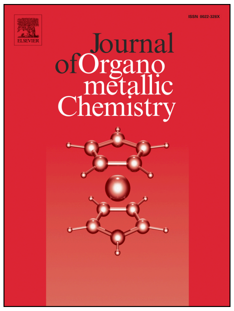

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Graphical Abstract

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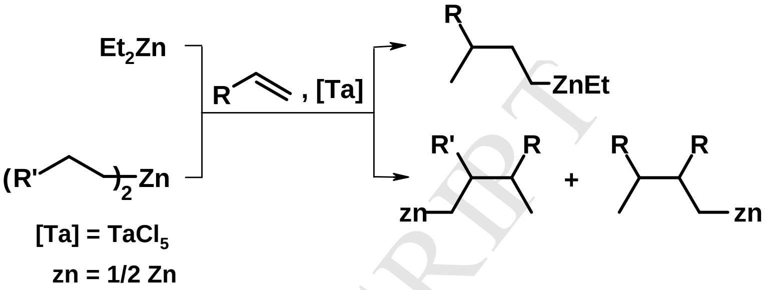

The tantalum-catalyzed carbozincation of 1-alkenes with zinc dialkyls

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Abstract

The $TaCl_5$-mediated reaction between monosubstituted alkenes and Et_2Zn affords 3-(R-substituted)-*n*-butylzincs in high yield (up to 92%) and regioselectivity. Organozinc reagents bearing a longer alkyl chain (R = Pr^{n}, Bu^{n}, Am^{n}, Hex^{n,}) react with 1-alkenes in the presence of $TaCl_5$ as the catalyst to give two types of organozinc compound having *iso*-alkyl structure. The probable mechanism of the carbozincation reaction implies the formation of β-substituted and β,β'-disubstituted tantalacyclopentanes as the key intermediates. The thermodynamic probability of the mechanistic elementary stages for the ethylzincation of terminal alkenes has been estimated using DFT PBE/SBK method

Keywords: Catalysis; Organozinc compounds; 1-Alkenes; Carbozincation; Tantalacyclopentanes; DFT calculations

1. Introduction

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As known, the catalytic systems based upon the compounds of copper [1], palladium [2], iron [3], nickel [4] and zirconium [5] are used in practical synthetic organic chemistry for the intramolecular and intermolecular carbozincation of alkenes. However, the assortment of the transition metal based catalysts as well as organozinc compounds (OZCs) remains limited. Therefore, the search of the new and efficient catalytic methods for the synthesis of various OZCs retains its high relevance.

We have previously reported [6] that the carbomagnesiation reactions of 1-alkenes and norbornenes with EtMgX (X = Cl, Et), Et_3Al or *n*-alkylmagnesiums in the presence of $TaCl_5$ lead to new types of organometallic compounds.

In this paper, we wish to report the results of our investigation into the tantalum-catalyzed carbozincation reaction of 1-alkenes with zinc dialkyls such as Et_2Zn, $Pr^n{}_2Zn$, $Bu^n{}_2Zn$, $Am^n{}_2Zn$ and Hex^nZn, thus greatly enhancing their potential in synthetic organic and organometallic chemistry.

2. Results and Discussions

In 2000, E. Negishi and coworkers have studied the carbozincation reaction between monosubstituted alkenes and diethylzinc in the presence of a catalyst generated *in situ* from Cp_2ZrCl_2 and EtMgBr at room temperature in tetrahydrofuran [5]. As shown, the resultant diisoalkylzinc derivatives were the classic carbometalation products (Scheme 1).

Scheme 1. Carbozincation of alkenes with Et_2Zn in the presence of Cp_2ZrCl_2 and EtMgBr.

Our ongoing research confirmed that $TaCl_5$ is able to effectively catalyze the reaction of 1-alkenes with Et_2Zn. However, the end products differ from those obtained under carbozincation involving Cp_2ZrCl_2 and EtMgBr. Thus, the model reaction of 1-octene with Et_2Zn (1:1 ratio) in the presence of $TaCl_5$ under optimized conditions (1-octene: [Ta] = 100:5, 20 ºC, 4 h, hexane) led to the OZC **1b** in 90% overall yield, based on the olefin (Scheme 2).

Scheme 2. The carbozincation reaction of 1-alkenes with Et_2Zn catalyzed by $TaCl_5$.

Hydrolysis of **1b** with dilute hydrochloric acid HCl (8%) resulted in the formation of 3-methyl nonane **2b**, whereas deuterolysis of the reaction mixture led to monodeuterated hydrocarbon **3b**. In an analogous fashion, 1-hexene and 1-decene entered into the tantalum-catalyzed reaction with Et_2Zn furnishing OZCs **1b** and **1c** in high yields (Table 1).

The yields of the end products **1a−c** were determined by GLC of their hydrolysis products **2a−c** with *n*-undecane as the internal standard. The structure of the obtained OZCs **1a−c** was proved by analysis of the one-dimensional (^{1}H, ^{13}C) NMR and chromato-mass spectra recorded for their hydrolysis **2a−c** and deuterolysis **3a−c** products.

Table 1. The effect of initial reagent ratio, reaction time and the solvent nature on the product yield in the carbozincation reaction between 1-alkenes and Et_2Zn mediated by $TaCl_5$ catalyst.

Reaction conditions: $TaCl_5$:Et_2Zn = 5:100, 20 ^{o}C, [Et_2Zn] = 2 mmol/mL.
*Based on starting 1-alkene

As seen from Table 1, the carbozincation reaction of 1-alkenes using Et_2Zn in the presence of $TaCl_5$ in nonpolar solvents (hexane, benzene, and toluene) furnishes the organozinc compound **1** in good yields. The polar solvents with stronger coordinating properties (diethyl ether, tetrahydrofuran) will contribute to the stabilization of (blocking) the catalytic system as reflected in the work of D. R. Armstrong and co-workers [7] thus reducing significantly the yield of the end products.

Scheme 3. The proposed catalytic cycle of the carbozincation reaction of 1-alkenes with Et_2Zn mediated by $TaCl_5$.

Considering the experimental results and the data obtained previously, we propose the transformation sequences (catalytic cycle), which may provide favorable pathways for reactants giving rise to the final carbozincation products from 1-alkenes and Et_2Zn in the presence of $TaCl_5$ as the catalyst (Scheme 3).

According to the scheme, at the first stage, the reaction between $TaCl_5$ and Et_2Zn leads to tantalum diethyl **4**. The latter transforms to the ethylene complex **5** due to the β-hydride transfer followed by the elimination of the ethane molecule. The coordination of the alkene molecule with **5** induces the formation of bis(alkene) complex **6**, which can transform to the tantalacyclopentane intermediate **7** through the intramolecular oxidative cyclization. Transmetallation of **7** by the additional Et_2Zn molecule resulted in Zn,Ta-bimetallic complex **8,** transformation of which affords the desired isoalkylzinc **1** as a result of β-hidride transfer.

For comparison, the carbomagnesiation of 1-alkenes with EtMgX in the presence of $TaCl_5$ resulted in the formation of two types of organomagnesiums as we have shown previously [6], (Scheme 4).

