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Hydrosilylation of non-1-ene with phenylsilane in the presence of yttrium and lutetium bisguanidinate hydride complexes

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Some regularities of hydrosilylation of non-1-ene with phenylsilane catalyzed by yttrium and lutetium bisguanidinate hydride complexes $\{[(Me_3Si)_2NC(NR)_2]_2Ln(\mu\text{-}H)\}_2$ (Ln = Y, Lu; R = Pr^i, Cy (Cy is cyclohexyl)) have been studied. The addition of $PhSiH_3$ to the double bond of non-1-ene in the presence of a $\{[(Me_3Si)_2NC(NPr^i)_2]_2Y(\mu\text{-}H)\}_2$ complex has the first order in olefin and zero order in phenylsilane. This indicates that the insertion of non-1-ene into the Ln—H bond is a rate determining stage of the process, whereas the metathesis of the Ln—C σ-bond upon the action of phenylsilane proceeds rapidly. The first example of successive double alkylation of phenylsilane with an olefin catalyzed by a rare-earth metal complex with the formation of tertiary silane has been discovered.

Key words: hydrosilylation, alkenes, phenylsilane, organosilicon compounds, yttrium complexes, lutetium complexes, kinetics.

Hydrosilylation of unsaturated substrates catalyzed by transition metal complexes is one of the most simple and atom-saving methods for the functionalization of olefins,[1] selective organic synthesis (for example, of small cycles[2]), as well as preparation of silicon-containing polymers.[3] By now, platinum complexes are the most widely studied among catalysts of hydrosilylation of olefins.[4—9] However, these catalysts have a number of disadvantages, in particular, they do not provide high chemo- and regioselectivity. For instance, when primary silanes $RSiH_3$ are used as the silylating agents[4] the reaction proceeds with the formation of a mixture of products of both hydrosilylation ($RR'SiH_2$, RR'_2SiH, and RR'_3Si) and hydration ($R'H$) of olefins. Catalysts based on the light transition metals,[10,11] actinides,[12] and rare-earth elements[2,13—26] exhibit considerably higher selectivity in the hydrosilylation processes of olefins with primary and secondary silanes, however, their lower activity, together with sensitivity to oxygen and air moisture (and frequently with thermal instability), considerably limits their application. The first examples of the use of the sandwich-type rare-earth element alkyl complexes as catalysts in the hydrosilylation reactions were published[27] in 1989. Results of subsequent studies confirmed the high potential[2,26] of these compounds. Earlier,[2,26] using cyclopentadienyl derivatives as examples it was demonstrated that the nature of the metal atom coordination sphere can significantly affect the rate and regioselectivity of hydrosilylation. For instance, going from the biscyclopentadienyl ligand system to the *ansa*-bound biscyclopentadienyl one and the use of a rare-earth metal with larger ionic radius allowed one to significantly increase the rate and selectivity (addition according to the Markovnikov rule) of hydrosilylation of α-olefins.[15] Replacement of biscyclopentadienyl ligand system with the *ansa*-bound cyclopentadienylphosphide one and the use of a lutetium complex $[Me_2Si(C_5Me_4)(\mu\text{-}PCy)\text{-}LuCH_2SiMe_3]_2$ (Cy is cyclohexyl) as the catalyst allow one, retaining a high rate of hydrosilylation of hex-1-ene with phenylsilane, to change regioselectivity of the process and exclusively obtain Markovnikov addition products.

At the same time, catalytic activity of related complexes containing no cyclopentadienyl ligands remains virtually uninvestigated. Lately, a tendency for search of new noncyclopentadienyl ligand systems has been outlined,[28] which is aimed on the increase in stability of the rare-earth metal derivatives with retaining high reactivity, the higher stability of catalysts to functional groups of substrates, broadening a possibility of design of the metal atom coordination sphere in the complex, as well as control of catalytic activity of metal complexes and selectivity of the processes. There are new reports on the synthesis of the rare-earth metal alkyl and hydride complexes, stabilized by amide,[23,29,30] silylamide,[31] silanolate,[32] amidinate,[33] bisphenolate[34] ligands, and all of them were successfully used as catalysts of hydrosilylation of olefins.

