Review

HOMOGENEOUS ZIRCONIUM BASED CATALYSTS IN ORGANIC SYNTHESIS

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I.   INTRODUCTION

There are many examples of the application of organozirconium compounds as reactive intermediates and their role in modern organic synthesis has been reviewed [1-3]. On the other hand, these species are only begining to emerge as homogeneous catalysts, being used rather timidly and infrequently, compared to the traditional catalysts containing palladium and nickel compounds. The present paper aims to show a number of advantages demonstrated by the homogeneous zirconium catalysts in the linear oligomerization of 1,3-dienes and olefins, and in cyclopropanation, hydroalumination, and some other reactions. Furthermore, these new catalysts are today the only suitable ones for the carbometallation of acetylenes by trialkylalanes and zinc dialkyls, for the carbomagnesation or β-alkylation of α-olefins by dialkylaluminium halides, and for the hydrometallation of olefin hydride. These reactions can hardly be effectively carried out with the use of other transition metals.

The present most popular area of the application of zirconium complexes is the catalyzed hydro- and carbometallation of unsaturated compounds, providing a route to a broad variety of organic reagents containing aluminium, magnesium, or zinc. All these reagents are readily capable of a large number of subsequent chemical transformations, again sometimes under the influ-

ence of the transition metal complexes, and catalyzed hydro- and carbometal-
lation reactions comprise a highly promising path in novel synthetic strate-
gy making extensive the use of alkenes and acetylenes.

The authors hope that their efforts here to generalize and classify
the available information concerning the use of the homogeneous catalysts,
involving zirconium containing substances, for performing transformations
of unsaturated and organometallic compounds, will attract the attention of
research workers to the potential of these reactants.

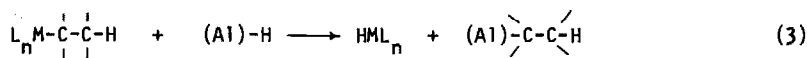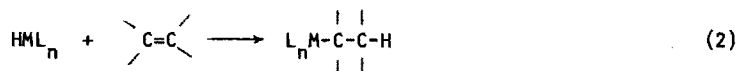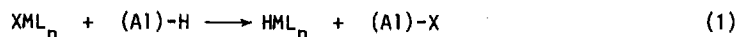## II. HYDRO- AND CARBOMETALLATION

A. Hydrometallation of Olefins

The first attempts to enlarge the scope of hydroalumination by intro-
ducing metal-complex catalysts were made by Asinger in the middle of the
1960s [4,5]. He used Ti(IV) and Zr(IV) [$ZrCl_4$, $Zr(acac)_4$, $ZrOCl_2$] compounds
as catalysts to convert mixtures of isomeric linear olefins into primary
alcohols by hydroalumination of the former by iso-Bu_3Al or iso-Bu_2AlH at 110°C
followed by oxidation.

In this case the catalyst plays the limited role of shifting the inter-
nal double bond toward the end of the hydrocarbon chain, because no catalyst
is needed for hydroalumination of α-olefins to occur sufficiently rapidly
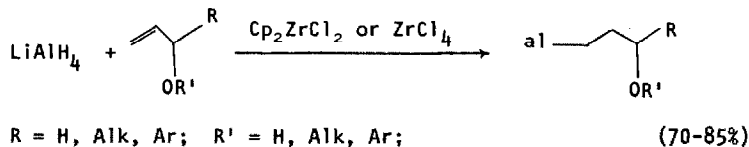under these conditions.

Ten years later Sato and coworkers made a prominent contribution in
this field by discovering the mild catalytic hydroalumination of olefins by
$LiAlH_4$ with the participation of transition metal complexes [6]. The termi-
nal double bonds are hydroaluminated with perfect regioselectivity to form
primary lithium tetraalkylalanates exclusively. The entire reaction pro-
ceeds via obviously the following consecutive stages:(1) generation of tran-
sition metal complexes; (2) hydrometallation of olefins by these complexes;
(3) transmetallation accompanied by the recovery of the initial hydride
complexes.

$$M = Ti, Zr$$

$$XML_n + (Al)-H \longrightarrow HML_n + (Al)-X \qquad (1)$$

$$HML_n + C=C \longrightarrow L_nM-C-C-H \qquad (2)$$

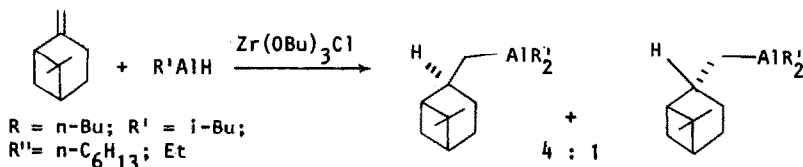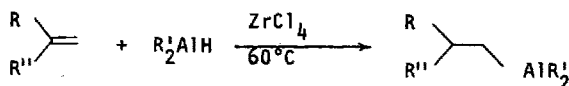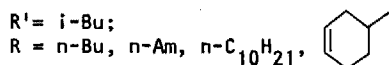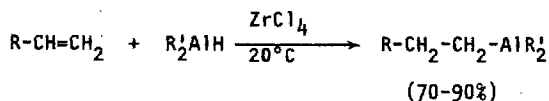$$L_nM-C-C-H + (Al)-H \longrightarrow HML_n + (Al)-C-C-H \qquad (3)$$

$TiCl_4$ is the most active catalyst for hydroalumination of mono-, di-,
and trisubstituted olefins, but the zirconium based catalysts remain prefer-
rable in some cases. Thus, the presence of $ZrCl_4$ ensures the selective hy-
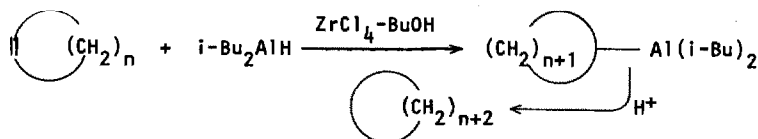
droalumination of terminal double bond in polyenes [6,7], though α,β-disubstituted double bonds (except in cyclopentene) do not react with $LiAlH_4$ under these conditions in the absence of the catalyst. Allylic alcohols and ethers react smoothly with $LiAlH_4$ in the presence of only zirconium catalysts, $ZrCl_4$ being more effective for the hydroalumination of the alcohols, and Cp_2ZrCl_2 for that of the ethers indicated [8,9].

$$LiAlH_4 \; + \; \overset{R}{\underset{OR'}{\diagup}} \quad \xrightarrow{\quad Cp_2ZrCl_2 \; or \; ZrCl_4 \quad} \quad al \overset{R}{\underset{OR'}{\diagup}}$$

R = H, Alk, Ar; R' = H, Alk, Ar;   (70-85%)

Both linear and cyclic olefins are selectively hydroaluminated by iso-Bu_2AlH over the zirconium-based catalysts while in the presence of titanium compounds polymerization mainly occurs. The reaction of iso-Bu_2AlH with α-olefins catalyzed by $ZrCl_4$ is complete in 3-6 hs at 20°C while α,β- as well as β,β'-disubstituted olefins react at a somewhat higher temperature (ca.60°C); it is therefore possible to hydroaluminate the terminal double bonds selectively [10].

$$R-CH=CH_2 \; + \; R'_2AlH \; \xrightarrow[20°C]{ZrCl_4} \; R-CH_2-CH_2-AlR'_2$$

$$(70-90\%)$$

R'= i-Bu;
R = n-Bu, n-Am, n-$C_{10}H_{21}$, $\bigcirc$

$$\overset{R}{\underset{R''}{\diagup}}\!=\!\diagdown \; + \; R'_2AlH \; \xrightarrow[60°C]{ZrCl_4} \; \overset{R}{\underset{R''}{\diagdown}}\!\diagup\!\overset{}{\underset{AlR'_2}{}}$$

$$\bigcirc\!\!=\!\!\overset{R}{} \; + \; R'AlH \; \xrightarrow{Zr(OBu)_3Cl} \; \underset{}{\overset{H}{\diagdown}}\!\!\overset{}{AlR'_2} \; + \; \underset{}{\overset{H}{\diagup}}\!\!\overset{}{AlR'_2}$$