Scheme 4. Carbomagnesiation of 1-alkenes with EtMgX catalyzed by $TaCl_5$.

2.1 DFT study

To explain the observable regularities of the reaction between alkenes and diethylzinc in the presence of tantalum(V) salts as the catalysts, the following transformation sequences have been proposed (Scheme 5), and Gibbs energies ΔG of the elementary stages for the reaction of $RCH=CH_2$ with Et_2Zn in the presence of $TaCl_5$ catalyst have been calculated (Table 2).

According to the scheme, at the first step, the reaction of Et_2Zn with $TaCl_5$ gives the organotantalum compound Cl_3TaEt_2 (eq. 1), which then transforms to π-complex between ethylene and tantalum pentachloride **A** (eq. 2). The formation of such coordination complexes is typical behavior of transition metals [8]. This reaction is endothermic and occurs most likely due to high heat effect of the previous stage. The next stage includes the formation of the substituted tantalacyclopentane as the key intermediate **B** (eq. 3).

The experiment has shown that the reaction of *n*-alkenes with Et_2Zn mediated by tantalum pentachloride furnishes only one product **D-1**. In order to clarify this reaction pathway we have examined two further interactions between intermediate **B** and Et_2Zn, which occur: a) without breaking, that is, retention of the chemical bond between the tantalum atom and the alkyl fragment R (eq. 4) to afford product **C-1,** and b) with breaking of the above Ta–C bond giving compound **C-2** (eq. 5).

Complete theoretical treatment of the reaction mechanism requires taking into account the solvent effects and complexation of organozinc compounds (the last one are readily interact with solvent and each other resulting in domeric and oligomeric species [7]. That is why, we consider only with thermodynamic parameters of the elementary steps, shown in Scheme 5, which is the first approximation for our further mechanistic studies.

The quantum chemical study has shown that the alternative channels of the reaction are exothermic and characterized by the similar magnitudes of ΔG (differences were about 6–10 kJ/mol). A very small difference between the lengths of the nonequivalent Ta−C bonds (*ca*. 2.150 and 2.130 Å) indicates equal probability of their involvement in the reaction between tantalacyclopentane **B** and the organozinc compound (Fig. 1).

Fig. 1. Calculated bond distances (Å) in the tantalacyclopentane ring of the intermediate **B** (R = Bu^n).

However, there is a significant difference between the thermodynamic parameters of the reactions involving compounds **C-1** and **C-2**. As shown in Scheme 5, the final stages of the catalytic cycle (eq. 6 and eq. 7) include regeneration of the active π-complex **A** and the formation of the end products **D-1** and **D-2** respectively.

According to calculations by PBE/SBK, these compounds exhibit different stability. Thus, in the case of R = Bu^n, the magnitude of $\Delta G < 0$ for both reactions (eq. 6 and eq. 7), whereas the difference between Gibbs energies (ca. ~18.0 kJ/mol) provides evidence for the formation of **D-1**.

The difference in Gibbs energies should correlate with the activation barriers of steps 6 and 7 leading to the D-1 and D-2, respectively. ~~However, ΔG for these reactions acquired different signs with an increase in the length of the alkyl chain R (Table 2). The formation of **D-2** is endothermic (eq. 7), whereas the formation of **D-1** is exothermic, that is, characterized by evolution of heat (eq. 6).~~

Hence, the experimental identification of only one reaction product **D-1** was due to its greater thermodynamic stability.

Scheme 5. Elementary steps of the catalytic cycle for the 1-alkene ethylzincation.

Probably, the difference in D-1 vs. D-2 thermodynamic stability reflects the balance of weak (both repulsive and attractive) interactions between Zn atom and the alkyl chain. We can qualitatively describe the origin of dissimilarity of zinc and magnesium cases (Scheme 4). Magnesium has greater covalent radius (radii for Mg and Zn, having two covalent bonds, are 139 and 118 pm, respectively [9]. This should enhance steric repulsion in the case of Mg. However, according to the Pauling scale of electronegativity [10], Zn is more electronegative compared to Mg (1.65 vs. 1.31). The last fact should enhance intramolecular attraction of the alkyl chain and Mg atom. The direct estimation of these effects on the stability of two isomeric species in the Zn and Mg cases requires high-cost computational techniques with conformational analysis and will be done in our further study.

Table 2. The calculated changes in Gibbs energy for the key stages of the tantalum-catalyzed carbozincation reaction between alkenes (R = Bu^n, Hex^n, Oct^n) and Et_2Zn (kJ/mol).

We have examined the reactivity of other Zn di-*n*-alkyls such as $Pr^n{}_2Zn$, $Bu^n{}_2Zn$, $Pent^n{}_2Zn$ and $Hex^n{}_2Zn$ in the tantalum-catalyzed reaction with 1-alkenes.

Thus, the interaction between model $Bu^n{}_2Zn$ and 1-hexene (20 ºC, 7 h, $Bu^n{}_2Zn$:1-alkene:$TaCl_5$ = 100:100:5) afforded OZCs **9a** and **10a** (40:60 ratio) in 84% yield (Scheme 6). The end products **9b** and **10b** (85%) have been obtained from 1-octene under the same reaction conditions. The yield and the molar ratio of the resultant OZCs were found by calculating the g.l.c. peak areas of their hydrolysis products. The structures of the end products were confirmed by analysis of the ^1H and ^{13}C NMR as well as chromatography-mass spectra of their hydrolysis (**11a,b** and **12a,b**) and deuterolysis (**13a,b** and **14a,b**) products.

On the example of the reaction of 1-octene with $Bu^n{}_2Zn$ we have studied the influence of the initial reagent ratio, temperature, process duration, concentration of the catalyst and solvent nature on the yield and selectivity of the end products **9b** and **10b.** The results obtained are given in Table 3.

Table 3. Effect of reagent ratio and solvent nature on the product yield and selectivity of the reaction of 1-octene with $Bu^n{}_2Zn$ in the presence of $TaCl_5$.

Reaction conditions: $TaCl_5$: $Bu^n{}_2Zn$ = 5:100, 20 ºC, 7 h, [$Bu^n{}_2Zn$] = 1.0 mmol/mL.
*Based on starting 1-alkene

Scheme 6. The reaction of 1-alkenes with $Bu^n{}_2Zn$ catalyzed by $TaCl_5$.

The elevated temperatures (65−70 °C) favored the predominant formation of **10b** (**9b**:**10b** = 10:90, total yield of **9b**+**10b** = 89%). At low temperatures (1-octene: $Bu^n{}_2Zn$: [Ta] = 100:100:5, 5 h, 0 ºC), the total yield of the OZCs obtained did not exceed 20%. However, in this case, the OZC **9b** was the major product in the reaction mixture (**9b**:**10b** = 60:40)

We have also studied the effect of ethereal solvents (tetrahydrofuran (THF), diethyl ether (Et_2O), 1,4-dioxane) on the yield of organozinc compounds. As shown in Table 3 (entries 6, 7, and 8), these solvents tend to reduce the product yield being not greater than 45%.

