Translated from *Uspekhi Khimii*, **55**, 191-224 (1986) U.D.C. 542.97:547; 313:547,254,6

Zirconium Complexes in Synthesis and Catalysis

U.M.Dzhemilev, O.S.Vostrikova, and A.G.Ibragimov

Data on the use of organometallic complexes of zirconium as key intermediates in organic synthesis and the catalysis of the transformations of alkenes, dienes, and acetylenes have been systematised. The hydrozirconation of unsaturated compounds and the reactions of alkyl- and alkenylzirconium complexes with electrophilic reagents, α,β-unsaturated ketones, aryl and vinyl halides, and salts of transition and non-transition metals have been examined. The use of zirconium complexes as catalysts in the homogeneous hydrogenation, isomerisation, linear dimerisation, and oligomerisation of alkenes and dienes, and the hydro- and carbometallation of the latter, have been considered. The mechanisms of these reactions have been discussed. The bibliography contains 147 references.

CONTENTS

I. Introduction 66
II. The synthesis and transformations of alkyl- and alkenylzirconium complexes 66
III. Catalysis by zirconium complexes 74

I. INTRODUCTION

Many of the most important achievements in organic chemistry in the last 15–20 years have been associated in some way with the use of transition metal complexes. Among these complexes, an increasingly important place is occupied by zirconium compounds, which have a number of unique properties enabling them to be used as highly reactive reagents in organic synthesis, and also as effective catalysts for transformations of unsaturated hydrocarbons and organometallic compounds. The discovery of the reaction of organozirconium intermediates with transition metal complexes, involving the transfer of alkyl or alkenyl substituents from the zirconium atom to other metals, has made it possible to carry out the stereoselective synthesis of compounds with a definite structure, whose preparation by other methods is extremely complicated.

Extensive material on the use of zirconium complexes in synthesis and catalysis has now accumulated, and studies in this field are being carried out actively in the Soviet Union and abroad. Although some aspects of the use of zirconium derivatives in organic synthesis have been discussed in two reviews,[1,2] there is a large amount of material which did not appear in these reviews. A large amount of data on the use of zirconium compounds as homogeneous metal-complex catalysts (published mainly in the last five years) has not yet been discussed and systematised.

The present review gives the most important results of studies of the use of organozirconium compounds in organic synthesis and metal-complex catalysis, published chiefly in the last ten years. The polymerisation of unsaturated compounds on zirconium-containing catalysts is not examined.

II. THE SYNTHESIS AND TRANSFORMATIONS OF ALKYL- AND ALKENYLZIRCONIUM COMPLEXES

1. The Hydrozirconation of Unsaturated Compounds

About ten years ago it was established[3,4] that bis(cyclopentadienyl)zirconium chloride hydride $Cp_2Zr(Cl)H$ (I) and bis(cyclopentadienyl)zirconium dihydride Cp_2ZrH_2 react readily with alkenes or acetylenes to give fairly stable alkyl and alkenyl complexes of zirconium. Subsequently, Schwartz and co-workers[1] developed a number of promising schemes for the use of hydrozirconation products as active intermediates in organic synthesis. In the last ten years, hydrozirconation has become popular in organic synthesis, chiefly as a result of these studies, as indicated by the fact that the hydride complex (I) is often referred to in the chemical literature as the "Schwartz reagent".[5]

The hydrozirconation of linear and cyclic alkenes by bis(cyclopentadienyl)zirconium chloride hydride (I) takes place under mild conditions and with high yields, giving alkyl complexes $Cp_2Zr(Cl)R$. The latter, unlike their lower homologues, are fairly stable.[6] The hydrozirconation of alkenes using $Cp_2Zr(Cl)H$ or Cp_2ZrH_2 takes place strictly as a 1,2-addition and is highly regioselective, reacting with both mono- and disubstituted alkenes to give only the primary alkylzirconium complexes, which are readily split by electrophiles (Table 1).

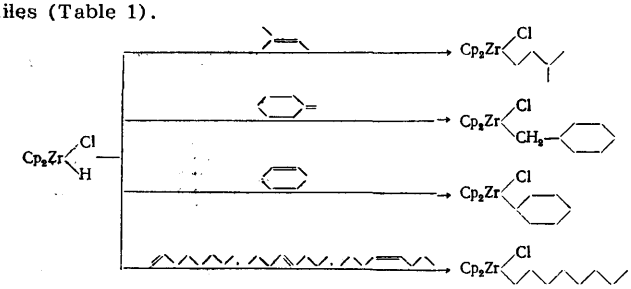


Table 1. Hydrozirconation of alkenes using compound (I).[6]

Alkene	Electrophilic reagent	Reaction product	Yield, %*
Oct-1-ene or oct-4-ene	HCl (dil.)**	octane	100
Ditto	Br_2	1-bromo-octane	96
»	I_2	1-iodo-octane	91
»	$PhICl_2$	1-chloro-octane	65
»	$MeC(O)Cl$	decan-2-one	80
2-Methylbut-1-ene	Br_2	1-bromo-3-methylbutane	100
»	$MeC(O)Cl$	5-methylhexan-2-ol	72
Cyclohexene	Br_2	bromocyclohexane	95

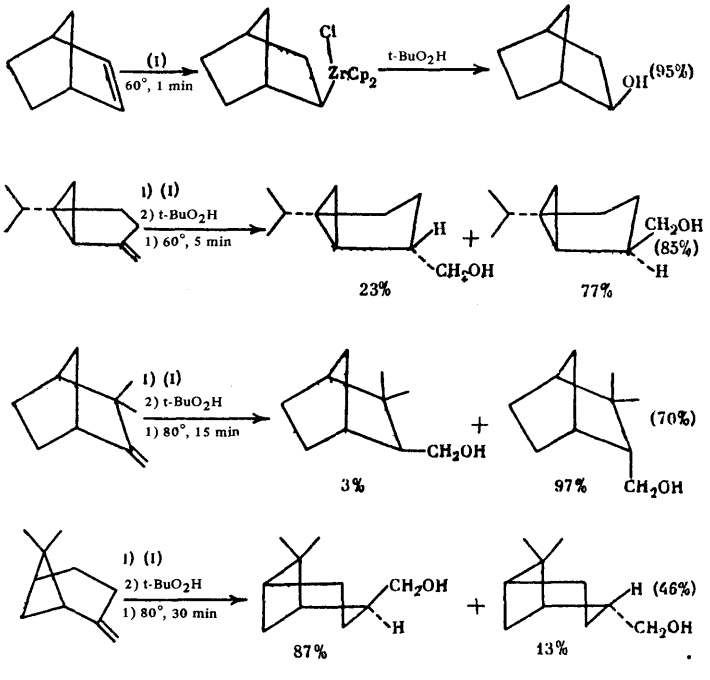
*Calculated for Cp_2ZrCl_2.
**Temperature 0°.

It is noteworthy that the hydride complexes of zirconium give exclusively primary alkylzirconium organic metallic compounds, irrespective of the position of the double bond

in the original alkene. Under hydrozirconation conditions, repeated addition and elimination of hydride complexes of zirconium probably take place, giving finally the thermodynamically most stable primary alkylzirconium complexes. These transformations take place fairly rapidly and under mild conditions, unlike the corresponding reactions of organoboron and organoaluminium compounds.[7,8] For example, the hydrozirconation of symmetrical disubstituted alkenes containing 24–42 carbon atoms gives only primary alkylzirconium complexes.[9] To obtain the optimum yields (50–80%) of the desired products in these experiments, however, the reaction must be carried out for 1–6 d at 40°.

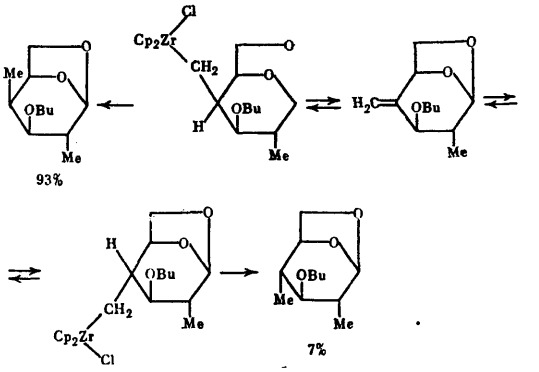
According to Schwartz's data, the relative rate of the hydrozirconation of alkenes decreases in the order: α-alkene > *cis*-alkene > *trans*-alkene > exocyclic alkene > cyclic alkene > trisubstituted alkene; the last three alkenes react with $Cp_2Zr(Cl)H$ at temperatures not lower than 40°.[1,6] Bulky groups in the substituted alkenes probably create steric hindrance to the approach of the zirconium hydrides, which have a "sandwich" structure, to the reaction centre. Thus tetrasubstituted alkenes and also methylcyclohexene and cyclo-octene do not react with $Cp_2Zr(Cl)H$ even when kept at 40° for a long time.[6]

In a series of bicyclic hydrocarbons with double bonds shielded to different extents, the rate of hydrozirconation decreases sharply in the order: norbornene > sabinene > camphene > β-pinene,[10] and the addition of the hydride complex (I) takes place chiefly on the least shielded side. The highest stereoselectivity of the addition is observed for camphene.

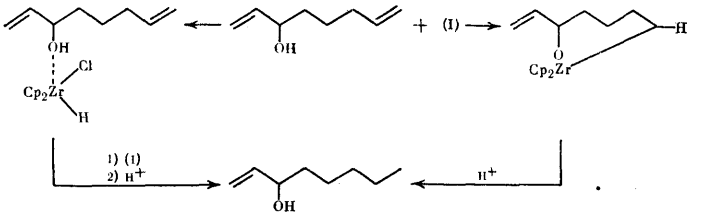


The anomalously high yield of 10-isothujanol in the oxidation of the hydrozirconation products of sabinene was attributed[10] to electronic factors.

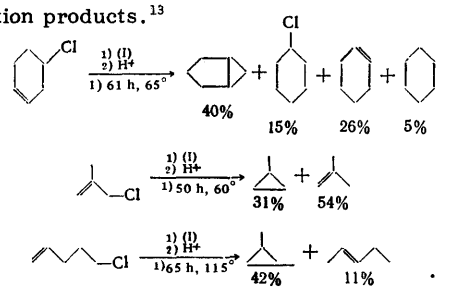
Hydrozirconation with subsequent protolysis made it possible to carry out the stereoregulated reduction of a methylene derivative of a monosaccharide in the synthesis of the C(9)–C(19) fragments of the antibiotics oleandonolide and erythronolide B.[11]



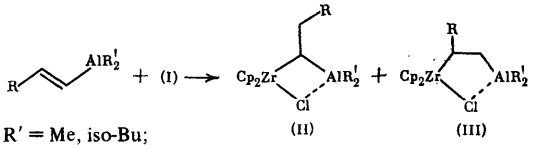
In this case the predominant formation of the thermodynamically more favourable galacto-isomer indicates that kinetic factors have a decisive influence. The hydrozirconation of unsaturated compounds is not only highly regiospecific but also highly selective. In particular, the hydrozirconation of non-conjugated dienols takes place exclusively at the double bond farthest from the hydroxyl group.[12] The high selectivity of this reaction is evidently due to the formation of a complex of the dienol with the hydride (I), which then reacts with a second $Cp_2Zr(Cl)H$ molecule at the sterically least hindered C(7)–C(8) vinyl group. It is not excluded that in these experiments, intramolecular hydrozirconation involves the formation of an alkoxyzirconium hydride according to the scheme:



In the reaction of $Cp_2Zr(Cl)H$ with various γ-halogenoalkenes, cyclopropane derivatives are formed in addition to the dehalogenation products.[13]

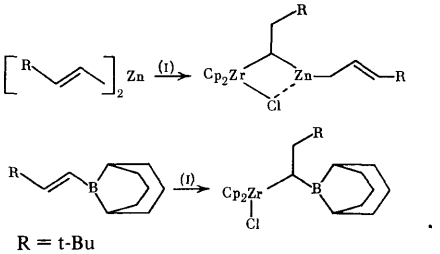


Complex (I) can hydrozirconate not only the simplest alkenes and dienes but also unsaturated organoaluminium, -zinc, and -boron compounds.[14] The hydrozirconation of alkenyldialkylalanes by $Cp_2Zr(Cl)H$ gives a bimetallic complex containing a bridging chloride ligand. The regioselectivity of the addition of the hydride (I) to the double bond depends on the size of the alkyl substituents on it.



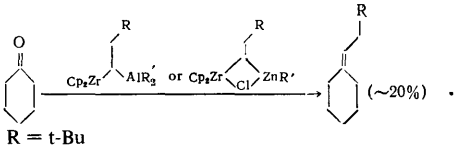
R′ = Me, iso-Bu;
R = t-Bu, (II) : (III) = >20 : 1
R = n-Bu, (II) : (III) = 3 : 2
R = Me, (II) : (III) = 1 : 2 .

Dineohexenylzinc forms with $Cp_2Zr(Cl)H$ an analogous bimetallic cyclic complex, whereas the neohexenyl derivative of borane reacts with compound (I) according to the usual scheme.[14]



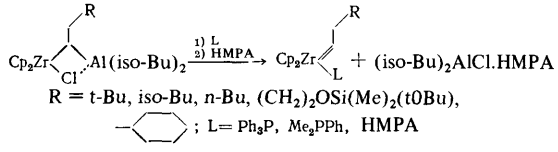
R = t-Bu

The zirconium complexes obtained are of interest as analogues of "Wittig's reagent" in carbonylalkenylation.[14]



R = t-Bu

More active analogues of "Wittig's reagent" are the carbene complexes of zirconium formed by the reaction of the above zirconium–aluminium complexes with a mixture of hexamethylphosphamide (HMPA) and a stabilising ligand (for example PhP_3, Me_2PPh, or an excess of HMPA).[15]



R = t-Bu, iso-Bu, *n*-Bu, $(CH_2)_2OSi(Me)_2(t0Bu)$, ; L= Ph_3P, Me_2PPh, HMPA

The reagents obtained convert esters and ketones into the corresponding alkenes in 78–100% yield.