R = n-Bu; R' = i-Bu;   4 : 1
R''= n-C_6H_{13}; Et

In interactions of $ZrCl_4$ and aliphatic alcohols or zirconium tetraalkoxydes, mixed chloroalkoxides are formed which catalyze the hydroalumination of cycloolefins with iso-Bu_2AlH quite effectively [12]. The highest activity has been demonstrated by the catalysts obtained using n-BuOH.

$$\overset{\bigcirc}{(CH_2)_n} \; + \; i\text{-}Bu_2AlH \; \xrightarrow{ZrCl_4\text{-}BuOH} \; (CH_2)_{n+1}\!\!-\!\!Al(i\text{-}Bu)_2$$

$$(CH_2)_{n+2} \xleftarrow{\quad} \overset{}{\underset{H^+}{}}$$

The rate of hydroalumination of cycloolefins by iso-Bu_2AlH depends on the ring size and decreases in the series $C_5 > C_6 > C_7 > C_{12} > C_8$ (See Table 1). The rate of addition of iso-Bu_2AlH to norbornene is extremely high while olefins with a trisubstituted double bond like methylcyclobutene and methylcyclododecene do not react.
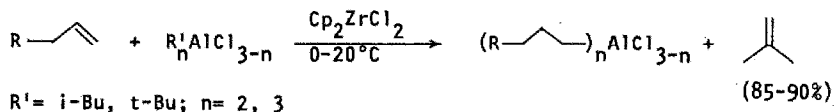
TABLE 1: Hydroalumination of Cycloolefins by iso-Bu_2AlH.

Olefin: iso-Bu_2AlH: $ZrCl_4$: n-BuOH = 50:50:1:4; solvent: hexane.

Olefin	Yield based on cycloalkene, %	T °C	Reaction time, h
cyclopentene	100	20	6
cyclohexene	99.5	20	8
cyclohexene	100	40	2
cycloheptene	82.6	20	24
cyclooctene	20	20	24
cyclooctene	20	60	12
cyclododecene (cis + trans)	59.2	20	21
norbornene	100	0	1
methylcyclobutene	0	20	24
methylcyclododecene	0	20	24

As a hydroalumination agent, iso-Bu_2AlH has a disadvantage compared to $LiAlH_4$ as the ballast iso-Bu groups complicate further synthetic transformations of the intermediate hydroalumination products.

It should be also noted, that the hydroalumination of olefins containing electron-donor substitutents is difficult to perform [13].

The application of Cp_2ZrCl_2 as a catalyst enables the use of iso-Bu_3Al, tert-Bu_3Al, and iso-Bu_2AlCl as hydroalumination reagents [13-15], all the Al-bonded alkyls taking part in the reaction.

$$R\text{---}\diagup\diagdown \quad + \quad R'_n AlCl_{3-n} \quad \xrightarrow[0-20°C]{Cp_2ZrCl_2} \quad (R\text{---}\diagup\diagdown\text{---})_n AlCl_{3-n} \quad + \quad \diagup\diagdown$$

R' = i-Bu, t-Bu; n= 2, 3   (85-90%)

The yields of the hydrometallation products amount to 85-99%, decreasing to 50% on change of Cp_2ZrCl_2 for $ZrCl_4$ [14].

A number of advantages are inherent to the method which has been developed, as compared to hydroalumination carried out by aluminium hydrides in the absence of a catalyst. In particular, the required reaction conditions are surprisingly mild (0-20°C), and olefins bearing different functions (OH, PhS, Br) can be introduced in the reaction [13,14].

The hydroalumination of olefins by iso-Bu$_2$AlCl catalyzed by Cp$_2$ZrCl$_2$ [11, 15] offers a convenient pathway to the higher dialkylaluminium halides which unlike the corresponding trialkylalanes cannot be obtained by the non-catalyzed hydroalumination of olefins.
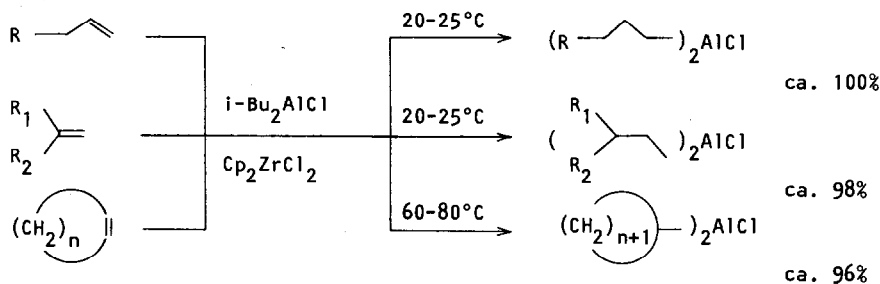
The terminal olefins react quite readily with iso-Bu$_2$AlCl at 20-25°C while cycloolefins require 60-80°C for the above reaction. It should be noted, that in the presence of Cp$_2$ZrCl$_2$ of Zr(OBu)$_4$, β,β'-disubstituted olefins react similarly with Et$_3$Al or Et$_2$AlCl though the expected hydro-alumination products are formed in rather low yields [16, 17].

R, R'= Alk; R''= Et; n= 2, 3   (25-30%)
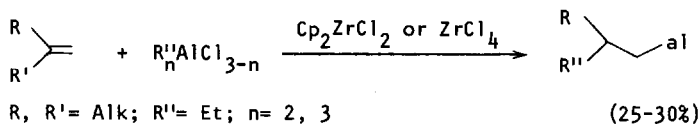
Negishi suggested a mechanism of the hydroalumination of olefins by trialkylalanes catalyzed by Cp$_2$ZrCl$_2$, comprising the stages of (1) alkyla-tion; (2) isobutylene elimination; (3) hydrozirconation; and (4) transmetal-lation [13, 14].
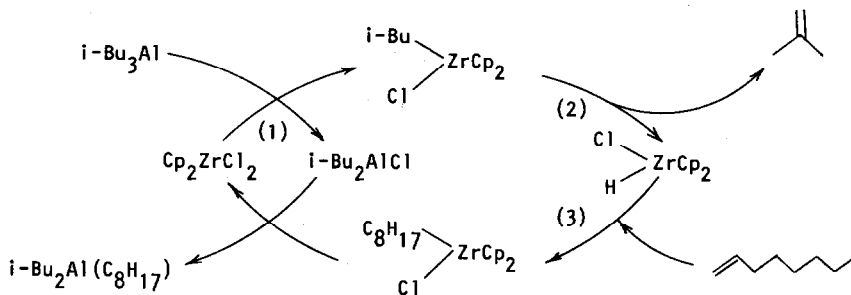
However, the last stage here does not agree with Schwartz's data [18] as he found the alkyl zirconium complexes unlike the alkenyl ones to be ac-tive in transmetallation with AlCl$_3$ rather than with alkylaluminium halides. In interactions with zirconium based catalysts, iso-Bu$_3$Al may form either

mixed Zr-Al hydride complexes [18, 19] or aluminium hydrides of the type R_nAlH_{3-n} which further react with olefins. This assumption is supported by the fact that an isobutylene molecule is eliminated from iso-Bu_3Al in the presence of a catalytic amount of $ZrCl_4$ to give iso-Bu_2AlH [16]. Linear radicals are not eliminated under the same conditions thus affording higher di-(n-alkyl)-aluminium hydrides from iso-Bu_3Al [16, 20].
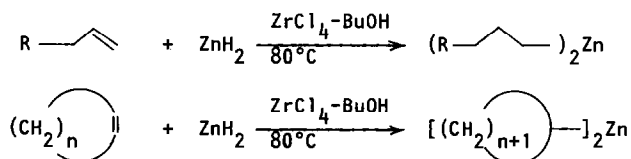
$$i\text{-}Bu_3Al \xrightarrow[30-40°C]{ZrCl_4} i\text{-}Bu_2AlH + \text{\Large\Lambda} \quad (ca. 98\%)$$

