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Highly Efficient and Reusable Alkyne Hydrosilylation Catalysts Based on Rhodium Complexes Ligated by Imidazolium-Substituted Phosphine

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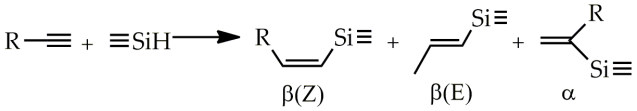
Abstract: Rhodium complexes ligated by imidazolium-substituted phosphine were used as catalysts in the hydrosilylation of alkynes (1-heptyne, 1-octyne, and phenylacetylene) with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) or triethylsilane (TES). In all cases, the above complexes showed higher activity and selectivity compared to their precursors ($[Rh(PPh_3)_3Cl]$ and $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$). In the reactions with aliphatic alkynes (both when HMTS and TES were used as hydrosilylating agents), β(Z) isomer was mainly formed, but, in the reaction of phenylacetylene with TES, the β(E) product was formed. The catalysts are very durable, stable in air and first and foremost insoluble in the reactants which facilitated their isolation and permitted their multiple use in subsequent catalytic runs. They make a very good alternative to the commonly used homogeneous catalysts.

Keywords: hydrosilylation; alkynes; heterogeneous catalysis; rhodium catalysts; ionic liquids

1. Introduction

Vinylsilanes and siloxanes due to a relatively low cost of their synthesis, low toxicity, and good chemical stability are valuable raw materials applied in many organic syntheses such a nucleophilic substitution, alkylation [1,2], and coupling [3,4]. However, the course of the above syntheses and formation of desired products are influenced by the kind and purity of isomer of vinyl organosilicon derivative employed. This is why various methods are developed for the synthesis of the aforementioned derivative to ensure high regio- and stereoselectivity of vinylsilanes and siloxanes formed. One of the most popular and commonly applied (also on a commercial scale) methods of synthesis of organofunctional silicon compounds is hydrosilylation [5,6], which enables obtaining vinyl derivatives in the reaction with alkynes. However, the reaction course and the kind of products formed depend on many factors such as the type of alkyne (terminal or internal) and hydrogen silane (siloxane) as well as reaction conditions (temperature, time, the kind of solvent) and particularly the kind of catalyst used [7]. In the case of hydrosilylation of terminal alkynes, there is a possibility of the formation of three isomers β-(E), β-(Z), and α as shown in Scheme 1:



Scheme 1. The example hydrosilylation reaction of terminal alkynes with hydrosilanes.

The kind of isomer formed depends on the way of ≡Si–H addition to the C≡C triple bond. In the former two cases, the silicon atom bonds to the terminal carbon atom which results in β-(E) isomer (if *cis*-addition occurs) or β-(Z) isomer (if *trans*-addition occurs). On the other hand, the reverse addition leads to the geminal vinyl silane (α isomer) as an internal adduct.

As mentioned above, the catalyst has a significant influence on the reaction course. The catalysts used for alkyne hydrosilylation are diverse simple compounds and complexes of transition metals such as Rh [8], Pt [9,10], Ru [11], Ni [12], Co [13], and Ir [13]. Their activity in many cases is high, but they differ in selectivity [7].

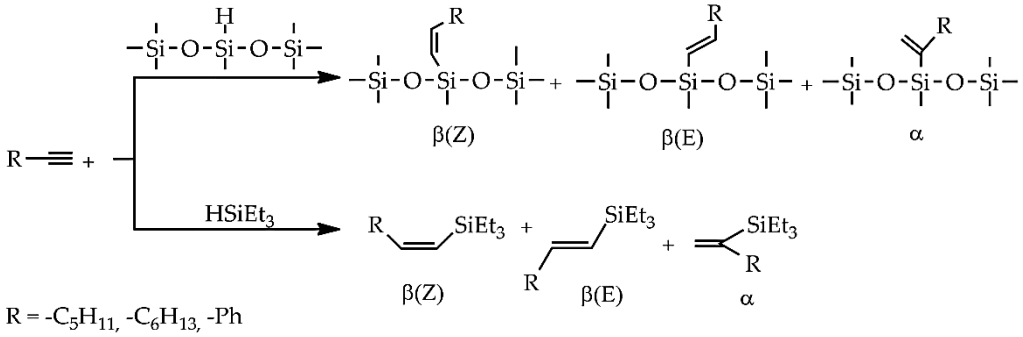
For instance, platinum catalysts (including Karstedt's catalyst), which are among the most popular catalysts for hydrosilylation, in the case of the reaction with terminal alkynes preferentially form β(E) isomer as the main product and, to a small extent, also α isomer. On the other hand, β(Z) isomer is not formed (or formed only in negligible amounts) in the reactions catalyzed by platinum catalysts [14], whereas rhodium catalysts favor mainly the formation of β(Z) product [8], except for cationic rhodium complexes, e.g., [{Rh(cod)$_2$}BF$_4$/PPh$_3$], in the presence of which the hydrosilylation reactions result in the formation of predominant amounts of the β(E) product [15,16]. In the literature, there are reports on the effect of different factors on the stereoselectivity of the reaction of hydrosilylation conducted in the presence of rhodium complexes. They include the kind of the structure of starting compounds [17], the type of solvent [16,18] as well as the way and sequence of adding reactants [19–21]. On the basis of the above data, some conclusions can be drawn that will enable directing the reaction to the desired isomer. For example, the reactions of silanes with electron-donor substituents (e.g. trialkylsilanes) and terminal alkynes not containing bulky substituents (with a large steric hindrance) result mainly in the formation of β(Z) isomer, whereas the reactions of silanes with electron-withdrawing substituents (e.g. alkoxy- or chlorosilanes) lead preferentially to the formation of β(E) isomer [20,22]. This effect is enhanced when an alkyne contains large substituents. Quite a large group of catalysts used in the hydrosilylation of terminal alkynes consists of various rhodium(I)-NHC complexes which in most cases catalyze the selective formation of β(Z) product [23–25]. However, if the steric hindrance caused by substituents both in NHC ligand and alkyne is large, then the formation of mostly β(E) product is possible [26]. The use of complexes with NHC ligands, as well as the addition of other ligands (e.g., phosphines) that are sensitive to various contaminants and are unstable in the presence of oxygen and moisture, results in the necessity of performing the reaction in a closed system in the atmosphere of inert gases while maintaining an appropriate level of purity of the reagents [12,23,27]. This is why researchers keep searching for new catalysts that are characterized by high activity and selectivity as well as stability and resistance to contaminants. An alternative solution can be heterogeneous catalysts.

