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NEW ACHIEVEMENTS IN THE USE OF ZIRCONIUM COMPLEXES IN THE CHEMISTRY OF ORGANO-ALUMINIUM AND MAGNESIUM COMPOUNDS

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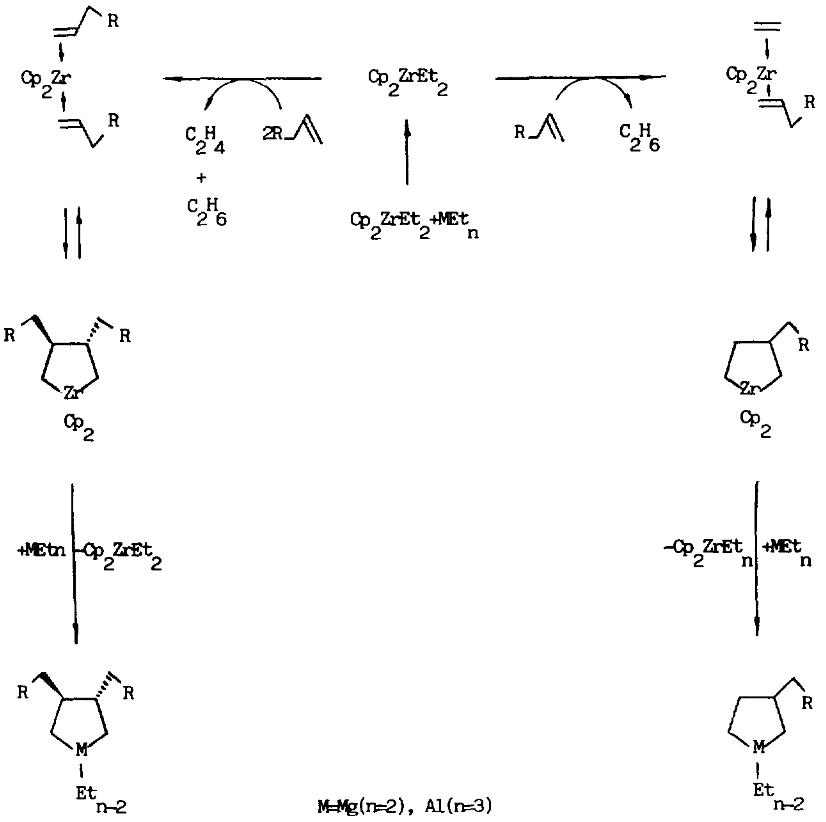
ABSTRACT : This paper describes some applications of a new reaction of catalytic cyclometallation of α-olefins, norbornenes and their derivatives, and 1,2-disubstituted acetylenes with organomagnesium and organoaluminium compounds effected by zirconium catalysts, leading to a series of five and macrocyclic heterocycles containing magnesium and aluminium.

INTRODUCTION

For the last 10-15 years the most outstanding achievements in a field of synthetic organic and organometallic chemistry concerned the use of zirconium complexes in synthesis and catalysis. Chemo-, regio- and stereoselective syntheses of organometallic compounds of nontransition metals have been realized exploiting the unique properties of zirconiumcontaining catalysts which can take part in transmetallation reactions of alkyl, alkenyl and alkynyl substituents from zirconium to other metals. Major contributions to the development of these investigations were made by Negishi[1], Sato[2], Ashby[3] and ourselves. The investigations and results obtained by us[4] in the field of the use of zirconium catalysis in the chemistry of olefins, 1,3-dienes, acetylenes and organometallic compounds of transition metals led (at the beginning of 1987) to an idea of transmetallation of zirconacyclopentanes formed in situ from low-valence zirconium and olefin complexes with the use of AlR_3 or MgR_2 to give the related five-membered organoaluminium and magnesium heterocycles. We hoped that realization of this reaction would give substituted alumina- and magnesiumcyclopentanes with catalytic amounts of zirconium complexes according to the Scheme :



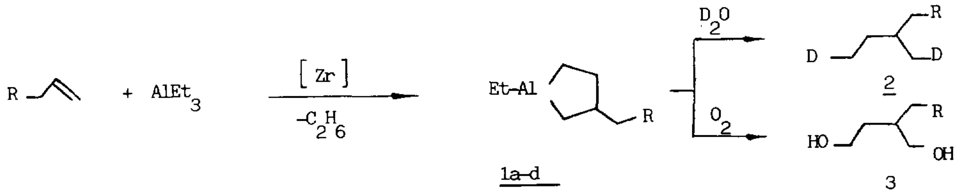
Then we have carried out the reactions involving an interaction of α-olefins with $AlEt_3$ or $MgEt_2$ in the presence of Cp_2ZrCl_2 in the catalytic manner. The reaction was termed olefin catalytic cyclometallation. Negishi[5], Takahashi[6], Hoveyda[7], Waymouth[8], Buchwald[9], Fagan[10], Erker[11] are making progress in this approach.

This paper describes the application of the new reaction to the cyclometallation of linear and cyclic olefins, 1,2-disubstituted acetylenes of various structures with the use of alkyl- and haloalanes, organoalkylmagnesium compounds in the presence of zirconium complexes as catalysts.

