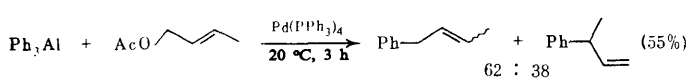
Allyl halides and acetate also afford excellent yields of cross-coupling products with vinylalanes in the presence of Pd-complexes.[148–149]



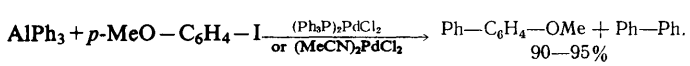
The reaction of allyl halides with vinylalanes is also catalysed by copper salts.[150]



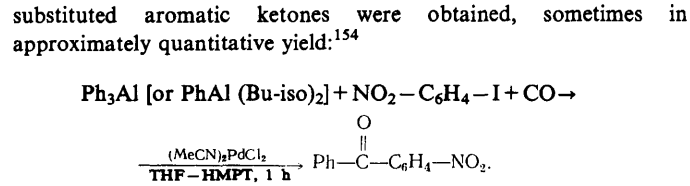
Examples of Pd-catalysed cross-coupling of arylalanes with allylic and aryl electrophiles are known:[151]



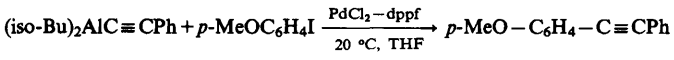
The coupling of arylalanes with aryl halides proceeds more selectively.[152,153] The reaction is of preparative value for the synthesis of substituted biphenyls (DMSO, 55 °C, 1 h).



By conducting this reaction in the presence of carbon monoxide, substituted aromatic ketones were obtained, sometimes in approximately quantitative yield:[154]

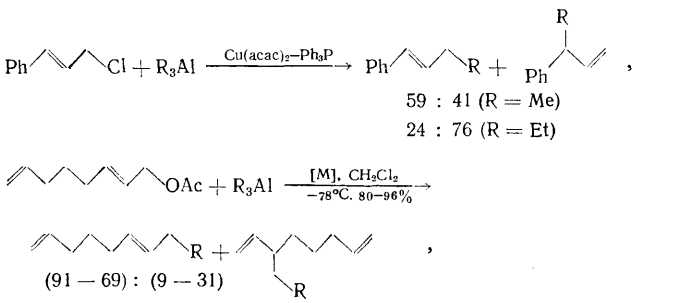


Cross-coupling of alkynylalanes normally proceeds non-selectively due to the formation of a large amount of product derived by homo-coupling.



The maximum yield (42%) was achieved by using a catalyst containing diphenylphosphinoferrocene (dppf).[153]

The reaction of alkylalanes and lithium tetraalkylaluminates with allylic electrophiles can, in principle, be conducted in the absence of catalyst; however, the selectivity and yield of coupling products are not high. Reaction is favoured by using copper-containing catalysts, and in a number of cases there is an effect on selectivity.[155–159]



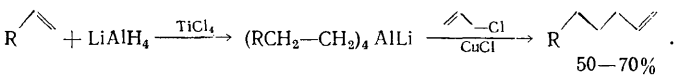
R = n-C_6H_{13}, *i*-Bu, Et; [M] = CuBr, CuCl, $FeCl_3$.



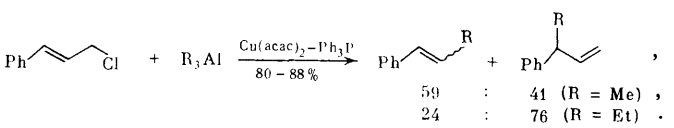
$n = 2, 3$; R = Alk.

The best results were obtained by using CuBr and $FeCl_3$ as catalysts; with Pd-containing catalysts the selectivity is worse, although they have been successfully used in the cross-coupling of alkylalanes with certain halogenonucleosides (8-bromoadenosine and 5-bromouridine).[160]

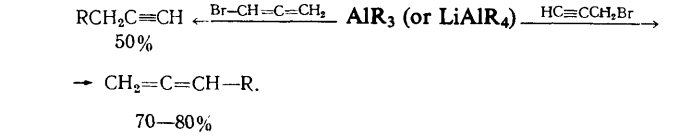
Lithium tetraalkylaluminates react in a similar manner with allyl halides in the presence of mono- and di-valent copper salts [CuCl, CuBr, CuI, CuCN, $CuCl_2$ and $Cu(OAc)_2$]. Contrasting with trialkylalanes, which participate by donating only one alkyl group, tetralkylaluminates transfer all four ligands.[34]