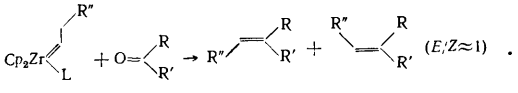
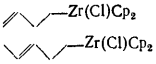
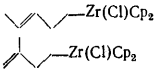
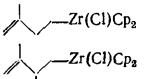
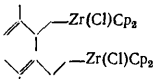
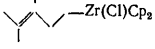
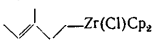
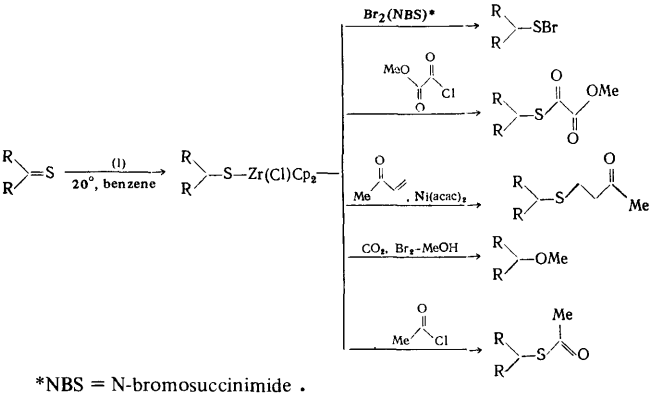


Table 2. Hydrozirconation of 1,3-dienes using compound (I).[1,18]

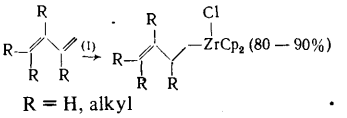
1,3-Diene	Product
	
	
	
	
	
	 (10:1)

An attempt has been made to hydrozirconate heteroalkenes, in particular Schiff bases, in order to subsequently transform them into amides.[16] It was found, however, that complex (I) does not add on to a C=N bond but transforms Schiff bases into enamides and imides, apparently via a Zr–enamide complex. At the same time, aromatic and aliphatic thioketones, including the α, β-unsaturated compounds, are smoothly hydrozirconated by $Cp_2Zr(Cl)H$ at room temperature to give compounds with a Zr–S bond, which can readily be converted into various sulphur-containing compounds under very mild conditions.[17]



*NBS = N-bromosuccinimide .

Unlike monoalkenes, 1,3-dienes undergo hydrozirconation much more slowly (by a factor of ~50) to give γ,δ-unsaturated zirconium complexes.[18] The reaction takes place mainly by the 1,2-addition of complex (I) at the sterically least hindered double bond of the diene (Table 2).



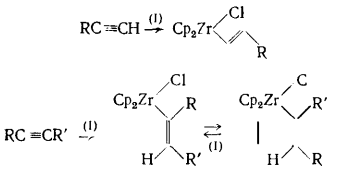
R = H, alkyl

Thus "Schwartz's reagent" as a hydrometallating agent is superior not only to the hydrides of boron and aluminium, which in the case of 1,3-dienes give a complex mixture of products,[19,20] but also to the hydrides of most transition metals, which react with conjugated dienes to form both 1,2- and 1,4-addition products.[21]

A review by Schwartz[1] contains the only mention of the possibility of carrying out the reaction between 2,4-dienes and three equivalents of $Cp_2Zr(Cl)H$, but no data on the structure of the products are given. There are no published data on the hydrozirconation of allenes.

The protonation of Vitamin D_3 and its 5*E*-isomer illustrates the possibility of hydrozirconating conjugated trienes.[22] The activity of the hydride complex (I) in this reaction is greater than that of 9-borabicyclononane. Irrespective of the structure of the original trienes, hydrolysis gave a mixture of the 5*E*- and 5*Z*-dihydrovitamins, indicating that the reaction is accompanied by 5*Z* ⇄ 5*E* isomerisation. Thus the sterically more hindered 5*Z*-isomer is hydrozirconated much more slowly. This reaction is apparently the only example of the hydrozirconation of 1,3-dienes containing functional substituents.[22]

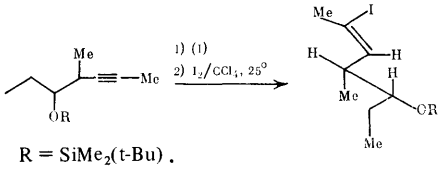
The addition of $Cp_2Zr(Cl)H$ to acetylenes is ~70–100 times more rapid than that to alkenes with analogous structures. Monosubstituted acetylenes form exclusively the 1*E*-alkenylzirconium complexes, and the disubstituted compounds give a mixture of the two possible isomers, the ratio of which depends on the structure of the alkyl substituents;[23,24] 1-alkenylzirconium complexes, unlike their alkyl analogues, do not undergo the above isomerisation, which takes place with the migration of the zirconium atom to the end of the carbon chain.



R = H, Me; R′ = Et, n-Pr, iso-Pr, n-Bu, iso-Bu, t-Bu.

In a number of cases, in the hydrozirconation of unsymmetrical disubstituted acetylenes with bulky substituents, the addition of complex (I) is highly regioselective.

Thus the hydrozirconation of 4-methyl-5-(dimethyl-t-butylsiloxy)-hept-2-one with one equivalent of compound (I) gave a single alkenylzirconium complex, which was readily converted into the corresponding halogenoalkene by treatment with I_2.[25]



R = $SiMe_2$(t-Bu).

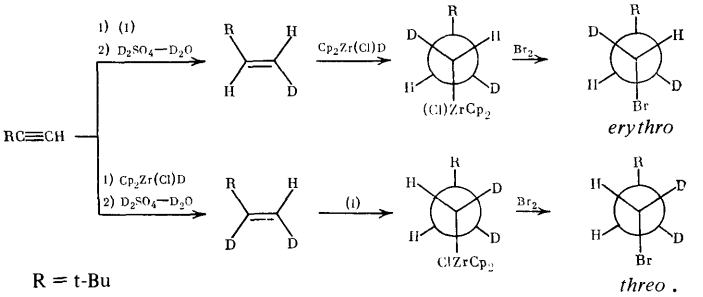
It should be noted that in the hydrozirconation of acetylenes with an excess of compound (I), stereo- and regioselective isomerisation of the resulting alkenyl complexes of zirconium is observed, giving organometallic compounds in which the zirconium atoms are situated predominantly on the least shielded side.[1,23]

Published data on the hydrozirconation of acetylenes indicate that $Cp_2Zr(Cl)H$ is currently one of the most active and regioselective reagents, capable of hydrometallating acetylenes, including those containing such functional substituents as Cl, OH, OR, CO_2H, C≡N, CO_2R, and in the case of the last two groups no appreciable reduction is observed in the reaction.[26] Thus $Cp_2Zr(Cl)H$ acts as a universal, highly active, and selective hydrometallating agent for a wide range of unsaturated compounds.

It has recently been shown possible to use $Cp_2Zr(Cl)H$ and its derivatives as reducing agents. Thus for example "Schwartz's reagent" (I) reduces cyclic ketones stereoselectively to the corresponding axial alcohols.[27] The mixed zirconium hydride $Cp_2Zr(Cl)BH_4$ has been proposed[28] for the selective reduction of aldehydes and ketones in the presence of carboxylic acids, esters, nitriles, and nitroalkanes. This reducing agent is more selective than the known derivatives $LiAlH_4$, boranes, and trialkyl borohydrides, and does not require the use of an inert atmosphere.

2. Reactions of Alkyl- and Alkenylzirconium Complexes with Electrophilic Reagents

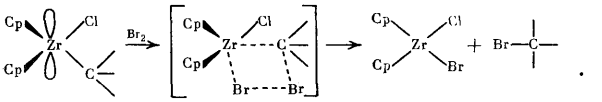
Alkyl- and more particularly alkenylzirconium complexes are convenient intermediates in the functionalisation of unsaturated compounds. One of the simplest ways of functionalising these compounds is by the stereospecific splitting of Zr–C bonds by electrophilic reagents. This process has been studied in considerable detail for a wide range of electrophilic reagents. Alkyl or alkenyl halides are readily formed by the reaction of the corresponding alkyl- and alkenylzirconium complexes with halogens and *N*-halogenosuccinimides. For the example of the reaction of bromine with the *erythro*- and *threo*-forms of the complex $Cp_2Zr(Cl)CHD–CHD–CMe_3$ it was shown that the formation of the alkyl halide molecules takes place with preservation of the configuration of the substituents on the carbon atom joined to Zr, indicating that the reaction involves a cyclic intermediate state.[2,29]



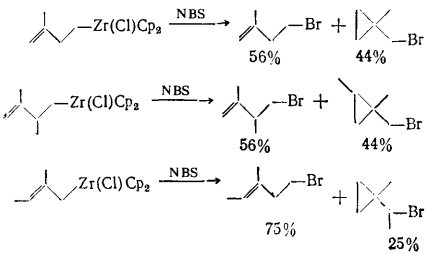
R = t-Bu

threo.

According to the proposed mechanism, the electrophilic reagent reacts with the substrate to form a cyclic intermediate complex using an unoccupied low-lying orbital of zirconium; this facilitates frontal attack at the Zr–C bond, and the subsequent polarisation of the coordinated electrophilic reagent leads to the rupture of this bond.



Similar reactions with Br_2 and N-bromosuccinimide (NBS) are undergone by alkyl- and alkenylzirconium complexes, the latter with preservation of the geometry of the double bond.[18,29] An exception is provided by 3-alkenylzirconium complexes containing, in addition to the double bond, alkenyl substituents on the C(3) atom. Under the influence of NBS, they are partly converted into cyclopropylalkyl bromides.[18]

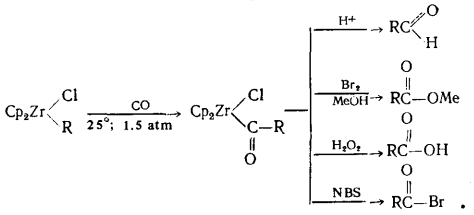


According to Schwartz's data,[29,30] alkylzirconium complexes are oxidised at the Zr–C bond in satisfactory yields by O_2, H_2O_2, alkyl hydroperoxides, and peroxyacids. In the later paper,[31] however, it was noted that in the oxidation of C_8–C_{30} alkylzirconium complexes, reproducible high (~70%) yields of primary alcohols can be obtained only using anhydrous t-butyl hydroperoxide. The use of a 70% solution of the hydroperoxide in water gives mainly hydrocarbons, and the yields of alcohols are low, and decrease with increase in the length of the hydrocarbon chain. The formation of appreciable quantities of unsaturated hydrocarbons was also observed in the oxidation of the products of the hydrozirconation of β-pinene and camphene by a 95% aqueous solution of t-butyl hydroperoxide.[10]

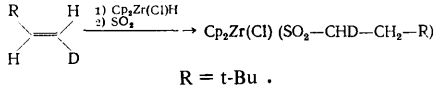
The presence, in the hydrocarbon group of the alkyl peroxide complexes, of double bonds separated by several carbon atoms from the metal atom has practically no influence on the oxidation, whereas the 1*E*-alkenylzirconium complexes cannot be oxidised smoothly.[1]

A convenient method for functionalising unsaturated compounds via the preparation of alkyl- and alkenylzirconium complexes is by the reaction of the latter with CO.[18,32] It is suggested that this reaction involves the rapid and reversible coordination of CO to the central metal atom to give a coordinatively unsaturated carbonyl complex $Cp_2Zr(Cl)(R)-CO$, in which the alkyl substituent migrates slowly to the active CO ligand.[2,32]

The relative ratio of formation of acyl complexes of zirconium depends markedly on the nature and structure of the alkyl substituent.[1] The acyl complexes can readily be selectively converted into aldehydes, carboxylic acids, esters, or acid halides, according to the scheme:



The analogous reaction of alkyl complexes of zirconium with CO_2 and SO_3 has not yet been carried out. Coordinatively saturated O,O′-sulphinate complexes of zirconium have been obtained using SO_2.[29]

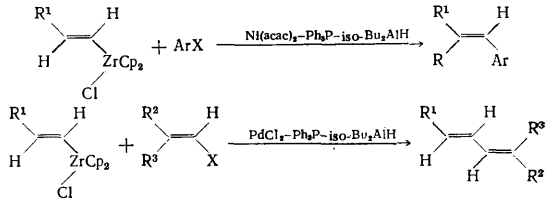


R = t-Bu .

In an excess of SO_2, this reaction is more complex.[33] $Cp_2Zr.(Cl)CH_3$ reacts similarly with NO_2 to give a zirconium complex of methylnitrosohydroxylamine.[34]

3. Alkenylzirconium Complexes in Cross-Coupling Reactions with Aryl and Vinyl Halides

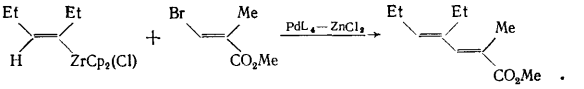
Negishi and co-workers were the first to establish that 1*E*-alkenylzirconium complexes in the presence of catalytic quantities of nickel or palladium compounds react readily with aryl[35] and vinyl[35–37] halides to give respectively derivatives of the arylethylene or dienes in 97–98% yield. The reaction is highly stereospecific (not less than 97%).



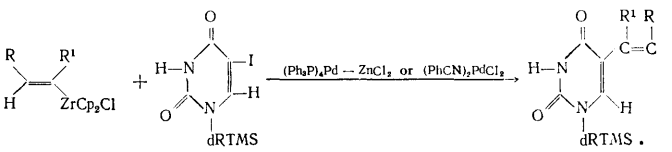
X = Cl, Br, I .

