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Organic Chemistry

Copper-Catalyzed Selective Silicon Insertion into Carbon-Carbon Bonds of Aluminacyclopentanes

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(Presented by Academy Member Vladimer Tsitsishvili)

Abstract. A method for obtaining 1-vinyl-1-methyl-3-alkylsilacyclopentanes and 1,1–methylvinyl-trans-3,4,-di(alkyl)cyclopentanes is described. The process involves the interaction of α-olefins with triethylaluminum (TEA) and ethylaluminum dichloride (EADC) in the presence of zirconocene dichloride (Cp_2ZrCl_2) catalysts at room temperature for 8 hours. Subsequently, tetrahydrofuran (THF), methylvinyldichlorosilane, and copper (I) chloride were added at -5°C, and the reaction mixture was stirred at room temperature for additional 10 hours. The technical result of this method is the production of new organosilicon compounds that can be used in the manufacturing of polymer products. To characterize the compounds obtained, ^{1}H NMR, ^{13}C NMR and mass spectroscopy methods were used. © *2026 Bull. Natl. Acad. Sci. Georg.*

Keywords: silicon-containing compounds, organosilicon chemistry, regioselective synthesis silacyclopentanes

Introduction

Major advances in the field of organosilicon chemistry (OSC) are largely due to the introduction and development of industrial methods for OSC synthesis. Organosilicon compounds are widely used due to their unique properties. They are widely used in the production of sealants, cosmetics, household chemicals (Pakuła et al., 2023), construction materials (Grabowska and Koniorczyk, 2022), agriculture (Silva et al., 2023; Schaller et al., 2024), and other industrial applications (Satenov, 2025). Over the past 10-15 years, along with the well-known classical methods of organosilicon compound synthesis, new reactions have become widely used that open up simple, practically one-step pathways to the synthesis of unique bimetallic C-, Si-containing compounds, the functionalization of which via an active C-C bond allows silanes with a carbon-heteroatom bond of a given structure to be obtained (Shainyan, 2020; Turks, 2020; Richter and Oestreich, 2019; Tyagi, 2020; Ge, 2022). In this regard, the development of new effective methods for designing acyclic and cyclic silanes, including those containing functional groups with the participation of metal complex catalysts, is an important and urgent task.

The aim of this study is to develop new methods for constructing metal-carbon, heteroatom-carbon, and carbon-carbon bonds based on the reactions of unsaturated silanes with ‘non-hydride’ organoaluminum compounds (AOCs) using metal complex catalysts.

Materials and Methods

General reaction procedures and reagents. The reaction products were analyzed using a Chrom-5 gas chromatograph (katharometer, FID, SE-30 stationary phase, 2000x3 mm column, operating temperature 50-300°C, carrier gas – helium) or a Chrom-5 chromatograph (Katharometer, FID, PEG-6000 stationary phase, 2000x3 mm column, operating temperature 50-170°C, carrier gas – helium). Mass spectra were recorded on an MX-1306 spectrometer with an ionizing electron energy of 70 eV and an ionization chamber temperature of 200°C. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Tesla BS-567 spectrometer (100 MHz). Data for ^{1}H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (J, reported as values in hertz (Hz)), and integration. ^{13}C NMR spectra were obtained on JEOL FX-90Q (22.5 MHz) and Bruker AM-300 spectrometers (75.46 MHz) with broadband suppression of protons and in the “monoresonance” mode with partial preservation of the Overhauser effect.

All reagents for the synthesis (olefins, methylvinyldichlorosilane, dimethyl ether, THF), purchased from Aldrich. Ether solvents were kept over NaOH, passed through Al_2O_3, refluxed over sodium turnings, and distilled in a stream of argon over $LiAlH_4$. All reactions were carried out in oven-dried three necked vessels under argon (Ar) atmosphere. Each reaction vessel was equipped with a magnetic stir bar and a three-way cock to maintain a positive pressure of inert atmosphere (Ar). Reagents sensitive to the atmosphere were transferred via syringe as necessary. The reactions at room temperature were conducted at 21~22ºC (the ambient temperature). The yields of 1,1- methylvinyl-3-(alkyl)silacyclopentanes and 1,1-methylvinyl-trans-3,4-silacyclopentanes were determined by GLC analysis of the products after treated with 10% HCl.