When involving other zinc *n*-dialkyls of the homologous series (e.g. $Pr^n{}_2Zn$, $Pent^n{}_2Zn$ and $Hex^n{}_2Zn$), the reaction under consideration retained all its regularities. As in the case of $Bu^n{}_2Zn$, two types of OZCs resulted from the reaction (Scheme 7). The total yield of the end products **15** and **10** remained sufficiently high and reached 81−85%.

Scheme 7. The $TaCl_5$-catalyzed reaction of 1-octene with Zn *n*-dialkyls

Other alkenes such as 1-octene and 1-decene demonstrated almost the same activity in this reaction. It should be noted that the reaction between 1-alkene and zinc dialkyl having the same number of carbon atoms furnished only one OZC. Thus, the reaction of 1-hexene with $Hex^n{}_2Zn$ (1-hexene: $Hex^n{}_2Zn$: [Ta] = 100:100:5, 20 ºC, 7 h, hexane) gave the OZC **10a** as the sole product (Scheme 8).

Scheme 8. The reaction of 1-hexene with $Hex^n{}_2Zn$ in the presence of $TaCl_5$.

The structure and composition of the synthesized OZCs, our experimental findings on the catalytic carbomagnesiation and carboalumination of alkenes mediated by $TaCl_5$, as well as the published data on the synthesis, transformations, and applications of tantalum complexes [11] allow proposing the catalytic cycle for the reaction under consideration through the tantalacyclopentane intermediates. The possible routes for the formation of OZCs from 1-alkenes and zinc *n*-dialkyls in the presence of $TaCl_5$ as the catalyst are represented in Scheme 9.

Scheme 9. The catalytic cycle for the $TaCl_5$-catalyzed reaction of 1-alkenes with Zn *n*-dialkyls

According to the scheme, the interaction between $TaCl_5$ and the initial OZC affords tantalum dialkyl **17**. Elimination of the appropriate alkane molecule gives alkene-tantalum π-complex **18** as a result of β-hydride transfer. Alkylation of **18** and subsequent transalkylation of bis-alkene-tantalum π-complex **19** in the presence of the initial alkene through the formation of the intermediate **20** furnish bis-alkene-tantalum π-complex **21** with two molecules of initial alkene.

Intramolecular oxidative cyclization of **19** and **21** affords β,β'-dialkyl-substituted tantalacyclopenetanes **22** and **23** respectively.

The transmetallation reaction of the latter intermediates with the original OZC gives the corresponding Zn,Ta-bimetallic complexes **24** (route 1) and **25** (route 2). Their subsequent transformations finally lead to the OZCs **26** and **27** as a result of intramolecular β-hydride transfer.

3. Conclusions

In conclusion, we have shown that the carbozincation reaction of 1-alkenes with Et_2Zn in the presence of $TaCl_5$ led to the regioselective formation of 3-(R-substituted)-*n*-butylzincs in high yields (up to 92%). Thermodynamic probability of elementary stages of the proposed mechanism for this reaction agrees well with the experimental data.

The tantalum-catalyzed reaction of 1-alkenes with Zn *n*-dialkyls ($Pr^n{}_2Zn$, $Pent^n{}_2Zn$ and $Hex^n{}_2Zn$) furnished two types of organozinc compounds having *iso*-alkyl structure. The proposed mechanistic schemes imply the formation of the β- and β,β'-substituted tantalacyclopentanes as the key intermediates. The investigations into the tantalum-catalyzed carbozincation reaction of 1-alkenes with Zn dialkyls resulted in the development of the catalytic procedure, which can serve as the effective method for the synthesis of the new types of organozinc compounds.

The catalytic carbozincation reaction of unsaturated compounds mediated by the simplest and readily available zinc organometallics opens new possibilities for the construction of carbon-carbon and metal-carbon bonds that, in turn, may contribute to the design of the mild and convenient regioselective, stereoselective, and chemoselective processes to obtain the desired organic and organometallic compounds including those of natural compound structure.

4. Experimental

All reactions were carried out under dry argon atmosphere. 1-Alkenes having a purity of no less than 99.8% were distilled over $Bu^i{}_3Al$ in a stream of argon prior to use. Hydrocarbon solvents (hexane, benzene, and toluene) were purified as described in Ref. [12]. Ethereal solvents (Et_2O, THF) pre-dried over KOH, refluxed over sodium-wire for 2 h and distilled from $LiAlH_4$ in a stream of argon. Organozinc reagents (Et_2Zn, $Pr^n{}_2Zn$, $Bu^n{}_2Zn$, $Am^n{}_2Zn$, $Hex^n{}_2Zn$) were synthesized as described in Ref. [13]. Commercially available $TaCl_5$ (purity 99.8%) was purchased from Aldrich and used as received.

Chromatographic analysis of the hydrolysis and deuterolysis products was performed on SHIMADZU GC-2014 instrument (column 2 m*3 mm, 5% SE-30 on Chromaton N-AW-HMDS (0.125-0.160 mm)) as the stationary phase, helium as a carrier gas (30 mL min^{-1}), temperature programming from 50 to 300 ºC at a rate of 8 ºC min^{-1} with *n*-undecane as the internal standard. The one-dimensional (^1H, ^{13}C) and two dimensional homo- (COSY) and heteronuclear (HSQC, HMBC) NMR spectra were recorded in $CDCl_3$ on a spectrometer Bruker Avance 400 [400.13 MHz (^1H) and 100.62 MHz (^{13}C)] at 298 K in accordance with standard Bruker pulse sequences. Chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Infrared spectra (IR) were recorded using FT-IR spectrometer Bruker Vertex 70v (liquid film). Chromato-mass spectrometric analysis of compounds was performed on SHIMADZU GCMS-QP 2010 instrument (SUPELCO SLB™- 5 ms, 60000 mm*0.25 μm, helium as the carrier gas, temperature programming 260 ºC at a rate of 5 ºC min^{-1}, the temperature of the ion source 260 ºC [EI, 70 eV]). Elemental analysis of the samples was carried out using Carlo Erba Elemental Analyzer model 1106.

Computational Details. Gibbs energies of the reaction steps were calculated by density functional theory (DFT) method with PBE functional [14] and Stevens-Basch-Krauss pseudopotential [15] implemented in Priroda 6 program [16]. The structures of all the reaction participants have been optimized with no restrictions on the symmetry. Gibbs energies of the reactions have been calculated as differences of total energies of products and reactants taking into account zero-point vibration energies and thermal corrections (T = 293 K).

*4.1. Synthesis of 3-methylheptane, **2a**, 3-methylnonane, **2b**, and 3-methylundecane, **2c***

4.1.1. General procedure

A glass reactor, under a dry argon atmosphere at 0 ^{o}C, was charged under stirring with hexane (10 mL), 1-hexene (20 mmol, 1.68 g) (or 1-octene, or 1-decene), Et_2Zn (20 mmol, 2.47 g, ~2 mL) and $TaCl_5$ (1.0 mmol, 0.36 g). The temperature was raised to 20 ^{o}C and the mixture was stirred for additional 4 h. Then, the reaction mixture was cooled to 0 ºC and quenched by an 8% HCl. The organic layer was separated. The aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organics were washed with $NaHCO_3$ (until neutral) and dried over $MgSO_4$. The mixture of products **2a, 2b** and **2c** was separated by fractional distillation and identified reliably by comparison with the known samples [17].