RESULTS AND DISCUSSION

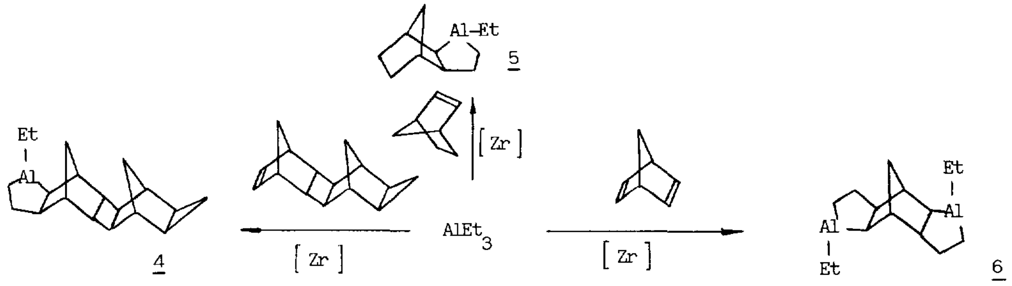
1. CATALYTIC CYCLOALUMINATION OF α-OLEFINS AND NORBORNENES WITH THE USE OF $AlEt_3$ AND HIGHER TRIALKYLALANES AlR_3

We have stated that the reaction of catalytic cycloalumination found by us[12] proceeds with high regio- and stereoselectivity giving substituted aluminacyclopentanes in high yields under mild conditions. The α-olefins with alkyl, alkenyl, aryl substituents and O-, N-, and S-containing functional groups were found to react with $AlEt_3$.



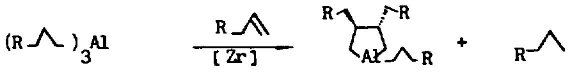
a: R=Ph; b: R=$-(CH_2)_2-CH=CH-CH_2NEt_2$; c: R=$-(CH_2)_2-CH=CH-CH_2OCH_3$; d:R=$-(CH_2)_2-CH=CH-CH_2OH$;

The structures of synthesized metallacycles 1 were established by spectral methods and identification of the products of deuterolysis 2 and oxidation 3. Norbornene and its derivatives containing sufficiently activated double bonds were found to react easily with $AlEt_3$ in THF in the presence of Cp_2ZrCl_2 (2-3 mol %) to be transformed into polycyclic organoaluminium compounds (4-6). The cyclometallation of norbornenes was carried out with high stereoselectivity to give polycyclic organoaluminium compounds with exo-configuration of aluminacyclopentane[14].



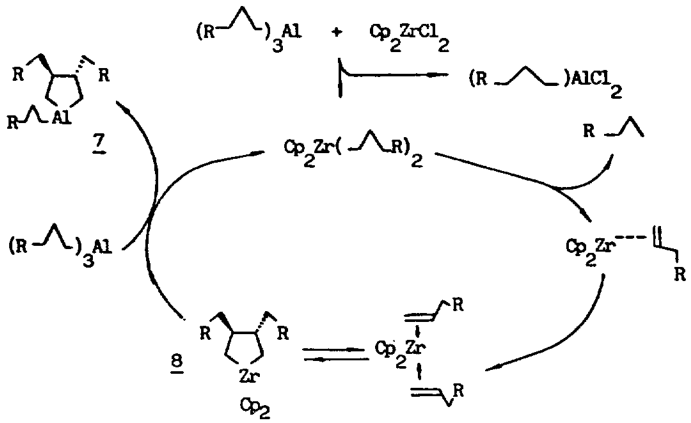
The next studies showed that in the interaction of α-olefins with higher trialkylalanes (olefin-AlR_3=2:1) in the presence of 3-5 mol% Cp_2ZrCl_2 or $ZrCl_4$ as a catalyst, trans-3,4-dialkylsubstituted aluminacyclopentanes were formed with high regio- and stereoselectivity in 55-95% yields (25°C, 10h)[15].

The formation of trans-3,4-dialkylsubstituted ACPs from α-olefins and higher trialkylalanes in the presence of a catalytic amount of Cp_2ZrCl_2 may proceed via zirconacyclopentanes 8, which undergo transmetallation with trialkylalanes to give the corresponding ACPs 7.

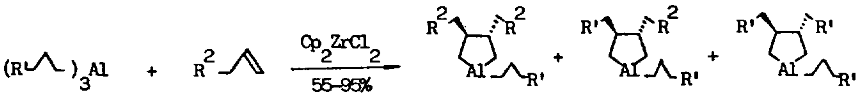


7 a-c

a: $R=C_3H_7$; b: $R=C_5H_{11}$; c: $R=C_8H_{17}$

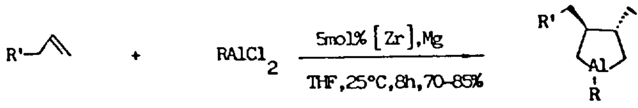


The α-olefin cycloalumination of higher trialkylalanes with α-olefins containing different alkyl groups gives a mixture of three trans-3,4-disubstituted ACPs 9-11 in a 1:2:1 ratio.