$$i\text{-}Bu_3Al + 2R \diagup\!\!\!\diagdown \xrightarrow[20°C]{Cp_2ZrCl_2} (R \diagup\!\!\!\diagdown)_2Al(i\text{-}Bu) \longrightarrow$$

$$\xrightarrow[30-40°C]{ZrCl_4} (R \diagup\!\!\!\diagdown)_2AlH \quad (ca. 96\%)$$
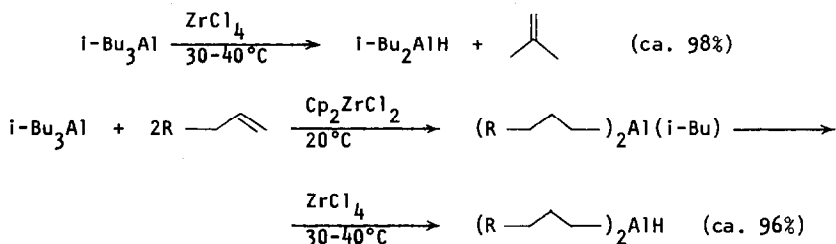
During the recent 2-3 years a number of papers have been published which show, that it is possible to carry out the hydrometallation of olefins by zinc or magnesium hydrides or hydride complexes under the action of zirconium catalysts [11, 21-24]. In particular, the hydrometallation of both linear and cyclic olefins by zinc hydrides has been thoroughly investigated [23]. A complex obtained by mixing $ZrCl_4$ with n-BuOH (1:4) proved to be the most active catalyst for this reaction which is carried out at 80°C in aromatic or aliphatic hydrocarbon media. Terminal olefins react with ZnH_2 to form exclusively primary zinc dialkyls in a yield of 54-65% based in the olefin (See Table 2), while the yields of the corresponding "hydrozincation" products from cycloolefins never exceeds 20% level.

$$R \diagup\!\!\!\diagdown + ZnH_2 \xrightarrow[80°C]{ZrCl_4\text{-}BuOH} (R \diagup\!\!\!\diagdown)_2Zn$$

$$(CH_2)_n \bigcirc || + ZnH_2 \xrightarrow[80°C]{ZrCl_4\text{-}BuOH} [(CH_2)_{n+1} \bigcirc]_2Zn$$

The formation of zinc dialkyls during hydrozincation is accompanied by the separation of metallic zinc and the evolution of hydrogen, and of corresponding alkanes. This can be explained in terms of the lability of the intermediate alkylzinc hydrides under the reaction conditions.
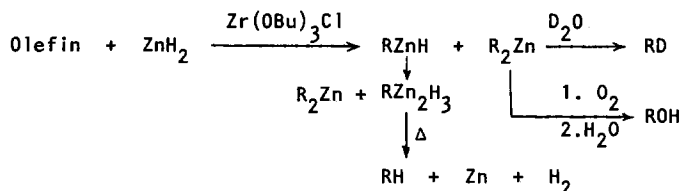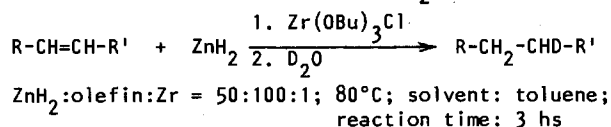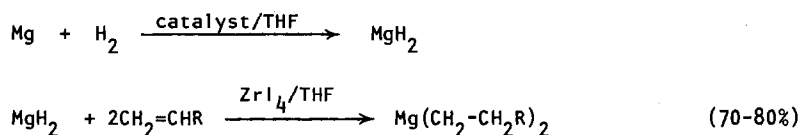
$$Olefin + ZnH_2 \xrightarrow{Zr(OBu)_3Cl} RZnH + R_2Zn \xrightarrow{D_2O} RD$$

$$R_2Zn + RZn_2H_3 \quad \begin{array}{c} 1.\ O_2 \\ \hline 2.H_2O \end{array} ROH$$

$$\downarrow \Delta$$

$$RH + Zn + H_2$$

TABLE 2. Hydrometallation of Olefins by ZnH_2

$$R-CH=CH-R' + ZnH_2 \xrightarrow[\text{2. } D_2O]{\text{1. } Zr(OBu)_3Cl} R-CH_2-CHD-R'$$

ZnH_2:olefin:Zr = 50:100:1; 80°C; solvent: toluene; reaction time: 3 hs

Starting olefin	Reaction mixture deuterolysis product composition, %		
	Unreacted olefin	H-alkane	D-alkane
1-hexene	–	35	65
1-nonene	11	29	60
1-decene	12	30	58
1-octene	8	38	54
cyclohexene	70	10	20
cyclooctene	79	6	15

Oxydation of the hydrozincation products with oxygen, followed by hydrolysis, gave nor the expected alkyl hydroperoxydes, but the corresponding primary alcohols [25], evidently because of the effect of zirconium catalyst. Zirconium tetrahalides, of which ZrI_4 appeared to be the most potent, catalyze the regioselective hydromagnesation of ethylene and higher α-olefins with metallic magnesium in the presence of chromium- or titanium-based catalysts [22].

$$Mg + H_2 \xrightarrow{\text{catalyst/THF}} MgH_2$$

$$MgH_2 + 2CH_2=CHR \xrightarrow{ZrI_4/THF} Mg(CH_2-CH_2R)_2 \qquad (70\text{-}80\%)$$

However, Ashby has shown [26] that the zirconium-based catalysts, unlike Cp_2TiCl_2, fail to activate a similar reaction of olefins with the "active" MgH_2 obtained by reducing Et_2Mg with $LiAlH_4$. Both Cp_2ZrCl_2 and $ZrCl_4$ catalyze the regioselective hydromagnesation of α-olefins by diethylamino-magnesium hydride but the activity thereof is in this case lower than that of Cp_2TiCl_2 [24].

$$Et_2NMgH + \diagup\!\!\!\diagdown\!\!-R \xrightarrow[\text{60°C, THF}]{Cp_2ZrCl_2 \text{ or } ZrCl_4} Et_2NMg-\diagup\!\!\!\diagdown\!\!-R \quad (ca.\ 30\%)$$
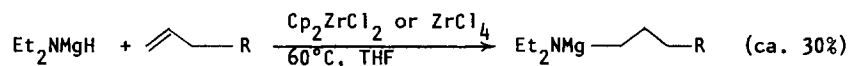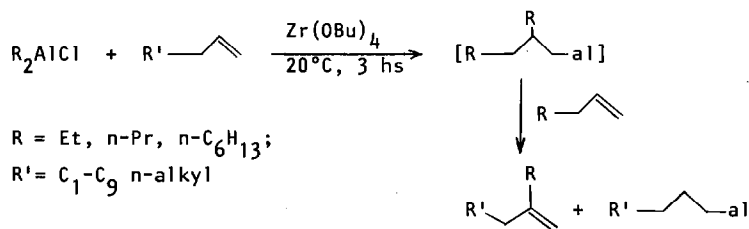
B. Carbometallation of Olefins

Only the zirconium-based catalysts can promote selective and mild carbometallation of α-olefins by organic compounds of Al and Mg which are completely inactive under any conditions in the absence of a catalyst.

3-Methylene alkanes together with the corresponding di-(n-alkyl)-alu-

minium halides are selectively formed by interaction of diethylaluminium chloride with α-olefins in the presence of $Zr(OBu)_4$ [16, 27].