Synthesis of 3-alkyl-substituted aluminacyclopentanes. In a 50 ml glass three necked reactor mounted on a magnetic stirrer in an argon atmosphere, at a temperature of ~ 0°C, 100 mmol of terminal alkene (hexene-1 or okten-1), 5 mmol of Cp_2ZrCl_2 are placed, 100 mmol of $AlEt_3$ is added slowly, stirred 8 hours at room temperature (21-22°C). Individual 3-alkyl-substituted aluminacyclopentanes were obtained.

Synthesis of 1,1-methylvinyl-3(*n*-alkyl)silacyclopentanes. The reactions were conducted in a 50 ml glass three-necked reactor mounted on a magnetic stirrer in an argon atmosphere. 10 mmol of aluminacyclopentane, synthesized according to the above procedure, was added at -5°C to 10 ml of THF and loaded with 20 mmol of methylvinyldichlorosilane and 12 mmol of CuCl. The temperature was slowly raised to room temperature and stirred for 10 hours. At the end of the reaction, it was hydrolyzed with a 10% HCl solution. The organic layer was extracted with ether, washed with Na_2CO_3 until neutral, and dried over $CaCl_2$.

1,1-methylvinyl-3(*n*-butyl)silacyclopentane (2 a): Yield: 60 %. Boiling point = 88 ℃ (40 mm Hg). NMR ^{1}H (δ, ppm): 0.09 (s, 3H, $SiCH_3$), 0.89 (m, 3H, CH_3), 0.63-1.78 (m, 13H, CH, CH_2), 5.14-6.12 (m, 3H, CH=). NMR ^{13}C (δ, ppm): 133.16 d (C^1), 136.61 d (C^2), -0.80 s (C^3), 10.90 t (C^4), 27.09 t (C^5), 30.28 d (C^6), 19.79 t (C^7), 35.81 t (C^8), 29.37 t (C^9), 23.06 t (C^{10}), 14.22 k (C^{11}). Mass spectrum, m/z: 182 [M^+].

1,1-methylvinyl-3(*n*-hexyl)silacyclopentane (2 b): Yield: 58 %. Boiling point = 108 ºC (20 mm Hg.). NMR ^{1}H (δ, ppm): 0.07 (s, 3H, $SiCH_3$), 0.83 (m, 3H, CH_3) 0.62-1.70 (m, 17H, CH, CH_2), 5.34-6.34

(m, 3H, CH=). NMR ^{13}C (δ, ppm): 132.96 d (C^1), 136.67 d (C^2), -0.67 c (C^3), 11.29 t (C^4), 27.09 t (C^5), 30.47 d (C^6), 19.16 t (C^7), 34.38 t (C^8), 26.90 t ($C^{9,10}$), 31.90 t (C^{11}), 23.39 t (C^{12}), 14.02 k (C^{13}). Mass spectrum, m/z: 210 [M^+].

Synthesis of 1-ethyl-trans-3,4-di(n-alkyl)aluminacyclopentanes. In a 50 ml three necked glass reactor mounted on a magnetic stirrer in an argon atmosphere, at a temperature of ~ 0°C, 10 ml. THF, 20 mmol of α – olefines (okten-1 or decene-1), 1.0 mmol of Cp_2ZrCl_2, 10 mmol Mg are placed, 15 mmol of $EtAlCl_2$ is added slowly, stirred 8 hours at room temperature (21-22°C). Individual 1-ethyl-trans-3,4-di(n-alkyl)aluminacyclopentanes were obtained.

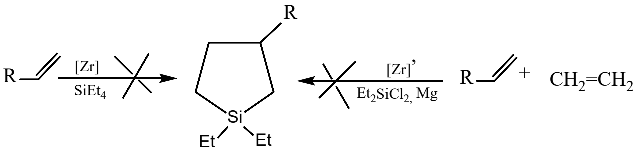
Synthesis of 1,1-methylvinyl-trans-3,4-silacyclopentanes. The study was conducted in a 50 ml three-necked glass reactor mounted on a magnetic stirrer under an argon atmosphere. 10 mmol of 1-ethyl-trans-3,4-di(n-alkyl)aluminacyclopentane, synthesized according to the above procedure, was added at -5°C to 10 ml of THF and loaded with 20 mmol of methylvinyldichlorosilane and 20 mmol of CuCl. The temperature was slowly raised to room temperature and stirred for 10 hours. At the end of the reaction, it was hydrolyzed with a 10% HCl solution. The organic layer was extracted with ether, washed with Na_2CO_3 until neutral, and then dried over $CaCl_2$.