9 10 11

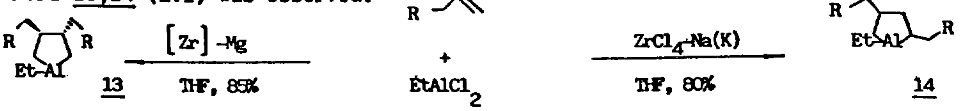
To explore the possibilities of using dihaloalanes ($RAlCl_2$), ($ROAlCl_2$),(R_2N-$AlCl_2$) and (RS-$AlCl_2$) as cyclometallation reagents and to produce new types of ACPs, we have studied the reaction of the above organoaluminium compounds (OACs) with C_6-C_{11} α-olefins in the presence of catalytic amounts (5 mol %) of Cp_2ZrCl_4. A generation of zirconacenes in these reactions was carried out by the reaction of Cp_2ZrCl_2 or $ZrCl_4$ with Mg(Na, K, Ca) in THF at 25°C for 6-8 hours. The reaction did not proceed in hydrocarbon solvents (benzene, xylene or hexane), and in Et_2O the ACP yields were no more than 20% In the interaction of $EtAlCl_2$, $EtOAlCl_2$ and $EtSAlCl_2$ with 1-hexene, 1-octene, 1-undecene or allylbenzene (in ratio of olefin:Al=2:1) the related ACPs 12 were produced in the presence of Cp_2ZrCl_2 (5 mol %) in 70-85% yields [16].



12

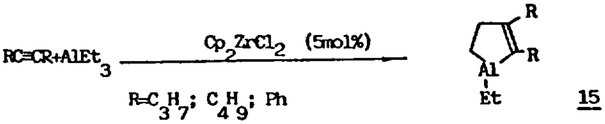
a:R=Cl; b:R=OEt; c:R=NEt_2; d:R=SEt; R'=C_3H_7; C_5H_{11}; C_8H_{17}; Ph

It should be noted that only trans-3,4-disubstituted ACPs were produced with the use of Cp_2ZrCl_2-Mg as a catalyst of cycloalumination, and in the experiments with $ZrCl_4$-Na (K) the formation of regioisomeric mixtures of trans-3,4- and 2,4-disubstituted ACPs 13,14 (2:1) was observed.



13 14

We have managed to synthesize cis-2,3-dialkyl (phenyl)aluminacyclopent-2-enes 15 in 75-80% yields, representing a novel class of cyclic OACs by the replacement of olefins with 1,2-disubstituted acetylenes (5 mol % Cp_2ZrCl_2, THF, 25°C, 10-12 hours)[17].



15

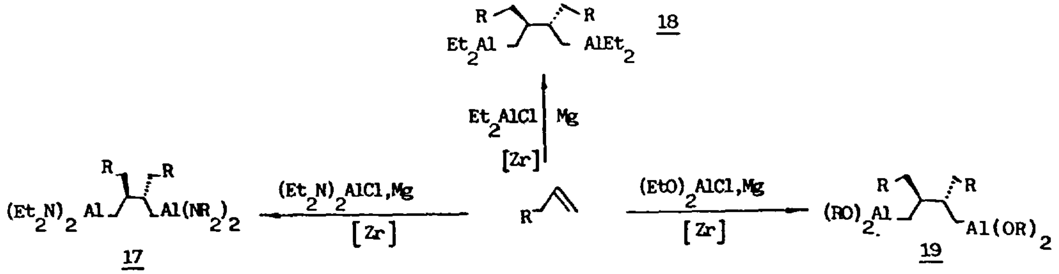
2. REGIO- AND STEREOSELECTIVE SYNTHESIS OF THREO-2,3-DIALKYLSUBSTITUTED 1,4-DIALUMINAALKANES

The results obtained by us on olefin cyclometallation by dihaloalanes to the corresponding ACPs suggested that transmetallation of zirconacyclopentane compounds formed in situ with the use of monohaloalanes (R_2AlCl) would yield the corresponding 1,4-dialuminium compounds according to the Scheme below

16

This reaction could be effected with Cp_2ZrCl_2 or $ZrCl_2$ catalysts. High yields of threo-2,3-dialkyl-1,4-dialuminabutanes 16 could be observed with the use of Cp_2ZrCl_2-Mg in THF in ratio of olefin-R_2AlCl=1:1.

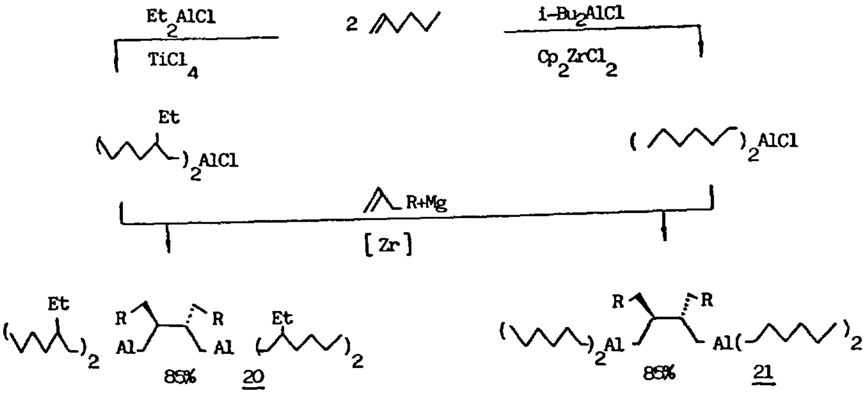
Together with dialkylhaloalanes, $(Et_2N)_2AlCl$ and $(EtO)_2AlCl$ also need for the reaction with α-olefins (1-hexene, 1-octene, 1-undecene, dialkylbenzene, vinylcyclohex-1-ene). The 1,4-dialuminabutanes of the structures 17-19 were produced under suitable conditions



25°C, 10h, THF

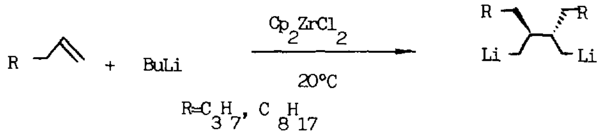
R=C_3H_7, C_5H_{11}, C_8H_{17}, Ph

The reaction developed above was shown to be of some generality, and dialkylhaloalanes of various structures can be incorporated to give the corresponding 1,4-dialuminabutanes 20-21.