Earlier,[35—37] we have reported on the synthesis of new lanthanide bisguanidinate hydride complexes $\{[(Me_3Si)_2NC(NR)_2]_2Ln(\mu\text{-}H)\}_2$ (Ln = Y, Nd, Sm, Gd, Yb, Lu, R = Pr^i; Ln = Y, Lu, R = Cy), which demonstrated high catalytic activity in polymerization and hydrosily-

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lation of olefins. The present work is devoted to the study of kinetic regularities of hydrosilylation of non-1-ene with phenylsilane upon catalysis with bisguanidinate hydride complexes $\{[(Me_3Si)_2NC(NR)_2]_2Ln(\mu\text{-}H)\}_2$ (Ln = Y, Lu; R = Pr^i, Cy).

Results and Discussion

We found that yttrium and lutetium hydride complexes $\{[(Me_3Si)_2NC(NR)_2]_2Ln(\mu\text{-}H)\}_2$ (Ln = Y, R = Pr^i (**1**); Ln = Lu, R = Pr^i (**2**); Ln = Y, R = Cy (**3**); Ln = Lu, R = Cy (**4**)) containing diisopropyl and dicyclohexyl guanidinate ligands catalyze hydrosilylation of non-1-ene with phenylsilane and provide, together with the high rate at room temperature, a high regioselectivity, exclusively leading to the formation of anti-Markovnikov addition product.[32]

It is known[2,13,14,20,26] that in hydrosilylation of olefins catalyzed by the rare-earth metal alkyl and hydride derivatives of metallocene series, a hydride complex is the active catalytic species. In this case, depending on the size of cyclopentadienyl ligand coordinated with the lanthanide atom, both the monomeric and dimeric hydride complexes can be the intermediates. In another words, dissociation of usually dimeric hydride derivatives in a number of cases is not a necessary prerequisite for the catalytic reaction to proceed.[20] To study chemical properties of new bisguanidinate hydride derivatives **1**—**4**, it seemed interesting to study some regularities (including kinetic) of the hydrosilylation reaction of non-1-ene with phenylsilane in their presence.

Hydrosilylation of non-1-ene with phenylsilane in the presence of complexes **1**—**4** was performed on a preparative scale in hexane at room temperature with the molar ratio of substrates 1 : 1 ($C^0_{PhSiH_3} = C^0_{non\text{-}1\text{-}ene} = 0.309$ mol L^{-1}) and 2 mol.% of the catalyst. It was found that all four catalysts possess close activities and the reactions come to completion within for ~12 h.

The study of hydrosilylation products by NMR spectroscopy and GLC showed that for all the catalysts, the reaction proceeds with exclusive formation of phenyl(non-1-yl)silane, the anti-Markovnikov addition product (Scheme 1).

Scheme 1

$$C_7H_{15}CH{=}CH_2 + PhSiH_3 \xrightarrow{[LnH]} n\text{-}C_9H_{19}SiH_2Ph$$

This is confirmed by the fact that in the ^1H and $^{13}C\{^1H\}$ NMR spectra of the reaction products, all the groupings of the product are represented by a single set of signals. The protons on the silicon atom SiH_2 are found as a triplet at δ 4.39 ($^3J_{H,H}$ = 3.6 Hz), resulting from the splitting on two methylene protons of the alkyl substituent. No signals related to the second possible isomer were found in the NMR spectra.

It should be noted that complexes **1**—**4** have proved inactive in catalysis of hydrosilylation of styrene and norbornene.

For the study of kinetic regularities of the hydrosilylation reaction of non-1-ene with phenylsilane, yttrium bisguanidinate hydride complex $\{[(Me_3Si)_2NC(NPr^i)_2]_2Y(\mu\text{-}H)\}_2$ (**1**) has been chosen as a test catalyst. As it is known, the lanthanide hydride complexes catalyze polymerization of α-olefins,[28,38] as well as dehydration—oligomerization of primary silanes,[15,31] that can complicate study of the hydrosilylation reactions. In order to clarify a possibility of occurring these side reactions in the system non-1-ene—$PhSiH_3$—complex **1**, we studied a behavior of each reagent in the presence of the catalyst. It was found that complex **1** does not catalyze oligomerization of non-1-ene and dehydration—oligomerization of $PhSiH_3$ at room temperature in hexane or benzene. This allows us to exclude a possibility of the side reaction to affect kinetic characteristics of the hydrosilylation process with a high degree of probability.