In the case of substituted allyl halides, reaction takes place as a rule non-selectively, being accompanied by allyl rearrangement:[161,162]

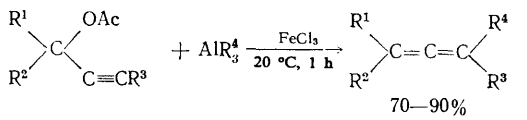


At the same time, products of rearrangement predominate on reaction of propargyl and allenyl halides with alkylalanes and alkylaluminates in the presence of CuCl at 0 °C during 5 h; the result is an original preparative route to primary allenes and acetylenes.[163–166]



The reaction of substituted propargyl acetates with trialkylalanes and

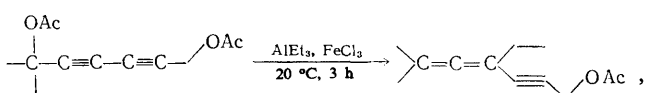
alkenyldialkylalanes proceeds readily in the presence of $FeCl_3$ (in this case being a more active catalyst than Pd or Cu salts), thereby providing a suitable method for preparing substituted allenes, including functionalised vinylallenes, diallenes and allenynes. A variety of different OACs may participate in the reaction. The obtained vinylallenes are of practical value as synthons for the preparation of a number of natural products with a cyclopentanone residue.[167–171]

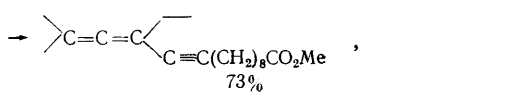


70—90%

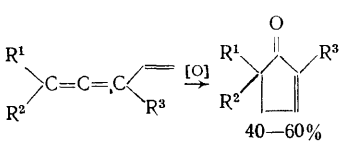
R^1, R^2 = Me, Et, $CH{=}CH_2$; R^3 = H, $CH{=}CH_2$;

R^4 = Et, Me, *i*-Bu, n-C_6H_{13};





73%

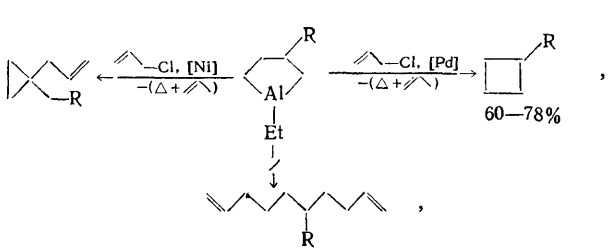


40—60%

R^1, R^2, R^3 = H, Alk.

It is worth noting that reaction takes place preferably at the electrophilic centre of the propargyl group even in the presence of an allyl group (when R′ = $-CH{=}CH_2$).

Allyl halides react in an unusual manner with aluminacyclopentanes, the formation of which has been mentioned in the previous section under cyclometallation.[12,113] Thus, interaction of substituted aluminacyclopentanes with allyl chloride in the presence of palladium complexes affords mono-substituted cyclobutanes,[172] while allylcyclopropanes are obtained in the presence of nickel catalysts.[173]



60—78%

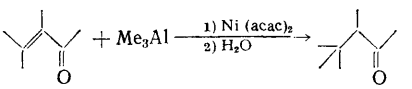
R = Alk.

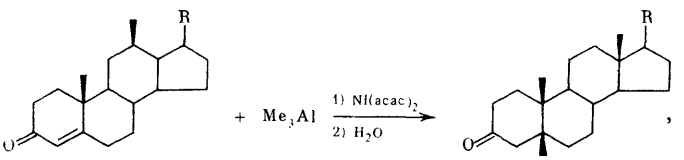
Reaction is accompanied by the evolution of a mixture of propylene and cyclopropane.

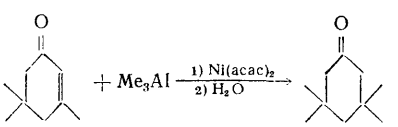
V. Catalytic reactions of organoaluminium compounds with carbonyl-containing compounds

1. Conjugate addition

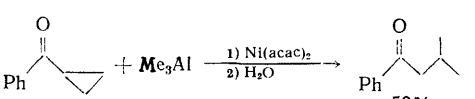
It is known that reduction and alkylation of enones can proceed by both 1,2- and 1,4-addition. Both types of reaction are known with organoaluminium reagents. Selective 1,4-addition of Me_3Al to enones can be achieved in the presence of $Ni(acac)_2$.[174–176]