The reaction opens a simple and efficient route to synthesize a novel series of 1,4-dialuminium compounds from α-olefins and suitable alkylhaloalanes in the presence of catalysts.

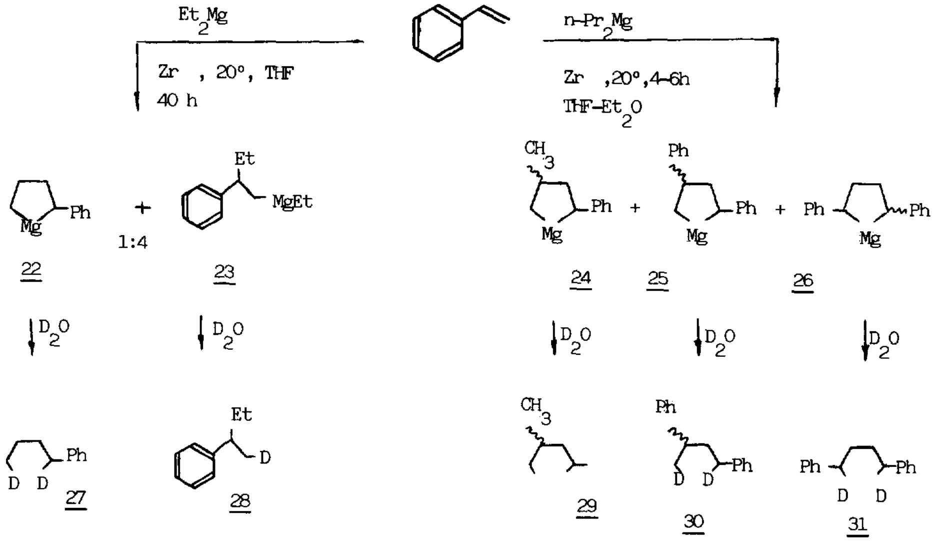
Recently we have carried out a similar reaction of BuLi with α-olefins catalyzed by Cp_2ZrCl_2.



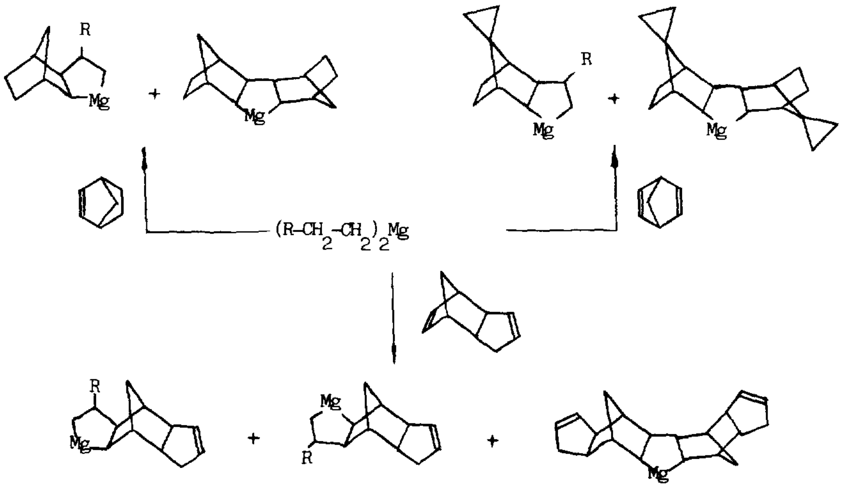
3. OLEFIN CYCLOMAGNESIATION

In 1989 we reported a catalytic cyclometallation on organomagnesium compounds (OMCs) and olefin cyclomagnesiation with the use of $(alk)_2Mg$ under the influence of catalytic amounts of Cp_2ZrCl_2 [18]. A styrene cyclomagnesiation by Et_2Mg in THF was found to proceed via formation of 2-phenylmagnesiocyclopentane 22 along with the products of carbomagnesiation 23 of initial olefin [19].

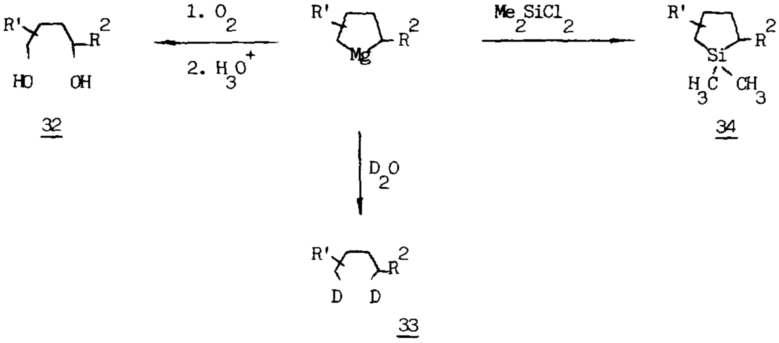
When Et_2Mg was replaced with Pr_2Mg, the reaction was directed to the formation of regioisomeric magnesiumcyclopentanes 24-26 in 98% yield. After deuterolysis hydrocarbons 27-31 were identified.