The rate of hydrosilylation of non-1-ene with phenylsilane in the presence of yttrium hydride complex **1** was studied by ^1H NMR spectroscopy. The reaction was performed at the molar ratio of substrates 1 : 1 in benzene-d_6 at 20±0.5 °C in the presence of 2 mol.% of complex **1** ($C^0_{PhSiH_3} = C^0_{non\text{-}1\text{-}ene} = 0.309$ mol L^{-1}). The reaction progress was monitored by the decrease in the signal intensities corresponding to the SiH_3 group of phenylsilane, the olefin protons of non-1-ene, as well as by the increase of the signal intensities of the silylene protons SiH_2 in the forming phenylnonylsilane.

Kinetic curves were built based on the NMR spectroscopic data, which show the change in concentrations of the reaction mixture components versus time (Fig. 1).

These dependencies are linear in the $\ln[C/C^0]—t$ coordinates, *i.e.*, the reaction has the overall first order (Fig. 2).

Particular orders of the reaction in phenylsilane and non-1-ene were determined using method of steady-state concentrations. To determine the order in one of the reagents, the reaction was performed in the presence of a five-fold molar excess of another, that allowed us to neglect the change in its concentration during the process.

It was found that the dependence of the concentration of non-1-ene from time under these conditions is linear in the $\ln[C]—t$ coordinates (Fig. 3). This fact is an evidence that the reaction has the first order in non-1-ene.

It turned out that the reaction has the zero order in phenylsilane, since the dependence of the concentration of phenylsilane from time is a straight line (Fig. 4).

Based on the fact that the reaction has the zero order in $PhSiH_3$ and its rate does not depend on its concentration, it can be concluded that the rate determining stage of the process is the insertion of non-1-ene into the Y—H

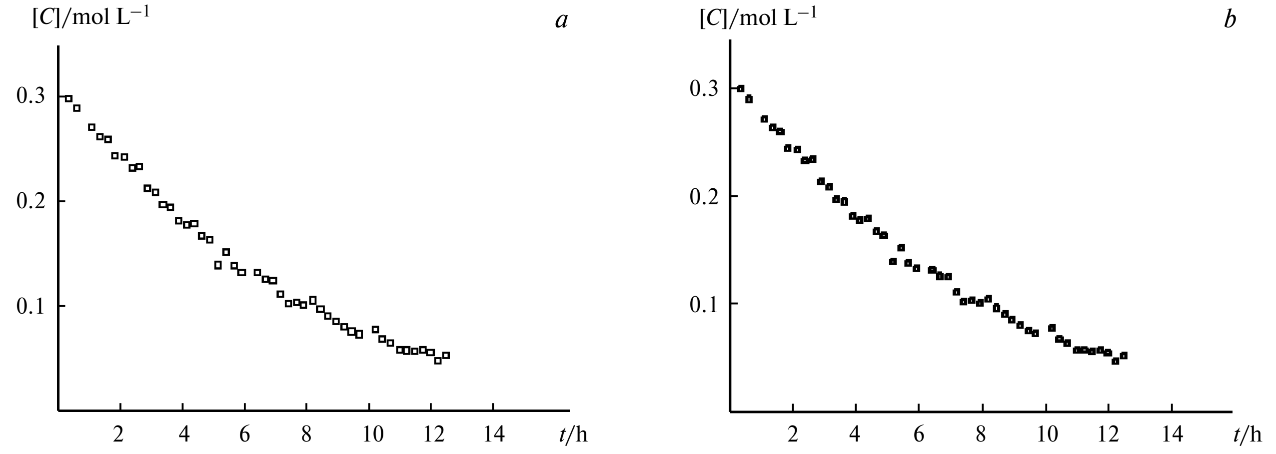


Fig. 1. Concentrations of $PhSiH_3$ (*a*) and non-1-ene (*b*) versus time in the hydrosilylation ($T = 20\pm0.5$ °C, C_6D_6, $C_{cat} = 0.0062$ mol L^{-1}, $C^0_{PhSiH_3} = C^0_{non\text{-}1\text{-}ene} = 0.309$ mol L^{-1}).