Our research group has been involved for several decades in the development of new catalysts for hydrosilylation. The application of ionic liquids as immobilizing agents for transition metal complexes is an interesting aspect of the above research [28–34]. In all the cases, ionic liquids played the role of a solvent and immobilizing agent for metal complexes which provided a biphasic system with reagents. All the above systems were very effective in the hydrosilylation of olefins. However, ionic liquids can also be employed in another way, i.a. as structural components of the complexing ions [35,36]. Very recently, we have obtained rhodium and platinum complexes with phosphine ligands that were functionalized with imidazolium ionic liquids [37]. As precursors of the above complexes, we have employed Wilkinson's catalyst or *bis*[chloro(1,5-cyclooctadiene)rhodium(I)]. Catalytic studies of olefin hydrosilylation proved very high activity, durability, and stability of the obtained catalysts as well as the possibility of their multiple use [35].

In this paper, we present the results of the study on the catalytic activity of rhodium complexes with phosphine ligands functionalized with ionic liquids for reactions of hydrosilylation of terminal alkynes. Our study was aimed at determining the effect of the kind of catalyst, olefin, and hydrosilylating agent on the yield and selectivity of the hydrosilylation process as well on multiple use of the same portion of the catalyst.

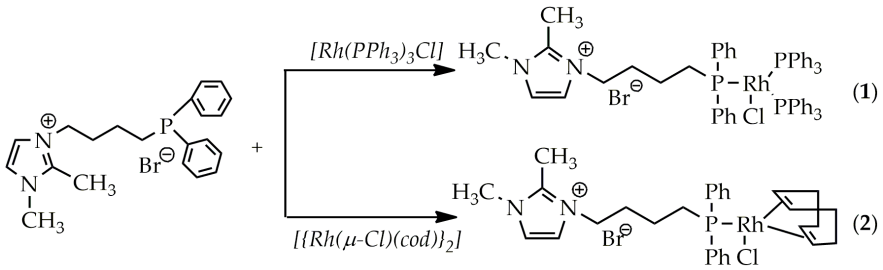
2. Results and Discussion

The reaction of alkyne hydrosilylation was studied according to Scheme 2, using three kinds of alkynes.



Scheme 2. The reactions of the hydrosilylation of alkynes studied.

We have employed aliphatic alkynes differing in their chain length, 1-heptyne and 1-octyne, as well as an alkyne that contains an aromatic ring in its structure, namely phenylacetylene. Hydrosilylating agents were 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) and triethylsilane (TES). The former of the compounds, due to its high stability, is frequently employed in the synthesis of organosilicon compounds. Moreover, it is a good model compound for obtaining vinylpolysiloxanes, whereas triethylsilane, due to its electron donor properties is a popular reducing agent and a starting material for obtaining vinylsilanes. As catalysts for the above reactions, we have employed Rh(I) complexes that have been recently obtained by our research group. They contain phosphine ligands in which imidazolium ionic liquid is a substituent. Synthesis of the ligands was described in our earlier paper [37], whereas syntheses of rhodium complexes (**1** and **2**) ligated by these ligands are presented in Scheme 3.



Scheme 3. Syntheses of rhodium complexes ligated by imidazolium-substituted phosphine.

For the sake of comparison, the catalytic study also included both precursors of rhodium catalysts, i.e., Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$ and cyclooctadiene rhodium complex $[\{Rh(cod)(\mu\text{-}Cl)\}_2]$. The complexes were highly active for hydrosilylation of alkenes and, for this reason, we tested their effectiveness in the reactions with alkynes. Phosphine complexes (**1** and **2**), contrary to the starting complexes (precursors), are insoluble in reactants. Moreover, they are characterized by high thermal stability [38] and resistance to oxidation and moisture. This is why they can be used without the necessity of reagent purification and under normal conditions (in the presence of air in open systems).

At the initial stage, when optimizing hydrosilylation reaction conditions, we performed test reactions in the presence of Wilkinson's catalyst and determined that the optimal stoichiometric ratio of reactants is [HSi≡]:[RC≡CH] = 1.3:1. The excess of HSi≡ enabled obtaining the considerably higher conversion of alkyne. Moreover, test reactions were conducted at different temperatures and the optimum reaction temperature appeared to be 90 °C. For example, when the reaction of 1-octyne with HMTS was carried out at 60 °C for four hours, the alkyne conversion was 11%, whereas at 90 °C the conversion reached 100% already after one hour. Such results were obtained at the catalyst

concentration of 1×10^{-3} mol/L mol HSi≡. For this reason, to compare the activity of all the catalysts studied, the ratio [HSi≡]:[RC≡CH]:[cat] = $1.3{:}1{:}2 \times 10^{-3}$ was used. Results of our earlier studies of the reaction of hydrosilylation conducted in the presence of commercially available rhodium catalysts have shown that the optimal reaction time is one hour. However, to verify these results in the presence of the catalysts tested in the present study, we carried out FT-IR in situ analysis for two catalytic systems (the complex **1** and the Wilkinson's catalyst) that enabled us to monitor the reaction course in real time. As test reactions, we have chosen reactions of HTMS and 1-octyne. During the experiments, we kept track of the decay of the HSi≡ band originated from HMTS (913 cm^{-1}) and the increase in the band originated from the C=C bond (1600 cm^{-1}) that shows the formation of the hydrosilylation reaction product (Figure S41 and Figure S42 in Supplementary Materials). To determine the reaction profiles, we have used the HSi≡ conversion calculated as a change in the area of the HSi≡ band (Figure 1). Non-stoichiometric amount of the above reactant, which is also shown by the presence of the remainder of the HSi≡ band (Figure S41 and Figure S42), was taken into account during the determination of the reaction profiles and converted to the stoichiometric amount.

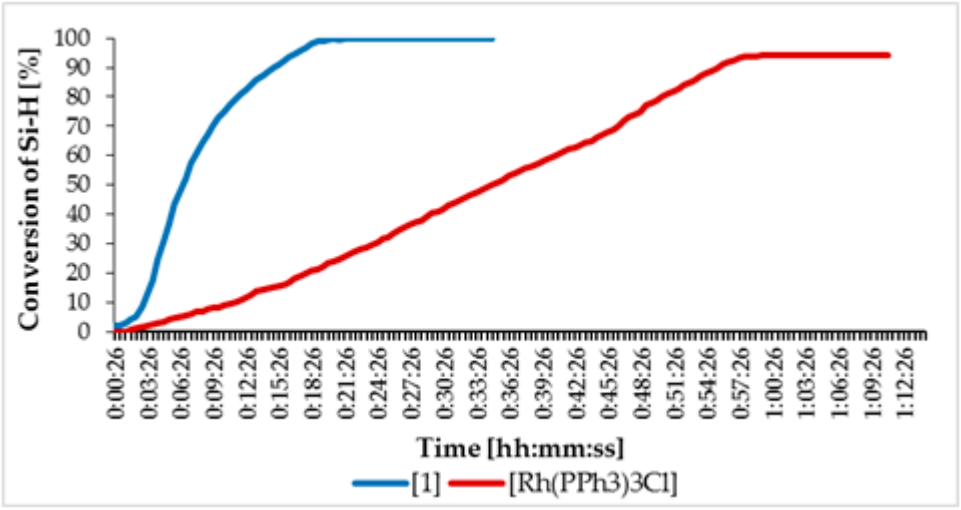


Figure 1. The dependence of the conversion of Si–H on time for the reaction of 1-octyne with 1,1,1,3,5,5,5-heptamethyltrisiloxane in the presence of catalyst **1** and Wilkinson's catalyst.