This process may be represented as consecutive carbo- and hydroalumination stages,

$$R_2AlCl + R' \diagup\!\!\!\diagdown \xrightarrow[20°C, 3\ hs]{Zr(OBu)_4} [R\diagdown\!\!\!\diagup\!\!-al]$$

$R = Et, n-Pr, n-C_6H_{13};$
$R' = C_1-C_9$ n-alkyl

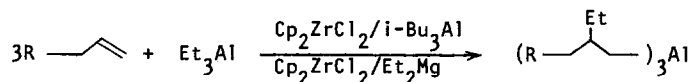$$R'\diagdown\!\!\!\diagup + R'\diagup\!\!\!\diagdown\!\!-al$$

Irrespective of the ratio of the starting components and the reaction conditions the process cannot be terminated at the carbometallation stage, which, in all probability, suggests that both stages are promoted by the same catalytic complex [28].
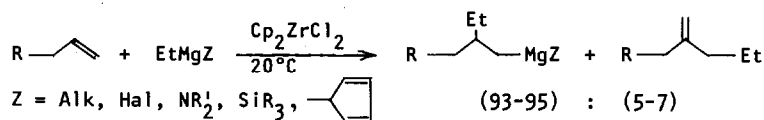
When some other di-(n-alkyl)-aluminium halides than Et_2AlCl [n-Pr_2AlCl, (n-$C_6H_{13})_2AlCl$] were used for the reaction [16], the yields of alkylation products decreased somewhat though the regioselectivity remained invariably high.

On the other hand, the hydrocarbon chain length in the α-olefin does not have much influence on the yield of the reaction products (See Table 3). Disubstituted olefins partially isomerize under these conditions without entering into the carboalumination itself [16].

$Zr(OBu)_4$ is the most active selective catalyst of the β-alkylation of α-olefins. In the presence of $ZrCl_4$ and $(C_5H_5N)_2ZrCl_2$, a mixture of the hydro- and carbometallation as well as of oligomerization products of the starting olefins is formed, while $Zr(acac)_4$ and Cp_2ZrCl_2 are completely inactive. At the same time, Cp_2ZrCl_2 aided by an equivalent amount of Et_2Mg or iso-Bu_3Al serves as a catalyst for the selective carboalumination of α-olefins by Et_3Al, which is not accompanied by the subsequent transformations [28].

$$3R\diagup\!\!\!\diagdown + Et_3Al \xrightarrow[Cp_2ZrCl_2/Et_2Mg]{Cp_2ZrCl_2/i-Bu_3Al} (R\diagdown\!\!\!\diagup\!\!\overset{Et}{\diagdown}\!\!-)_3Al$$

The use of Cp_2ZrCl_2 enables these authors for the first time to carbomagnesate regioselectively α-olefins by diethylmagnesium and also by the Grignard reagent and some of its analogues under mild conditions [29, 30].

$$R\diagup\!\!\!\diagdown + EtMgZ \xrightarrow[20°C]{Cp_2ZrCl_2} R\diagdown\!\!\!\diagup\!\!\overset{Et}{\diagdown}\!\!-MgZ + R\diagdown\!\!\!\diagup\!\!-Et$$

$Z = Alk, Hal, NR'_2, SiR_3, \diagdown\!\!\!\square$ (93-95) : (5-7)

TABLE 3. Interaction of α-Olefins with Et_2AlCl Catalyzed by $Zr(OBu)_4$

Al:olefin:Zr = 100:400:1; solvent: toluene;
reaction time: 3 h;

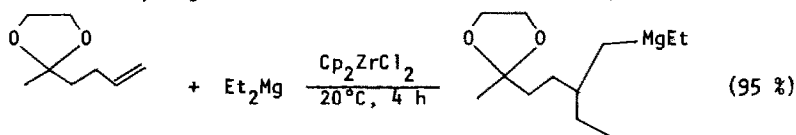| Starting olefin	Reaction temperature, °C	Reaction product			
		Hydrocarbon	Yield, %	Organoaluminium compound	Yield, %
1-hexene	20	3-methylene heptane	95	di-(n-hexyl)-aluminium chloride	95
1-octene	20	3-methylene nonane	90	di-(n-octyl)-aluminium chloride	90
1-decene	20	3-methylene undecane	85	di-(n-decyl)-aluminium chloride	85
1-dodecene	20	3-methylene tridecane	80	di-(n-dodecyl)-aluminium chloride	80
1,4Z-hexadiene	20	2-ethyl-1,4Z-hexadiene	65	di-(4-hexene-1yl)-aluminium chloride	65
3-methylene-heptane	40	ethylene	25	(3-methylheptyl)-ethylaluminium chloride	20
5-methylene undecane	60	ethylene	20	(2-butyloctyl)-ethylaluminium chloride	25

Unlike the β-alkylation of α-olefins by dialkylaluminium halides discussed above, the carbomagnesation is not complicated by subsequent hydrometallation. This method may be applied to the broad variety of α-olefins containing additional internal double bonds which remain intact as the reaction proceeds [30].

We also succeeded in carbomagnesation of a number of α-olefins bearing different functions and heteroatoms in the allylic position to the double

bond (See Table 4).

TABLE 4.   Carbometallation of Allylic Derivatives by Et_2Mg
over Cp_2ZrCl_2 Catalyst

$$R \diagup\!\!\diagup\!\!\searrow + Et_2Mg \xrightarrow{Cp_2ZrCl_2} R\diagup\!\overset{Et}{\diagdown}\!\diagdown MgEt$$

$R\diagup\!\!\diagup\!\!\searrow$:Mg:Zr = 200:300:3; solvent: diethyl ether;
temperature: 20°C
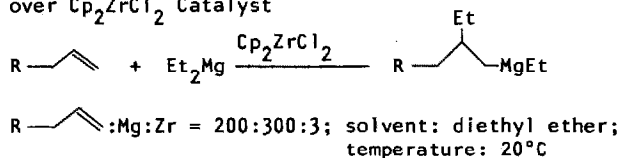
R	Yield, %	Reaction time, h
Me_3Si-	96	4
Et_2N-	100	4
$n-BuO-$	30	90
C_3H_5O-	30	60
C_3H_5S-	25	4
$HO-$	0	90
$PhO-$	0	90

As is seen, the electron-acceptor substitutents at the allylic carbon
decrease notably the activity of the double bond in the carbomagnesation,
but have no marked effect upon the regioselectivity of the process. The
course of the reaction is little influenced by functions separated from the
reactive centre by a greater distance (See also Table 5),

$$\overset{O\diagdown\diagup O}{\diagdown\!\!\diagup}\diagdown\!\!\diagup\!\!\searrow + Et_2Mg \xrightarrow[20°C, 4 h]{Cp_2ZrCl_2} \overset{O\diagdown\diagup O}{\diagdown\!\!\diagup}\diagdown\!\!\diagup\diagdown MgEt \quad (95\%)$$

The carbomagnesation can be carried out using both Et_2Mg and other
Grignard reagent analogues of the EtMgZ type, the activity of these falling
off in the series: $Et \approx Et_3Si \gg$ cyclopentadienyl $>$ (Ph)N(Et) $\approx$ Cl $>$ Br $\approx$
$N\!\bigcirc \approx Et_2N > J$. Compounds of the types EtMgOR, EtMgSR, $EtMgOC\lesssim_R^O$, EtMgF,
and EtMgC $\equiv$CR, show a total absence of reactivity in carbomagnesation [31].