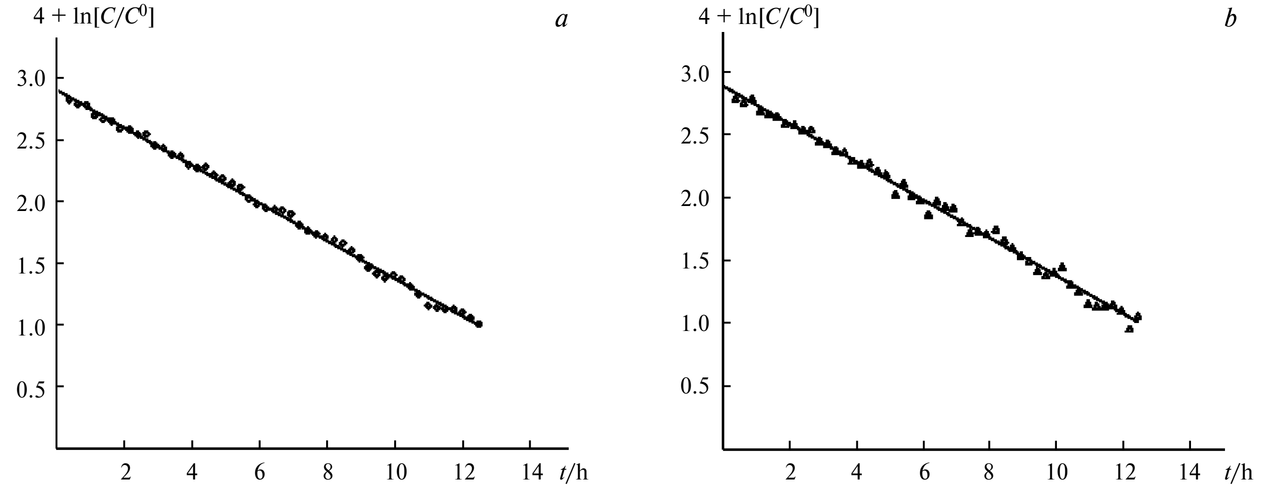


Fig. 2. Parameter $\ln[C/C^0]$ for phenylsilane (*a*) and non-1-ene (*b*) versus time in the hydrosilylation ($T = 20\pm0.5$ °C, C_6D_6, $C_{cat} = 0.0062$ mol L^{-1}, $C^0_{PhSiH_3} = 0.309$ mol L^{-1}, $C^0_{non\text{-}1\text{-}ene} = 0.3085$ mol L^{-1}).

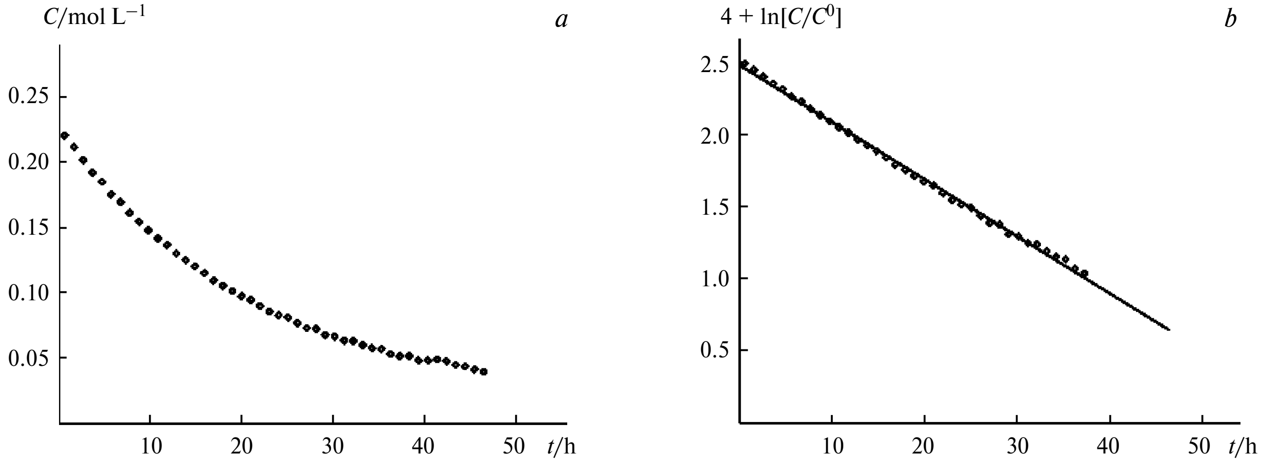


Fig. 3. Concentration of non-1-ene (*a*) and parameter $\ln[C/C^0]$ for non-1-ene (*b*) versus time in the hydrosilylation ($T = 20\pm0.5$ °C, C_6D_6, $C_{cat} = 0.0061$ mol L^{-1}, $C^0_{PhSiH_3} = 1.1325$ mol L^{-1}, $C^0_{non\text{-}1\text{-}ene} = 0.2265$ mol L^{-1}).