The measurements showed that the new complex **1** makes it possible to reach full conversion considerably faster than the Wilkinson's catalyst. In the case of the complex 1, full conversion was reached as early as after 15 min, whereas, in that of Wilkinson's catalyst, it took 55 min. Therefore, to compare the activity of all complexes in the same conditions and to achieve the highest conversion, we decided to conduct all the further reactions at 90 °**C** for 1 h in air in the open system without a solvent. The reactions of alkynes with HMTS were performed first. After the reaction completion, the catalyst was in the form of a fine suspension; therefore, its separation from the post-reaction mixture was carried out by centrifugation. After the separation, the post-reaction mixture was analyzed chromatographically and the obtained results are presented in Table 1.

Chromatographic and spectroscopic analyses of the post-reaction mixture showed the presence of isomers *β(Z)*, *β(E)* and *α*. The obtained results confirmed the high catalytic activity of rhodium phosphine complexes (**1**, **2**) in all the reaction systems (Table 1). The conversion in the reaction of hydrosilylation of aliphatic alkynes has been considerably higher (100%) than in the reaction with phenylacetylene (87%). Some surprise is relatively low activity and selectivity (and its lack in the case of the reaction with phenylacetylene) of the catalyst [{Rh(μ-Cl)(cod)}$_2$] since this complex belongs to the most active catalysts for hydrosilylation of alkenes [6,7]. New rhodium complexes (**1** and **2**) do not lead to the formation of α isomer, but only to β isomers. For the majority of the complexes studied (except for the catalyst [{Rh(μ-Cl)(cod)}$_2$]), *cis* isomer is overwhelmingly formed, which is

in agreement with results obtained for other rhodium complexes. However, selectivities obtained in reactions conducted in the presence of the catalysts **1** and **2** are higher than those observed in the case of reactions catalyzed by precursors of the rhodium catalysts. One can also notice that, in the case of aliphatic alkynes, the selectivity towards β(Z) isomer increases with the chain growth. It is modest growth, albeit the chain lengths of both alkynes differ only by one carbon atom. When comparing selectivities of the catalysts **1** and **2**, one can observe that in each case the catalyst **1** is characterized by a higher selectivity. To a large extent, it can be explained by differences in the structure and steric hindrance of both complexes. Taking into consideration the mechanism of catalysis occurring in analogous phosphine and cyclooctadiene complexes [7], one can assume that, in the case of the complex **1**, the activation of the catalyst occurs through the detachment of one of the PPh_3 ligands, whereas in that of the complex **2** the rupture of one coordinative bond in the cyclooctadiene group occurs. Thereby, the steric hindrance in the complex **2** is greater than that in the complex **1** which results in a decrease in the selectivity and the formation of a large amount of the *trans* isomer.

Table 1. Conversion of alkynes and selectivity for isomers in the hydrosilylation of RC≡CH with HMTS.

Catalyst	R					
	–C_5H_{11}		**–C_6H_{13}**		**–Ph**	
	Conv. [%]	**α/β(Z)/β(E) [%]**	**Conv. [%]**	**α/β(Z)/β(E) [%]**	**Conv. [%]**	**α/β(Z)/β(E) [%]**
[$Rh(PPh_3)_3Cl$]	100	5/80/15	94	0/95/5	99	0/94/6
1	100	0/91/9	100	0/96/4	70	0/100/0
[{Rh(μ-Cl)(cod)}$_2$]	100	0/54/46	95	12/50/38	0	0
2	100	0/88/12	100	0/89/11	87	0/86/14

[RC≡CH]:[HSi≡]:[cat] = 1:1.3:2 × 10^{-3}; T = 90 °C, t = 1 h.

The catalytic study on the reaction between phenylacetylene and HMTS has shown that the catalyst **1** (where Wilkinson's catalyst was the metal precursor) was characterized by a higher selectivity towards the *cis* product (100%) compared to that of its precursor (in the case of the precursor the *trans* product was formed as well). Hydrosilylation of phenylacetylene catalyzed by the complex **2** also results in the formation of the *cis* product; however, in that case, the selectivity was 86%. The formation of predominant amounts of the *cis* isomer is frequently observed for hydrosilylation reactions catalyzed by neutral rhodium complexes [6,7].

Analogous measurements of catalytic activity were carried out for hydrosilylation of alkynes with triethylsilane. In addition, in this case, the catalysts **1** and **2**, contrary to their precursors, were insoluble in the reactants; therefore, after the reaction, the catalyst was isolated from the mixture by centrifugation. Then, the composition of the post-reaction mixture was determined by using chromatographic analysis and results of the determination are presented in Table 2.

Table 2. The conversion of alkynes and selectivity to isomers in the hydrosilylation of RC≡CH with TES.

Catalyst	R					
	–C_5H_{11}		**–C_6H_{13}**		**–Ph**	
	Conv. [%]	**α/β(Z)/β(E) [%]**	**Conv. [%]**	**α/β(Z)/β(E) [%]**	**Conv. [%]**	**α/β(Z)/β(E) [%]**
[$Rh(PPh_3)_3Cl$]	87	0/95/5	79	0/97/3	88	0/25/75
1	100	0/93/7	95	0/95/5	89	0/17/83
[{Rh(μ-Cl)(cod)}$_2$]	85	20/76/4	97	21/79/0	0	0
2	100	0/89/11	100	0/92/8	96	0/53/47

[RC≡CH]:[HSi≡]:[cat] = 1:1.3:2 × 10^{-3}; T = 90 °C, t = 1 h.