*4.2. Synthesis of 1-deutero-3-methylheptane, **3a**, 1-deutero-3-methylnonane, **3b**, and 1-deutero-3-methylundecane, **3c***

4.2.1. General procedure

The $TaCl_5$-catalyzed reaction of 1-alkene (1-hexene, 1-octene, and 1-decene) with Et_2Zn was implemented according to the general procedure 4.1.1. The obtained reaction mixtures were treated by 8% DCl in D_2O. Compounds **3a, 3b** and **3c** were separated by fractional distillation. Spectral data for **3a**: Bp. 56 ºC (80 mm Hg), IR (ν, см$^{-1}$): 2175 (C-D). ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.45 (m, 1H, CH), 1.29 (m, 2H, CH_2), 1.20 (m, 2H, CH_2), 1.16 (m, 2H, CH_2), 1.12 (m, 2H, CH_2), 0.87 (t, 3H, CH_3, ^{3}J= 7.2 Hz), 0.86 (m, 2H, CH_2D), 0.83 (q, 3H, CH_3, ^{3}J=6.4 Hz). ^{13}C NMR ($CDCl^3$, in ppm, 100.62 MHz): δ= 36.60 (C^4), 34.70 (C^3), 29.40 (C^2), 28.60 (C^5), 22.75 (C^6), 18.60 (C^7), 14.09 (C^8), 10.80 (C^1, t, $^1J_{C\text{-}D}$= 19.0 Hz). MS, m/z: 115 (M^+). Elemental Anal. Calc. for: C, 83.48; H, 14.78; D, 1.74%. Found: C, 83.44; H+D, 16.48%. Spectral data for **3b**: Bp. 75 ºC (30 mm Hg), IR (ν, см$^{-1}$): 2175 (C-D). ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.12-1.45 (m, 13H, CH_2, CH), 0.86-0.97 (m, 8H, CH_3, CH_2D). ^{13}C NMR ($CDCl_3$, in ppm , 100.62 MHz): δ= 36.78 (C^4), 35.45 (C^3), 32.09 (C^7), 29.83 (C^6), 29.50 (C^2), 27.20 (C^5), 22.79 (C^8), 19.16 (C^{10}), 14.09 (C^9), 11.04 (C^1, t, $^1J_{C\text{-}D}$= 19.0 Hz). MS, m/z: 143 (M^+). Elemental Anal. Calc. for: C, 83.92; H, 14.68; D, 1.40%. Found: C, 84.15; H+D, 15.75%. Spectral data for **3c**: Bp. 110 ºC (30 mm Hg), IR (ν, см$^{-1}$): 2175 (C-D). ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.43 (m, 1H, CH), 1.35 (m, 16H, CH_2), 0.93 (m, 8H, CH_3, CH_2D). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 34.40 (C^2), 34.40 (C^4), 32.02 (C^5), 30.14 (C^6), 29.79 (C^7), 29.51 (C^3), 29.47 (C^8), 27.20 (C^9), 22.73 (C^{10}), 19.10 (C^{12}), 18.79 (C^1, t, $^1J_{C\text{-}D}$= 19.0 Hz), 13.99 (C^{11}). MS, m/z: 171 (M^+). Elemental Anal. Calc. for: C, 84.21; H, 16.62; D, 1.17%. Found: C, 84.19; H+D, 15.73%.

*4.2. Synthesis of 2,4-dimethyloctane, **11a**, 5,6-dimethyldecane, **12a**, 3,4-dimethyldecane, **11b**, 7,8-dimethyltetradecane, **12b**, 1-deutero-2-ethyl-3-methylheptane, **13a**, 1-deutero-2-butyl-3-methylheptane, **14a**, 1-deutero-2-ethyl-3-methylnonane, **13b**, and 1-deutero-2-hexyl-3-methylnonane, **14b***

4.2.2. General procedure

A glass reactor, under dry argon atmosphere at 0 ºC, was charged under stirring with $TaCl_5$ (2.5 mmol, ~ 0.9g), 1-hexene or 1-octene (50 mmol), hexane (50 mL), and freshly prepared $Bu^n{}_2Zn$ (50 mmol). The temperature was raised to 20 ºC, and the mixture was stirred for additional 7 h. Then the reaction mixture was quenched by an 8% HCl in H_2O or DCl in D_2O to identify the resulting OZCs. The organic layer was separated. The aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organics were washed with $NaHCO_3$ (until neutral) and dried over