1,1-Methylvinyl-trans-3,4-di(n-hexyl)silacyclopentane (4 a): Yield: 55 %. Boiling point = 110 ºC (1 mm Hg.). NMR ^{1}H (δ, ppm): 0.13 (s, 3H, $SiCH_3$), 0.67-0.90 (m, 6H, CH_3), 0.70 (m, 4H, CH_2), 1.10-1.44 (m, 22H, CH, CH_2). NMR ^{13}C (δ, ppm): 133.55 d (C^1), 136.29 d (C^2), -0.74 s (C^3), 14.48 t ($C^{4,7}$), 36.72 d ($C^{5,6}$), 35.09 t ($C^{8,14}$), 27.81 t ($C^{9,15}$), 29.89 t ($C^{10,16}$), 32.10 t ($C^{11,17}$), 22.87 t ($C^{12,18}$), 14.22 k ($C^{13,19}$).

1,1-methylvinyl-trans-3,4-di(n-octyl)silacyclopentane (4 b): Yield: 50 %. Boiling point = 152 ºC (1 mm Hg.). NMR ^{1}H (δ, ppm): 0.17 (s, 9H, $SiCH_3$), 0.62-0.92 (m, 6H, CH_3) 0.74 (m, 4H, CH_2), 1.08-1.52 (m, 30H, CH, CH_2); NMR ^{13}C (δ, ppm): 133.22 d (C^1), 136.67 d (C^2), -0.56 s (C^3), 14.78 t ($C^{4,7}$), 37.68 d ($C^{5,6}$), 37.22 t ($C^{8,16}$), 36.62 t ($C^{9,17}$), 35.10 t ($C^{10,18}$), 27.46 t ($C^{11,19}$), 32.24 t ($C^{12,20}$), 23.42 t ($C^{13,21}$), 22.86 t ($C^{14,22}$), 14.46 k ($C^{15,23}$).

Results and Discussion

To advance research in the field of catalytic cyclometallation of olefins and acetylenes using alkyl derivatives of non-transition metals to form corresponding metal cycles, we hypothesized the possibility of direct cyclosilylation of unsaturated compounds using $RR'SiCl_2$ to obtain silacyclopentanes or silacyclopentanes in a one-pot process:



All our attempts at cyclosilylating olefins or 1,2-disubstituted acetylenes using $SiEt_4$ or Et_2SiCl_2 in the presence of a chlorine ion acceptor (activated metallic Mg) under the action of Ti or Zr complex-based catalysts were unsuccessful. We were unable to obtain silacyclopentanes regardless of changes in catalyst concentration, monomer ratio, and reaction conditions.

During these studies, we discovered that aluminacyclopentanes synthesized *in situ* react quite easily with R_2SiCl_2 under the action of copper-containing complex catalysts to form the corresponding silacyclopentanes. This results in the replacement of the aluminum atom in the initial aluminacyclopentanes with silicon atoms, leading to the formation of silacyclopentanes.

Subsequent experiments were focused on finding the optimal conditions for this reaction and creating highly active catalysts capable of selectively performing transmetalation process. The goal was to develop a one-step preparative method for the synthesis of practically important silacyclopentanes.

The studies showed that the alkylaluminacyclopentanes generated *in situ* can undergo transmetalation with RR'$SiCl_2$ in the presence of metal complex catalysts. Among the catalysts tested based on Fe compounds ($Fe(acac)_3$, $FeCl_3$), Co ($CoCl_2$, $Co(CH_3COO)_2$, $Co(acac)_2$), Ni ($NiCl_2$, $Ni(acac)_2$), Cu ($Cu(acac)_2$, CuCl, CuI, CuBr), Rh ($RhCl_3$), the best results were obtained with the participation of monovalent copper salts (Table).