Attempts to extend the range of application of this reaction encountered serious difficulties. In particular, the formation of molecules of cross-coupled dienes, which takes place without complications in the case of β-monosubstituted alkenyl derivatives of zirconium, is extremely non-selective and gives low yields when the alkenyl substituents in the zirconium compounds are α, β- and β,β′-disubstituted. These difficulties were overcome by increasing the activity of the catalyst using promoting additives. The additives were salts of metals with electronegativities comparable with that of Zr, Ni, or Pd, but a much smaller atomic radius (Cu, Zn, Cd, Sn, In, Ti). Zn and Co salts were found to be most effective.

For example, the reaction between a 1*E*-alkenyl complex of zirconium and methyl β-bromomethacrylate in the presence of 5% $Pd(Ph_3P)_4$ after 6 h gives an ester of 2-methyl-4-ethyl-2*E*, 4*E*-heptadienoic acid in 22% yield, whereas with the "tandem" $(Ph_3P)_4Pd-ZnCl_2$ (1:1) the required product is formed in ~80% yield in 1 h.[38,39]

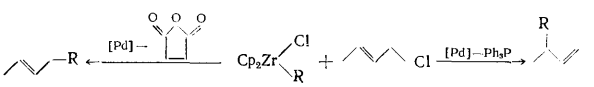


The same catalyst was used in the synthesis of 5*E*-alkenyl-substituted 2-deoxyuridines by cross-coupling 5-iodo-O-3′,5′-bis(trimethylsilyl)deoxyuridine with α-substituted alkenylzirconium complexes obtained from disubstituted acetylenes. In the case of less hindered alkenylzirconium complexes, the most active cross-coupling catalyst was found to be the complex $(PhCN)_2PdCl_2$.[26]



where dTRMS represents O-3′,5′-bis(trimethylsilyl)deoxyribose.

The influence of the nature of the ligands on the regioselectivity of the reaction has been demonstrated for the example of the cross-coupling of alkenylzirconium complexes with allyl halides and allyl acetates in the presence of bis-π-crotylpalladium chloride.[40] The introduction of phosphine ligands into the palladium catalyst promotes the coupling of the allyl fragment at the sterically more hindered end, whereas the addition of maleic anhydride favours the formation of the coupling products with the other structure.

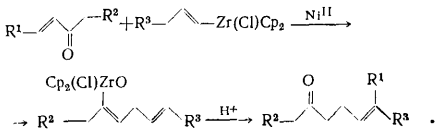


[Pd] = bis-π-allylpalladium chloride .

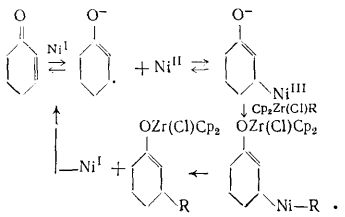
A similar influence of the ligands is observed in the coupling of alkenylzirconium compounds with stoichiometric quantities of π-allylpalladium chloride complexes. This made it possible to carry out an elegant regioselective synthesis of 20(S)-cholestan-3-one and 20(R)-cholestan-3-one.[41,42]

4. The Reactions of Alkenylzirconium Complexes with α,β-Unsaturated Ketones and the Transformations of Zirconium O-Enolates

Individual alkenyl complexes of zirconium react with α,β-unsaturated ketones even in the absence of catalysts, but the reaction is very slow, and the yields of required products are low.[43] Attempts to catalyse this reaction by transition metal complexes have been unsuccessful, probably because of the low activity of alkylzirconium complexes in *trans*-metallation. At the same time, the addition of 1*E*-alkenylzirconium complexes to enones is successfully catalysed by Ni compounds.[44,45] The corresponding β-alkenyl-substituted ketones are formed in high yield.

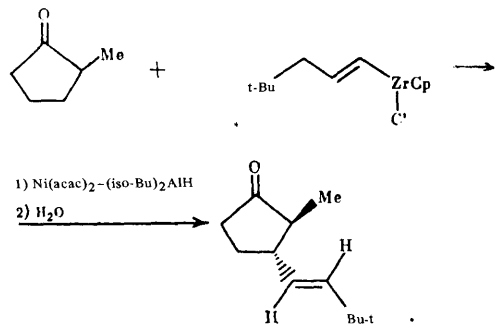


The catalytic systems obtained by reducing Ni compounds with $(iso\text{-}Bu)_2AlH$ are more active catalysts than nickel(II) salts. Moreover, an electrochemical study of the reaction of alkenylzirconium complexes with α,β-unsaturated ketones showed that this reaction, like the cross-coupling of vinyl complexes of zirconium with aryl and vinyl halides, is catalysed by nickel(I) complexes. On the basis of the results obtained, the following mechanism was proposed for the alkylation of enones.[46,47]

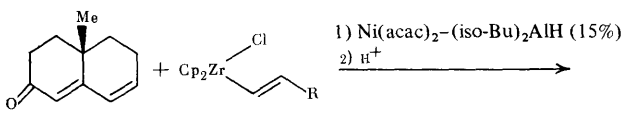


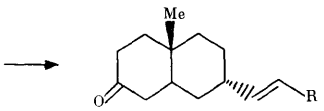
According to this scheme, the first stage involves the transfer of an electron from Ni^I to the enone, followed by the oxidative addition of the ketyl to Ni^{II}, giving a σ-bonded complex of Ni^{III} with the enone. The subsequent transformations of this complex as a result of *trans*-metallation and reductive elimination give the Zr enolate with the simultaneous regeneration of Ni^I.

The yield of the products of the 1,4-addition of 1*E*-alkenylzirconium complexes to enones is influenced considerably by the structure of the original ketone. The reaction gives good yields with most cyclic and acyclic ketones (Table 3), but in the case of $\Delta^{1(9)}$-octen-2-one and 10-methyl-$\Delta^{1(9)}$-octenone the yields of the products of the coupled addition do not exceed 33% and 70% respectively. Like the cuprate method, the addition of alkenylzirconium complexes to α-substituted cyclic enones gives the *trans*-disubstituted ketones with the same stereochemistry.[45]

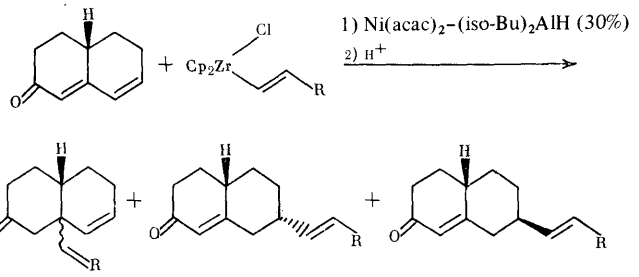


The selectivity of the alkylation of dienones depends to a marked extent on their structure. For example, the addition of alkenylzirconium complexes to 10-methyl-1(9),7-hexalin-2-one takes place selectively to give a single isomer, whereas in the case of non-substituted 1(9),7-hexalin-2-one, a mixture of regio- and stereoisomers is obtained.[47]





62% (R = n-Bu)
77% (R = t-Bu)

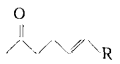
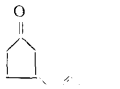
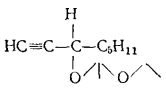
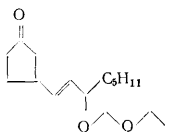
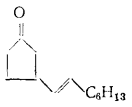
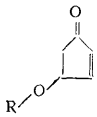
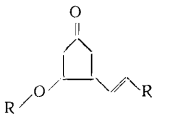
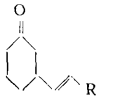
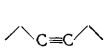
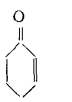
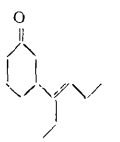
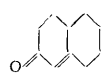
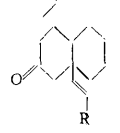
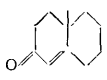
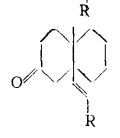


3% (R = n-Bu)
8% (R = t-Bu)

27% (R = n-Bu)
13% (R = t-Bu)

19% (R = n-Bu)
15% (R = t-Bu) .

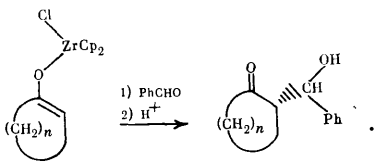
Table 3. Addition of alkenylzirconium complexes to α,β-enones, catalysed by nickel salts*.[44,45]

Acetylene	α,β-Enone	Product	Yield, %
HC≡C—R			>35
HC≡C—R			78
			59
HC≡CC$_6$H$_{13}$			49
HC≡C—R			76,9
HC≡C—R			77
			6—10
HC≡C—R			32,2
HC≡C—R			<10

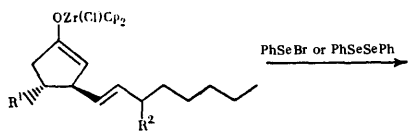
*R = t-Bu.

The highly reactive zirconium enolates formed have been made the basis of promising methods for obtaining β-keto- and homoallyl alochols of definite structure, used as synthones in the synthesis of natural compounds. Thus hydrozirconation and the coupled addition of alkenylzirconium complexes to cyclopentenone derivatives have been used to synthesise analogues of prostaglandins.[45,48]

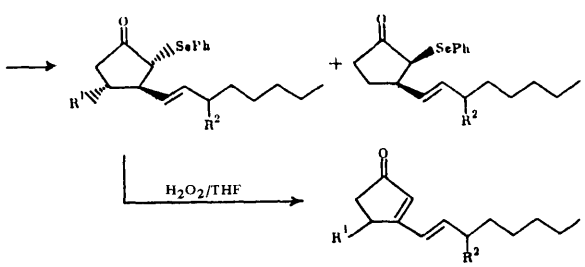
Attempts to use alkyl and allyl halides to introduce a substituent into the α-position of β-substituted Zr enolates were unsuccessful, but Zr cyclopentenolate reacts readily with a solution of monomeric formaldehyde in ether, to give after hydrolysis α-hydroxymethylcyclopentenone in 70% yield. When formaldehyde is replaced by acetaldehyde, the yield of desired products decreases sharply,[48] evidently as a result of steric hindrance, since non-substituted Zr O-cycloalkenolates react readily with benzaldehyde.[49]



The reaction of zirconium O-enolates with selenium derivatives (PhSeBr, Ph–Se–Se–Ph) gives α-phenylselenylcyclopentanones, used as synthones in the preparation of analogues of prostaglandins.[50]

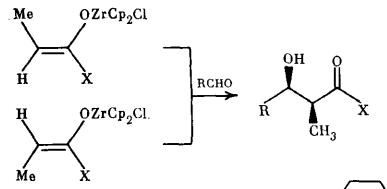


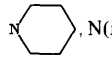
$R^1 = OC(Me)_2Ph$, $R^2 = (OCH_2)_2Ph$



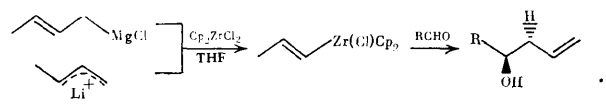
The use of zirconium O-enolates opens up an original approach to diastereoselective aldol condensation, which is generally carried out using prochirally pure enolates or enolates enriched in one of the isomers, which are difficult to obtain. Thus *Z*-enolates usually react with carbonyl compounds to give *erythro*-adducts, and *E*-enolates give *threo*-adducts. Since in the enolates of cyclic ketones the double bond has a fixed *E*-geometry, the preparation of *erythro*-aldols from these materials is complicated.

In 1980, almost simultaneously, two groups of workers reported that zirconium O-enolates, irrespective of their geometry and the nature of the substituents, react with aldehydes to give β-hydroxyketones, esters, and amides, with predominantly the ***erythro***-configuration.[49,51,52]



X = SBu-t, OMe, Ph, Et, OBu-t, , N(iso-Pr)$_2$;
R = Ph, n-Pr, iso-Pr, $C(CH_3)=CH_2$.

An interesting feature is that crotyl derivatives of zirconium, which can readily be obtained from crotylmagnesium chloride or crotyl-lithium and Cp_2ZrCl_2 in THF, react with aromatic and aliphatic aldehydes to give high yields of β-methylhomoallyl alcohols with predominantly the *threo*-configuration (yield 85–95%, selectivity 73–94%).[54]



5. Reactions of Alkyl- and Alkenylzirconium Complexes with Salts of Transition and Non-transition Metals

Considerable progress in the chemistry of organozirconium compounds was made with the discovery of the reaction involving the stereospecific transfer of a σ-bonded organic ligand from a zirconium atom to a metal atom which together with its ligand environment is more electronegative than the species $Cp_2Zr(Cl)^-$. The use of this reaction made it possible to overcome the difficulty of the low reactivity of alkyl- and alkenylzirconium complexes towards alkylating electrophilic reagents.