Based on the performed measurements, one can say that in all the cases the reactions catalyzed by the complexes **1** and **2** resulted in higher yields than those catalyzed by the precursors. In the case of hydrosilylation of aliphatic alkynes, an analogous tendency is observed as that occurring for the

reactions with HMTS, i.e., that the selectivity towards the formation of *cis* isomers increases with the growth of chain lengths. In addition, a bit higher effectiveness of the complex **1**, compared to the complex **2**, was established. A relatively low activity was also confirmed and, in particular, low selectivity in the reactions catalyzed by the complex [{Rh(μ-Cl)(cod)}$_2$]. However, the most interesting results were observed in the case of the reaction between TES and phenylacetylene. Apart from the total lack of activity of the complex [{Rh(μ-Cl)(cod)}$_2$], in other cases, a change in the selectivity to the predominant formation of the *trans* isomer was found. As it was mentioned earlier, the preference for the formation of a particular isomer is determined by steric and induction effects. On the one hand, the phenyl group makes some steric hindrance, but in the reaction with HMTS, which is also a bulky molecule, the *cis* isomer is preferentially formed. In this case, the steric effects are enhanced by the induction effects because triethylsilane is a strong electron-donor agent and, as a result of the interaction with phenyl group (from phenylacetylene), it favors the formation of the *trans* product. Similar effects were observed in the reaction of hydrosilylation of phenylacetylene with dimethylphenylsilane in the presence of Rh-NHC complexes [20]. The predominant formation of the *trans* product is not surprising in the case of platinum catalysts, but in that of rhodium catalysts, it is a rare case [8,16].

As was already mentioned, rhodium complexes (**1** and **2**) were insoluble in the reactants what enabled their isolation from the post-reaction mixture. However, due to the high dispersion of the catalyst which formed a fine suspension and sedimented very slowly, the separation of the catalyst from the post-reaction mixture was ineffective. For this reason, we employed a rotary centrifuge which enabled the fast separation of the catalyst from the mixture. The isolated catalyst was reused in the subsequent catalytic runs, and its activity was determined. The isolation and reusing were performed for the complex **1** which was characterized by higher activity and selectivity in all the above reactions. As a test reaction, we chose hydrosilylation of 1-octyne with HMTS. After each catalytic run, the mixture was centrifuged, followed by the collection of products (colorless and clear liquid) with a syringe. The products were subjected to chromatographic and spectral analyses and the isolated catalyst was reused in a next catalytic run carried out after a fresh portion of the reaction substrates was added. In this way, we conducted five catalytic runs and the obtained results are presented in Table 3.

Table 3. The conversion and selectivity for hydrosilylation of 1-octyne with HMTS in subsequent catalytic runs catalyzed by the same portion of the catalyst **1** isolated from the post-reaction mixture by centrifugation.

No. of Catalytic Run	Conv. of Alkyne [%]	Selectivity α/β(Z)/β(E) [%]
1	100	0/96/4
2	95	0/91/9
3	90	0/88/12
4	70	0/86/14
5	65	0/86/14

[RC≡CH]:[HSi≡]:[cat] = 1:1.3:2 × 10^{-3}; T = 90 °C, t = 1 h.

The results show that catalytic activity of the complex **1** in subsequent catalytic runs is very high, particularly in the first three runs. In the further runs, the conversion of 1-octyne decreases which can be explained by a gradual loss of catalyst as a result of incomplete centrifugation, i.e., only partial catalyst isolation. The slow sedimentation of the catalyst was the reason for which centrifugation was carried out only for a few minutes. The evaluation of the centrifugation effectiveness was based on the visual observation of the separation of two phases. This appeared to be not quite appropriate. This is why we decided to check it by using a different means of isolation. The post-reaction mixture was subjected to filtration followed by placing the filter with the precipitate in the reaction mixture and repeating the catalytic run. The conversion and selectivity in the subsequent runs are presented in Table 4. No significant reduction in the conversion was observed, contrary to the case when the catalyst was reused after centrifugation. This allows supposing that the decrease in the conversion observed previously was the effect of the incomplete isolation.

Table 4. The conversion and selectivity for hydrosilylation of 1-octyne with HMTS in subsequent catalytic runs catalyzed by the same portion of the catalyst **1** isolated from the post-reaction mixture by filtration.

No. of Catalytic Run	Conv. of Alkyne [%]	Selectivity α/β(Z)/β(E) [%]
1	100	0/96/4
2	98	0/94/6
3	98	0/94/6
4	95	0/92/8
5	93	0/90/10

[RC≡CH]:[HSi≡]:[cat] = 1:1.3:2 × 10^{-3}; T = 90 °C, t = 1 h.

A deterioration of selectivity in subsequent runs was also observed. It can be caused by catalyst modification which occurs with time. Taking into consideration that the concentration of β(E) isomer increases (which according to the literature data is observed for complexes with a bulky steric hindrance), one can suppose that, in subsequent catalytic cycles, due to weakly coordinating properties of imidazolium substituent, binding of reagents or aggregation of the complex occur which results in a larger steric hindrance. However, the possibility of at least fivefold use of the same portion of catalyst significantly reduces the necessary amount of the catalyst and thereby decreases the synthesis costs.

3. Materials and Methods

3.1. Materials

All the reagents used in the presented experiments, such as 1-octyne (97%), 1-heptyne (98%), phenylacetylene (98%), 1,1,1,3,5,5,5-heptamethyltrisiloxane (97%), triethylsilane (99%), and n-decane (99%), were supplied by Sigma Aldrich (Poznań, Poland) and used as received. Wilkinson's catalyst and chloro(1,5-cyclooctadiene)rhodium(I) dimer were also purchased from Sigma Aldrich (Poznań, Poland).

3.2. Analytical Techniques

The yield of the product of hydrosilylation of alkynes was determined by using a Clarus 680 gas chromatograph (Perkin Elmer, Shelton, CT, USA) equipped with a 30 m capillary column Agilent VF-5ms (Santa Clara, CA, USA) and TCD detector, employing the following temperature program: 60 °C (3 min.), 10 °C min^{-1}, and 290 °C (5 min.). Characteristic retention times were used for partial identification of the obtained products. The GC-MS analysis was conducted using a Varian 3300 chromatograph (Mundelein, IL, USA) equipped with a 30 m DB-1 capillary column connected to the Finnigan Mat 700 mass detector (Mundelein, IL, USA). For the products obtained, NMR spectra were made with Bruker BioSpin (400 MHz) spectrometer (Ettlingen, Germany) using $CDCl_3$ and CD_3CN as a solvent, with tetramethylsilane as the internal standard. Proton chemical shifts are shown in parts per million (δ ppm). The FT-IR in situ measurements were performed using a Mettler Toledo ReactIR 15 instrument (Giessen, Germany). The spectra were recorded with 256 scans for 1 h at 30 s intervals with the resolution of 1 cm^{-1}. Changes in the intensity of the bands at 913 cm^{-1} and 1600 cm^{-1} were recorded using an ATR probe with a diamond window. During the experiments, the decay of the HSi≡ band originated from HMTS (913 cm^{-1}) and the increase in the band originated from the C=C bond (1600 cm^{-1}) that shows the formation of the hydrosilylation reaction product (Figure S41 and Figure S42 in Supplementary Materials) were tracked. CHN elemental analyses were performed on an elemental analyzer Vario EL III (Elementar Analysensysteme GmbH, Langenselbold, Germany).