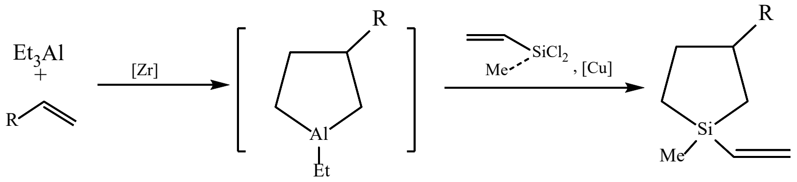
Table. Dependence of the yield of silacyclopentane 2a on copper halides

[Cu]	Yield of silacyclopentane 2a, %
CuCl	60
CuI	45
CuBr	40
Without catalyst	-

Reaction conditions: [Al]:1,1-methylvinyldichlorosilane: [Cu]= 10:20:12, ~21-22°C, 10 h, THF.

For example, when 1-ethyl-3(n-butyl)aluminacyclopentane interacts with a double excess of methylvinyldichlorosilane in the presence of both stoichiometric and catalytic (~12% mol) amounts of CuCl at room temperature (~21-22°C) for 10 hours in THF media, 1,1-methylvinyl-3-(n-butyl)silacyclopentane is formed with a yield of ~60% 2a.

Without a catalyst (CuCl), the reaction does not proceed (Scheme 1).



1 a, b

2 a, b

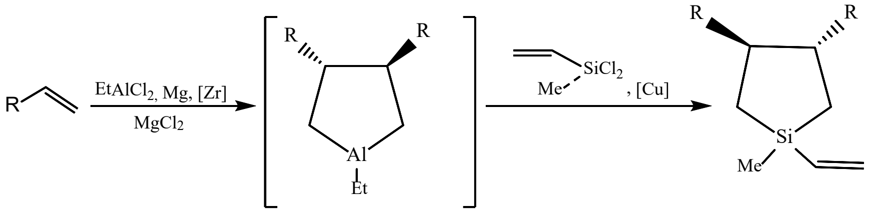
[Zr]= Cp_2ZrCl_2, a: R=*n*-C_4H_9, b: R=*n*-C_6H_{13}, [Cu] = CuCl.

Scheme 1. Synthesis of 1,1-methylvinyl-3(*n*-alkyl)silacyclopentanes.

The desired products are formed only with the participation of Et_3Al and the catalyst Cp_2ZrCl_2. In the presence of other aluminum compounds (e.g., Et_2AlCl, $EtAlCl_2$, i-Bu_3Al, i-Bu_2AlCl, i-Bu_2AlH) or other catalysts $ZrCl_4$, $Zr(OBu)_4$, Cp_2TiCl_2, $TiCl_4$, $Ti(OBu)_4$, the desired products (2) are not formed. A necessary condition for obtaining the desired products (2) is the presence of the starting compound methylvinyldichlorosilane (for the formation of the silacyclopentane fragment) and the catalyst CuCl. Conducting the reaction in the presence of a catalyst Cp_2ZrCl_2 greater than 6 mol% and CuCl above 15% relative to the olefin does not lead to a significant increase in the yield of products (2). Using a catalyst Cp_2ZrCl_2 less than 4 mol % and CuCl less than 5 mol % in the reaction reduces the yield of 1-vinyl-1-methyl-3-alkylsilacyclopentanes (2), which is associated with a decrease in catalytically active centers in the reaction mixture. The experiments were carried out at room temperature (21-22°C).

At higher temperatures (e.g., 60°C), the amount of side products increases slightly. At lower temperatures (e.g., 0°C), the reaction rate decreases. Changing the ratio of the starting reagents to increase the content of triethylaluminum (Et_3Al) or 1-methyl-1-vinyldichlorosilane relative to α-olefin does not lead to a significant increase in the yield of desired products (2). A decrease in the amount of starting reagents relative to α-olefin reduces the yield (2).

Positive results in the catalytic metallation of 3-alkylaluminacyclopentanes allowed us to carry out regio- and stereoselective synthesis of trans-3,4-dialkylsilacyclopentanes. Thus, the interaction of 1-ethyl-trans-3,4-di(n-hexyl)aluminacyclopentane (3a) with a double excess of 1,1-methylvinyldichlorosilane under the optimal conditions found (THF, ~20°C, 10 h, 20 mol % CuCl), 1,1-methylvinyl-trans-3,4-di(n-hexyl)silacyclopentane (4a) was obtained with a yield of ~55 % according to Scheme 2.