The first example of the use of these reagents to form a carbon–carbon bond was the reaction of alkyl- and alkenylzirconium complexes with $AlCl_3$, discovered in 1976.[54]

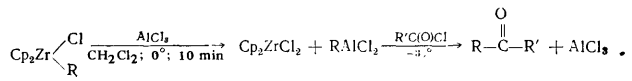


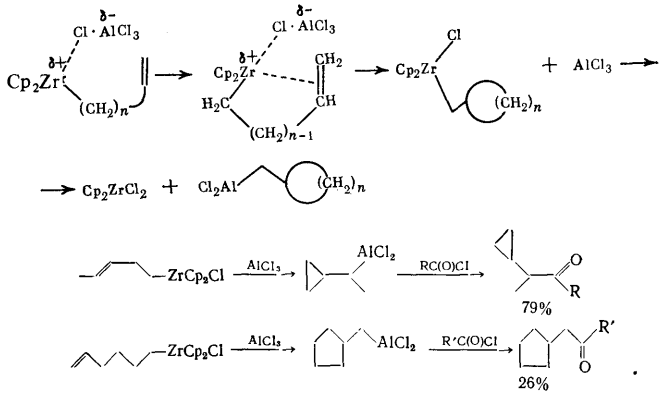
Table 4. Hydroalumination of cyclo-alkenes using $(iso\text{-}Bu)_2$.AlH (alkene : Al : $ZrCl_4$: n-BuOH = 50 : 50 : 1 : 4; hexane).[107]

Alkene	Yield*, %	T, °C	*t*, h
Cyclopentene	100	20	6
Cyclohexene	99.5	20	8
Cyclohexene	100	40	2
Cycloheptene	82.6	20	24
Cyclo-octene	20	20	24
Cyclo-octene	20	60	12
Cyclododecene (*cis* + *trans*)	59.2	20	21
Norbornene	100	0	1
Methylcyclobut-1-ene	0	20	24
Methylcyclododec-1-ene	0	20	24

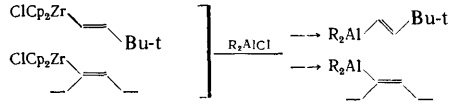
*Calculated for the cycloalkane.

The alkyl- or alkenylaluminium chlorides formed were used as acylating agents to obtain ketones, including enones, which cannot be synthesised by the direct acylation of the corresponding alkenyl-zirconium complexes (Table 4).

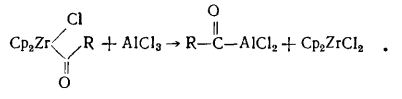
As a rule, the configuration of the double bonds of the alkenyl complexes remains unchanged in *trans*-metallation and subsequent transformations. In a number of cases, however, the reaction with ω-alkenylzirconium complexes is more complicated, and is accompanied by intramolecular cyclisation. This method was used to obtain a number of ketones which are difficult to prepare.[43]



According to Ref. 43, the reaction of alkylzirconium complexes with $AlCl_3$ is much slower than that of the corresponding alkenyl derivatives. Moreover, alkyl complexes of zirconium react with an excess of $AlCl_3$ to form exclusively monoalkylaluminium chlorides, whereas the alkenyl complexes may give mono-, di-, and trialkenylalanes, depending on the Zr : Al ratio. This method has been used to obtain mixed dialkenylalanes with different structures.

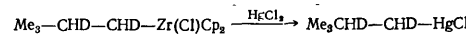


Acyl complexes of Zr react similarly with $AlCl_3$ to give acyldihalogenoalanes, which are of interest as potential equivalents of the acyl anion.[55]

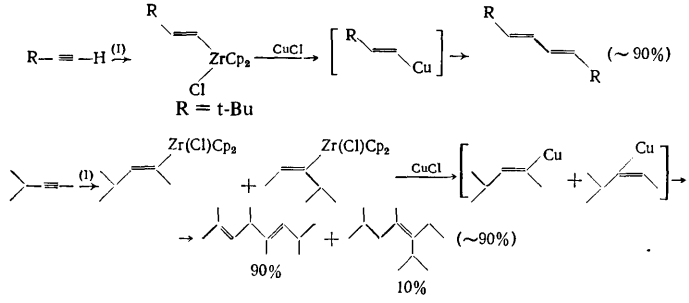


Special experiments with deuteriated alkylzirconium complexes showed that *trans*-metallation takes place predominantly with preservation of the configuration of the substituents on the carbon atom joined to the metal. This indicates a similarity between the mechanisms of *trans*-metallation and the splitting of the Zr–C bond by heteroatomic electrophilic reagents, discussed above.[43] *trans*-Metallation has been used to prepare alkyl and alkenyl complexes of a number of transition and non-transition metals.

Thus partly deuteriated *threo*- and *erythro*-alkylzirconium complexes react with $HgCl_2$ to give alkylmercury chlorides in ~50% yield with a high degree of stereoisomeric purity (≥80%).[56]



Alkenyl complexes of zirconium undergo an analogous reaction with copper salts; the configuration of the double bonds in the alkenyl groups remains unchanged. The alkenyl compounds of copper formed are extremely unstable, and decompose even at 0° to give *E,E*-conjugated dienes.[57]

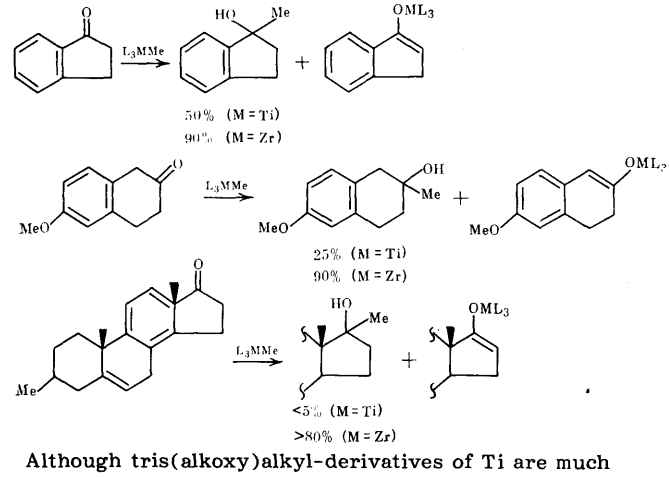


An analogous reaction is observed when copper salts are replaced by $PdCl_2$, but the yields of conjugated dienes in this case do not exceed 60%. Alkylzirconium complexes do not react with Cu and Pd salts under the conditions described.

According to Ref. 47, the reaction of alkenylzirconium complexes with $Ni(acac)_2$ also gives conjugated dienes, but no experimental details were given. A review by Schwartz[2] mentions (referring to unpublished results) that *trans*-metallation with Sn^{IV} and Zn^{II} compounds is possible in principle. *trans*-Metallation reactions using other transition and non-transition metals can undoubtedly be expected, and this will extend significantly the range of application of these methods in directed organic synthesis.

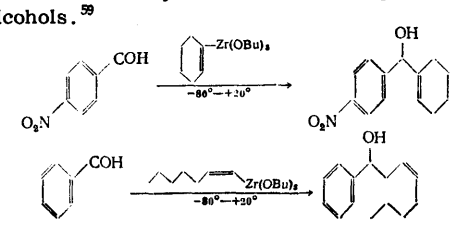
6. Alkoxyalkyl-complexes of Zirconium as Stable and Highly Selective Alkylating Agents

A new class of highly selective and stable alkylating agents for carbonyl compounds was recently proposed,[58–60] namely alkoxyalkyl-complexes of titanium and zirconium, obtained by the reaction of $(RO)_3MCl$ (where M = Ti, Zr) with lithium or magnesium alkyls. These reagents, particularly the Zr derivatives, are fairly stable, and differ from classical alkylating agents in their low basic strength and higher stereo- and regiospecificity, and also their selectivity, which makes it possible, for example, to alkylate aldehydes selectively in the presence of ketones with the same structure.[58,59]



Although tris(alkoxy)alkyl-derivatives of Ti are much less basic than organolithium or organomagnesium compounds, they are insufficiently nucleophilic for the successful alkylation of ketones which are readily enolised. The zirconium compounds $(RO)_3ZrR'$ successfully combine an exceptionally low basic strength with highly nucleophilic properties, so that they can be used for the selective alkylation of ketones which are readily enolised, including those containing various additional substituents. Moreover, alkoxyalkyl-compounds of titanium containing vinyl or α-branched hydrocarbon

groups decompose under the conditions of the reaction with carbonyl compounds, leading to a decrease in the yield of alkylation products. At the same time, the corresponding zirconium derivatives are more stable, and can, for example, convert aromatic aldehydes into the corresponding unsaturated alcohols.[59]



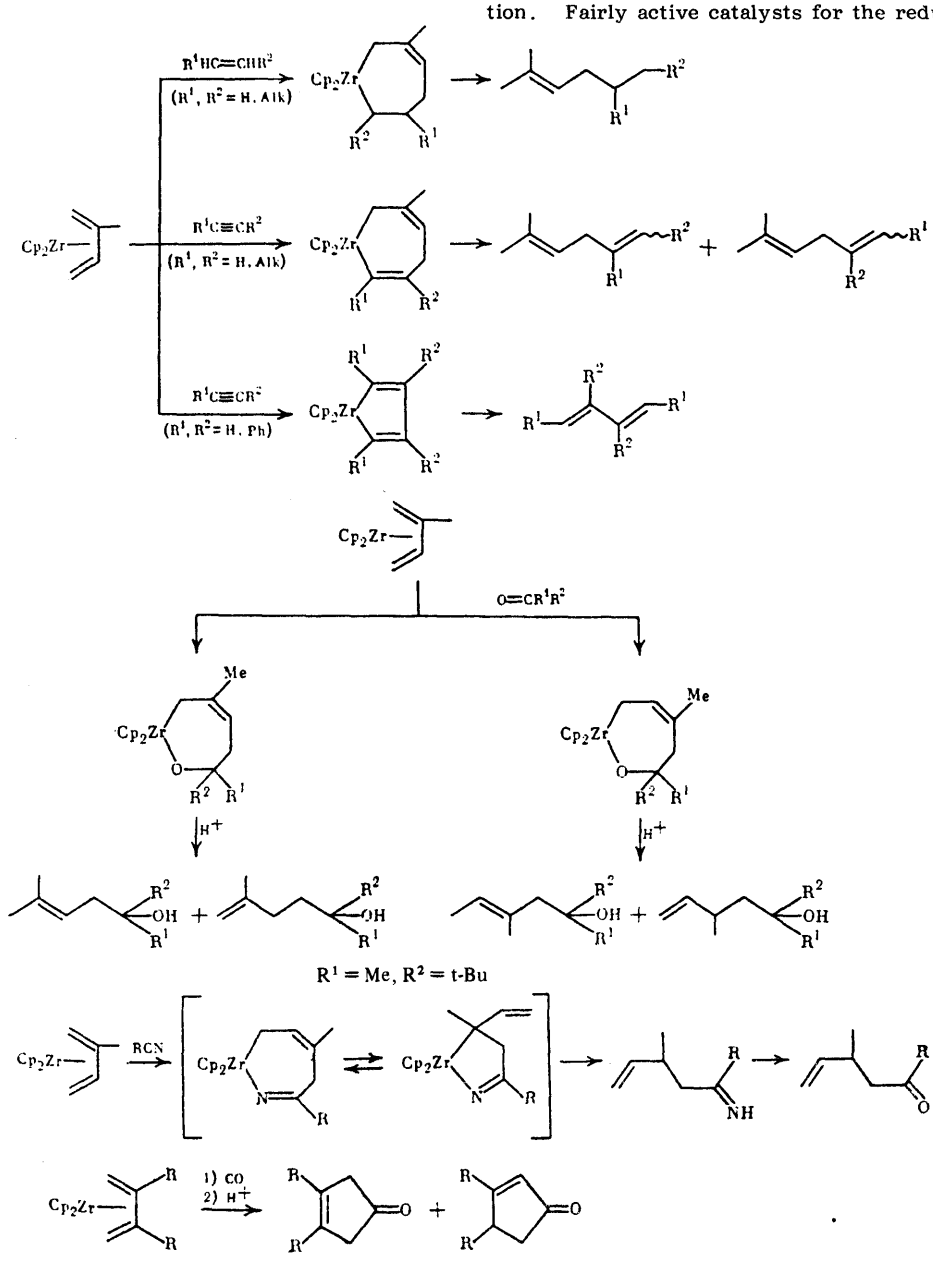
Another class of promising organozirconium reagents, synthesised in the last 2–3 years from σ,π-complexes of zirconium, should be noted. These complexes have a unique reactivity, and are being studied intensively by several groups of workers.[60–70] The most interesting reactions are given below.

III. CATALYSIS BY ZIRCONIUM COMPLEXES

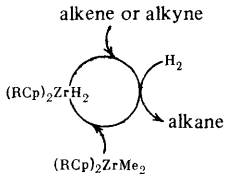
1. Transformations of Alkenes and Dienes, Catalysed by Zirconium Complexes

In spite of the fact that organozirconium compounds are firmly established in synthetic organic chemistry as active intermediates, their use as metal-complex catalysts in organic synthesis, apart from polymer chemistry, has only recently attracted extensive attention from research workers both in the Soviet Union and abroad.