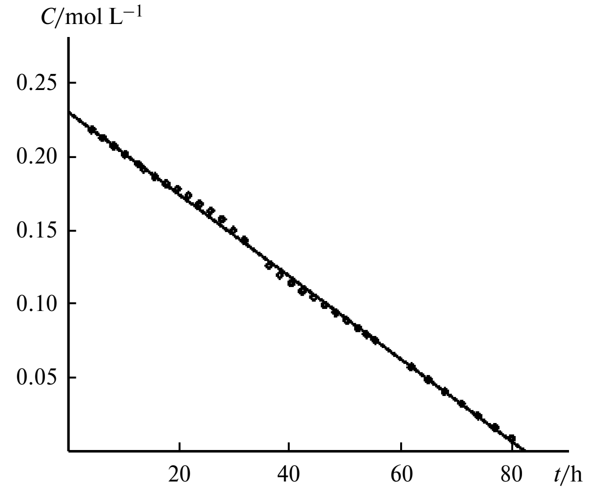


Fig. 4. Concentration of $PhSiH_3$ versus time in the presence of a five-fold molar excess of non-1-ene (T = 20±0.5 °C, C_6D_6, $C_{cat} = 0.0045$ mol L^{-1}, $C^0_{PhSiH_3} = 0.2191$ mol L^{-1}, $C^0_{non\text{-}1\text{-}ene} = 1.1093$ mol L^{-1}).

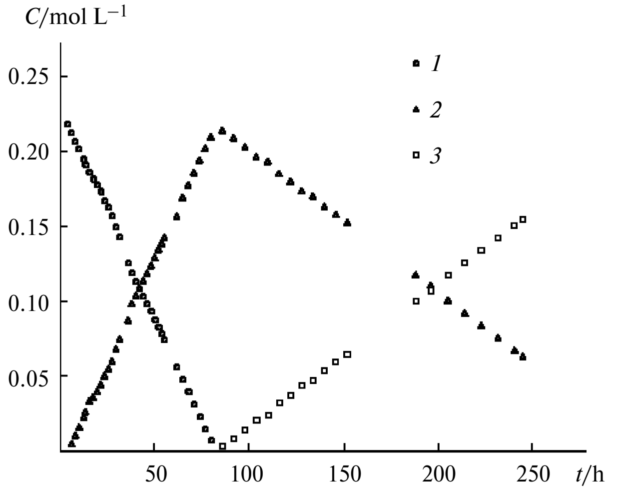


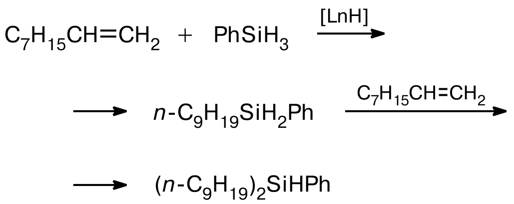
Fig. 5. Current concentrations of $PhSiH_3$ (*1*), Ph(n-C_9H_{19})SiH_2 (*2*) and Ph(n-C_9H_{19})$_2$SiH (*3*) versus time in the hydrosilylation (T = 20±0.5 °C, C_6D_6, C_{cat} = 0.0045 mol L^{-1}, $C^0_{PhSiH_3}$ = 0.2191 mol L^{-1}, $C^0_{non\text{-}1\text{-}ene}$ = 1.1093 mol L^{-1}).

bond of the catalyst, whereas the metathesis reaction of the Y—C σ-bond upon the action of phenylsilane proceeds rapidly.

It should be noted that the first order in olefin and zero order in silane were also observed in the case of hydrosilylation of oct-1-ene with $PhMeSiH_2$ in the presence of $[(Bu^tC_5H_4)_2LnH]_2$ (Ln = Tb, Yb, Lu),[20] whereas the reaction of hex-1-ene with $PhMeSiH_2$ catalyzed by a $[MeC_6H_3N(Me_2SiBu^t)]_2YMe(THF)_2$ complex has the first order in silane and zero in olefin.[31] Addition of $PhSiH_3$ to the double bond of 2-phenylbut-1-ene in the presence of (R)-$Me_2Si(C_5Me_4)$[(–)-menthylCp]$SmCH(SiMe_3)_2$ has also the first order in silane and zero in olefin.[15] The facts indicated clearly demonstrate that, depending on the structure of the olefin and silane, as well as on the nature of the catalyst, different steps of the catalytic cycle can determine the overall rate of the process.