3.3. Synthesis of Transition-Metal Based Complexes

Transition-metal based complexes were prepared using the Schlenck technique. In the Schlenck's tube equipped with a magnetic stirrer, a portion of rhodium precursor ($[Rh(Cl)(PPh_3)_3]$ or $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$) with phosphine ligand (3-(4-(diphenylphosphanyl)butyl)-1,2-dimethylimidazolium

bromide) was dissolved in toluene. The mixture was stirred for 24 h at room temperature and, after filtration, evaporation of the solvent, and drying under vacuum, the final product was obtained. The detailed synthesis procedures of rhodium ({1,2-dimethyl-3-(diphenylphosphine) butylimidazoliumbromide}bis(triphenylphosphine)chloridorhodium(I) (**1**) and {1,2-dimethyl-3-(diphenylphosphine)butylimidazoliumbromide}(η^4-cycloocta-1,5-diene)chloride-rhodium(I)) (**2**) were previously reported by our research group [37]. Spectroscopic characterization and elemental analysis of these complexes are presented in Supplementary Materials.

3.4. General Procedure for Catalytic Tests

The catalytic activity of Rh phosphine-ligated complexes was tested in the hydrosilylation of 1-heptyne, 1-octyne, and phenylacetylene with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) or triethylsilane (TES). The hydrosilylation reactions were carried out in the special glass reaction vessel, which was a 5 mL reactor with a side connector for sampling. The reactor was equipped with condenser and magnetic stirrer. In addition, 2×10^{-3} mol of catalyst, 1 mmol of alkyne derivative, 1.3 mmol of HMTS or TES, and 0.5 mmol of n-decane as an internal standard were placed into the reaction vessel. The reaction was carried out at 90 °C under air with vigorous stirring for 1 h. Then, the reaction mixture was cooled, centrifuged, and subjected to GC analysis to determine the reaction yield. The obtained retention times for particular isomers were used for partial identification of hydrosilylation products. The products were isolated and subjected to NMR and GC-MS analyses. The obtained spectroscopic data were compared with the literature data [8,12,18,38–43].

1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)Hept-1-Enyl)]Trisiloxane

^{1}H NMR ($CDCl_3$)ppm: β (Z): 0.10–0.14 (m, 21H, Si–CH_3), 0.92 (t, J = 8.2 Hz, 3H, –CH_3), 1.37 (m, 6H, C=C–CH_2–$(CH_2)_3$), 2.22 (m, 2H, C=C–CH_2), 5.34 (dd, J = 14.8, 4.8 Hz, 1H, C=CH–), 6.37 (dt, J = 14.6, 7.4 Hz, 1H, –CH=C), β(E): 5.53 (ddt, J = 21.7, 18.7, 1.5 Hz, 1H, C=CH–), 6.16 (dt, J = 18.7, 6.3 Hz, 1H, –CH=C–). **^{13}C NMR** ($CDCl_3$)ppm: β (Z): 1.81 (–Si–CH_3), 13.79 (–CH_3), 22.56 (C–CH_3), 29.12 (C–C–C–), 31.84 (–C–C–CH_3), 33.34 (C=C–C), 127.03 (Si-C=C–), 150.52 (–C=C–), β (E): 127.6 (Si–C=C–), 149.2 (–C=C–). **^{29}Si NMR** ($CDCl_3$)ppm: −35.37 (–$OSiCH_3$), 7.45 (–$OSi(CH_3)_3$).

GC-MS: β(Z): 305 (3%, $[(–OSi(CH_3)_3)_2SiC_7H_{14}]^+$), 247.5 (5%, $[(–OSi(CH_3)_3)_2SiCH_3CH=CH_2]^+$), 229.5 (3%, $[–OSi(CH_3)_3SiCH_3C_7H_{14}]^+$), 221 (100%, $[(-OSi(CH_3)_3)_2SiCH_3]^+$), 208.9 (17% $[((CH_3)_3SiO)SiOH(CH_3)_2SiO]^{2+}$), β(E): 305 (3%, $[(–OSi(CH_3)_3)_2SiC_7H_{14}]^+$), 247.5 (7%, $[(–OSi(CH_3)_3)_2SiCH_3CH=CH_2]^+$), 229.5 (3%, $[–OSi(CH_3)_3SiCH_3C_7H_{14}]^+$), 221 (100% $[(OSi(CH_3)_3)_2SiCH_3]^+$), 208.9 (23% $[((CH_3)_3SiO)SiOH(CH_3)_2SiO]^{2+}$) α: 305 (2.3%, $[(–OSi(CH_3)_3)_2SiCH_3C_6H_{12}]^+$), 247.5 (5% $[(–OSi(CH_3)_3)_2SiCH_3CH=CH_2]^+$), 221 (100%, $[(–OSi(CH_3)_3)_2SiCH_3]^+$), 208.9 (31%, $[((CH_3)_3SiO)SiOH(CH_3)_2SiO]^+$).

1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)Oct-1-Enyl)]Trisiloxane

^{1}H NMR ($CDCl_3$) ppm: β (Z): 0.10–0.15 (m, 21H, Si–CH_3), 0.91 (t, J = 6.9 Hz, 3H, –CH_3), 1.29–1.45 (m, 8H, C=C–CH_2–$(CH_2)_4$), 1.95–2.13 (m, 2H, C=C–CH_2), 5.37 (dt, J = 14.2, 1.2 Hz, 1H, C=CH–), 6.31 (dt, J = 14.5, 7.4 Hz, 1H, –CH=C), β(E): 5.49 (dt, J = 18.7, 1.5 Hz, 1H, C=CH–), 6.16 (dt, J = 18.7, 6.3 Hz, 1H, –CH=C). **^{13}C NMR** ($CDCl_3$)ppm: 1.71–2.01 (–Si–CH_3), 14.35 (–CH_3), 22.67 (C–CH_3), 29.11, 29.62 (C–C–C–), 31.86 (–C–C–CH_3), 36.60 (C=C–C), 126.93 (Si–C=C–), 150.47 (–C=C–). **^{29}Si NMR** ($CDCl_3$)ppm: −35.39 (–$OSiCH_3$), 8.07 (–$OSi(CH_3)_3$).