The use of zirconium complexes as hydride-transfer catalysts has been studied in considerable detail. Thus a number of hydride complexes of zirconium(IV), fixed on activated silica gel, are highly active catalysts of the isomerisation of alkenes under mild conditions in thermodynamically equilibrium mixtures of the *cis*- and *trans*-isomers.[72] The hydrogenation of alkenes on these complexes is much slower than isomerisation. Fairly active catalysts for the reduction of alkenes

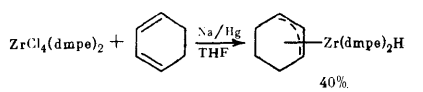


and acetylenes have been based on the zirconium complexes $RCp_2ZrR'_2$, where R' = H, Me; R = Me, Me_2CH, Me_3C.[73,74] The hydrogenation takes place by the following catalytic cycle:



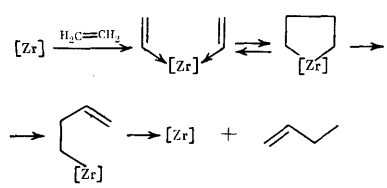
Attempts to use the optically active complexes $(R^*Cp)_2ZrR'_2$ for the asymmetric hydrogenation of the prochiral alkenes α-ethylstyrene and 2-ethylhex-2-ene were not successful. The yield of optically active hydrocarbons in these experiments did not exceed 2%, evidently because of the large distance between the chiral and reactive centres of the catalyst.[74]

High catalytic activity in hydride transfer was shown by stable low-valent zirconium complexes obtained by reducing $ZrCl_4$ with sodium amalgam in the presence of bis(dimethylphosphino)ethane (dmpe), cyclohexa-1,3-diene, or butadiene in THF solution.[75] The complexes synthesised in this way are highly active catalysts of the disproportionation of cyclohexa-2,3-dienes to cyclohexene and benzene, and of the reduction of mono0 and disubstituted alkenes and acetylenes to the corresponding alkanes.[75]



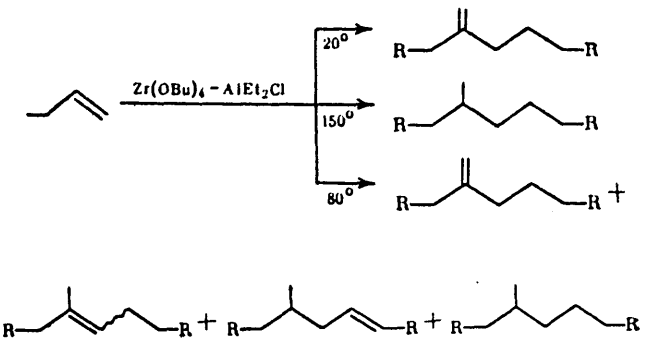
It is suggested that these processes involve the redox couples $Zr^{IV} \rightleftarrows Zr^{II}$; $Zr^{II} \rightleftarrows Zr^0$, which are the catalytically active centres in these reactions. The butadiene complex of zirconium $[Zr(C_4H_6)_2(dmpe)_2]$.dmpe catalyses the oligomerisation of various alkenes and dienes.[76]

From an an analysis of the structure of the oligomers obtained, and their distribution with respect to composition, a mechanism was proposed for the transformation of alkenes,[76] assuming the formation of five-membered metal-containing rings, which are responsible for the formation of the unsaturated hydrocarbon molecules:

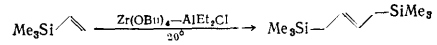


The above zirconium complexes have not found extensive preparative applications, however, since they are difficult to obtain. More promising catalysts for these purposes were obtained by the reaction of accessible zirconium compounds (halides, alkoxides, acetylacetonates) with alkylhalogenoalanes. These catalysts were used to develop highly selective and effective methods for copolymerising ethylene with propylene, or converting ethylene into but-1-ene[77–79] or into higher alkenes, including α-alkenes with controlled molecular weight.[79,80]

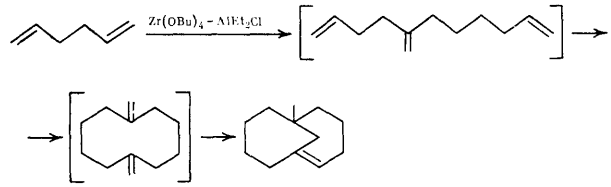
The two-component catalytic system $Zr(OBu)_4$–$AlEt_2Cl$ brings about the highly selective transformation of higher α-alkenes into unsymmetrical methylene-alkanes in high yields.[81,82] The reaction is sensitive to the structure of the original alkene and the temperature of the process. Increase in the length of the hydrocarbon group (C_6–C_{10}) in the α-alkene decreases considerably the yield of corresponding methylene-alkanes. On the other hand, with increase in the reaction temperature (100–150°), the yield of dimers increases, but dimerisation is accompanied by simultaneous isomerisation and hydrogenation of the unsaturated hydrocarbons formed.



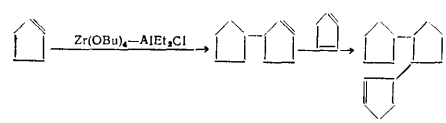
This catalytic system did not enable the authors cited to carry out the dimerisation of α-alkenes containing substituents in the α- or β-positions to the double bond. This catalyst selectively converts trimethylvinylsilane into 1,4-bis(trimethylsilyl)but-1-end.[81]



The dimerisation of hexa-1,5-diene is more complex, and gives a ~25% yield of a bicyclic hydrocarbon, identified as 6-methyl[4,4,1]bicycloundec-1-ene.[83,84]

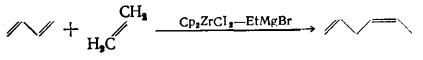


When Et_2AlCl in the catalytic system is replaced by $EtAlCl_2$, it is possible to carry out the dimerisation and trimerisation of cyclic C_5–C_{12} alkenes, whose activity in this reaction decreases in the order $C_5 > C_8 > C_7 > C_{12} > C_6$.[85]

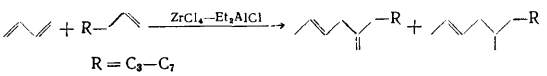


Unlike the homodimerisation of α-alkenes, the codimerisation of the latter with butadiene in the presence of zirconium complex catalysts takes place at a high temperature. Butadiene, however, having a greater coordinating power than α-alkenes, reacts with the central atom of the catalyst to form fairly stable complexes, in which the dissociation of the diene molecules and the approach and activation of the monoalkenes can take place only at a high temperature. Evidence in support of this suggestion is provided by the fact that the homodimerisation of hex-1-ene under the influence of zirconium catalysts at 20–60° is readily inhibited by the addition of butadiene.[86]

In particular, butadiene reacts with ethylene in the presence of the catalytic system Cp_2ZrCl_2–EtMgBr at 140–155° to give the single hydrocarbon hexa-1,4Z-diene in 20% yield.[87]

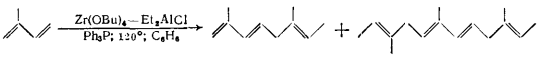


Higher α-alkenes do not react with butadiene on this catalyst, but the catalytic system $ZrCl_4$–Et_2AlCl (1 : 10) makes it possible to carry out at 120° the codimerisation of butadiene with hex-1-ene, oct-1-ene, non-1-ene, and dec-1-ene to give the corresponding 2*E*,5-methylene alkenes.[80]

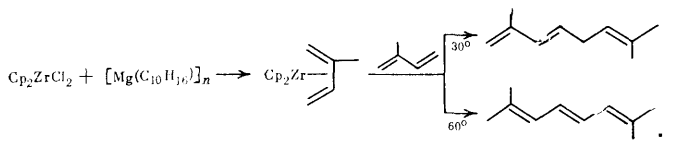


The codimerisation is accompanied by the homodimerisation of both original monomers, so that the yield of codimers does not exceed 15–20%. The mono-unsaturated codimers are evidently produced by the reaction of the initially formed 2,5-dienes with the organoaluminium component of the catalyst under the conditions of the reaction.[86]

In 1969, Japanese workers reported for the first time the possible use of the multicomponent catalytic systems $Zr(OBu)_4$–Et_2AlCl–Ph_3P and $Zr(C_3H_5)_4$–$Et_3Al_2Cl_3$ as catalysts of the linear dimerisation of isoprene to give 2,6-dimethylocta-1,3*E*,6*E*-triene.[88,89] In addition to the latter, the reaction gave a mixture of trimers, in which the concentration of 3,6,10-trimethyldodeca-2,5,7,10-tetraene was ~90%.[90]

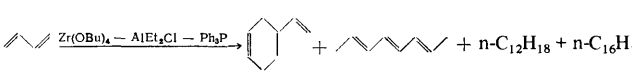


Later, more active catalysts were obtained, making it possible to increase the conversion of isoprene in this reaction to 90–95%.[91–93] The direction of the dimerisation of isoprene is changed completely by using the catalyst bis(cyclopentadienyl)isoprenylzirconium, which, depending on the reaction temperature, converts the original diene into 2,7-dimethylocta-1,3,6-triene or 2,7-dimethylocta-2,4,6-triene.[63]



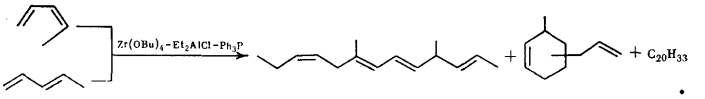
Subsequently, the authors of the present review established that three-component zirconium-containing catalysts can be used successfully for the dimerisation of other conjugated dienes with different structures.[94–97]

In the presence of the catalyst $Zr(OBu)_4$–$AlEt_2Cl$–Ph_3P, butadiene gives a mixture of linear and cyclic hydrocarbons consisting of 4-vinylcyclohexene, octa-2,4,6-triene, and isomeric tri- and tetramers of butadiene, differing in the positions of the double bonds.[94,95]

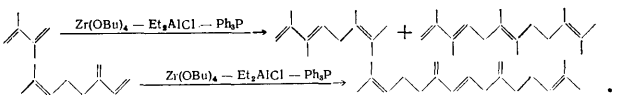


At the same time, the σ,π-complexes of zirconium formed by the reaction of $(C_8H_8)_2ZrCl_2$ with C_3H_5MgCl convert butadiene with an exceptionally high selectivity into octa-1,3*E*,6*Z*-triene.[98,99]

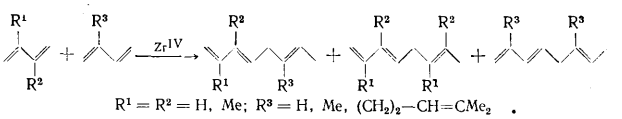
The reaction with *cis*- and *trans*-piperylenes gave 4,8-dimethyltrideca-2*E*,5*E*,7*E*,10*Z*-tetraene and a mixture of six-membered dimers and unidentified tetramers in the ratio 45 : 20 : 35.[95]



The oligomerisation of 2,3-dimethylbutadiene gives 2,3,6,7-tetramethylocta-1,3,6-triene and 2,3,6,7,10,11-hexamethyldodeca-1,3,6,10-tetraene. Myrcene is dimerised with a high selectivity to give the linear dimer 2,14-dimethyl-6-methylene-10 ethylidenepentadeca-2,7,13-triene.



The homodimerisation of farnesene gives a complex mixture of linear dimers and isomers of the original hydrocarbon.[94,95] Zirconium catalysts have made it possible to carry out the codimerisation of mono- and disubstituted conjugated dienes with different structures according to a "head-to-tail" scheme.



It is suggested[95] that the formation of linear dimers and codimers from 1,3-dienes takes place via the formation of bis-π-allyl and σ,π-allyl complexes of zirconium.

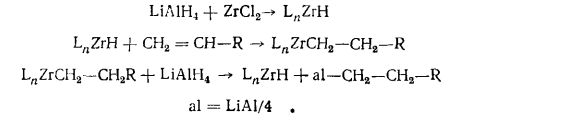
Thus of the catalysts known at present for the linear dimerisation and codimerisation of conjugated dienes, the zirconium complexes are the most universal, and can be used for the directed synthesis of polyenes with definite structures.

2. The Hydro- and Carbometallation of Alkenes, Dienes, and Acetylenes Under the Influence of Zirconium Catalysts

The first attempts to extend the range of application of hydroalumination using metal-complex catalysts were made by Asinger, who, in particular, used Ti and Zr compounds to convert a mixture of isomeric n-alkenes into primary alcohols by hydroalumination with tri-isobutylaluminium at 120° with subsequent oxidation of the higher organoaluminium compounds formed.[100]

The greatest progress in this field was made as a result of the discovery by Sato in the late nineteen-seventies[101,102] of the $ZrCl_4$-catalysed hydroalumination of alkenes by $LiAlH_4$ under mild conditions. Mono- and β,β'-disubstituted α-alkenes react selectively to give the corresponding lithium tetra-alkylalanates. Linear and cyclic α,β-disubstituted hydrocarbons, except cyclopentene, do not react with $LiAlH_4$ under these conditions.

According to Ref.103, the reaction takes place with the formation of intermediate hydride complexes of Zr, which hydrozirconate the alkenes, giving alkyl complexes of Zr, and subsequent *trans*-metallation leads to the regeneration of the original hydrides.



It was later established[101] that hydroalumination is catalysed not only by $ZrCl_4$ but also by Cp_2ZrCl_2, VCl_4, Cp_2TiCl_2, and $TiCl_4$, the last of these being the most effective catalyst. Its use made it possible to carry out the hydroalumination of alkenes with di- and trisubstituted double bonds under mild conditions, using not only $LiAlH_4$ but also AlH_3, $AlClH_2$, and $AlHCl_2$.

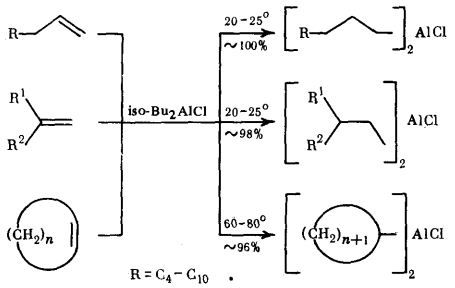
In a number of cases, however, the use of zirconium catalysts is still preferable. For example, allyl alcohols and their ethers react smoothly with $LiAlH_4$ only in the presence of Zr salts, $ZrCl_4$ is more effective for the hydroalumination of alcohols, and Cp_2ZrCl_2 is more effective for the hydroalumination of esters.[104,105]

The authors of the present review established[106,107] that Zr salts catalyse the hydroalumination of linear and cyclic alkenes under the influence of $(iso\text{-}Bu)_2AlH$ under mild conditions. The most effective catalysts of this reaction were found to be the mixed zirconium chloride alkoxides formed *in situ* by the reaction of $ZrCl_4$ with aliphatic alcohols or of $ZrCl_4$ with $Zr(OR)_4$. The activity of the zirconium catalysts decreases in the order: $Zr(OR)_nCl_{4-n} > ZrCl_4 > Zr(OR)_4 \geq Cp_2ZrCl_2$.[107] The rate of hydroalumination of cycloalkenes depends on the size of the ring, and decreases in the order: cyclopentene > cyclohexene > cycloheptene > cyclododecene > cyclo-octene (Table 4).