During determination of the reaction order in phenylsilane in the presence of excess non-1-ene, it was found that hydrosilylation does not stop at the step of Ph(n-C_9H_{19})SiH_2 formation. The latter reacts with the second molecule of non-1-ene, leading to the tertiary silane Ph(n-C_9H_{19})$_2$SiH (Scheme 2). This is indicated by the decrease in the integral intensity of the characteristic triplet at δ 4.39 related to the protons SiH_2, and by appearance of the signal at δ 4.32 in the ^{1}H NMR spectrum of the reaction mixture. The growing signal related to the SiH group is a quintet due to the splitting of the proton on the four hydrogen atoms of the methylene groups of two n-nonyl substituents. From the curve of concentrations of $PhSiH_3$ and Ph(n-C_9H_{19})SiH_2 versus time (Fig. 5), it is seen that initially all the primary phenylsilane is consumed and only then the secondary silane Ph(n-C_9H_{19})SiH_2 would react. The picture observed correlates with the known fact indicating that the primary silanes are much more reactive in the hydrosilylation reactions as compared to the secondary.[33]

Scheme 2



$$C_7H_{15}CH{=}CH_2 + PhSiH_3 \xrightarrow{[LnH]} n\text{-}C_9H_{19}SiH_2Ph \xrightarrow{C_7H_{15}CH=CH_2} (n\text{-}C_9H_{19})_2SiHPh$$

When the reaction of $PhSiH_3$ with excess of non-1-ene has been carried out in the presence of complex **1** on a preparative scale, the tertiary silane Ph(n-C_9H_{19})$_2$SiH was isolated in 91% yield.

This result is interesting by the fact that usually for the lanthanide-containing catalytic systems, hydrosilylation with participation of primary silanes is limited to the single addition of one olefin molecule to the double bond, and secondary silanes formed do not further react. The fact described above is the first example of double addition of alkenes to phenylsilane in the presence of the rare-earth metal complexes, which leads to the formation of tertiary silane.

In conclusion, we found that yttrium and lutetium bisguanidinate hydride complexes are efficient and selective catalysts for the hydrosilylation of non-1-ene with phenylsilane. The reactions proceed at room temperature in quantitative yields and with exclusive formation of anti-Markovnikov addition product. Addition of $PhSiH_3$ to the double bond of non-1-ene in the presence of a $\{[(Me_3Si)_2NC(NPr^i)_2]_2Y(\mu\text{-}H)\}_2$ complex has the first order in olefin and the zero in phenylsilane. This is an evidence that the rate determining stage of the process is the insertion of non-1-ene into the Ln—H bond, whereas metathesis of the Ln—C σ-bond upon the action of phenylsilane is a fast process. In addition, we found the first example of successive double alkylation of phenylsilane with an olefin catalyzed by the rare-earth metal complex with the formation of tertiary silane.

Experimental

All the manipulations on the synthesis and isolation of products were performed *in vacuo* using standard Schlenk technique. Tetrahydrofuran after drying with potassium hydroxide was distilled over sodium benzophenone ketyl. Hexane and benzene were dried by reflux and distillation over sodium metal. Phenylsilane was dried with calcium hydride, degassed and condensed into the reaction tube directly before use. Non-1-ene, styrene, and *N*,*N*´-diisopropylcarbodiimide were degassed *in vacuo* and used after drying over molecular sieves A4. Commercial reagent *N*,*N*´-dicyclohexylcarbodiimide was used as purchased. Benzene-d_6 was dried with metallic sodium, degassed, and condensed *in vacuo*; $CDCl_3$ was used as purchased. NMR spectra were recorded on a Bruker DPX 200 spectrometer (200 (^1H) and 50 MHz (^{13}C)). Liquid chromatography was performed on a KNAUER chromatograph (a Separon SGXC 18 column, $MeCN—H_2O$ was an eluent). The reaction progress was monitored on a Tsvet 530 gas-liquid chromatograph.