$MgSO_4$. Individual products and their monodeuterated derivatives were separated by fractional distillation. Spectral data for **11a**: Bp. 68ºC (30 mm Hg). ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 0.93-1.31 (m, 8H, 4CH_2), 0.83-0.92 (m, 12H, 4CH_3), 0.82-0.88 (m, 2H, 2CH). NMR ^{13}C ($CDCl_3$, in ppm, 100.62 MHz): δ= 38.13, 37.82, 36.75, 35.24, 27.06, 22.81, 17.43, 16.65, 14.12, 12.33. MS, m/z: 142 (M^+). Elemental Anal. Calc. for: C, 84.51; H, 15.49. Found: C, 84.47; H, 15.46%. Spectral data for **12a**: Bp. 62 ºC (2.5 mm Hg). ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 0.98-1.31 (m, 12H, 4CH_3), 0.82-0.94 (m, 14H, 6CH_2, 2CH). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 36.89, 35.64, 28.21, 22.72, 16.91, 15.49. MS, m/z: 170 (M^+). Elemental Anal. Calc. for: C, 84.51; H, 15.49. Found: C, 84.47; H, 15.48%. Spectral data for **11b**: Bp. 105 ºC (30 mm Hg). ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.08-1.44 (m, 14H, CH, CH_2), 0.73-0.96 (m, 12H, CH_3). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 38.55, 36.32, 35.00, 32.00, 29.73, 27.68, 27.52, 22.71, 14.29, 14.03, 13.88, 11.31. MS, m/z: 170 (M^+). Elemental Anal. Calc. for: C, 84.71; H, 15.29. Found: C, 84.68; H, 15.27%. Spectral data for **12b**: Bp. 158 ºC (30 mm Hg). ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.17-1.44 (m, 22H, CH, CH_2), 0.86 (t, 6H, CH_3), 0.73 (d, ^1J= 6.6 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 36.54, 34.93, 31.96, 29.70, 27.67, 27.70, 14.36, 14.11. MS, m/z: 226 (M^+). Elemental Anal. Calc. for: C, 84.96; H, 15.04. Found: C, 84.92; H, 15.01%. Spectral data for **13a**: Bp. 69 ºC (30 mm Hg). $IR_{\nu CO}$ (cm^{-1}, in thin film): 2185 (C-D). ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.08-1.44 (m, 10H, CH, CH_2), 0.77-0.88 (m, 11H, CH_3, CH_2D). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 37.66, 36.41, 35.25, 34.95, 25.82, 21.71, 13.58, 12.65 (t, $^1J_{C-D}$=19Hz), 11.10. MS, m/z: 143 (M^+). Elemental Anal. Calc. for: C, 83.90; H+D, 16.10. Found: C, 83.82; H, 16.05%. Spectral data for **14a**: Bp. 102 ºC (30 mm Hg). $IR_{\nu CO}$ (cm^{-1}, in thin film): 2185 (C-D). ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.09-1.44 (m, 14H, CH, CH_2), 0.75-0.95 (m, 11H, CH_3, CH_2D). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 36.51, 36.24, 36.11, 34.21, 27.92, 22.63, 14.01, 12.41 (t, $^1J_{C-D}$=19Hz), 12.40. MS, m/z: 171 (M^+). Elemental Anal. Calc. for: C, 84.21; H+D, 15.79. Found: C, 84.17; H, 15.74%. Spectral data for **13b**: Bp. 105 ºC (30 mm Hg). $IR_{\nu CO}$ (cm^{-1}, in thin film): 2175 (C-D). ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.08-1.44 (m, 14H, CH, CH_2), 0.88 (t, J_{H-H}= 7 Hz, 3H, CH_3), 0.86 (t, J_{H-H}= 7 Hz, 3H, CH_3), 0.74 (d, J_{H-H}= 7 Hz, 2H, CH_2D), 0.73 (d, J_{H-H}= 7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 38.41, 36.25, 34.95, 31.98, 29.71, 27.66, 27.50, 22.71, 14.12, 13.94, 13.65 (t, $^1J_{C-D}$=19Hz), 12.21. MS, m/z: 171 (M^+). Elemental Anal. Calc. for: C, 84.20; H+D, 15.80. Found: C, 84.16; H, 15.77%. Spectral data for **14b**: Bp. 159 ºC (30 mm Hg). $IR_{\nu CO}$ (cm^{-1}, in thin film): 2175 (C-D). ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.11-1.44 (m, 22H, CH, CH_2), 0.74-0.91 (m, 11H, CH_3, CH_2D). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 36.58, 36.50, 34.95, 34.94, 31.98, 29.68, 27.68, 22.71, 14.40, 14.11, 14.10 (t, $^1J_{C-D}$=19Hz). MS, m/z: 227 (M^+). Elemental Anal. Calc. for: C, 84.60; H+D, 15.40. Found: C, 84.56; H, 15.39%.

*4.3. Synthesis of 1-deutero-2,3-dimethylnonane, **16a**, 1-deutero-2-propyl-3-methylnonane, **16b**, and 1-deutero-2-butyl-3-methylnonane, **16c***

4.3.1. General procedure

A glass reactor, under a dry argon atmosphere at 0 ºC, was charged under stirring with $TaCl_5$ (2.5 mmol, ~ 0.9g), 1-octene (50 mmol, 5,6 g) and $Pr^n{}_2Zn$ (50 mmol, 0.8 M solution in hexane) or ($Pent^n{}_2Zn$, $Hex^n{}_2Zn$). (Further treatment of the reaction mixture was identical with the procedure described under *4.2.2*). Spectral data for **16a**: Bp. 104 ºC (30 mm Hg). $IR_{\nu CO}$ (cm^{-1}, in thin film): 2175 (C-D). ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.08-1.44 (m, 12H, CH, CH_2), 0.75-0.87 (m, 11H, CH_3, CH_2D). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 39.20, 33.92, 32.27, 32.08, 29.01, 27.65, 22.89, 21.78, 19.44 (t, $^1J_{C-D}$=19Hz), 16.61, 14.11. MS, m/z: 157 (M^+). Elemental Anal. Calc. for: C, 84.08; H+D, 15.92. Found: C, 84.05; H, 15.90%. Spectral data for **16b**: Bp. 118 ºC (30 mm Hg). $IR_{\nu CO}$ (cm^{-1}, in thin film): 2175 (C-D). ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.08-1.44 (m, 16H, CH, CH_2), 0.74-0.88 (m, 11H, CH_3, CH_2D). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 37.95, 35.91, 35.51, 34.15, 31.58, 28.80, 27.26, 22.21, 19.90, 14.25, 14.12, 13.65 (t, $^1J_{C-}$

$_D$=19Hz). MS, m/z: 185 (M^+). Elemental Anal. Calc. for: C, 84.32; H+D, 15.68. Found: C, 84.30; H, 15.65%. Spectral data for **16c**: Bp. 132 ºC (30 mm Hg). IR$_{\nu CO}$ (cm^{-1}, in thin film): 2175 (C-D). ^{1}H NMR ($CDCl_3$, in ppm, 400.13 MHz): δ= 1.09-1.46 (m, 18H, CH, CH_2), 0.75-0.89 (m, 11H, CH_3, CH_2D). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ= 36.81, 36.25, 34.71, 34.12, 31.68, 29.12, 27.86, 27.71, 22.61, 22.12, 14.26, 13.95, 13.68, 13.34 (t, $^1J_{C-D}$=19Hz). MS, m/z: 199 (M^+). Elemental Anal. Calc. for: C, 83.90; H+D, 16.10. Found: C, 83.87; H, 16.05%.

According to the data of Chromato-mass spectrometry and NMR spectroscopy, the deuterium incorporation in products **3a-c**, **13 a-b**, **14a-b,** and **16a-c** was no less than 97%.

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Table 1.

Entry	1-Alkene	Et_2Zn : alkene molar ratio	Solvent	Time, h	Yield* of **1**, %
1	1-Hexene	1:1	Hexane	4	89
2	1-Octene	1:1	Hexane	4	90
3	1-Decene	1:1	Hexane	4	87
4	1-Octene	1,5:1	Hexane	4	92
5	1-Octene	1:1	Tetrahydrofuran	4	35
6	1-Octene	1:1	Toluene	4	86
7	1-Octene	1:1	Benzene	4	89
8	1-Octene	1:1	Diethyl ether	4	15
9	1-Decene	1:1	Hexane	8	90
10	1-Octene	1:1	Hexane	12	92

Table 2.

Reaction	ΔG (kJ/mol) for various R		
	^{n}Bu	^{n}Hex	^{n}Oct
(3)	-38.2	-37.7	-39.9
(4)	-88.6	-90.0	-92.0
(5)	-82.0	-82.2	-83.0
(6)	-18.0	-16.2	-17.6
(7)	-0.2	+0.6	+2.9

Table 3.