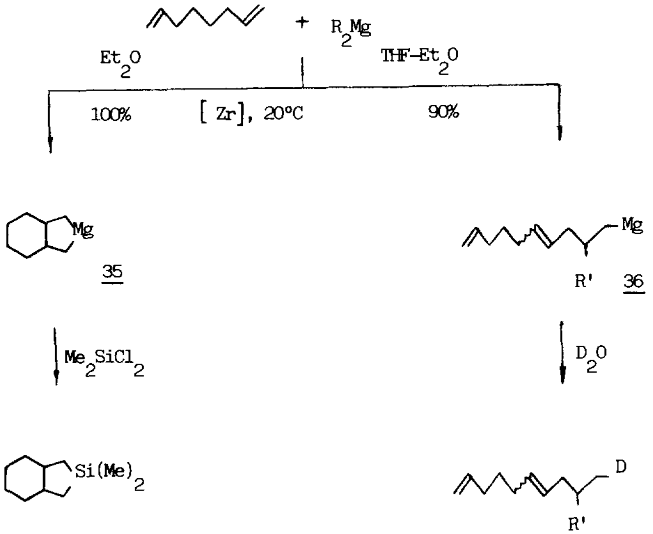
A catalytic carbomagnesiation of norbornene and its derivatives leading to polycyclic organomagnesium compounds (OMCs) was carried out in high yields [20].



Magnesiocyclopentanes were identified through their conversion via oxidation 32, deuterolysis 33 and transformation to the substituted silacyclopentanes 34.

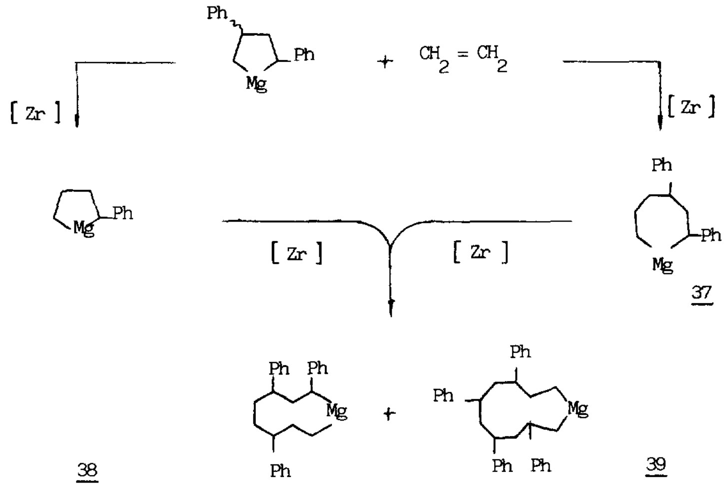


We have studied cyclomagnesiation of α,ω-dienes with n-alkylmagnesiums. A mixture of OMCs 35 and 36 (6:1) was formed from 1,7-octadiene and n-Pr_2Mg or n-Bu_2Mg in the presence of 3 mol % Cp_2ZrCl_2 (THF-OEt_2, 23°C) in a common yield of 90%. The 35 with a 100% selectivity may be prepared in the reaction in Et_2O.

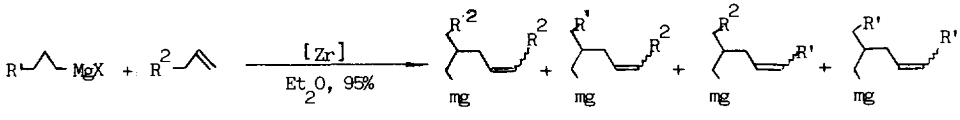


R=n-Pr, n-Bu; R'=Me, Et

A further study of olefin cyclomagnesiation with zirconium catalysts led to a synthesis of macrocyclic OMCs 37–39 by carbomagnesiation of ethylene and styrene using magnesiocyclopentanes.



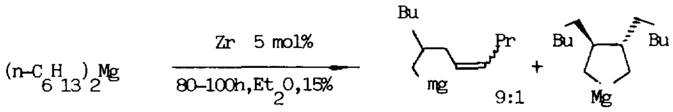
In contrast to styrene, norbornenes and α,ω-dienes, higher olefins were found to react with n-magnesioalkyls starting from n-Pr_2Mg to give a mixture of only linear organoalkenylmagnesium compounds 40–43, the hydrocarbon group of which is the products of the reaction of the initial OMCs and olefins[21].



40 41 42 43

$R'=R^2=H, C_3-C_{11}, Ph;\ X=C_2H_5+C_6H_{13}$

Higher dialkylmagnesium derivatives were shown to give alkenyl 44 and cyclic OMCs 45 in the absence of olefins catalyzed by Cp_2ZrCl_2. However, a common yield of these products were no more than 15%.



44 45

EXPERIMENTAL

All solvents and initial unsaturated compounds were distilled repeatedly before use and then dried over celites. Transition metal salts and complexes used as catalysts were purified by recrystallyzation or sublimation under dry argon. The synthesized compounds were analyzed chromatographically using Chrom-6 in He flow, 1200x3mm column, 5% SE-30 or 15% PEG-600 on N-AW chromatone. ^{13}C-NMR spectra of cyclic and acyclic OMCs and OACs, and hydrolysis, deuterolysis and oxidation products were recorded on a Brucker AM-300 spectrometer (^{13}C-75,46 MHz, ^{1}H-300 MHz). The solutions diluted in Et_2O with C_6D_6 addition were used for the internal stabilization of a field. TMS was used as an internal standard.