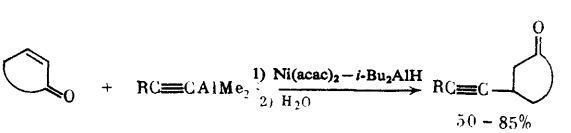
Cyclopropyl ketones react in a similar manner under these conditions:[175]



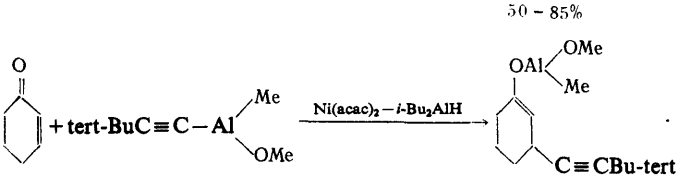
50%

All such additions are normally complicated by the formation of high molecular-weight products derived by aldol condensation.

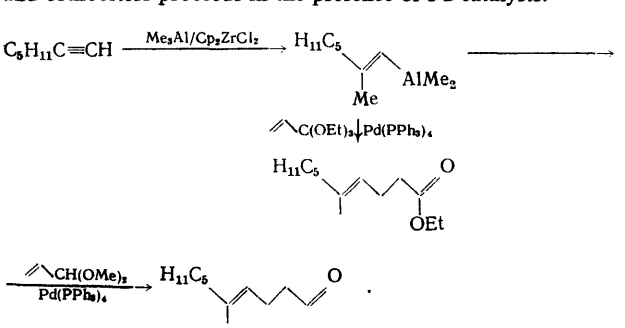
Dialkylalkynylalanes react with α,β-enones by donating only an alkyl group.[177,178] In order to obtain high yields of the alkynyl adduct, the catalyst must be preliminarily reduced by *i*-Bu_2AlH:



50 - 85%

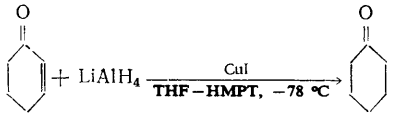


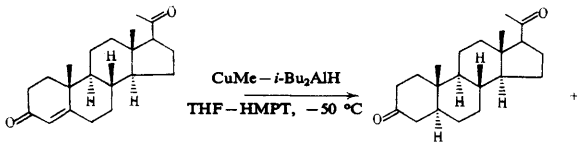
The analogous reaction of vinylalanes with α,β-unsaturated acetals and orthoesters proceeds in the presence of Pd-catalysts.[174]

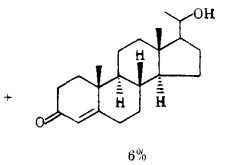


2. Conjugate reduction of enones

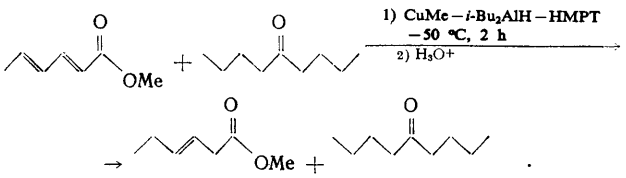
Conjugate reduction of α,β-unsaturated carbonyl compounds with *i*-Bu_2AlH [179] or $LiAlH_4$ [180] is catalysed by Cu(I) compounds, and proceeds in the presence of hexamethylphosphoramide (HMPT):







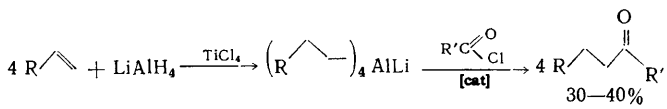
In the case of dienones, selective 1,6-reduction takes place even in the presence of an equivalent amount of saturated carbonyl compound:[180]



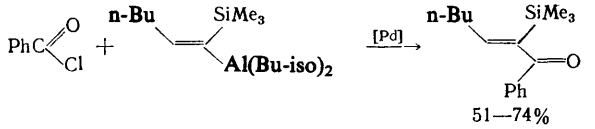
Triisobutylaluminium reacts with α,β-unsaturated ketones in the same way, but in the presence of nickel complexes.[181]

3. Synthesis of ketones

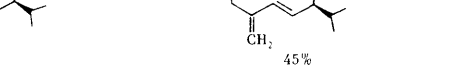
The interaction of OACs with acyl chlorides in the presence of transition metal salts may be applied as an effective method of preparing ketones:[35,182,183]