GC-MS: β(Z): 317 (25%, $[(–OSi(CH_3)_3)_2SiCH=CH(CH_2)_5CH_3)]^+$), 221 (100%, $[(–OSi(CH_3)_3)_2SiCH_3]^+$), 208 (19% $[((CH_3)_3SiO)SiOH(CH_3)_2SiO]^+$), 134 (4%, $[–OSi(CH_3)_3\text{-}SiCH_3]^{2+}$), β(E): 317 (30%, $[(–OSi(CH_3)_3)_2SiCH=CH(CH_2)_5CH_3)]^+$), 221 (100%, $[(–OSi(CH_3)_3)_2SiCH_3]^+$), 208 (20% $[((CH_3)_3SiO)SiOH(CH_3)_2SiO]^+$), 134 (4%, $[–OSi(CH_3)_3\text{-}SiCH_3]^{2+}$), α: 317 (10%, $[(–OSi(CH_3)_3)_2SiCH=CH(CH_2)_5CH_3)]^+$), 221 (100%, $[(–OSi(CH_3)_3)_2SiCH_3]^+$), 208 (18% $[(CH_3)_3SiO)SiOH(CH_3)_2SiO]^+$), 134 (3.7%, $[\text{-}OSi(CH_3)_3\text{-}SiCH_3]^{2+}$).

1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-Phenylethenyl]Trisiloxane

^{1}H NMR (CD_3CN) ppm: β (Z): 0.10–0.24 (m, 21H, –$OSiCH_3$), 5.68 (d, J = 15.5 Hz, 1H, C=CH–Si), 7.31 (d, J = 15.7 Hz, 1H, HC=CH), 7.23–7.39 (m, 3H, C–C=C), 7.49–7.56 (m, 2H, C=C–C), β (E): 6.33 (d, J = 19.3 Hz, 1H, C=CH–Si), 7.04 (d, J = 19.3 Hz, 1H, SiC=CH). **^{13}C NMR** (CD_3CN) ppm: −0.5–1.05 (–$OSi(CH_3)_3$, –$OSiCH_3$), 127.86 (C=C–C), 128.02, 128.37, 129.37, 139.16, 147.38. **^{29}Si NMR** (CD_3CN)ppm: −37.04 (-$OSiCH_3$), 8.07 (–$OSi(CH_3)_3$).

GC-MS: β(Z): 324 (5%, [(–$OSi(CH_3)_3)_2SiCH_3$–CH=CH_2Ph]$^+$), 311 (6.5%, [(–$OSi(CH_3)_3)_2SiCH$=CH_2Ph]$^+$ 221 (18.7% [(–$OSi(CH_3)_3$-$SiCH_3$]$^+$), 208 (30%, [(–$OSi(CH_3)_3)_2Si$–]$^{2+}$), 161 (100%, [–$OSi(CH_3)$ –Si–CH=CH_2–]$^{2+}$), 149 (31%, [–$SiCH_3$–CH=CH_2–Ph]$^{2+}$), 104 (5.5%, [CH=CH_2–Ph]$^+$), 77.1 (6.3%, [–C_6H_5]$^+$), β(E): 324 (2%, [(–$OSi(CH_3)_3)_2SiCH_3$–CH=CH_2Ph]$^+$), 311 (5%, [(–$OSi(CH_3)_3)_2SiCH$=CH_2Ph]$^+$ 221 (100% [(–$OSi(CH_3)_3$-$SiCH_3$]$^+$), 208 (12%, [(–$OSi(CH_3)_3)_2Si$–]$^{2+}$), 161 (17%, [–$OSi(CH_3)$ –Si–CH=CH_2–]$^{2+}$), 149 (15%, [–$SiCH_3$–CH=CH_2–Ph]$^{2+}$), 104 (6%, [CH=CH_2–Ph]$^+$), 77.1 (5%, [–C_6H_5]$^+$).

(Z)-Triethyl(Hept-1-Enyl)Silane

^{1}H NMR ($CDCl_3$) ppm: β(Z): 0.63 (m, 4H, –CH_2–CH_3), 0.94 (m, 11H, –CH_3), 1.32 (m, 6H, –CH_2–CH_2–CH_2–), 2.15 (m, 2H, –C=C-CH_2–, J=4.8 Hz), 5.42 (dt, J = 14.1, 1.3 Hz 1H, Si–CH=C–), 6.41 (dt, J = 14.4, 7.3 Hz 1H, C=CH–), β(E): 5.59 (dt, J = 18.5, 1.4 Hz, 1H, Si–CH=C–), 6.08 (dt, J = 18.7, 6.3 Hz, 1H, C=CH–). **^{13}C NMR** ($CDCl_3$)ppm: β(Z): 4.73 (Si–CH_2–), 7.54 (Si–CH_2–CH_3), 14.04 (–CH_3), 22.61 (C–CH_3), 29.49 (–C–C–C–), 31.66 (–C–C–CH_3), 34.08 (C=C–C–), 124.89 (Si–C=C–), 150.38 (C=C–C–); **β (E):** 125.52 (Si–C=C–), 148.83 (C=C–C). **^{29}Si NMR** ($CDCl_3$)ppm: −2.83 (($C_2H_5)_3$SiH).

GC-MS: β(Z): 183 (100%, [–$Si(C_2H_5)_2HC$=$CH_2C_5H_{11}$]$^+$), 156 (5%, [SiC_2H_5HC=$CH_2C_5H_{11}$]$^+$), 115.1 (16%, [–$Si(C_2H_5)_3$]$^+$), 99 (37%, [HC=$CH_2C_5H_{11}$]$^+$), 89.1 (16%, [–$Si(C_2H_5)_2$]$^{2+}$); β(E): 183 (100%, [–$Si(C_2H_5)_2HC$=$CH_2C_5H_{11}$]$^+$), 156 (6%, [SiC_2H_5HC=$CH_2C_5H_{11}$]$^+$), 115.1 (14%, [–$Si(C_2H_5)_3$]$^+$), 99 (50%, [HC=$CH_2C_5H_{11}$]$^+$), 89.1 (28%, [–$Si(C_2H_5)_2$]$^{2+}$); **α:** 183 (100%, [–$Si(C_2H_5)_2HC$=$CH_2C_5H_{11}$]$^+$), 156 (5%, [SiC_2H_5HC=$CH_2C_5H_{11}$]$^+$), 115.1 (30%, [–$Si(C_2H_5)_3$]$^+$), 89.1 (70%, [–$Si(C_2H_5)_2$]$^{2+}$).