When α-olefins are carbomagnesated by higher magnesium di-n-alkyls
($n-Pr_2Mg$, $n-Bu_2Mg$, $n-Oct_2Mg$) the regioselectivity of the process remains
the same, but the respective methylalkenes and the dimers of olefins with
characteristic structure are abundantly formed together with the carbome-
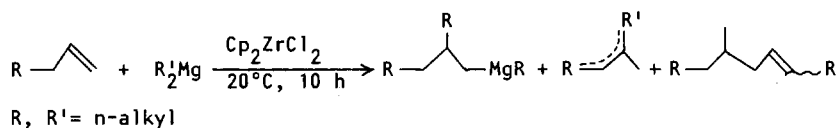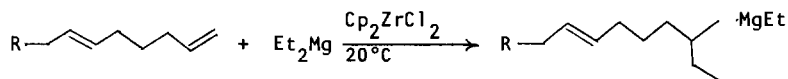tallation products [32].

$$R\text{---}CH=CH_2 \quad + \quad R_2'Mg \xrightarrow[20°C, 10 h]{Cp_2ZrCl_2} \quad R\text{---}\underset{R}{\overset{R}{CH}}\text{---}MgR \; + \; R=\overset{R'}{\diagup} \; + \; R\text{---}CH=CH\text{---}R$$

R, R'= n-alkyl

TABLE 5.

$$R\text{---}CH=CH\text{---}CH_2CH=CH_2 \quad + \quad Et_2Mg \xrightarrow[20°C]{Cp_2ZrCl_2} \quad R\text{---}CH=CH\text{---}CH\text{---}MgEt$$

R	Yield, %	Reaction time, h
	98	6
N-	98	4
O-	95	4
HO-	98	4
MeO-	95	4
PhO-	90	4

C. Carboalumination of Acetylenes

In 1978, Negishi and coworkers [13, 33] were the first to use Cp_2ZrCl_2 to catalyze both regio- and stereoselective cis-carboalumination of terminal acetylenes by trimethylaluminium.

$$RC\equiv CH \quad + \quad Me_3Al \xrightarrow[20°C, 6 h]{Cp_2ZrCl_2} \quad \underset{Me}{\overset{R}{C}}=\underset{AlMe_2}{\overset{H}{C}}$$
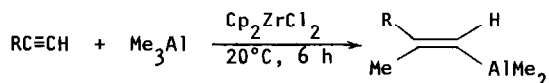
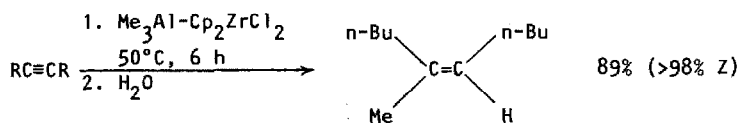R = n-alkyl, alkenyl, alkydienyl, vinyl, homoallyl, aryl, phenyl;

This is a general type reaction with 95-100% regioselectivity and yields amounting to 90-100%, involving acetylenes with linear and branched alkyl and alkenyl substituents. The carbometallation of propargyl and homopropargyl derivatives containing electron-donor functions is characterized by invariably high stereoselectivity [34].
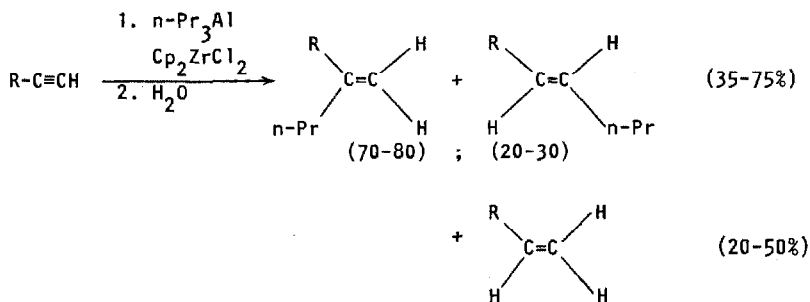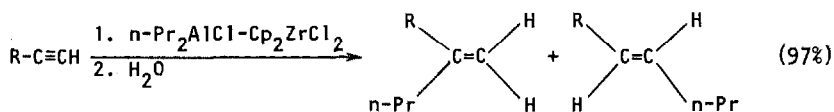
$$Z(CH_2)_nC\equiv CH \xrightarrow{Me_3Al\text{-}Cp_2ZrCl_2} \underset{Me}{\overset{Z(CH_2)_n}{C}}=\underset{AlMe_2}{\overset{H}{C}}$$
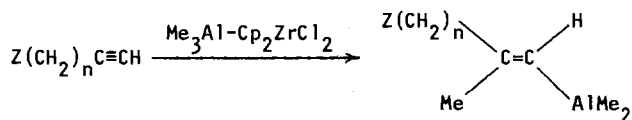
Z = OH, OSiMe$_2$(t-Bu), PhS; I
n = 1,2

Symmetrically disubstituted acetylenes also show high yields and re-
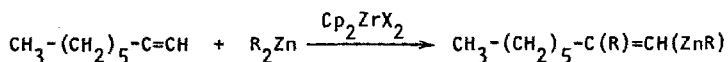gioselectivity in this reaction [33].

$$RC\equiv CR \xrightarrow[\text{2. } H_2O]{\substack{\text{1. } Me_3Al-Cp_2ZrCl_2 \\ 50°C, 6\ h}} \underset{Me}{\overset{n\text{-Bu}}{\diagdown}} C=C \underset{H}{\overset{n\text{-Bu}}{\diagup}} \qquad 89\% \ (>98\%\ Z)$$

A change of trimethylaluminium for other tri-(n-alkyl)-alanes results
in a considerable decrease both in regioselectivity and yields [14],

$$R-C\equiv CH \xrightarrow[\text{2. } H_2O]{\substack{\text{1. } n\text{-Pr}_3Al \\ Cp_2ZrCl_2}} \underset{n\text{-Pr}}{\overset{R}{\diagdown}} C=C \underset{H}{\overset{H}{\diagup}} + \underset{H}{\overset{R}{\diagdown}} C=C \underset{n\text{-Pr}}{\overset{H}{\diagup}} \qquad (35\text{-}75\%)$$

$$(70\text{-}80) \quad ; \quad (20\text{-}30)$$

$$+ \underset{H}{\overset{R}{\diagdown}} C=C \underset{H}{\overset{H}{\diagup}} \qquad (20\text{-}50\%)$$

The use of di-(n-alkyl)-aluminium halide for carbometallation prevents
the competing hydrometallation [35].

$$R-C\equiv CH \xrightarrow[\text{2. } H_2O]{\text{1. } n\text{-Pr}_2AlCl-Cp_2ZrCl_2} \underset{n\text{-Pr}}{\overset{R}{\diagdown}} C=C \underset{H}{\overset{H}{\diagup}} + \underset{H}{\overset{R}{\diagdown}} C=C \underset{n\text{-Pr}}{\overset{H}{\diagup}} \qquad (97\%)$$

Recently a similar reaction has been performed [36] between zinc di-
n-alkyls and mono- or disubstituted acetylenes catalyzed by bis-cyclopenta-
dienyl zirconium halides Cp_2ZrX_2, the catalyst activity decreasing in the
series $Cp_2ZrI_2 > Cp_2ZrBr_2 > Cp_2ZrCl_2$.

$$CH_3-(CH_2)_5-C\equiv CH + R_2Zn \xrightarrow{Cp_2ZrX_2} CH_3-(CH_2)_5-C(R)=CH(ZnR)$$

R = Alkyl

The reaction proceeds according to the cis-pattern, its stereoselecti-
vity being ca. 98%. The maximal regioselectivity (ca. 95%) has been noted
in the case of dimethylzinc while with other zinc di-n-alkyls it does not
exceed 70-80%. Though zirconium plays a catalytic role in this reaction,
satisfactory yields of the "carbozincation" products can only be achieved
using an equivalent or even greater amount of Cp_2ZrCl_2 with respect to the
alkylating reagent.

The literature available fails to give any information concerning the possibility of carrying out a similar reaction with the participation of magnesium or boron alkyls.