Palladium complexes [$Pd(PPh_3)_4$ and $Pd(OAc)_2.2PPh_3$] are the best catalysts for the selective synthesis of ketones from OACs containing alkenyl or alkynyl groups, whereas Ru-, Rh- and Ni-complexes were ineffective.[183]

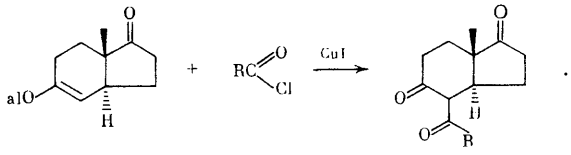


Trialkylalanes afford a better yield of ketones than tetraalkylaluminates,[182] and react not only with acyl chlorides but also with thiolocarboxylic acid esters:



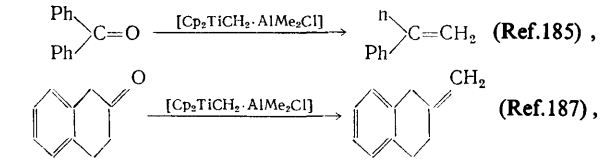
X = Cl, SPh; R^1 = Ph, $CH_2=CH-(CH_2)_8-$; R^2 = Me, Et, *i*-Bu.

In addition, copper(I) salts catalyse the formation of 1,3-diketones from acyl chlorides and aluminium enolates:[184]



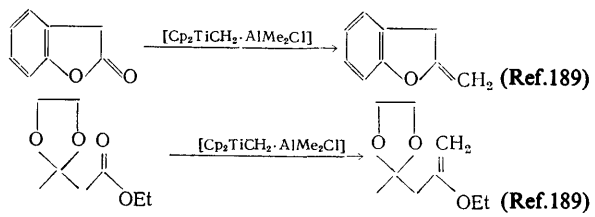
4. Methylenation of carbonyl compounds

Tebbe's reagent ($Cp_2TiCH_2.AlMe_2Cl$), prepared *in situ* by treatment of Cp_2TiCl_2 with Me_3Al,[185,186] has proved to be useful for the methylenation of a variety of carbonyl compounds. It can serve as an alternative to the traditional Wittig reagent, notably for the methylenation of readily enolisable ketones which are unstable under the strongly basic conditions of the Wittig synthesis.



(Ref.188)

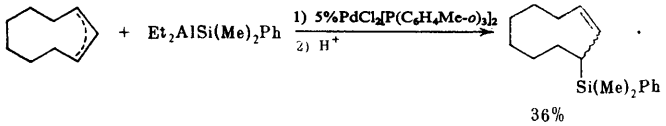
Esters and lactones are simply converted to the corresponding enolethers which may then react further:[189,190]



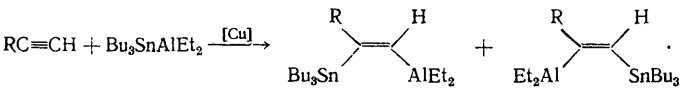
VI. Catalytic reactions across the aluminium-heteroatom bond

This section will be devoted to some interesting reactions related to carbometallation and cross-coupling which were discussed earlier; however, we shall be considering here reaction across the aluminium-heteroatom bond, rather than the aluminium-carbon bond (even in cases where the OAC contains both aluminium-heteroatom and aluminium-carbon bonds). In this way, a variety of hetero-functions

can be introduced into an organic compound. Thus, silylalumination of the allene group of 1,2-cyclononadiene with dimethyl(phenyl)silyldiethylalane in the presence of a Pd-catalyst affords a 3-dimethyl(phenyl)silyl-1-cyclononene:[191]

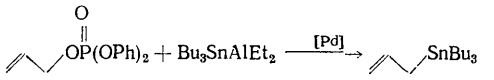


By interaction of mono-substituted acetylenes with dialkyl(stannyl)-alanes in the presence of Cu(I) salts (CuCN, CuI) or Pd(O)-complexes, stannylalumination of the triple bond takes place rather than carboalumination:[192–195]