(Z)-Triethyl(Oct-1-Enyl)Silane

^{1}H NMR ($CDCl_3$)ppm: β(Z): 0.55 (m, 4H, –CH_2–CH_3), 0.96 (t, 3H, –CH_3), 0.98 (m, 11H, –CH_2–CH_3), 1.31–1.46 (m, 8H, –$(CH_2)_4$–), 1.96–2.17 (m, 2H, –C=C–CH_2–), 5.39 (dd, J = 13.8, 6.1 Hz, 1H, Si–CH=C–), 6.39 (dt, J = 14.4, 7.3 Hz, 1H, C=CH–), β (E): 5.59 (dt, J = 18.7, 1.5 Hz, 1H, –CH=C–), 6.02 (dt, J = 18.7, 6.3 Hz, 1H, C=CH–), α: 5.29 (ddd, J = 12.2, 9.9, 3.8 Hz,1H, –CH=C–). **^{13}C NMR** ($CDCl_3$)ppm: β(Z): 3.55 (Si–CH_2–), 7.41 (Si–CH_2–CH_3), 14.07 (–CH_3), 22.63 (C–CH_3), 28.80 (–C–C–C–), 29.66 (–C–C–C–),), 31.38 (–C–C–CH_3), 32.78 (C=C–C–), 126.00 (Si–C=C–), 150.36 (C=C–C–), β(E): 125.48 (Si–C=C–), 148.82 (C=C–C–). **^{29}Si NMR** ($CDCl_3$)ppm: −5.78 (($C_2H_5)_3$SiH).

GC-MS: β(Z): 197 (100%, [$SiEt_2C_8H_{15}$]$^+$), 141.3 (2% [$SiEt_3$CH=CH]$^+$), 115.1 (72.5%, [$SiEt_3$]$^+$), 85.1 (6%, [C_6H_{11}]$^+$), β(E): 197 (100%, [$SiEt_2C_8H_{15}$]$^+$), 141.3 (15% [$SiEt_3$CH=CH]$^+$), 115.1 (15%, [$SiEt_3$]$^+$), 85.1 (26%, [C_6H_{11}]$^+$), **α:** 197 (100%, [$SiEt_2C_8H_{15}$]$^+$), 141.3 (12% [$SiEt_3$CH=CH]$^+$), 115.1 (30%, [$SiEt_3$]$^+$), 85.1 (25%, [C_6H_{11}]$^+$).

(E)-Triethyl(Phenyl-1-Ethene)Silane

^{1}H NMR (CD_3CN) ppm: β(E): (CD_3CN) ppm: 0.72–1.04 (m, 15H, –$Si(Et)_3$), 6.50 (d, J = 19.3 Hz, 1H, C=CH–Si), 6.97 (d, J = 19.3 Hz, 1H, HC=C–Si), 7.29 (m, 1H, C=C–C), 7.37 (m, 2H, C=C–C), 7.50 (m, 2H, C–C=C), β(Z): 5.79 (d, J=15.2 Hz, 1H, C=CH–Si) **^{13}C NMR** (CD_3CN) ppm: 3.33 (–$SiCH_2CH_3$), 7.12 (–$SiCH_2$–), 125.95 (C=C–C–), 126.32, 127.89, 128.48, 138.53, 145.19 **^{29}Si NMR** (CD_3CN)ppm: 0.55 (–$Si(Et)_3$).

GC-MS: β(E): 189 (100%, [$Si(C_2H_5)_2$–HC=CH_2-Ph], 134.1 (25%, [Si–HC=CH_2Ph]$^{3+}$), 115.1 (5%, [–$Si(C_2H_5)_3$]$^+$), 104 (25%, [HC=CH_2–Ph]$^+$), β(Z): 189 (100%, [$Si(C_2H_5)_2$–HC=CH_2–Ph], 134.1 (52%, [Si–HC=CH_2Ph]$^{3+}$), 115.1 (10%, [–$Si(C_2H_5)_3$]$^+$), 104 (30%, [HC=CH_2-Ph]$^+$).

3.5. General Procedure for Catalyst Isolation and Tests with Subsequent Catalytic Runs

The catalytic activity of the complex **1** in subsequent catalytic cycles was tested in the hydrosilylation of 1-octyne with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS). The hydrosilylation reaction was conducted in a glass reaction vessel equipped with a condenser and magnetic stirrer. In addition, 2×10^{-3} mol of catalyst, 1 mmol of 1-octyne, 1.3 mmol of HMTS, and 0.5 mmol of n-decane as an internal standard were placed into the reaction vessel. The reaction was carried out at 90 °C under air with vigorous stirring for 1 h. Then, the reaction mixture was cooled and centrifuged for a few minutes or filtered. Next, the whole amount of product was collected with a syringe equipped with a needle, followed by subjecting to GC analysis to determine the reaction yield. For the catalyst isolated by centrifugation, that remained in the reaction vessel, another portion of the same substrates was added, whereas, for filtered post-reaction mixture, the filter with isolated catalyst was added to the new portion of reagents. In both cases, the isolated catalyst was not subjected to any washing or regeneration. The aforementioned operation was repeated five times, in order to perform five catalytic runs.

4. Conclusions

The modification of the starting rhodium complexes $[Rh(PPh_3)_3Cl]$ and $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ with the phosphine ligand containing imidazolium ionic liquid as a substituent resulted in obtaining complexes **1** and **2** which are insoluble in the reactants used in the hydrosilylation react on. The above complexes are very durable and stable in air which facilitates their use. Both complexes showed a very high catalytic activity for alkyne hydrosilylation. A complete conversion of alkynes was achieved already after 1 h from the beginning of the reaction. However, the FT-IR in situ analysis of the reactions catalyzed by the complex **1** and the Wilkinson's catalyst has shown that, in the case of the former catalyst, full conversion can be achieved in a considerably shorter time (15 min), whereas, in that of the Wilkinson's catalyst, it requires 55 min. The above studies are a preliminary step to the determination of the kinetics of hydrosilylation of alkynes in the presence of the new rhodium catalysts which we are going to carry out in the immediate future. Three alkynes (1-heptyne, 1-octyne and phenylacetylene) were subjected to hydrosilylation with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) or triethylsilane (TES). In all the cases, the complexes **1** and **2** were more active than their precursors. In the reactions of hydrosilylation of aliphatic alkynes catalyzed by both complexes, mainly *β(Z)* isomers are formed, which is typical of the major part of rhodium catalysts applied hitherto. In addition, selectivities achieved in this case are higher than those observed for reactions catalyzed by their precursors and range from 89 to 96%. Additionally, a small increase in the selectivity is observed with alkyne chain growth. When comparing selectivities obtained for both catalysts, one can notice that complex **1** is characterized by a higher selectivity. In the reactions with aliphatic alkynes, the effect of the kind of hydrosilylating agent was not observed; both in the reactions with HMTS and TES, *cis* isomer is mainly formed. A somewhat different situation occurs in the hydrosilylation of phenylacetylene, where, depending on the kind of hydrosilylating agent, either *cis* or *trans* isomer predominates. In the reaction with HMTS, the isomer *β(Z)* prevails, whereas, in that with TES, the *β(E)* product is formed. This is caused, besides the steric effect of the phenyl group, also by strongly electronegative nature of triethylsilane whose interaction with phenyl group results in the predominant formation of the *trans* isomer. It is also worth mentioning that the catalyst **2** was active both in reactions with HMTS and TES, whereas its precursor was inactive (maybe because of too mild reaction conditions or too short reaction time).