Entry	1-octene: $Bu^n{}_2Zn$ molar ratio	Solvent	Total yield* of 9b+10b, %	Product selectivity, %	
				9b	**10b**
1	1:1	hexane	85	40	60
2	2:1	hexane	49	20	80
3	3:1	hexane	30	8	92
4	1:1.5	hexane	90	45	55
5	1:3	hexane	93	50	50
6	1:1	THF	40	43	67
7	1:1	Et_2O	30	90	10
8	1:1	1,4-dioxane	45	80	20
9	1:1	toluene	84	42	58

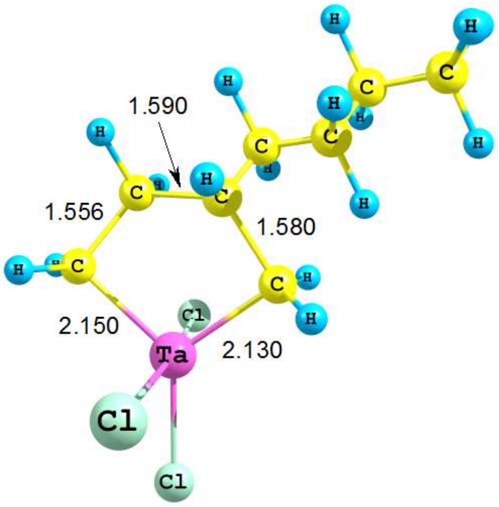
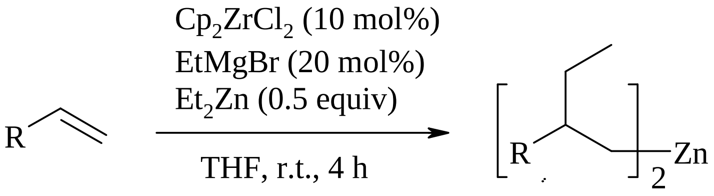
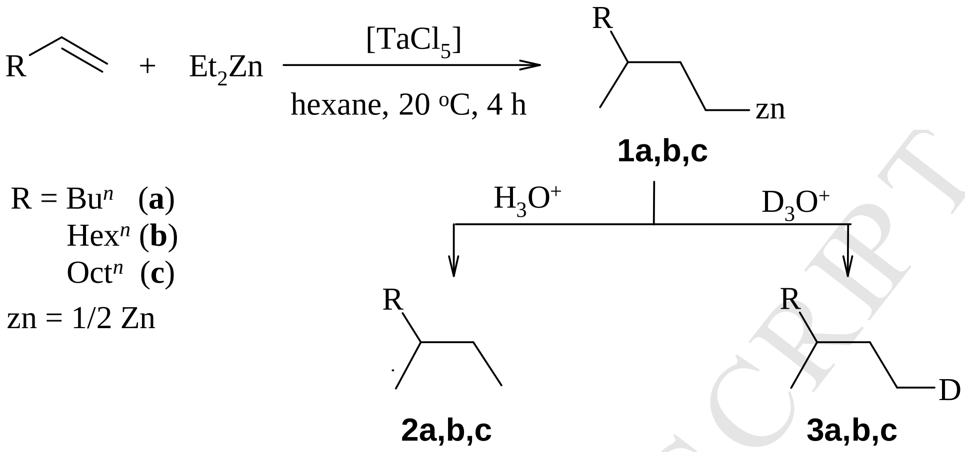


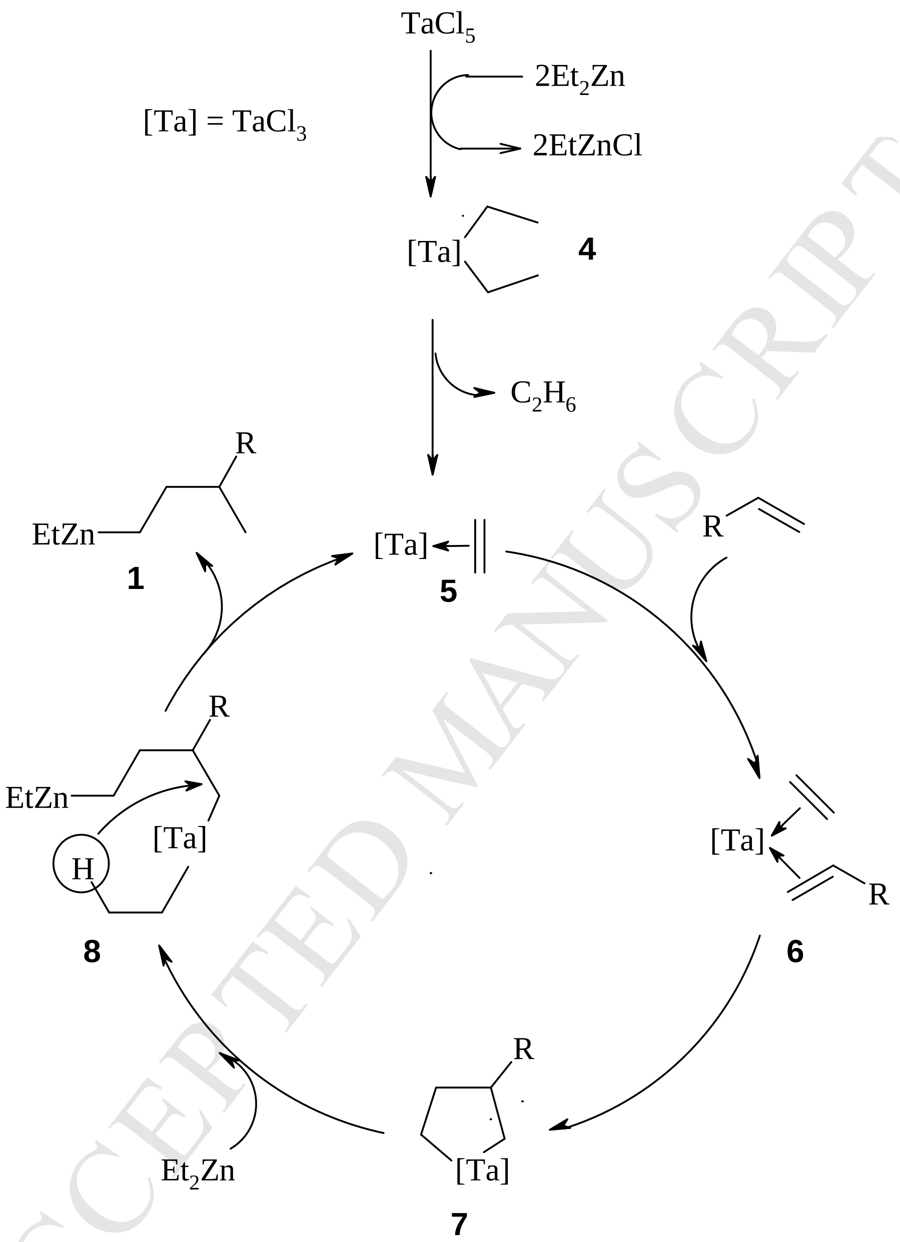
Fig. 1



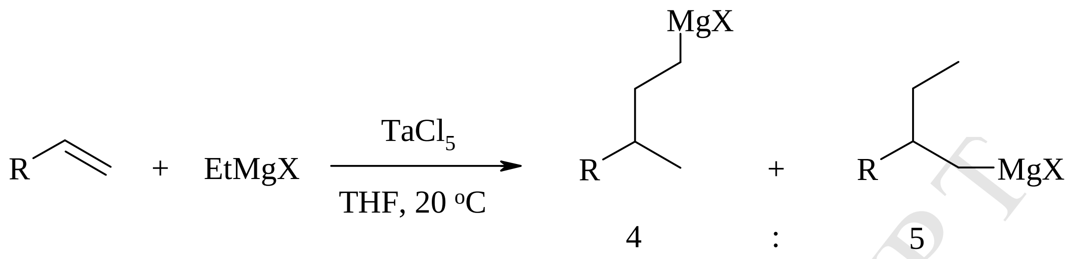
Scheme 1


R
+
Et$_2$Zn
[TaCl$_5$]
hexane, 20 °C, 4 h
R
zn
1a,b,c
R = Bu^n (a)
Hex^n (b)
Oct^n (c)
zn = 1/2 Zn
H$_3$O$^+$
D$_3$O$^+$
R
R
D
2a,b,c
3a,b,c