Reaction of equimolar amounts of non-1-ene and $PhSiH_3$ on a preparative scale

Hydrosilylation of non-1-ene with $PhSiH_3$ in the presence of $\{[(Me_3Si)_2NC(NPr^i)_2]_2Y(\mu\text{-}H)\}_2$ (1). Phenylsilane (0.20 mL, 1.6 mmol) and non-1-ene (0.28 mL, 1.6 mmol) were added to a solution of complex **1** (0.0418 g, 0.0316 mmol) in hexane (5 mL). The reaction mixture was stirred for 12 h at room temperature. To stop the reaction, 1-bromobutane (1 mL) was added to the reaction mixture. The solution was filtered, volatile organic compounds were evaporated *in vacuo* at room temperature. A liquid residue of the high-boiling products was distilled at reduced pressure (0.05 Torr, 180—210 °C) to yield $Ph(n\text{-}C_9H_{19})SiH_2$ (0.34 g, 91%). Found (%): C, 76.34; H, 11.23. $C_{15}H_{26}Si$. Calculated (%): C, 76.84; H, 11.18. ^1H NMR ($CDCl_3$), δ: 0.93 (br.m, 5 H, CH_3 + $SiCH_2$); 1.31 (br.m, 14 H, CH_2); 4.39 (t, 2 H, SiH_2, $^2J_{H,H}$ = 3.6 Hz); 7.41—7.63 (m, 5 H, SiC_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 10.1 ($SiCH_2$, C(8)); 14.2 (CH_3, C(16)); 22.8, 25.2, 29.3, 29.4, 29.6, 31.9, 32.9 (CH_2); 127.9, 129.5, 135.3, 132.9 (C_{Ar}). IR (KBr), ν/cm^{-1}: 454, 505, 563, 662, 699, 635, 840, 938, 1115, 1169, 1252, 1299, 1378, 1589, 1638, 1813, 1879, 1950, 2130, 3015, 3051, 3069.

Hydrosilylation of non-1-ene with $PhSiH_3$ in the presence of $\{[(Me_3Si)_2NC(NPr^i)_2]_2Lu(\mu\text{-}H)\}_2$ (2). Phenylsilane (0.44 mL, 3.5 mmol) and non-1-ene (0.62 mL, 3.5 mmol) were added to a solution of complex **2** (0.1034 g, 0.0690 mmol) in hexane (5 mL). The reaction time was 12 h. The reaction mixture was quenched and the product was isolated as described above. The yield of $Ph(n\text{-}C_9H_{19})SiH_2$ was 0.77 g (94%).

Hydrosilylation of non-1-ene with $PhSiH_3$ in the presence of $\{[(Me_3Si)_2NC(NCy)_2]_2Y(\mu\text{-}H)\}_2$ (3). Phenylsilane (0.32 mL, 2.6 mmol) and non-1-ene (0.45 mL, 2.6 mmol) were added to a solution of complex **3** (0.0869 g, 0.0528 mmol) in hexane (5 mL). The reaction time was 12 h. The reaction mixture was quenched and the product was isolated as described above. The yield of $Ph(n\text{-}C_9H_{19})SiH_2$ was 0.57 g (94%).

Hydrosilylation of non-1-ene with $PhSiH_3$ in the presence of $\{[(Me_3Si)_2NC(NCy)_2]_2Lu(\mu\text{-}H)\}_2$ (4). Phenylsilane (0.34 mL, 2.7 mmol) and non-1-ene (0.47 mL, 2.7 mmol) were added to a solution of complex **4** (0.0983 g, 0.0540 mmol) in hexane (5 mL). The reaction time was 12 h. The reaction mixture was quenched and the product was isolated as described above. The yield of $Ph(n\text{-}C_9H_{19})SiH_2$ was 0.61 g (96%).

Reaction of $PhSiH_3$ with a five-fold molar excess of non-1-ene on a preparative scale