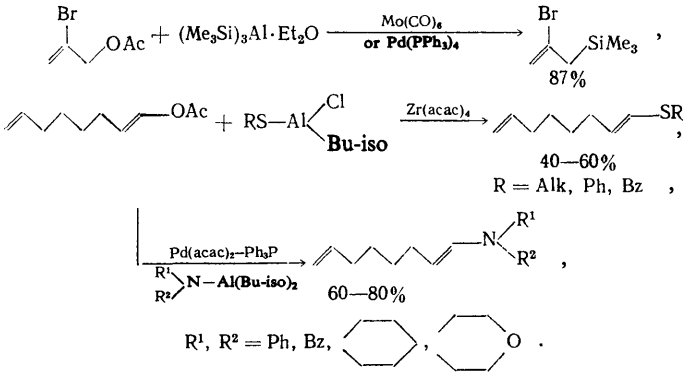


Reaction is noteworthy for its high regio- and stereo-selectivity (80–92%). Contrasting with carbometallation, stannylalumination can be performed on acetylenes which possess tetrahydro-2-pyranyloxy-, hydroxy-, acetoxy-, and benzyloxy-groups.

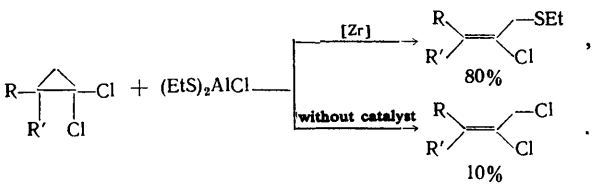
By interaction of (tributylstannyl)diethylalane with allyl phosphates, cross-coupling takes place with the formation of allylstannanes:[196]



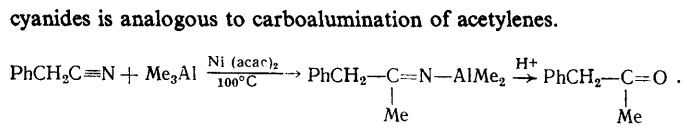
Similar reactions can also be achieved by fission of Al–Si [197], Al–N and Al–S bonds.[198,199]



Finally, by interaction of *gem*-dichlorocyclopropanes with bis(ethylthio)aluminium chloride in the presence of Zr-catalysts, a high yield of the corresponding allyl thioethers was obtained, i.e. the chlorocyclopropane here performs the function of an allyl halide equivalent.[200]



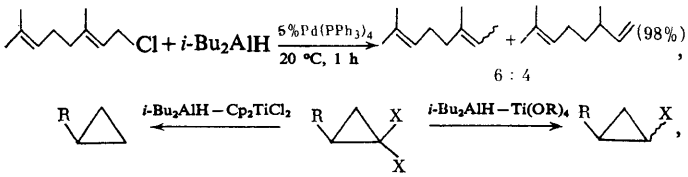
Addition of Me_3Al to the nitrile bond of alkyl, aryl and benzyl cyanides is analogous to carboalumination of acetylenes.



Reaction is more selective and milder in the presence of Ni-complexes[201] than without catalyst.

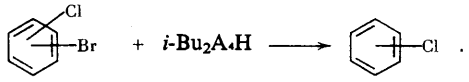
VII. Other catalytic reactions involving organoaluminium compounds

In the presence of palladium complexes,[202] as well as those of Ti, Zr and Hf,[202–207] *i*-Bu_2AlH effectively dehalogenates various types of halogenated hydrocarbon under mild conditions. These include allyl,[202] alkyl,[204] aryl[204] and cyclopropyl halides:[203–207]

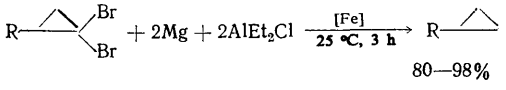


$$ArCH_2X + i\text{-}Bu_2AlH \xrightarrow{[Ti,\ Zr,\ Hf]} Ar{-}CH_3.$$

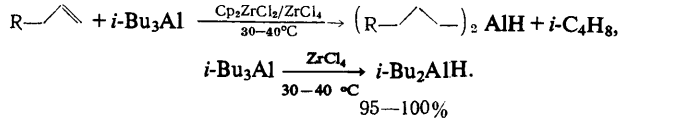
In the case of aryl bromides containing aromatic chlorine, it is possible to replace the bromine with retention of the C–Cl bond.[204]



Complete dehalogenation of dibromocyclopropanes can be achieved with a mixture of Et_2AlCl and powdered magnesium in the presence of $FeCl_3$ as catalyst.[208]



The synthesis of *i*-Bu_2AlH and certain higher dialkylaluminium hydrides was carried out under mild conditions with the aid of zirconium catalysts:[209,210]



Higher alkylaluminium chlorides have been obtained by catalytic telomerisation of ethylene with diethylaluminium or sesquiethylaluminium chloride, also in the presence of zirconium catalysts.[211]

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