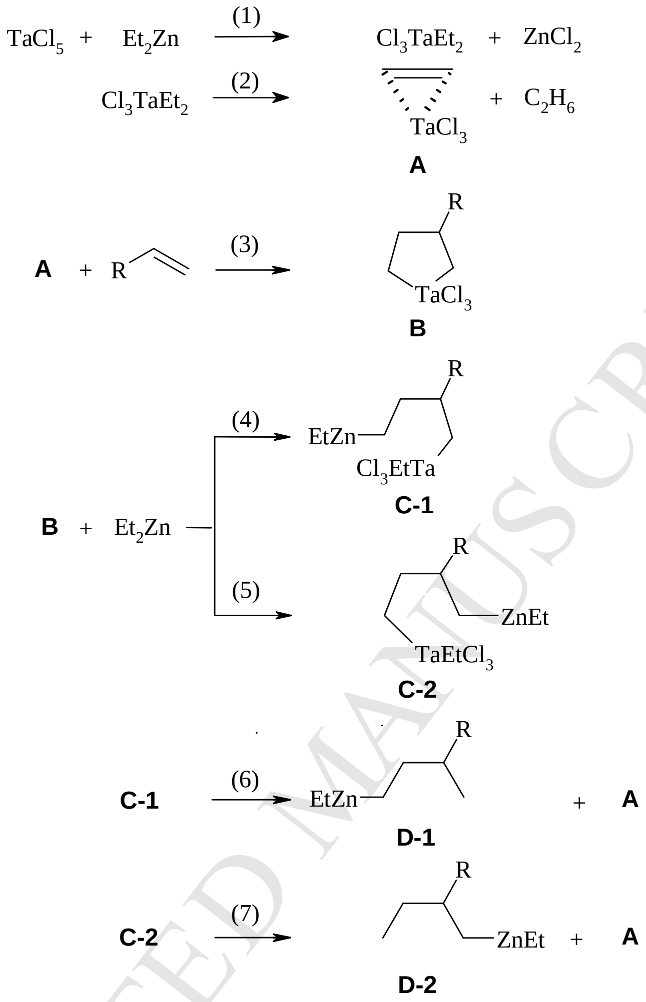
Scheme 2.


TaCl5
2Et2Zn
2EtZnCl
[Ta] = TaCl3
[Ta]
4
C2H6
R
EtZn
1
[Ta]
5
R
[Ta]
R
6
R
[Ta]
7
Et2Zn
EtZn
R
[Ta]
H
8

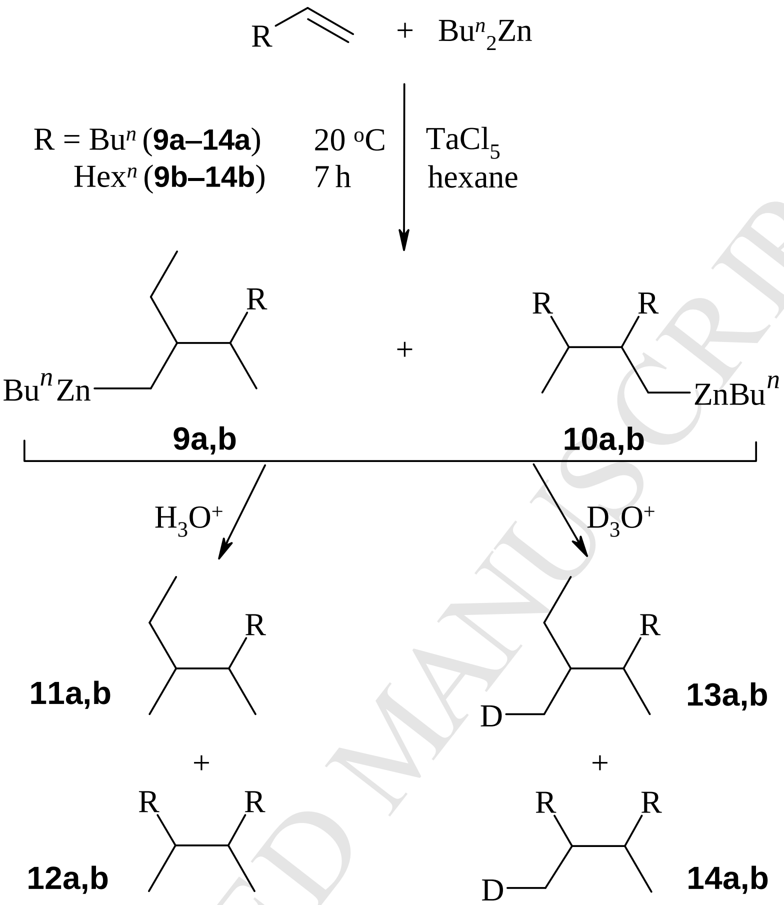
Scheme 3



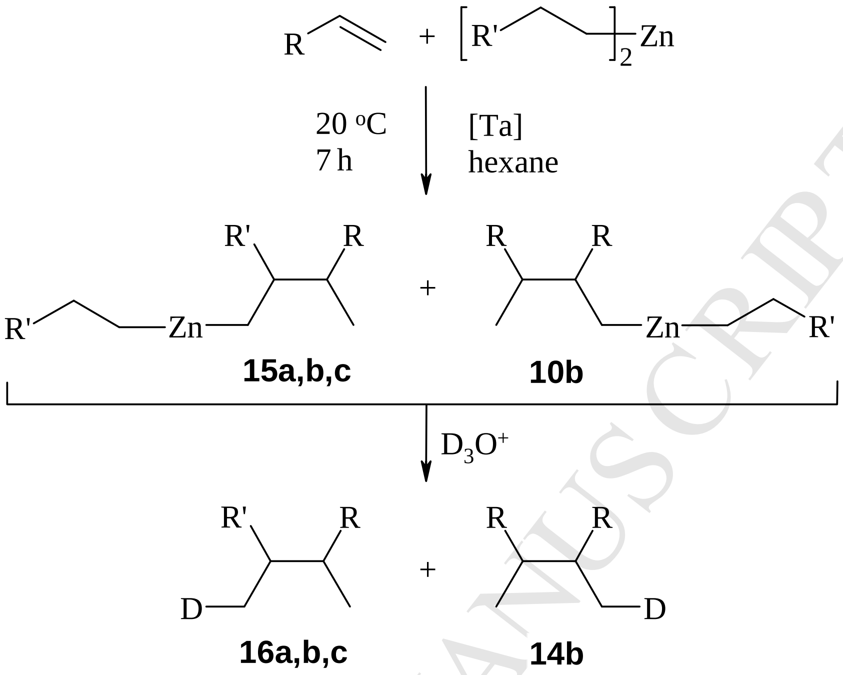
Scheme 4


TaCl5 + Et2Zn
(1)
Cl3TaEt2 + ZnCl2
Cl3TaEt2
(2)
TaCl3 + C2H6
A
A + R
(3)
R
TaCl3
B
B + Et2Zn
(4)
EtZn
R
Cl3EtTa
C-1
(5)
R
ZnEt
TaEtCl3
C-2
C-1
(6)
EtZn
R
D-1
+ A
C-2
(7)
R
ZnEt + A
D-2

Scheme 5.