Hydrosilylation of non-1-ene with $PhSiH_3$ in the presence of $\{[(Me_3Si)_2NC(NPr^i)_2]_2Y(\mu\text{-}H)\}_2$ (1). Phenylsilane (0.20 mL, 1.6 mmol) and non-1-ene (1.36 mL, 7.9 mmol) were added to a solution of complex **1** (0.0418 g, 0.032 mmol) in hexane (5 mL). The reaction mixture was stirred for 24 h. To stop the reaction, 1-bromobutane (1 mL) was added to the reaction mixture. The solution was filtered, volatile organic compounds were evaporated *in vacuo* at room temperature. A liquid residue of high-boiling products was distilled at reduced pressure (0.05 Torr, 180—210 °C) to yield $Ph(n\text{-}C_9H_{19})_2SiH$ (0.34 g, 91%). Found (%): C, 80.12; H, 12.51. $C_{24}H_{44}Si$. Calculated (%): C, 79.92; H, 12.30. ^1H NMR ($CDCl_3$), δ: 0.93 (br.m, 10 H, CH_3 + $SiCH_2$); 1.31 (br.m, 28 H, CH_2); 4.39 (quint, 1 H, SiH, $^2J_{H,H}$ = 3.3 Hz); 7.41—7.63 (m, 5 H, SiC_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 11.9 ($SiCH_2$); 14.1 (CH_3); 22.7, 24.5, 29.3, 29.4, 29.5, 31.9, 33.3 (CH_2); 127.9, 129.1, 134.7, 136.2 (C_{Ar}). IR (KBr), ν/cm^{-1}: 466, 701, 732, 822, 940, 1013, 1115, 1169, 1260, 1300, 1378, 1408, 1426, 1465, 1589, 1734, 1759, 1813, 1876, 1949, 2109, 3015, 3049, 3070.

Hydrosilylation of non-1-ene with $PhSiH_3$ in the presence of $\{[(Me_3Si)_2NC(NPr^i)_2]_2Lu(\mu\text{-}H)\}_2$ (2). Phenylsilane (0.11 mL, 0.9 mmol) and non-1-ene (0.77 mL, 4.5 mmol) were added to a solution of complex **2** (0.0287 g, 0.019 mmol) in hexane (5 mL). The reaction time was 24 h. The reaction mixture was quenched and the product was isolated as described above. The yield of $Ph(n\text{-}C_9H_{19})_2SiH$ was 0.29 g (91%).

Hydrosilylation of non-1-ene with $PhSiH_3$ in the presence of $\{[(Me_3Si)_2NC(NCy)_2]_2Y(\mu\text{-}H)\}_2$ (3). Phenylsilane (0.32 mL, 2.6 mmol) and non-1-ene (2.28 mL, 13.2 mmol) were added to a solution of complex **3** (0.0869 g, 0.053 mmol) in hexane (3 mL). The reaction time was 24 h. The reaction mixture was quenched and the product was isolated as described above. The yield of $Ph(n\text{-}C_9H_{19})_2SiH$ was 0.32 g (93%).

Hydrosilylation of non-1-ene with $PhSiH_3$ in the presence of $\{[(Me_3Si)_2NC(NCy)_2]_2Lu(\mu\text{-}H)\}_2$ (4). Phenylsilane (0.09 mL, 0.7 mmol) and non-1-ene (0.6 mL, 3.5 mmol) were added to a solution of complex **4** (0.0253 g, 0.014 mmol) in hexane (5 mL). The reaction time was 24 h. The reaction mixture was quenched and the product was isolated as described above. The yield of $Ph(n\text{-}C_9H_{19})_2SiH$ was 0.24 g (94%).

Hydrosilylation of non-1-ene with phenylsilane in the presence of complex 1 (NMR-monitoring)

Hydrosilylation of non-1-ene with $PhSiH_3$ with the ratio of reagents 1 : 1. Phenylsilane (0.045 mL, 0.36 mmol) and non-1-ene (0.061 mL, 0.36 mmol) were added to a weighted amount of complex **1** (0.009 g, 0.0068 mmol, 2 mol.%) dissolved in benzene-d_6 (1 mL). The reaction was monitored by NMR for 3 days.

Hydrosilylation of non-1-ene with $PhSiH_3$ in the presence of a five-fold excess of non-1-ene. Phenylsilane (0.06 mL, 0.5 mmol) and non-1-ene (0.45 mL, 2.6 mmol) were added to a weighted amount of complex **1** (0.0138 g, 0.0104 mmol, 2.1 mol.%) dissolved in benzene-d_6 (1 mL). The reaction was monitored by NMR for 3 days.

Hydrosilylation of non-1-ene with the excess of phenylsilane. Phenylsilane (0.24 mL, 1.9 mmol) and non-1-ene (0.066 mL, 0.39 mmol) were added to a weighted amount of complex **1** (0.0102 g, 0.0077 mmol, 1.8 mol.%) dissolved in benzene-d_6 (1 mL). The reaction was monitored by NMR for 3 days.

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