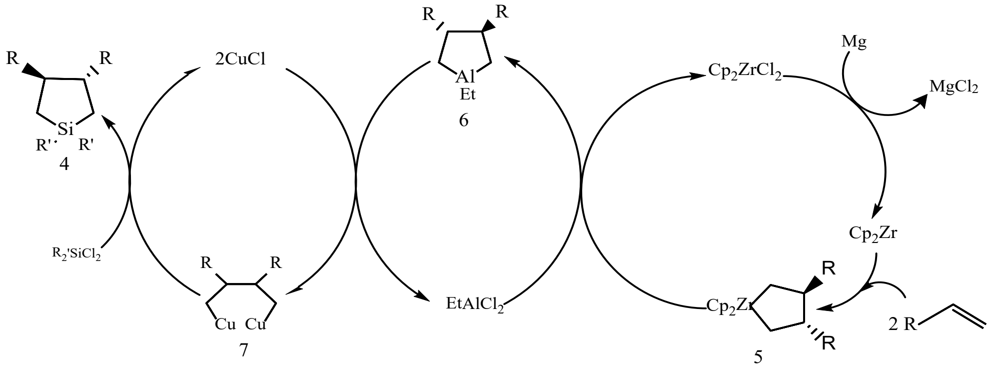
3 a-b 4 a-b

[Zr]= Cp_2ZrCl_2, a: R=n-C_6H_{13}, b: R=n-C_8H_{17}, [Cu] = CuCl.

Scheme 2. Synthesis of 1,1-methylvinyl-trans-3,4-silacyclopentanes.

One of the advantages of the developed method is the production of silacyclopentanes with high regio- and stereoselectivity based on available Et_3Al or $EtAlCl_2$, α-olefins, and silicon dihalides without preliminary isolation of substituted aluminacyclopentanes formed under reaction conditions (Scheme 3).

Apparently, the general scheme of the Cp_2ZrCl_2- and CuCl-catalyzed reaction consists of two catalytic cycles, which include the selective generation of zirconacyclopentane intermediates 5, the formation of substituted aluminacyclopentanes 6, the formation of intermediate 1.4-dicuprate reagents 7, and their subsequent transmetalation with silicon dihalides leads to silacyclopentanes 4 according to Scheme 3.



Scheme 3. Catalytic cycle of silacyclopentane formation.

The results obtained show that copper halide-catalyzed transmetalation of substituted aluminacyclopentanes with alkylhalides silicon opens up a new promising route to the synthesis of previously difficult-to-obtain 3-alkyl or trans-3,4-dialkylsilacyclopentanes with high regio- and stereoselectivity.

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ორგანული ქიმია

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(წარმოდგენილია აკადემიის წევრის ვ. ციციშვილის მიერ)

ნაშრომში აღწერილია 1-ვინილ-1-მეთილ-3-ალკილსილაციკლოპენტანებისა და 1,1–მეთილ-ვინილ-ტრანს-3,4-დი(ალკილ)ციკლოპენტანების მიღების მეთოდი. პროცესი მოიცავს α-ოლეფინების ურთიერთქმედებას ტრიეთილალუმინსა (TEA) და ეთილალუმინის დიქლორიდთან (EADC) ცირკონოცენის დიქლორიდის (Cp_2ZrCl_2) კატალიზატორის თანდასწრებით, ოთახის ტემპერატურაზე 8 საათის განმავლობაში. ამის შემდეგ რეაქციულ ნარევს დაუმატეს ტეტრაჰიდროფურანი (THF), მეთილვინილდიქლოროსილანი და სპილენძის(I) ქლორიდი –5°C ტემპერატურაზე, ხოლო შემდეგ ნარევი ურიეს ოთახის ტემპერატურაზე დამატებით 10 საათის განმავლობაში. აღნიშნული მეთოდის ტექნიკური შედეგია ახალი ორგანოსილიციუმის ნაერთების მიღება, რომლებიც შეიძლება გამოყენებულ იქნეს პოლიმერული პროდუქტების წარმოებაში. მიღებული ნაერთების დასახასიათებლად გამოყენებულ იქნა ^{1}H NMR, ^{13}C NMR და მას-სპექტროსკოპიის მეთოდები.

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