SYNTHESIS OF α-SUBSTITUTED ALUMINA-CYCLOPENTANES 1 : A 50 mL flask equipped with a magnetic stirrer under dry argon was charged with Cp_2ZrCl_2 (0.0524 g, 0.2 mmol), allylbenzene (1.18 g, 10 mmol) and $AlEt_3$ (1.368 g, 12 mmol). The reaction mixture was stirred for 10 h at 23-25°, hydrolyzed with 5% HCl to give 2-benzylbutane (1.20 g, 82%).

A 50 mL flask was charged with Cp_2ZrCl_2 (0.0876 g, 0.3 mmol), $AlEt_3$(3.534 g, 31 mmol) in hexane (3 mL). The flask was cooled to 0°, and 2,7-octadien-1-ol (1.26 g, 10 mmol) was added dropwise to hexane (2 mL). The reaction mixture was heated to 20° and stirred for 6 h. A deuterolysis (5% DCl in D_2O) of OAC leads to 2-(hex-4-en-6-ol)-1,4-dideuterobutane (1.46 g, 92%).

A 50 mL flask was charged with Cp_2ZrCl_2 (0.0524 g, 0.2 mmol), $AlEt_3$ (2.51 g, 22 mmol) in hexane (3 mL). The flask was cooled to 0°, and diethyl-(2,3-octadienyl)amine was added dropwise to hexane (2 mL). The reaction mixture was heated to 20° and stirred for 16 h, hexane (20 mL) was added, cooled to 0°. The OAC obtained was oxidized with dried air on stirring, then for 1 h at 20-30à, and with oxygen for 3 h at 40-50°. The reaction mixture was treated with 5% NaOH. A water phase was saturated with K_2CO_3 and extracted with MeOH. The solvent was evaporated, and the residue was distilled in vacuo. 2-/6'-Diethylamino-(hex-4'-enyl)/-1,4-butandiol was isolated.

1-Ethyl-3-benzyl-1-aluminacyclopentane 1a. ^{13}C-NMR spectrum (δ): 15.0(t,C-2), 44.5(d,C-3), 35.4(t,C-4), 5.9(t,C-5), 1.4(t,C-6), 8.7(q,C-7), 48.3(t,C-8), 143.7(c,C-9), 127.8(d,C-10), 129.3(d,C-11), 125.8(d,C-12), 129.3(d,C-13), 127.8(d,C-14).

1-Ethyl-3-/6'-(diethylamino)-hex-4'-enyl/-1-aluminacyclopentane 1b. ^{13}C-NMR spectrum : 14.2(t,C-2),40.5 (d,C-3), 33.8(t,C-4), 6.0(t,C-5), 2.9(t,C-6), 9.6(q,C-7), 40.1(T,C-8), 27.5(t,C-9), 33.2(t,C-10), 121.7(d, C-11), 139.4(d,C-12), 56.4(t,C-13).

1-Ethyl-3-/6'-(metoxy)-hex-4'-enyl/-1-aluminacyclopentan 1c. ^{13}C-NMR : 13.6(t,C-2), 40.2(d,C-3), 33.6 (t,C-4), 5.8(t,C-5), 0.9(t,C-6), 9.2(q,C-7), 41.4(t,C-8), 28.0(t,C-9), 33.6(t,C-10), 122.9(d,C-11), 140.8 (d,C-12), 75.4(t,C-13), 57.5(q,C-14).

1-Ethyl-3-/6'-(diethylalumoxy)-hex-4'-enyl/-1-aluminacyclopentane 1d. ^{13}C-NMR spectrum : 12.5(t,C-2), 40.5(d,C-3), 33.7(t,C-4), 6.0(t,C-5), 0.5(t,C-6), 9.2(q,C-7), 41.0(t,C-8), 27.5(t,C-9), 32.9(t,C-10),127.0 (d,C-11), 137.5(d,C-12), 64.6(t,C-13), 1.5(t,C-14,C-16), 8.8(q,C-15,C-17).

1-Ethyl-3-/6'-(butylthio)-hex-4'enyl/-1-aluminacyclopentane 1e. ^{13}C-NMR spectrum : 14.1(t,C-2), 40.4(d, C-3), 35.7(t,C-4), 8.2(t,C-5), 1.2(t,C-6), 9.5(q,C-7), 40.6(t,C-8), 28.8(t,C-9), 33.7(t,C-10), 123.4(d,C-11), 137.8(d,C-12), 33.2(t,C-13), 30.8(t,C-14), 31.7(t,C-15), 22.4(t,C-16), 13.6(q,C-17).

1-Butylthio-7-deuteriomethyl-9-deuterionon-2-en 2e. Mass spectrum , m/z: 230 $/M/^+$. IR spectrum (v,cm^{-1}): 3075, 2940, 2870, 2190(C-D), 1645, 1470, 1385, 1285, 1235, 980, 930, 760. PMR spectrum (δ) : 0.84-0.98 (7H, m, CH_3, CH_2D), 1.10-1.73 (13H, m, CH, CH_2), 1.83-2.17 (2H, m, CH_2-C=), 2.44(2H, t, S-CH_2), 3.09(2H,d,S-CH_2-C=), 5.35-5.59(2H,m,CH=CH). ^{13}C-NMR spectrum : 32.6(t,C-1), 133.5(d,C-2), 126.1(d,C-3), 34.0(t,C-4), 27.0 (t,C-5), 36.2(t,C-6), 34.2(d,C-7), 29.4(t,C-8), 11.1(t,C-1), 19.0(t,C-10), 30.3(t,C-11), 31.6(t,C-12), 22.1 (t,C-13), 13.7(q,C-14).