Almost simultaneously and independently, Negishi[108] and the authors of the present review,[79,109] found that Cp_2ZrCl_2 catalyses the hydroalumination of mono- and disubstituted linear and cyclic alkenes under the influence of $(iso\text{-}Bu)_3Al$, $(t\text{-}Bu)_3Al$, and $(iso\text{-}Bu)_2AlCl$. The yields of the products of the hydrometallation of the alkenes are 85–99%. When Cp_2ZrCl_2 is replaced by $ZrCl_4$, the yields are lowered to 50%.

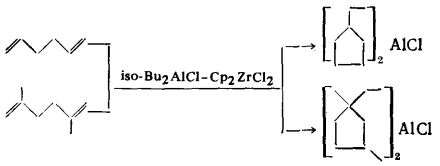
This reaction has a number of advantages over hydroalumination using dialkylaluminium hydrides, described above; in particular, it takes place under exceptionally mild conditions (0–20°) and can be carried out using alkenes containing electron-donor substituents (OH, SPh, Br), whose hydroalumination by Al hydrides is difficult.[111]

The hydroalumination of alkenes by $(iso\text{-}Bu)_2AlCl$, catalysed by Cp_2ZrCl_2, opens up a route to higher dialkylhalogenoalanes difficult to obtain.[109–111]

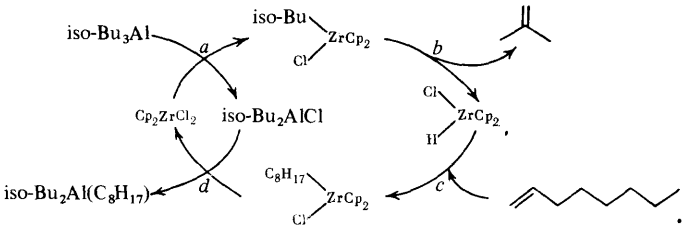


β,β′-Disubstituted alkenes are also selectively hydroaluminated by di-(n-alkyl)halogenoalanes and trialkylalanes.[112] Di-isobutylaluminium chloride reacts comparatively readily with α-alkenes at 20–25°, and with disubstituted and cyclic alkenes at 60–80°.[79]

Linear 1,5-dienes react with $(iso\text{-}Bu)_2AlCl$ in two stages. Hydroalumination takes place initially at one of the double bonds of the diene, after which intramolecular carbometallation gives the corresponding mono- and bicyclic halogenoalanes.[79]



A mechanism has been proposed for the catalysed hydroalumination of alkenes by trialkylalanes,[109,110] involving alkylation (*a*), the elimination of isobutylene (*b*), hydrozirconation (*c*), and *trans*-metallation (*d*):



This mechanism does not appear correct, however, since the regeneration of Cp_2ZrCl_2 from $Cp_2Zr(Cl)R$ and $(iso\text{-}Bu)_2$. .AlCl seems unlikely, because the concentration of the latter in the system is low. Moreover, according to Schwartz's data,[43] dialkylhalogenoalanes are inactive in *trans*-metallation with alkyl complexes of Zr. In the reaction conditions, under the influence of catalytic quantities of zirconium salts, trialkylalanes are probably succively split to give aluminium hydrides R_nAlH_{3-n}, which then bring about the hydroalumination of the alkenes or acetylenes. Evidence in support of this suggestion is provided by the fact that $(iso\text{-}Bu)_3Al$ in the presence of catalytic quantities of $ZrCl_4$ under mild conditions gives up a molecule of isobutylene, forming $(iso\text{-}Bu)_2AlH$.[79] Since groups with a normal structure are not eliminated under these conditions, the authors of the present review developed a catalytic method for obtaining higher dialkylaluminium hydrides:

$$iso\text{-}Bu_3Al \xrightarrow[30-40^\circ]{ZrCl_4} iso\text{-}Bu_2AlH + \underset{\sim 98\%}{\text{alkene}}$$

$$iso\text{-}Bu_3Al + 2R\text{-alkene} \xrightarrow[20^\circ]{Cp_2ZrCl_2} (R\text{-alkene})_2Al(iso\text{-}Bu) \xrightarrow[30-40^\circ]{ZrCl_4} \underset{\sim 96\%}{(R\text{-alkene})_2AlH}$$

Papers published in the last 4–5 years indicate that zirconium-containing catalysts can be used for the hydrometallation of alkenes by hydrides and hydride complexes of Mg and Zn.[111,115–117]

In particular, the hydrometallation of linear and cyclic alkenes by ZnH_2 has been studied in detail. The reaction is carried out at 80° in a medium of aromatic or aliphatic hydrocarbons. The most active catalyst of this reaction is $Zr(OBu)_3Cl$, obtained by the reaction of $ZrCl_4$ with $Zr(OBu)_4$. In addition to zinc dialkyls, the reaction products include metallic zinc, hydrogen, and saturated hydrocarbons; this was attributed[117] to the instability of the intermediate alkylzinc hydrides under the reaction conditions:

$$\text{alkene} + ZnH_2 \xrightarrow[PhMe,\ 80^\circ,\ 3\ h]{Zr(OBu)_3Cl} RZnH + R_2Zn \xrightarrow{1)\ O_2;\ 2)\ H^+} ROH$$

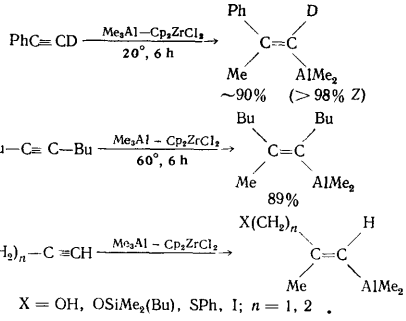
$$RZnH + R_2Zn \xrightarrow{D_2O} RD$$

$$RZnH + R_2Zn \xrightarrow{\Delta} RZnH_3 + R_2Zn \xrightarrow{\Delta} RH + H_2 + Zn$$

R = alkyl, cycloalkyl

An interesting feature is that oxidation of the reaction mass with oxygen gave not the expected alkyl hydroperoxides[118] but the corresponding primary alcohols, again evidently due to the influence of the zirconium catalysts.

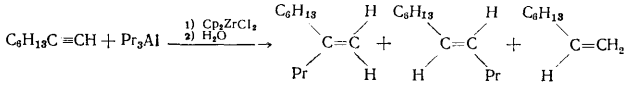
In 1978, Negishi and co-workers[110,119] carried out for the first time the Cp_2ZrCl_2-catalysed regio- and stereoselective *cis*-carboalumination of mono- and disubstituted acetylenes by trimethylaluminium. This reaction can be carried out with substituted acetylenes containing alkyl, alkenyl, and aromatic groups, including propargyl and homopropargyl derivatives. The carbometallation generally takes place with a high stereoselectivity, which reaches 95–100%.[110,119]



X = OH, $OSiMe_2(Bu)$, SPh, I; $n = 1, 2$.

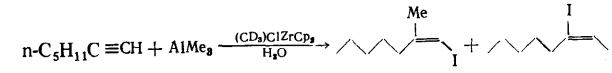
The carbometallation of monosubstituted acetylenes by Me_3Al, catalysed by Cp_2ZrCl_2, provides a simple and effective method of obtaining trisubstituted alkenes with the *cis*-configuration of the double bond, promising as synthones for the synthesis of natural products with the isoprene structure.[110]

The structure and nature of the carbometallating reagent have a much greater influence on the direction of the carboalumination of acetylene than the structure of the original acetylene. In particular, in the reaction of n-Pr_3Al with oct-1-yne, the regioselectivity of the process does not exceed 70–80%, and the yield of the carbometallation products is lowered to 35–75% as a result of the simultaneous competing reaction of hydroalumination.[110]

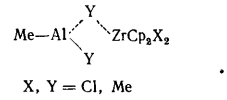


When Pr_3Al is replaced by $(iso\text{-}Bu)_3Al$ or $(t\text{-}Bu)_3Al$, only hydrometallation of the acetylenes is observed. The hydrometallation of both mono- and disubstituted acetylenes can be excluded by using the R_2AlCl–Cp_2ZrCl_2 system as the carbometallating reagent.[120] The mechanism of this extremely promising reaction and the role of Cp_2ZrCl_2 in it are still not clear.

On the basis of recent results,[121] Negishi rejected his earlier suggestion[122] that carbometallation involves successive *trans*-metallation, carbozirconation, and *trans*-metallation. Moreover, halogen–alkyl exchange between the Al and Zr atoms, which was previously regarded as a necessary condition for carbometallation, not only is not the decisive stage, but also favours the competing reaction of hydroalumination.[121] Thus in the bimetallic system Me_3Al–Cp_2. .Zr(Cl)Me, in contrast to the reagent Me_3Al–Cp_2ZrCl_2, halogen–alkyl exchange is not observed, but the rate of the carbometallation of the acetylenes is the same in both cases. In the carbometallation of hept-1-yne by the reagent Me_3Al–$Cp_2Zr(CD_3)Cl$, treatment of the reaction products with I_2 gives a quantitative yield of a mixture of 1-iodo-2-methylhept-1*E*-ene and 3-iodohept-2*Z*-ene. The concentration of the deuteriated alkenes in these experiments did not exceed 4%.

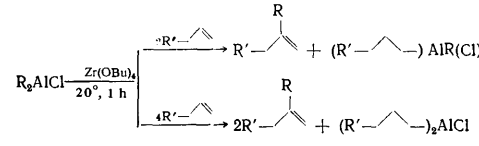


From these data, Negishi concludes that the zirconium-catalysed carboalumination of acetylenes by Me_3Al, at least in typical cases, involves direct carbometallation with the participation of zirconium complexes. It is suggested that the active intermediate is a bimetallic complex with the following structure:[121]

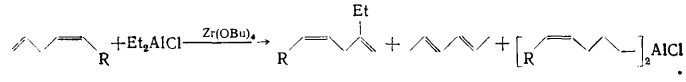


X, Y = Cl, Me

The authors of the present review were the first to establish that zirconium compounds also catalyse the carbometallation of α-alkenes by organoaluminium and organomagnesium compounds.[112 123–125] Thus the reaction of α-alkenes with dialkylaluminium halides in the presence of $Zr(OBu)_4$ leads to the selective formation of methylene-alkanes and the corresponding higher di-n-alkylaluminium halides; this can be attributed to successive carbo- and hydroalumination:[112]

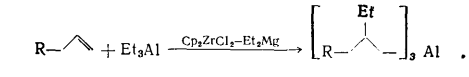


The size of the hydrocarbon group, and the presence of a localised disubstituted bond in the molecule of the original α-alkene, have no influence on the direction of the reaction, but in the last case the yield of reaction products is lower, because of the partial isomerisation of the original 1,4-diene to the 2,4-isomer.[112]



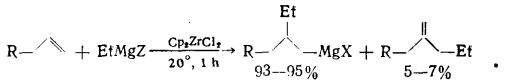
Under the conditions of this reaction, conjugated dienes polymerise, and β,β′-disubstituted alkenes, as noted above, give exclusively the hydroalumination products. The reagents with the most selective action are the dialkylhalogenoalanes.

The highest yields of carboalumination products were obtained using diethylaluminium chloride, whereas with increase in the length of the hydrocarbon group on the aluminium atom their yield decreases slightly.[112] A higher catalytic activity and selectivity of action in this reaction are shown by $Zr(OBu)_4$. In the presence of $ZrCl_4$ and $(C_5H_5N)_2ZrCl_2$, and also $TiCl_4$ and $Ti(OBu)_4$, a mixture of the products of hydro- and carbometallation, and also oligomerisation of the original alkenes, is formed, whereas Cp_2. .$ZrCl_2$ and $Zr(acac)_4$ were found to be completely inactive in this reaction. In the presence of an equivalent quantity of $(iso\text{-}Bu)_3Al$ or Et_2Mg, however, Cp_2ZrCl_2 catalyses the selective carboalumination of α-alkenes not only by diethylmagnesium but also by triethylaluminium. An interesting feature is that in this case the process stops at the carboalumination stage.[126,79]



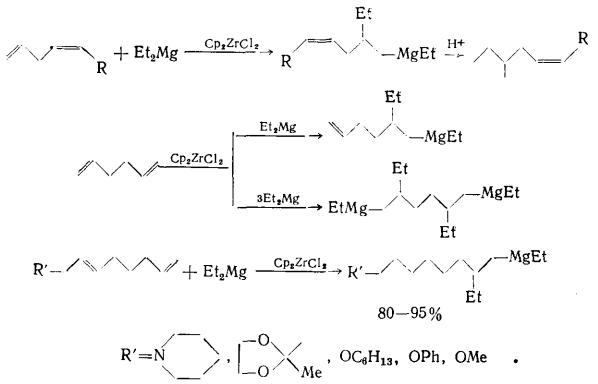
This reaction has been made the basis of a synthesis of 2-ethylhexanol from hex-1-ene and $AlEt_3$.[127]

The use of Cp_2ZrCl_2 made it possible to carry out under mild conditions the regioselective carbomagnesation of α-alkenes by Et_2Mg or EtMgX (where X = Cl, Br, I).[125,128] Unlike the reaction of α-alkenes with R_2AlCl described above, the process is not accompanied by subsequent hydrometallation. In this connection, the mechanism of formation of small quantities (5–7%) of β-alkylated alkenes under the conditions of the carbomagnesation is not yet clear. It should be noted that $ZrCl_4$ and $Zr(OBu)_4$ do not catalyse carbomagnesation; in their presence, the yield of hydromagnesation products is 3–5%. An interesting feature is that the action of Cp_2ZrCl_2 is completely blocked by the addition of equivalent quantities of hydrocarbons containing a triple bond or a conjugated system of double bonds.