The most important result of our study is proving the possibility of multiple uses of the same portion of the catalyst. Due to the heterogeneous nature of the complexes **1** and **2**, their isolation and reusing are feasible. The results of conducting five catalytic runs with the use of the same portion of catalyst show that the activity and particularly selectivity are high. It has been proved that the most efficient way of the catalyst isolation from the post-reaction mixture was filtration, which made it possible to reuse the catalyst five times with the preservation of its high activity. Generally,

the complexes **1** and **2** that contain the imidazolium- phosphine ligand are characterized by a higher catalytic activity than their precursors. According to the literature data, the rhodium complexes containing ligands with such heteroatoms as P–, N– or NHC– group (which are electron donors) show an increase in the selectivity and yield of the reaction due to a higher stabilization of the Rh-phosphine bond [44–46]. On the other hand, phosphine ligand with imidazolium ionic liquid has a significant effect on the heterogenization of the catalytic system. The obtained catalysts enable their easy isolation and reusability which is of substantial economic and ecological importance.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/6/608/s1, Figure S1: ^{1}H NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)hept-1-enyl)]trisiloxane. Figure S2: ^{13}C NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)hept-1-enyl)]trisiloxane. Figure S3: ^{29}Si NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)hept-1-enyl)]trisiloxane. Figure S4: ^{1}H NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)oct-1-enyl)]trisiloxane, Figure S5: ^{13}CNMR spectrum of 1,1,1,3,5,5,5-Heptamethyl -3-[(1Z)oct-1- enyl)]trisiloxane. Figure S6: ^{29}Si NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)oct-1-enyl)] trisiloxane. Figure S7: ^{1}H NMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]trisiloxane. Figure S8: ^{13}CNMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]trisiloxane. Figure S9: ^{29}SiNMR spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]-trisiloxane, Figure S10: ^{1}H NMR spectrum of (Z)- triethyl(hept-1-enyl)silane. Figure S11: ^{13}C NMR spectrum of (Z)-triethyl(hept-1-enyl)silane, Figure S12: ^{29}SiNMR spectrum of (Z)-triethyl(hept-1-enyl)silane. Figure S13: ^{1}H NMR spectrum of (Z)-triethyl(oct-1-enyl)silane. Figure S14: ^{13}C NMR spectrum of (Z)-triethyl(oct-1-enyl)silane. Figure S15: ^{29}Si NMR spectrum of (Z)-triethyl(oct -1-enyl)silane. Figure S16: ^{1}H NMR spectrum of (E)-triethyl(phenyl-1-ethene)silane. Figure S17: ^{13}C NMR spectrum of (E)-triethyl(phenyl-1-ethene)silane. Figure S18: ^{29}Si NMR spectrum of (E)-triethyl(phenyl-1-ethene)silane. Figure S19: GC chromatogram of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)hept-1-enyl)]-trisiloxane, 1,1,1,3,5,5,5-Heptamethyl-3-[(1E)hept -1-enyl)]trisiloxane and 1,1,1,3,5,5,5-Heptamethyl-3-[(α)hept-1-enyl)]trisiloxane. Figure S20: MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)hept-1-enyl)]trisiloxane. Figure S21: MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1E)hept-1-enyl)]trisiloxane. Figure S22: MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1α)hept-1-enyl)]trisiloxane. Figure S23: GC chromatogram of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)oct-1-enyl)]trisiloxane1,1,1,3,5,5,5-Heptamethyl -3-[(1E)oct-1-enyl)] trisiloxane and 1,1,1,3,5,5,5-Heptamethyl-3-[(1α)oct-1-enyl)]trisiloxane. Figure S24: MS spectrum of 1,1,1,3,5,5, 5-Heptamethyl-3-[(1Z)oct-1-enyl)]trisiloxane. Figure S25: MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1E)oct-1-enyl)]trisiloxane. Figure S26: MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1α)oct-1-enyl)]trisiloxane. Figure S27: GC chromatogram of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]trisiloxane and 1,1,1,3,5,5,5-Heptamethyl-3-[(1E)-2-phenylethenyl]trisiloxane. Figure S28: MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1Z)-2-phenylethenyl]trisiloxane. Figure S29: MS spectrum of 1,1,1,3,5,5,5-Heptamethyl-3-[(1E)-2-phenylethenyl]trisiloxane. Figure S30: GC chromatogram of (Z)-triethyl(hept-1-enyl)silane, (E)-triethyl(hept-1-enyl)silane and (α)-triethyl(hept-1-enyl)silane. Figure S31: MS spectrum of (Z)-triethyl(hept-1-enyl)silane. Figure S32: MS spectrum of (E)-triethyl(hept-1-enyl)silane. Figure S33: MS spectrum of (α)-triethyl(hept-1-enyl)silane. Figure S34: GC chromatogram of (Z)-triethyl(oct-1-enyl)silane, (E)-triethyl(oct-1-enyl)silane and (α)-triethyl(oct-1-enyl)silane. Figure S35: MS spectrum of (Z)-triethyl(oct-1-enyl)silane. Figure S36: MS spectrum of (E)-triethyl(oct-1-enyl)silane. Figure S37: MS spectrum of (α)-triethyl(oct-1-enyl)silane. Figure S38: GC chromatogram of (E)-triethyl(phenyl-1-ethene)silane and (Z)-triethyl(phenyl-1-ethene)silane. Figure S39: MS spectrum of (E)-triethyl(phenyl-1-ethene)silane. Figure S40: MS spectrum of (Z)-triethyl(phenyl-1-ethene)silane. Figure S41: FT-IR spectra with characteristic peaks at 1600 cm^{-1} and 913 cm^{-1} which change with time of the hydrosilylation reaction between 1-octyne and HMTS, carried out in the presence of the Wilkinson's catalyst. Figure S42: FT-IR spectra with characteristic peaks at 1600 cm^{-1} and 913 cm^{-1} which change with time of the hydrosilylation reaction between 1-octyne and HMTS, carried out in the presence of catalyst **1**.

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