The method for the carbometallation of terminal acetylenes, discussed above, is important in organic synthesis as it promises a convenient and stereoselective approach to mono- and bifunctional unsaturated synthons, which have been used by Negishi and coworkers as the basis of a new synthetic strategy directed toward natural products mainly of the terpenoid group. This is considered in detail in a review article [13].

It should be noted that the mechanism of the catalyzed carbometallation is far from clear enough. At least for the typical cases, the zirconium-catalyzed carboalumination of terminal acetylenes by trimethylaluminium is assumed to be a process of direct carboalumination aided by Cp_2ZrCl_2 (the precise function of which has not been determined yet) rather than of carbozirconation followed by transmetallation [37].

III. OLIGOMERIZATION OF UNSATURATED COMPOUNDS

A vast number of experimental data concerning homo- and cooligomerization of conjugated 1,3-dienes catalyzed by complexes of zirconium with organoaluminium or -magnesium reducing reagents has been accumulated.

In 1970, the Japanese research workers reported [38, 39] on the possibility of using catalytic systems of the types $Zr(OBu)_4$-Ph_3P-Et_2AlCl, $Zr(OBu)_4$-C_5H_5N-Et_2AlCl, and $Zr(C_3H_5)_4$-$Et_3Al_2Cl_3$ for the selective linear dimerization of isoprene into 2,6-dimethyl-1,3E,6E-octatriene.

Alongside with the latter, the formation of a mixture of trimers has been noted [40], of which 90% is represented by 3,6,10-trimethyl-2,5,7,10-dodecatetraene.
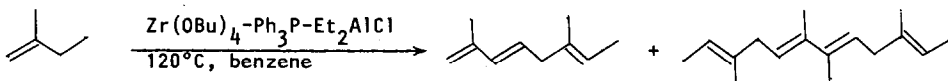

Somewhat later, more active zirconium-based catalysts were developed making it possible to increase the isoprene conversion into 2,6-dimethyl-octatriene up to 90-95% [41-43]. The isoprene linear dimers of differing structure are formed over a catalyst of the type Cp_2ZrCl_2-isoprenylmagnesium, the double bond position therein depending on the reaction temperature [44].
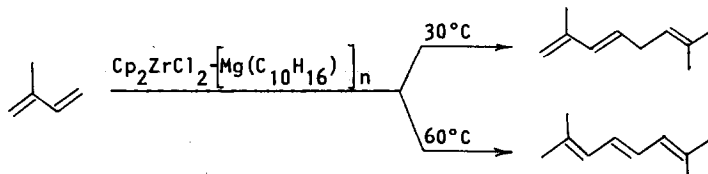
A number of later investigations [45-49] have shown that so far, of all the known catalysts for linear oligomerization of 1,3-dienes, those based on zirconium are the most versatile and can promote the linear oligomerization of conjugated dienes of various structure.

Thus, cyclooctatetraene dialkylzirconium formed on the interaction of $(COT)ZrCl_2$ with allylmagnesium chloride, catalyzes the stereospecific conversion of butadiene into 1,3E,6-octatriene. An intermediate bis-π-allyl complex has been isolated [49] from the reaction mixture.
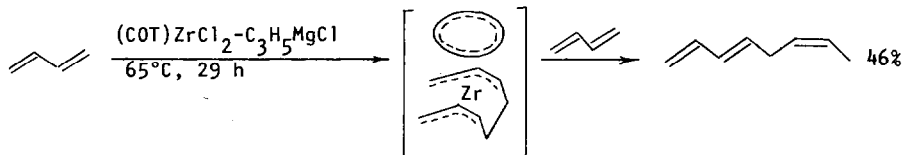

Over the catalytic system $Zr(OBu)_4$-Ph_3P-Et_2AlCl, at 100°C butadiene is converted into a mixture of hydrocarbons composed of 4-vinylcyclohexene (28%), 2,4,6-octatriene (48%), and of isomeric linear tri- and tetramers (24%) [45, 46].
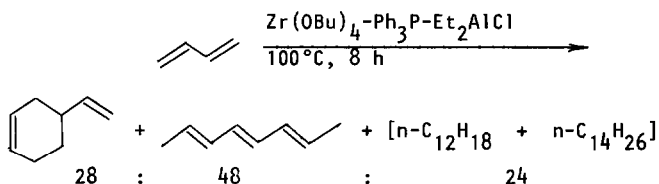

Cis- and trans-piperylenes gave rise to 4,8-dimethyl-2E,5E,7E,10Z-tridecatetraene, and a mixture of six-member dimers and unidentified tetramers in a total ratio of 45:20:35 [46].
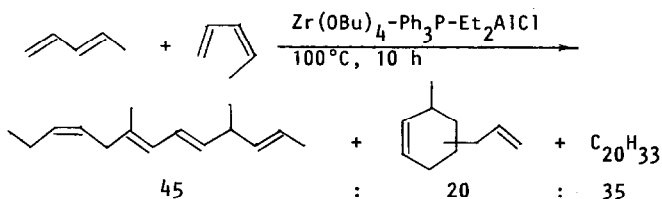

The oligomerization of 2,3-dimethylbutadiene leads to the formation of 2,3,6,7-tetramethyl-1,3,6-octatriene and 2,3,6,7,10,11-hexamethyl-1,3,6,10-dodecatetraene [46].
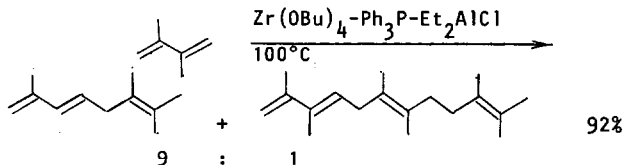
Myrcene dimerizes with high stereoselectivity to a linear dimer, identified as 2,14-dimethyl-6-methylene-10-ethylidene-2,7,13-pentadecatriene [46].
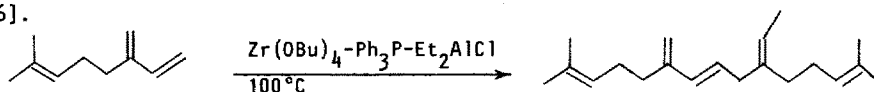
As is seen, the oligomerization of the 1,3-dienes listed above is catalyzed by similar zirconium-containing catalytic systems requiring no search for the optimal reaction conditions in each separate case. This made it possible to perform a "tail-head" codimerization of a number of conjugated dienes to 1,3,6-octatrienes [46, 50].

$R_1 = R_2 = H, CH_3$;
$R_3 = H, CH_3, -(CH_2)_2CH=C(CH_3)_2$
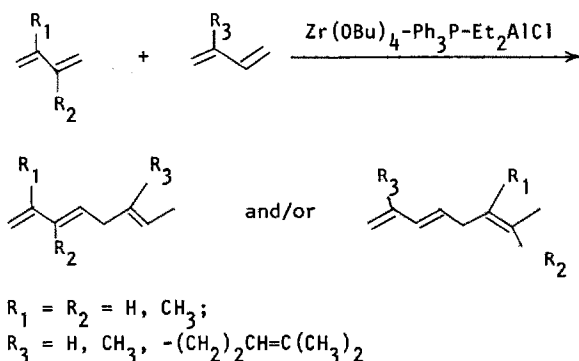
The substituents "geography" in the octatrienes formed depends in this case on the structures of the starting monomers. Thus, the conjugated diene system is retained in the butadiene moiety on interaction between mono- or disubstituted dienes and butadiene, while upon codimerization of 2-substituted dienes and 2,3-dimethylbutadiene it is directed into 2,3-disubstituted fragment. Conjugated 1,3-dienes, bearing different substituents at the C-2 atom, form both possible codimers in an approximately 1:1 ratio.
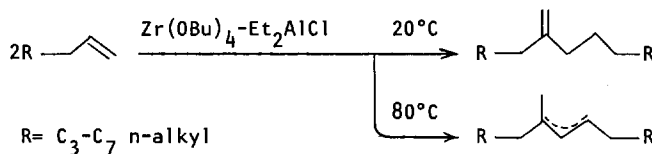
It was suggested that the formation of the linear dimers and codimers from 1,3-dienes proceeds via the stage of the intermediate bis-π-allyl and σ,π-allyl zirconium complexes [46].