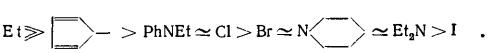
The reaction with the α-alkenes involves one ethyl group of the Et_2Mg molecule or half of the ethyl groups in EtMgX, and the latter reacts much more slowly than Et_2Mg. This suggested that under the reaction conditions, EtMgX disproportionates to MgX_2 and $MgEt_2$, which is then involved in the carbomagnesation.[128]

The method described is applicable to a wide range of α-alkenes containing internal double bonds and various functional substituents, and the regioselectivity of the process remains unchanged.



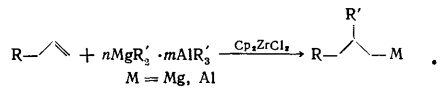
Electron-acceptor substituents on the allyl carbon atom lower considerably the activity of the double bond in carbomagnesation.

The complex Cp_2ZrCl_2 catalyses the carbomagnesation of α-alkenes under the influence of not only Et_2Mg and EtMgX but also a number of other important Grignard reagents RMgZ, where the rate of carbomagnesation decreases in the Z order:



Compounds of the type R'OMgR, RMgSR, RMgF, and $RMgC{\equiv}CR'$ are completely inactive in carbomagnesation.[129,130] In the case of higher magnesium alkyls R_2Mg (R = n-Pr, n-Bu, n-Oct), a considerable quantity of unsaturated organomagnesium compounds is formed in addition to the products of the direct carbometallation.[130]

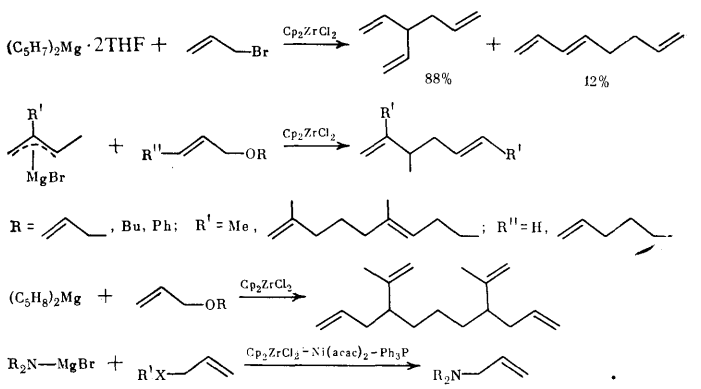
It was shown that the carbometallation of α-alkenes, catalysed by Zr salts, by bimetallic compounds in a hydrocarbon medium is possible in principle.[130]



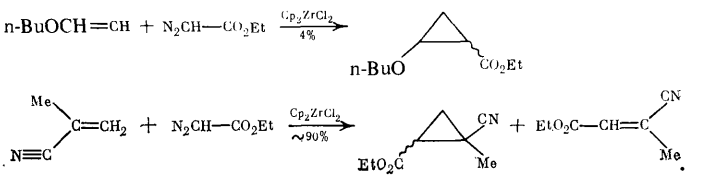
This reaction opens up extensive possibilities for the development of new effective technological carbo- and hydrometallating agents.

3. Other Examples of the Use of Zirconium-containing Catalysts

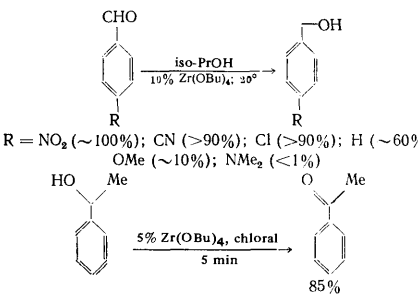
The cross-coupling of diene–magnesium complexes[131–133] and of alkenylmagnesium bromides and magnesium amides with allyl and aryl halides, catalysed by Cp_2ZrCl_2 and bimetallic catalysts,[132] are of undoubted interest and practical importance.



Two recent papers[134,135] describe the use of Cp_2ZrCl_2 to catalyse the cyclopropanation by diazoacetic ester of alkenes containing an activated double bond.



The use of zirconium tetra-alkoxides as catalysts of the Meerwein–Ponndorf–Varley reduction of carbonyl compounds or the Oppenauer oxidation of aromatic alcohols in the presence of chloral has been reported.[59]



While the present review was being prepared for publication, a number of papers on the topics of its sections were published. Thus the hydrozirconation of aliphatic and aromatic nitriles has been carried out; a heteroallyl structure

has been proposed for the complexes formed.[136] The Cp_2ZrCl_2–t-BuMgCl system has been proposed for the hydrozirconation of unsaturated compounds, and has been used to carry out for the first time the carbozirconation of 1,3-dienes.[137] The condensation of crotylzirconium complexes with aldehydes in the presence of BF_3, giving β-methylhomoallyl alcohols with predominantly the *threo*-configuration, has been described.[138] It has been shown that hydride complexes of cyclopentadienyl-zirconium can reduce the trichloromethyl groups in polychloroalkanes.[139] Studies directed towards increasing the activity of akylidene-zirconium complexes in carbonylalkenisation are continuing.[140] Zirconium(II) complexes have been used to convert ω-vinyl-1-silylalk-1-ones into zirconabicyclanes, which after treatment with CO give the corresponding α-silylbicyclopentenones.[141]

Interesting results have been obtained on hydro- and carbometallation involving zirconium-containing catalysts.[142–147]

The above results show the promising possibilities provided by the use of zirconium compounds in synthesis, including their use for the regio- and stereoselective synthesis of complex organic molecules. It is to be hoped that further studies in this field will make it possible to develop new and highly effective reagents and catalysts for organic synthesis.

REFERENCES

1. J.Schwartz and J.A.Labinger, Angew.Chem.Int.Ed. Engl., 1976, **15**, 333.
2. J.Schwartz, Pure Appl.Chem., 1980, **52**, 733.
3. P.C.Wailes and H.Weigold, J.Organometal.Chem., 1970, **24**, 405.
4. P.C.Wailes, H.Weigold, and A.P.Bell, J.Organometal. Chem., 1972, **43**, C32.
5. The Aldrich-Europe Catalog Handbook of the Fine Chemicals, 1981–1982, p.126.
6. D.W.Hart and J.Schwartz, J.Amer.Chem.Soc., 1974, **96**, 8115.
7. H.C.Brown and G.Zweifel, J.Amer.Chem.Soc., 1967, **89**, 561.
8. G.A.Tolstikov and V.P.Yur'ev, "Alyuminiiorganicheskii Sintez" (Organoaluminium Synthesis), Izd.Nauka, Moscow, 1979, p.20.
9. T.W.Gibson and L.Tulich, J.Org.Chem., 1980, **45**, 737.
10. M.S.Miftakhov, N.N.Sidorov, and G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2748.
11. A.F.Sviridov, M.S.Ermolenko, and N.K.Kochetkov, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2568.
12. C.Qian, K.Lui, and H.Zhou, in "Fundam.Res. Organomet.Chem.Proc.China–Japan–US. Trilateral Semin.Organomet.Chem., Edited by M.Tsutsui, Y.Ishii, and Y.N.Y.Huang, Van Nostrand Reinhold, New York, 1982, p.705; Chem.Abs., 1982, **97**, 182575.
13. W.Tam and M.F.Rettig, J.Organometal.Chem., 1976, **108**, C1.
14. F.W.Hartner and J.Schwartz, J.Amer.Chem.Soc., 1981, **103**, 4979.
15. F.W.Hartner, J.Schwartz, and S.M.Clift, J.Amer. Chem.Soc., 1983, **105**, 640.
16. K.S.Ng, D.E.Laycock, and H.Alper, J.Org.Chem., 1981, **46**, 2899.
17. D.E.Laycock and H.Alper, J.Org.Chem., 1981, **46**, 289.
18. C.A.Bertelo and J.Schwartz, J.Amer.Chem.Soc., 1976, **98**, 262.
19. B.M.Mikhailov and Yu.N.Bubnov, "Boroorganicheskie Soedineniya v Organicheskom Sinteze" (Organoboron Compounds in Organic Synthesis), Izd.Nauka, Moscow, 1977, p.315.
20. J.J.Partridge, N.K.Chadha, and M.R.Uskokovic, J.Amer.Chem.Soc., 1973, **95**, 532.
21. C.K.Brown, W.Mowat, G.Yagupsky, and G.Wilkinson, J.Chem.Soc., A, 1971, 850.
22. A.W.Messing, F.P.Ross, A.W.Norman, and W.H.Okamura, Tetrahedron Letters, 1978, 3635.
23. D.W.Hart, T.F.Blackburn, and J.Schwartz, J.Amer. Chem.Soc., 1975, **97**, 679.
24. P.C.Wailes, H.Weigold, and A.P.Bell, J.Organometal. Chem., 1971, **27**, 373.
25. E.J.Corey, E.J.Trybulski, L.S.Melvin, K.C.Nicolaou, J.A.Secrist, R.Lett, P.W.Sheldrake, I.R.Falck, D.I.Brunnelle, M.F.Haslanger, S.Kim, and S.Yoo, J.Amer.Chem.Soc., 1978, **100**, 4618.
26. P.Vincent, J.-P.Beaucourt, and L.Pichat, Tetrahedron Letters, 1982, **23**, 63.
27. E.Cesarotti, A.Chiesa, S.Maffi, and R.Ugo, Inorg. Chim.Acta, 1982, **64**(4), L207.
28. T.N.Sorrell, Tetrahedron Letters, 1978, 4985.
29. J.A.Labinger, D.W.Hart, W.E.Seibert, and J.Schwartz, J.Amer.Chem.Soc., 1975, **97**, 3851.
30. T.F.Blackburn, J.A.Labinger, and J.Schwartz, Tetrahedron Letters, 1975, 3041.
31. T.W.Gibson, Tetrahedron Letters, 1982, **23**, 157.
32. C.A.Bertelo and J.Schwartz, J.Amer.Chem.Soc., 1975, **97**, 228.
33. P.C.Wailes, H.Weigold, and A.P.Bell, J.Organometal. Chem., 1971, **33**, 181.
34. P.C.Wailes, H.Weigold, and A.P.Bell, J.Organometal. Chem., 1971, **34**, 155.
35. E.Negishi and D.E.Van Horn, J.Amer.Chem.Soc., 1977, **99**, 3168.
36. N.Okukado, D.E.Van Horn, W.L.Klima, and E.Negishi, Tetrahedron Letter, 1978, 1027.
37. H.Matsushita and E.Negishi, J.Amer.Chem.Soc., 1981, **103**, 2882.
38. E.Negishi, in "Aspects of Mechanism in Organometallic Chemistry", Edited by J.H.Brewster, Plenum Press, New York, 1978, p.285.
39. E.Negishi, N.Okukado, A.O.King, D.E.Van Horn, and B.I.Spiegel, J.Amer.Chem.Soc., 1978, **100**, 2254.
40. Y.Hayasi, M.Riediker, J.S.Temple, and J.Schwartz, Tetrahedron Letters, 1981, **22**, 2629.
41. J.S.Temple and J.Schwartz, J.Amer.Chem.Soc., 1980, **102**, 7382.
42. J.S.Temple, M.Riediker, and J.Schwartz, J.Amer. Chem.Soc., 1982, **104**, 1310.
43. D.B.Carr and J.Schwartz, J.Amer.Chem.Soc., 1979, **101**, 3521.
44. M.J.Loots and J.Schwartz, J.Amer.Chem.Soc., 1977, **99**, 8045.
45. J.Schwartz, M.J.Loots, and H.Kosugi, J.Amer.Chem. Soc., 1980, **102**, 1333.
46. F.M.Dayrit, D.E.Gladkowski, and J.Schwartz, J.Amer.Chem.Soc., 1980, **102**, 3976.
47. F.M.Dayrit and J.Schwartz, J.Amer.Chem.Soc., 1981, **103**, 4466.
48. M.J.Loots and J.Schwartz, Tetrahedron Letters, 1978, 4381.
49. Y.Yamamoto and K.Maruyama, Tetrahedron Letters, 1980, **21**, 4607.
50. J.Schwartz and Y.Hayasi, Tetrahedron Letters, 1980, **21**, 1497.
51. D.A.Evans and L.R.McGee, Tetrahedron Letters, 1980, **21**, 3975.