1-Diethylamino-7-hydroxymethyl-9-hydroxynon-2-en 3b. Mass spectrum, m/z 243 $/M/^+$. IR spectrum (v,cm^{-1}): 3370,2940, 2880, 1670, 1470, 1385, 1210, 1180, 1070, 990. PMR spectrum : 1.03(6H,t,CH_3, J=7 Hz), 1.26-1.80 (7H,m,CH,CH_2), 1.95-2.26(2H,m,CH_2-C=), 2.53(4H,q,N-CH_2,J=7 Hz), 3.04(2H,d,=C-CH_2-N,J=4 Hz), 3.54-3.98(4H,m, O-CH_2), 4.53(2H,c,OH), 5.42-5.64(2H,m,CH=CH). ^{13}C-NMR spectrum (δ): 54.9(t,C-1), 134.5(d,C-2), 126.1(d,C-3), 31.2(t,C-4), 26.5(t,C-5), 36.0(t,C-6), 39.4(d,C-7), 32.5(t,C-8), 60.5(t,C-9), 65.8(t,C-10), 46.2(t,C-11, C-13), 11.0(q,C-12,C-14).

SYNTHESIS OF POLYCYCLIC ALUMINACYCLOPENTANES : A 50 mL flask equipped with a magnetic stirrer under argon was charged with Cp_2ZrCl_2 (0.146 g, 0.5 mmol), bicyclo/2.2.1/heptene (0.94 g, 10 mmol) and $AlEt_3$ (1.368g, 12 mmol). The reaction mixture was stirred for 14 h. The OAC obtained was diluted with pentane (20 mL) and treated dropwise with 5% HCl at 0°, extracted with pentane. The residue was evaporated in vacuo. Exo-2-ethyl-bicyclo-32.2.1/heptane/ (1.22 g, 98%) was isolated.

3-Ethyl-exo-3-aluminatricyclo-/5.2.1.0^{2,6}/decane 5. ^{13}C-NMR spectrum (δ): 44.1(d,C-1), 30.6(d,C-2), 4.9(t,C-4), 36.8(t,C-5), 48.8(d,C-6), 39.3(d,C-7), 30.2(t,C-8), 34.3(t,C-9), 35.3(t,C-10), 1.9(t,C-11), 10.1(q,C-12).

SYNTHESIS OF 1, trans-3,4-TRIALKYLSUBSTITUTED ALUMINACYCLOPENTANES 7 : A 50 mL flask equipped with a magnetic stirrer under dry argon was charged with Cp_2ZrCl_2 (0.0876 g, 0.3 mmol), tris(n-octyl)aluminium obtained from i-Bu_3Al (2.38 g, 12 mmol) and 1-octene (4.0 g,, 36 mmol), then 1-octene (1.12 g, 10 mmol) was added. The reaction mixture was stirred for 10 h at 23-25°. A deuterolysis of the OAC leads to threo-7,8-bis(deuteriomethyl)teradecane (1.30 g, 58%). IR spectrum (v, cm^{-1}) : 2900, 2200, 1460, 1380, 1285. PMR spectrum (δ) : 0.62-0.95 m(10H,CH_3,CH_2D), 1.03-1.50 m (22H,CH,CH_2). ^{13}C-NMR spectrum (δ) : 14.08(t,C-1), 36.53(d,C-2), 34.97(t,C-3), 27.68(t,C-4), 29.73(t,C-5), 31.98(t,C-6), 22.71(t,C-7), 14.08(q,C-8). M^+ 228.

SYNTHESIS OF ALUMINASUBSTITUTED trans-3,4-DIALKYL(ARYL)ALUMINACYCLOPENTANES 12 : A 50 mL flask equipped with a magnetic stirrer under dry argon was charged with Cp_2ZrCl_2 (0.0876 g, 0.3 mmol), magnesium powder (0.24 g, 10 mmol), the corresponding olefin (20 mmol), THF (15 mL) and $AlCl_3$ (10 mmol). The reaction mixture was stirred for 10 h. The compound is 1-chlor-trans-3,4-dibutylaluminacyclopentane 12a. ^{13}C-NMR spectrum (δ): 11.78(t,C-2), 44.04(d,C-3), 39.27(t,C-4), 30.82(t,C-5), 23.62(t,C-6), 14.56(q,C-7).

SYNTHESIS OF 1-ETHYL-cis-2,3-DIALKYL(ARYL)ALUMINACYCLOPENT-3-ENES <u>15</u> : A 50 mL flask equipped with a magnetic stirrer under argon was charged with Cp_2ZrCl_2 (0.146 g, 0.5 mmol), $AlEt_3$ (2.85 g) and dec-5-yn (1.38 g, 10 mmol). The reaction mixture was stirred for 10 h at 23-25°. A hydrolysis of the OAC leads to 1-ethyl-2,3-dipropylaluminacyclopent-2-ene <u>15a</u>. ^{13}C-NMR spectrum (δ) : 158.9(s,C-2), 147.1(s,C-3), 35.4(t,C-4), 5.6(t,C-5), 1.6(t,C-6), 8.8(q,C-7), 35.2(t,C-8), 23.1(t,C-9), 15.0(q,C-10), 32.2(t,C-11), 22.5(t,C-12), 14.0(q,C-13).