Catalysts obtained by the interaction between zirconium and alanes are less active compared to the similar titanium containing systems of the Ziegler type. Hence, instead of polymerization, either highly selective homo- and codimerization of the simplest α-olefins or their oligomerization to higher α-olefins having controlled molecular mass can be effected under the action of such zirconium-based catalysts [16, 51-56]. The oligomerization of a number of olefins is also catalyzed by a more complicated zirconium complex [57] obtained by $ZrCl_4$ reduction by Na amalgam in the presence of bis-dimethylphosphinoethane and butadiene in THF. Based on the analysis of
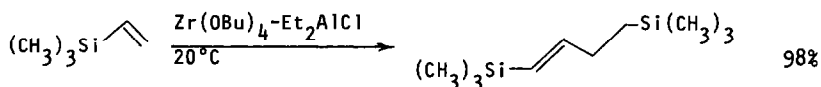
the structure and compositional distribution of the oligomers obtained, a mechanism has been proposed [57] providing for the formation of five-member metallocycles responsible for the generation of the dimeric molecules,

$$[Zr] \xrightarrow{CH_2=CH_2} [Zr] \rightleftharpoons [Zr] \longrightarrow [Zr] \longrightarrow [Zr] + \diagup\diagdown$$
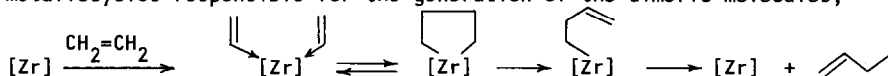
Higher α-olefins are selectively converted to unsymmetrical methylene alkanes [58, 59] over a two-component catalyst of $Zr(OBu)_4$-Et_2AlCl.

$$2R \diagup\diagdown \xrightarrow[\text{Zr(OBu)}_4\text{-Et}_2\text{AlCl}]{20°C} R \diagdown\diagup\diagdown R$$

$$R= C_3-C_7 \text{ n-alkyl} \qquad \xrightarrow{80°C} R \diagdown\diagup\diagdown R$$

The reaction is sensitive to the starting olefin structure and depends on the temperature. Thus, under the same conditions, trimethylvinylsilane selectively dimerizes to 1,4-bis-trimethylsilyl-1E-butene [59] whereas trimethylallylsilane is completely inactive [16].

$$(CH_3)_3Si \diagup\diagdown \xrightarrow[\text{20°C}]{\text{Zr(OBu)}_4\text{-Et}_2\text{AlCl}} (CH_3)_3Si \diagdown\diagup\diagdown\text{-Si(CH}_3)_3 \qquad 98\%$$

The $Zr(OBu)_4$-Et_2AlCl system mentioned catalyzes an unprecedented single stage conversion of 1,5-hexadiene to 6-methyl[4.4.1]-bicyclo-1-undecene [60, 61].

$$\diagup\diagdown\diagup\diagdown \xrightarrow[\text{40°C, 6 h}]{\text{Zr(OBu)}_4\text{-Et}_2\text{AlCl}}$$
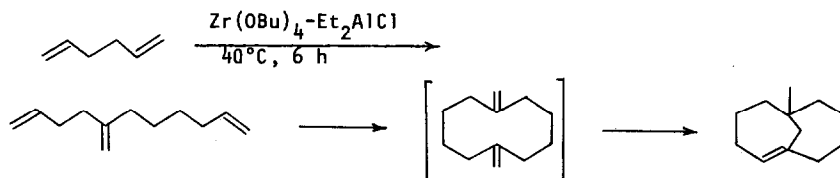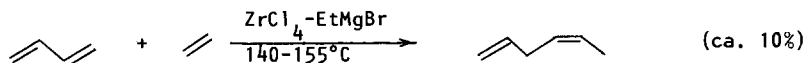
On the exchange of Et_2AlCl for $EtAlCl_2$ a complex is formed, catalyzing di- and oligomerization of cyclic olefins, the reactivity of which diminishes in the series $C_5>C_8>C_7>C_{12}>C_6$ [62].
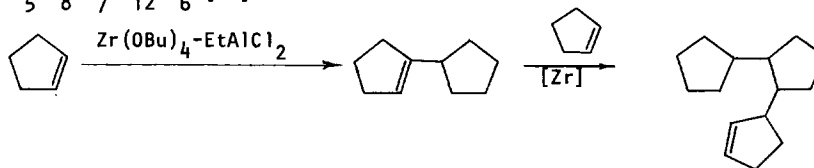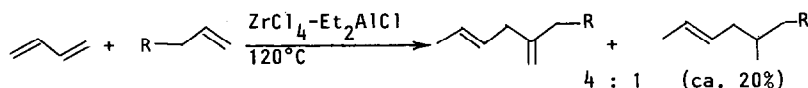
Unlike the homodimerization of α-olefins, their codimerization with butadiene in the presence of zirconium-based catalysts should be carried out at a somewhat higher temperature as, under mild conditions, butadiene, in all probability, forms rather stable coordinatively saturated complexes with the central atom of the catalyst and which have low activity in the reaction

concerned.

In fact, the catalyzed homodimerization of 1-hexene at 20-60°C is inhibited by the addition of butadiene in catalytic amount [63]. As a result, the ethylene and butadiene codimerization in the presence of a Cp_2ZrCl_2-EtMgBr catalytic system could be carried out only at 140-155°C to give the sole product, 1,4Z-hexadiene, the conversion amounting to ca. 10% [64].

$$\diagup\!\!\!\diagup + \diagup\!\!\!\diagup \quad \xrightarrow[\text{140-155°C}]{ZrCl_4\text{-EtMgBr}} \quad \diagup\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup \qquad \text{(ca. 10%)}$$

Higher α-olefins do not react with butadiene over this catalyst. The system $ZrCl_4$-Et_2AlCl, however, at 120°C catalyzes a codimerization of butadiene with 1-hexene, 1-octene, 1-nonene, and 1-decene [63],

$$\diagup\!\!\!\diagup + R\!\!-\!\!\diagup\!\!\!\diagdown \quad \xrightarrow[\text{120°C}]{ZrCl_4\text{-}Et_2AlCl} \quad \diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\text{-R} + \diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\text{-R}$$

$$4 : 1 \quad \text{(ca. 20%)}$$

A homodimerization of the starting monomers competes with the codimerization, the yield of codimers does not pass 15-20%.

IV. ZIRCONIUM COMPLEXES IN HYDRIDE TRANSFER REACTIONS

A number of examples of the application of zirconium compounds in hydride transfer reactions is known. Thus, some hydride complexes of four-valent zirconium supported on activated silica gel were reported [65] to be highly active catalysts for the isomerization of α-olefins into the respective thermodynamic cis-trans-isomeric mixtures. Over such catalysts, the hydrogenation of α-olefins proceeds considerably slower than isomerization. Cyclopentadienyl alkyl- and hydride zirconium complexes of the type $(RCp)_2ZrR'_2$, in which R'= H, Alk; R = H, Me, Me_3C, CH_2Ph, are sufficiently active catalysts for the hydrogenation of olefins and acetylenes [66-68].