52. D.A.Evans and L.R.McGee, J.Amer.Chem.Soc., 1981, **103**, 2876.
53. Y.Yamamoto and K.Maruyama, J.Amer.Chem.Soc., 1981, **22**, 2895.
54. D.B.Carr and J.Schwartz, J.Amer.Chem.Soc., 1977, **99**, 638.
55. D.B.Carr and J.Schwartz, J.Organometal.Chem., 1977, **139**, C21.
56. R.A.Budnik and J.K.Kochi, J.Organometal.Chem., 1976, **116**, C3.
57. M.Yoshifuji, M.J.Loots, and J.Schwartz, Tetrahedron Letters, 1977, 1303.
58. B.Weidman, C.Maycock, and D.Seebach, Helv. Chim.Acta, 1981, **64**, 1552.
59. B.Weidman and D.Seebach, Angew.Chem., 1983, **95**, 12.
60. M.T.Reetz, R.Steinbach, J.Westermann, R.Urz, B.Wenderoth, and R.Peter, Angew.Chem., 1982, **94**, 133.
61. A.Nakamura, H.Yasuda, Y.Kajihara, and K.Nagasuna, Chem.Letters, 1981, 719.
62. H.Yasuda, Y.Kajihara, K.Nagasuna, K.Mashima, K.Lee, and A.Nakamura, Organometallics, 1982, **1**, 388.
63. H.Yasuda, Y.Kajihara, K.Mashima, K.Nagasuna, and A.Nakamura, Chem.Letters, 1981, 671.
64. M.Akita, H.Yasuda, and A.Nakamura, Chem.Letters, 1983, 217.
65. K.Mashima, H.Yasuda, K.Asami, and A.Nakamura, Chem.Letters, 1983, 219.
66. U.Dorf, K.Engel, and G.Erker, Organometallics, 1983, **2**, 462.
67. A.Famili, M.F.Farona, and S.P.Thanedar, Chem. Communs., 1983, 435.
68. G.Erker, K.Engel, J.L.Atwood, and W.E.Hunter, Angew.Chem.Suppl., 1983(6), 675.
69. G.Erker, J.Wicher, K.Engel, and C.Krüger, Chem. Ber., 1982, 115, 3300.
70. G.Erker, K.Engel, C.Krüger, and A.-P.Chiang, Chem.Ber., 1982, **115**, 3311.
71. S.S.Wreford and J.F.Whitney, Inorg.Chem., 1981, **20**, 3918.
72. J.Schwartz and M.D.Ward, J.Molecular Catalysis, 1980(8), 465.
73. S.Couturier and B.Gautheron, J.Organometal.Chem., 1978, 157, C61.
74. S.Couturier, G.Tainturier, and B.Gautheron, J.Organometal.Chem., 1980, **195**, 291.
75. S.Datta, S.S.Wreford, R.P.Beatty, and T.J.McNeese, J.Amer.Chem.Soc., 1979, 101, 1053.
76. S.Datta, M.B.Fischer, and S.S.Wreford, J.Organometal.Chem., 1980, **188**, 353.
77. U.M.Dzhemilev, G.A.Tolstikov, S.R.Rafikov, M.A.Dalin, O.S.Vostrikova, A.G.Ibragimov, R.M.Masagutov, S.M.Maksimov, and G.E.Ivanov, USSR P.857 097, 1981.
78. U.M.Dzemilev, G.A.Tolstikov, S.R.Rafikov, G.I.Rutman, O.S.Vostrikova, A.G.Ibragimov, S.S.Shavanov, F.B.Gershanov, and S.A.Egoricheva, USSR P.941 340, 1982.
79. A.G.Ibragimov, Candidate's Thesis, Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa, 1981.
80. V.N.Belova, L.N.Russiyan, P.E.Matkovskii, V.N.Mel'nikov, M.P.Gerasina, F.S.D'yachkovskii, and M.A.Birkenshtein, "Kataliticheskie Reaktsii v Zhidkoi Faze. Tezisy Dokladov VII Vsesoyuznoi Konferentsii" (Summaries of Papers Presented at the Sixth All Union Conference on Catalytic Liquid-Phase Reactions), Part 2, Izd.Nauka, Alma-Ata, 1983, p.191.
81. O.S.Vostrikova, A.G.Ibragimov, G.A.Tolstikov, L.M.Zelenova, and U.M.Dzhemilev, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2320.
82. U.M.Dzhemilev, O.S.Vostrikova, A.G.Ibragimov, G.A.Tolstikov, and V.D.Buteev, USSR P.793972, 1980.
83. U.M.Dzhemilev, O.S.Vostrikova, G.A.Tolstikov, and A.G.Ibragimov, "Tezisy XII Mendeleevskogo S'ezda po Obshchei i Prikladnoi Khimii" (Summaries of Papers Presented at the Twelfth Mendeleev Congress of Pure and Applied Chemistry), Vol.4, Moscow, 1980, p.54.
84. O.S.Vostrikova and A.G.Ibragimov, "Tezisy Dokladov Konferentsii Molodykh Uchenykh" (Summaries of Papers Presented at the Conference of Young Scientists), Izd.Bashkir.Fil.Akad.Nauk SSSR, Ufa, 1981, p.26.
85. H.H.Bittrich, R.Bittrich, L.Sass, P.Zirz, P.Reich, and G.Zimmermann, J.prakt.Chem., 1981, 323, 177.
86. O.S.Vostrikova, A.G.Ibragimov, G.A.Tolstikov, L.M.Zelenova, and U.M.Dzhemilev, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1410.
87. Yu.B.Amerik, in collected papers "Novye Aspekty Neftekhimicheskogo Sinteza" (New Aspects of Petrochemical Synthesis), Izd.INKhS im.A.V.Topchieva, Moscow, 1978, p.28.
88. A.Misono, Y.Uchida, K.Furuhata, and S.Yoshida, Bull.Chem.Soc.Japan, 1969, **42**, 1383.
89. Y.Uchida, K.Furuhata, and S.Yoshida, Bull.Chem. Soc.Japan, 1971, 44, 1966.
90. A.Misono, Y.Uchida, K.Furuhata, and S.Yoshida, Bull.Chem.Soc.Japan, 1969, **42**, 2303.
91. H.Morikawa and T.Sato, Japan P.78-101 375, 1978.
92. H.Morikawa and S.Kitazume, US P.4 071 575, 1978.
93. H.Morikawa and S.Kitazume, Ind.Eng.Chem.Prod. Res.Dev., 1979, 18, 254; Chem.Abs., 1979, **91**, 193447.
94. Y.M.Dzhemilev, A.G.Ibragimov, O.S.Vostrikova, and G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser. Khim., 1979, 2071.
95. U.M.Dzhemilev, A.G.Ibragimov, O.S.Vostrikova, G.A.Tolstikov, and L.M.Zelenova, Zhur.Org. Khim., 1981, **17**, 2313.
96. A.G.Ibragimov, U.M.Dzhemilev, and O.S.Vostrikova, USSR P.997 798, 1982.
97. U.M.Dzhemilev, O.S.Vostrikova, A.G.Ibragimov, G.A.Tolstikov, and A.A.Panasenko, "Tezisy Dokladov Vsesoyuznoi Konferentsii Pamyati Akademika A.E.Favorskogo" (Summaries of Papers Presented at the Conference in Memory of Academician A.E.Favorskii), Leningrad, 1980, p.149.
98. H.J.Kablits and G.Wilke, J.Organometal.Chem., 1972, **44**, C49.
99. H.J.Kablits and G.Wilke, J.Organometal.Chem., 1973, **51**, 241.
100. F.Asinger, B.Fell, and R.Janssen, Chem.Ber., 1964, **97**, 2515.
101. F.Sato, S.Sato, and M.Sato, J.Organometal.Chem., 1976, **122**, C25.
102. F.Sato, S.Sato, H.Kodama, and M.Sato, J.Organometal.Chem., 1977, **142**, 71.
103. L.I.Shoer, K.I.Gell, and J.Schwartz, J.Organometal. Chem., 1977, **136**, C19.
104. F.Sato, Y.Tomuro, H.Ishikawa, and M.Sato, Chem. Letters, 1980, 99.
105. F.Sato, Y.Tomuro, H.Ishikawa, and M.Sato, Kenkyu Hokoku–Asahi Garasu Kogyo Gijutsu Shoreikai, 1980, **37**, 123; Chem.Abs., 1982, **95**, 80036.

106. U.M.Dzhemilev, O.S.Vostrikova, A.G.Ibragimov, and G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser. Khim., 1980, 2134.
107. G.A.Tolstikov, U.M.Dzhemilev, O.S.Vostrikova, and A.G.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 669.
108. E.Negishi and T.Yoshida, Tetrahedron Letters, 1980, **21**, 1501.
109. U.M.Dzhemilev, O.S.Vostrikova, A.G.Ibragimov, G.A.Tolstikov, and L.M.Zelenova, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 476.
110. E.Negishi, Pure Appl.Chem., 1981, **53**, 2333.
111. O.S.Vostrikova, A.G.Ibragimov, A.G.Tolstikov, R.M.Sultanov, and U.M.Dzhemilev, "Tezisy Dokladov II Vsesoyuznoi Konferentsii po Metalloorganicheskoi Khimii" (Summaries of Papers Presented at the Second All-Union Conference on Organometallic Chemistry), Gor'kii, 1982, p.58.
112. U.M.Dzhemilev, O.S.Vostrikova, A.G.Ibragimov, G.A.Tolstikov, and L.M.Zelenova, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 360.
113. A.G.Ibragimov, O.S.Vostrikova, and U.M.Dzhemilev, USSR P.1 085 981, 1984.
114. U.M.Dzhemilev, A.G.Ibragimov, and O.S.Vostrikova, USSR P.1 097 628, 1984.
115. U.M.Dzhemilev, L.Yu.Gubaidullin, and R.M.Sultanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 714.
116. B.Bogdanovic, M.Schwickardi, and P.Sikorsky, Angew.Chem., 1982, **94**, 206.
117. U.M.Dzhemilev, O.S.Vostrikova, and R.M.Sultanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 1195.
118. N.I.Sheverdina and K.A.Kocheshkov, "Metody Elementoorganicheskoi Khimii. Tsink, Kadmii" (Methods of Hetero-organic Chemistry. Zinc and Cadmium), Izd.Nauka, Moscow, 1964, p.44.
119. D.E.Van Horn and E.Negishi, J.Amer.Chem.Soc., 1978, **100**, 2252.
120. T.Yoshida, Chem.Letters, 1982, 293.
121. T.Yoshida and E.Negishi, J.Amer.Chem.Soc., 1981, **103**, 4985.
122. T.Yoshida and E.Negishi, J.Amer.Chem.Soc., 1981, **103**, 1276.
123. U.M.Dzhemilev, O.S.Vostrikova, G.A.Tolstikov, and A.G.Ibragimov, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2626.
124. O.S.Vostrikova and U.M.Dzhemilev, "Tezisy Dokladov Konferentsii Molodykh Uchenykh" (Summaries of Papers Presented at the Conference of Young Scientists), Izd.Bashkir.Fil.Akad.Nauk SSSR, Ufa, 1979, p.22.
125. U.M.Dzhemilev, O.S.Vostrikova, and R.M.Sultanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 219.
126. U.M.Dzhemilev, O.S.Vostrikova, and A.G.Ibragimov, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 201.
127. U.M.Dzhemilev and A.G.Ibragimov, USSR P.1 051 054, 1983.
128. U.M.Dzhemilev, O.S.Vostrikova, R.M.Sultanov, A.G.Kukovinets, and L.M.Khalilov, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 2053.
129. U.M.Dzhemilev, O.S.Vostrikova, and R.M.Sultanov, "Vsesoyuznoe Soveshchanie "Metalloorganicheskie Soedineniya Neperekhodnykh Metallov v Sinteze i Katalize". Tezisy Dokladov" (Summary of Papers Presented at the All Union Conference on Organometallic Compounds of Non-transition Metals in Synthesis and Catalysis), Perm', 1983, p.69.
130. U.M.Dzhemilev, O.S.Vostrikova, R.M.Sultanov, and A.G.Ibragimov, "IV Mezhdunarodnyi Simpozium po Gomogennomu Katalizu. Tezisy Dokladov" (Summaries of Papers Presented at the Fourth International Symposium on Homogeneous Catalysis), Vol.1, Leningrad, 1984, p.223.
131. U.M.Dzhemilev, A.G.Ibragimov, F.A.Saraev, D.M.Minsker, and E.V.Gribanova, "IV Mezhdunarodnyi Simpozium po Gomogennomu Katalizu. Tezisy Dokladov" (Summaries of Papers Presented at the Fourth International Symposium on Homogeneous Catalysis), Vol.1, Leningrad, 1984, p.259.
132. U.M.Dzhemilev, A.G.Ibragimov, D.L.Minsker, and F.A.Saraev, "Kataliticheskie Reaktsii v Zhidkoi Faze. Tezisy Dokladov VI Vsesoyuznoi Konferentsii" (Summaries of Papers Presented at the Sixth All Union Conference on Catalytic Liquid–Phase Reactions), Part 2, Alma-Ata, 1983, p.165.
133. H.Yasuda, M.Yamauchi, A.Nakamura, T.Sei, Y.Kai, N.Yasuoka, and N.Kasai, Bull.Chem.Soc.Japan, 1980, **53**, 1089.
134. W.H.Tamblyn, S.R.Hoffmann, and M.P.Doyle, J. Organometal.Chem., 1981, **216**, C64.
135. M.P.Doyle, R.L.Dorow, and W.H.Tamblyn, J.Org. Chem., 1982, **47**, 4059.
136. G.Erker, W.Frömberg, J.L.Atwood and W.E.Hunter, Angew.Chem., 1984, **96**, 72.
137. E.Negishi, J.A.Miller, and T.Yoshida, Tetrahedron Letters, 1984, **25**, 3407.
138. Y.Yamamoto, T.Komatsu, and K.Maruyama, J.Organomet.Chem., 1985, **285**, 31.
139. E.M.Brainina, E.I.Strunkina, N.A.Kuz'mina, and E.M.Grechkina, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 228.
140. S.M.Clift and J.Schwartz. J.Organometal.Chem., 1985, **285**, C5.
141. E.Negishi, S.J.Holmes, J.M.Tour, and J.A.Miller, J.Amer.Chem.Soc., 1985, **107**, 2568.
142. J.A.Miller and E.Negishi, Isr.J.Chem., 1984, **28**, 76.
143. J.A.Miller and E.Negishi, Tetrahedron Letters, 1984, **25**, 5863.
144. E.Negishi, D.E.Van Horn, T.Yoshida, and C.L.Rand, Organometallics, 1983, **2**, 563.
145. U.M.Dzhemilev and O.S.Vostrikova, J.Organometal. Chem., 1985, **285**, 43.
146. U.M.Dzhemilev, O.S.Vostrikova, and R.M.Sultanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 1430.
147. V.V.Gavrilenko, V.S.Kolesov, and L.I.Zakharkin, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 681.

Institute of Chemistry,
Bashkir Branch,
Academy of Sciences of the
USSR, Ufa