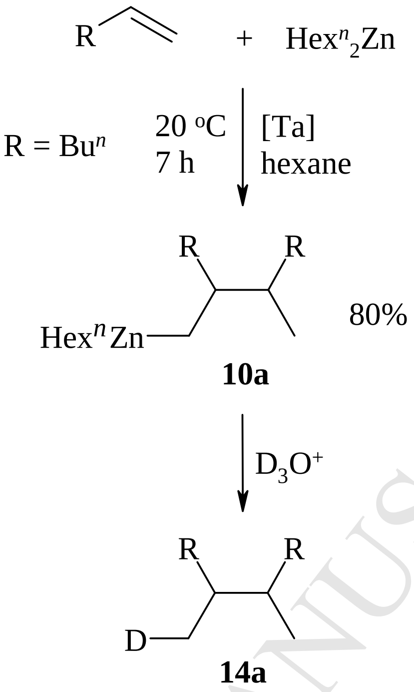

R
+ Bu$^n{}_2$Zn
R = Bu^n (**9a–14a**)
Hex^n (**9b–14b**)
20 °C
7 h
TaCl$_5$
hexane
R
Bu^{n}Zn
+
R
R
ZnBu^n
9a,b
10a,b
H$_3$O$^+$
D$_3$O$^+$
R
11a,b
R
D
13a,b
+
+
R
R
12a,b
R
R
D
14a,b

Scheme 6

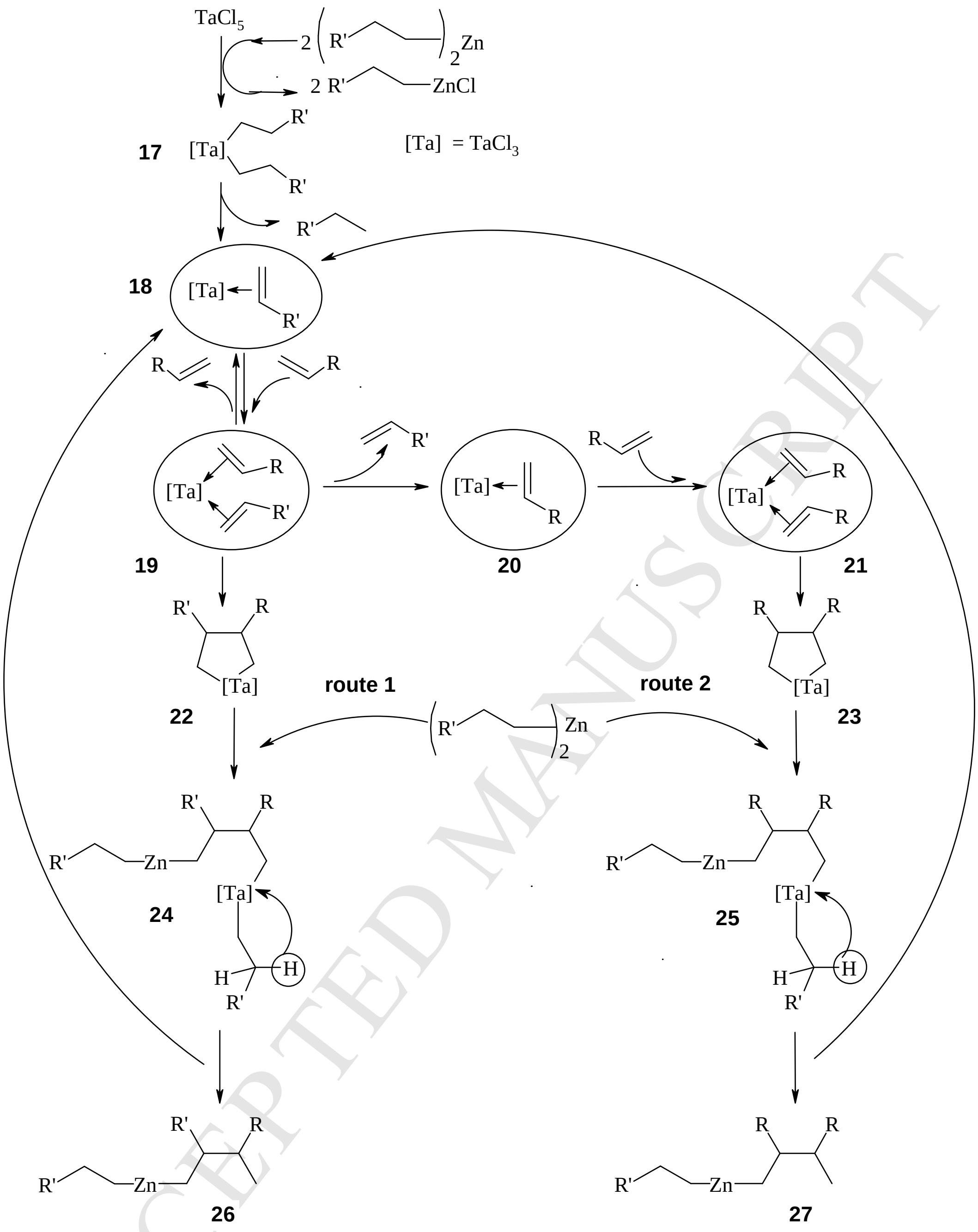


R = Hex^n, R' = CH_3 (**15a, 16a**)
R = Hex^n, R' = Pr^n (**15b, 16b**)
R = Hex^n, R' = Bu^n (**15c, 16c**)

Scheme 7.



Scheme 8.


TaCl5
2 (R')2Zn
2 R' ZnCl
17
[Ta]
[Ta] = TaCl3
18
19
20
21
22
23
route 1
route 2
24
25
26
27
Zn
H
R
R'

Scheme 9.

Highlights

- $TaCl_5$ regioselectively catalyzes the reaction of 1-alkenes with Et_2Zn.
- The ethylzincation reaction produces 3-(R-substituted)-*n*-butylzincs in high yield.
- DFT study confirms thermodynamic stability of the sole ethylzincation product.
- 1-Alkenes react with Zn *n*-dialkyls giving two types of organozincs.
- The β- and β,β′-substituted tantalacyclopentanes are proposed as key intermediates.