SYNTHESIS OF THREO-2,3-DISUBSTITUTED 1,4-dialuminabutanes <u>16</u> : A 50 mL flask at 0° was charged with Cp_2ZrCl_2 (0.0876 g, 0.3 mmol), magnesium powder (0.24 g, 10 mmol), α-olefin (20 mmol), THF (10 mL) and the corresponding chloralane (R_2AlCl) (20 mmol). The reaction mixture was stirred 8 h at room temperature. The compound is threo-2,3-dihexyl-1,4-bis/diethylalumina/butane <u>18</u>. ^{13}C-NMR spectrum (δ) : 11.50(t, C-1), 45.83 (d,C-2), 38.80(t,C-3), 28.35(t,C-4), 30.61(t,C-5), 32.78(t,C-6), 23.30(t,C-7), 14.39(q,C-8), 1.65(t,C-9),10.04 (q,C-10). Threo-2,3-dibutyl-1,4-bis/dihexylalumina/butane <u>21</u> . ^{13}C-NMR (δ) : 12.26(t,C-1), 46.30(d,C-2), 38.90(t,C-3), 31.12(t,C-4), 23.82(t,C-5), 15.18(q,C-6), 10.17(t,C-7), 25.92(t,C-8), 37.06(t,C-9), 32.95(t,C-10), 23.57(t,C-11), 15.04(q,C-12).

GENERAL PROCEDURE OF CYCLOMAGNESIATION OF NORBORNENES : Into a glass reactor (100mL) equipped with a magnetic stirrer were placed under argon 20 mmol of organomagnesium compounds ($n\text{-}Pr_2Mg$ or $n\text{-}Bu_2Mg$) in ether (1.2 mmol/mL), 20 mmol of the corresponding norbornene, 0.175 g(0.6 mmol) of Cp_2ZrCl_2, and 16.7 mL of THF. The resulting solution was stirred for 7-7 h at a specified temperature, cooled to 0°C, hydrolyzed with 5% HCl or DCl, extracted with ether (3 x 50 mL), dried with $MgSO_4$, evaporated, and the residue was analyzed by GLC. The following compounds were isolated from the reaction mixture by distillation in vacuo.
3-Deuterio-exo-2-(1-deuteriomethylethyl)bicyclo/2.2.1/heptane . B.p. 51°C(38 Torr). n_D^{20} 1.4546. IR spectrum (v, cm^{-1}) : 1460, 2185,(C-D), 2880, 2970. ^1H-NMR spectrum (δ, J,Hz) : 0.85(d,5H,CH_3,CH_2D, J=6.0), 1.05 1.7(m,10H,CHD, CH), 2.0-2.3(m,2H,CH). ^{13}C-NMR spectrum (δ,J,Hz) : 38.52(d,C-1), 50.46(d,C-2), 36.57(t,C-3, $J_{^{13}C\text{-}D}$ =19.5), 36.85(d,C-4), 28.54(t,C-5), 30.63(t,C-6), 35.47(t,C-7), 32.83(d,C-8),20.02(t,C-9, $J_{^{13}C\text{-}D}$ =19.5) 21.84(q,C-10). Mass spectrum, m/z : 140 /M/$^+$. 3,3'-Dideuterio-exc,exo-2,2'-bis-bicyclo/2.2.1/heptyl B.P. 62°C (4 Torr), n_D^{20} 1.5014. IR spectrum (v,cm^{-1}) : 1455, 2190(C-D), 2860,2960. ^1H-NMR spectrum (δ) : 0.9-1.8(m,16H, CH_2, CHD, CH), 2.0-2.25(m,4H,CH). ^{13}C-NMR spectrum (δ, J, Hz): 40.67(d,C-1), 47.97(d,C-2), 35.54(t,C-3), 36.55(d,C-4), 28.98(t,C-5), 30.29(t,C-6), 35.54(t,C-7, $J_{^{13}C\text{-}D}$ =19.5). Mass spectrum, m/z:192/M/$^+$.

CONCLUSION

Investigations carried out by us for the last 3-5 years in the field of a catalytic activation of metal-hydrocarbon and metal-hydrogen bonds in a series of organometallic compounds of main group metals (Li,Mg,Cd,Al,Ga,In,Sn) in olefin and acetylene reactions effected by zirconium complexes develop a novel type of catalytic reactions termed the reactions of catalytic cyclometallation, cyclomagnesiation, cyclocadmation, etc. The reactions described above have opened a new entry into metal-complex catalysis, organic and organometallic synthesis. High reactivities of the metal-hydrocarbon bonds in metallacycles of main group metals obtained by us transfor easily the metallacycles to 1,4-bifunctional compounds, heterocycles containing S,Se,P and Si, cyclopentanones, cyclopropanes, cyclobutanes, conjugated dienes, regular isoprenoids, pest pheromones and other natural products. It should be noted that the synthesis of metallacycles and their further transformations were carried out, as a rule, in one vessel, and the syntheses were called "one-vessel methods" of the high efficiency and easy preparation. Presently the reaction of catalytic cyclometallation is under study with a wide class of organometallic compounds of main group and transition metals in the presence of olefins, heteroolefins, conjugated dienes and acetylenes, and hence, we hope to have the new unexpected results.

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