The hydrogenation is represented by the following catalytic cycle,

alkene or alkyne

H_2

$(RCp)_2ZrH_2$

alkane
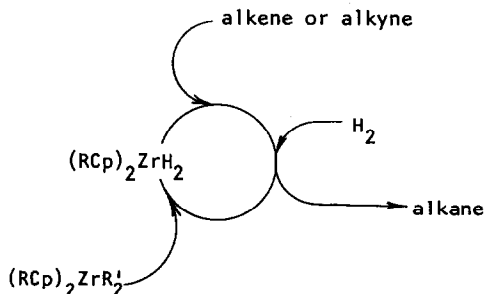
$(RCp)_2ZrR'_2$

Attempts to apply optically active complexes of the type $(R*Cp)_2ZrR_2$ to hydrogenate asymmetrically prochiral olefins brought little success. The yield of optically active hydrocarbons in the reported experiments [67] did not exceed 2% which was evidently due to the considerable distance separating the chiral and reactive centres in the catalyst.

Bis-cyclopentadienylzirconium dihydride (Cp_2ZrH_2) catalyzes the hydrogenation of naphthalene to a mixture of tetralin and dihydronaphthalene [68]. The latter reaction as well as olefin hydrogenation are catalyzed by a η, η'-naphthylzirconium(II) hydride complex which, however, has a lower activity compared to that of titanocene [68].
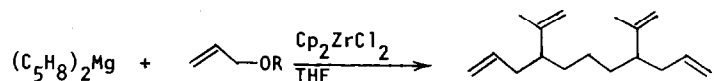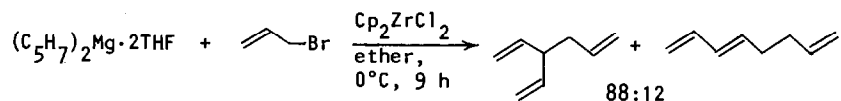
Prominent catalytic activity in hydride transfer has been demonstrated by stable complexes of low-valent zirconium prepared by the reduction of $ZrCl_4$ with sodium amalgam in the presence of bis-dimethylphosphinoethane (dmpe) and 1,3-cyclohexadiene or butadiene. They are highly effective catalysts for the metathesis of 1,3-cyclohexadiene into cyclohexane and benzene, and they also catalyze the hydrogenation of mono- and disubstituted olefins and acetylenes to give the corresponding alkanes [69].

$$ZrCl_4(dmpe)_2 \ + \ \bigcirc \xrightarrow[THF]{Na/Hg} \ \bigcirc\!\!-Zr(dmpe)_2H$$
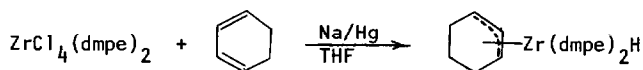
The existence of the redox pairs Zr(IV) $\rightleftarrows$ Zr(II); Zr(II) $\rightleftarrows$ Zr(0) performing the role of catalysis centres in such reactions was postulated [57, 69].

V. MISCELLANEOUS CATALYTIC REACTIONS INVOLVING ZIRCONIUM BASED COMPLEXES

Of high interest and practical value are the cross-coupling reactions of diene magnesium complexes [70, 71] as well as of alkenylmagnesium halides and magnesylamines with alkyl or aryl halides catalyzed by Cp_2ZrCl_2 or bimetallic catalysts containing zirconium [72].

$$(C_5H_7)_2Mg\cdot2THF \ + \ \diagup\!\!\!\!\diagdown\!\!-Br \xrightarrow[\substack{ether, \\ 0°C, \ 9 \ h}]{Cp_2ZrCl_2} \qquad + \qquad 88:12$$

$$(C_5H_8)_2Mg \ + \ \diagup\!\!\!\!\diagdown\!\!-OR \xrightarrow[THF]{Cp_2ZrCl_2}$$

Recently data have been published [73] concerning the use of zirconium complexes for catalyzing the cyclopropanation of olefins with diazoacetic ester. With Cp_2ZrCl_2, the target products are obtained in a high yield only with olefins with a sufficiently activated double bond [73], while the yield

of the n-butyl ether cyclopropanation does not exceed 4% [74].

The two-component catalytic systems containing $Zr(acac)_4$ and $AlEt_3$ or $(CH_3C_6H_4)P$, however, are not less active than the rhodium based catalysts [75].

96-98%

85-88%

$$\text{(cyclohexene)} + N_2CHCO_2Et \xrightarrow[80°C]{Zr(acac)_4-(CH_3C_6H_4)_3P} \text{(bicyclic)} \sim CO_2Et$$
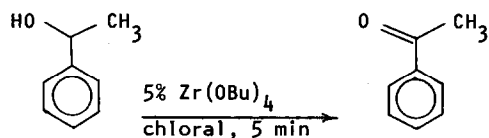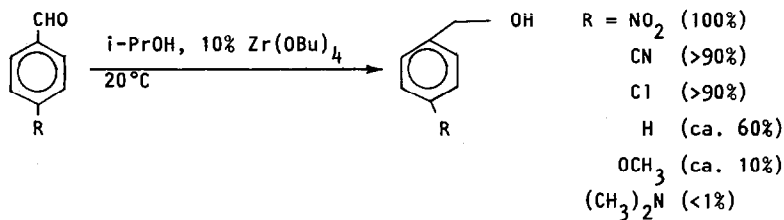
85-88%

The interaction of N-2,7-octadienylic derivatives of amines and dia-zoacetic ester over the same catalysts results in the formation of non-tri-vial aminoesters [75], the yields being over 70%.

$$X\text{(ring)}N\text{—}\diagup\diagdown\diagup\diagdown + N_2CHCO_2Et \xrightarrow[80°C]{Zr(acac)_4-(CH_3C_6H_4)_3P}$$

X = O, CH$_2$

$$\xrightarrow{} \quad X\text{(ring)}N\text{—}\underset{CH_2CO_2Et}{|}\diagdown$$

$$R_2N\text{—}\diagup\diagdown\diagup\diagdown + N_2CHCO_2Et \xrightarrow{Zr(acac)_4-(CH_3C_6H_4)_3P}$$

R = Me, Et

$$\xrightarrow{} R_2N\text{—}\underset{CH_2CO_2Et}{|}\diagdown$$
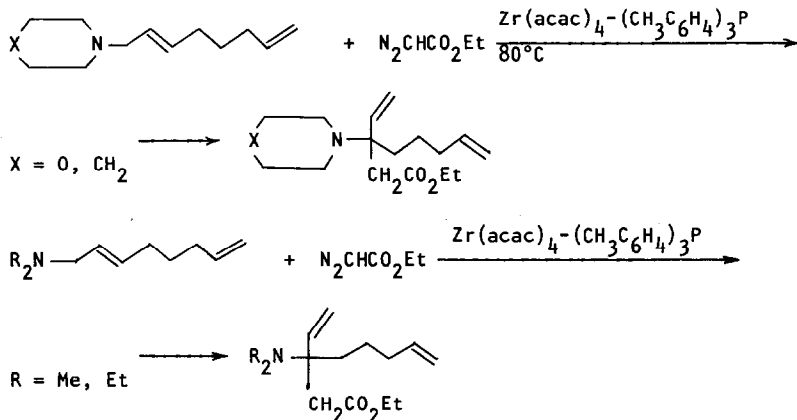
Some data are known about the application of zirconium tetraalkoxides as catalysts either for the selective reduction of carbonyl compounds by the Meerwein-Ponndorf-Verley method or for the oxidation of aromatic alcohols in the presence of chloral by the Oppenauer method [76].

$$\underset{R}{\overset{CHO}{\text{(benzene)}}} \xrightarrow[20°C]{i\text{-PrOH, 10\% Zr(OBu)}_4} \underset{R}{\text{(benzene)}}\text{—OH}$$

R = NO$_2$ (100%)
CN (>90%)
Cl (>90%)
H (ca. 60%)
OCH$_3$ (ca. 10%)
(CH$_3$)$_2$N (<1%)

$$HO\text{—}CH\text{(—CH}_3\text{)(benzene)} \xrightarrow[chloral, 5\ min]{5\%\ Zr(OBu)_4} O=C\text{(—CH}_3\text{)(benzene)}$$

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