

Supplementary information for:

A highly effective supported ionic liquid phase (SILP) catalysts – characterization and application to the hydrosilylation reaction

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Catalysts used in experiments

[Rh(PPh₃)₃Cl] and [Rh(μ-Cl)(cod)]₂ were purchased from Sigma Aldrich. [Rh(cod)(μ-OSiMe₃)₂] was prepared as described by Marciniak et. al.¹

Synthesis and analysis of Ionic Liquids (ILs)

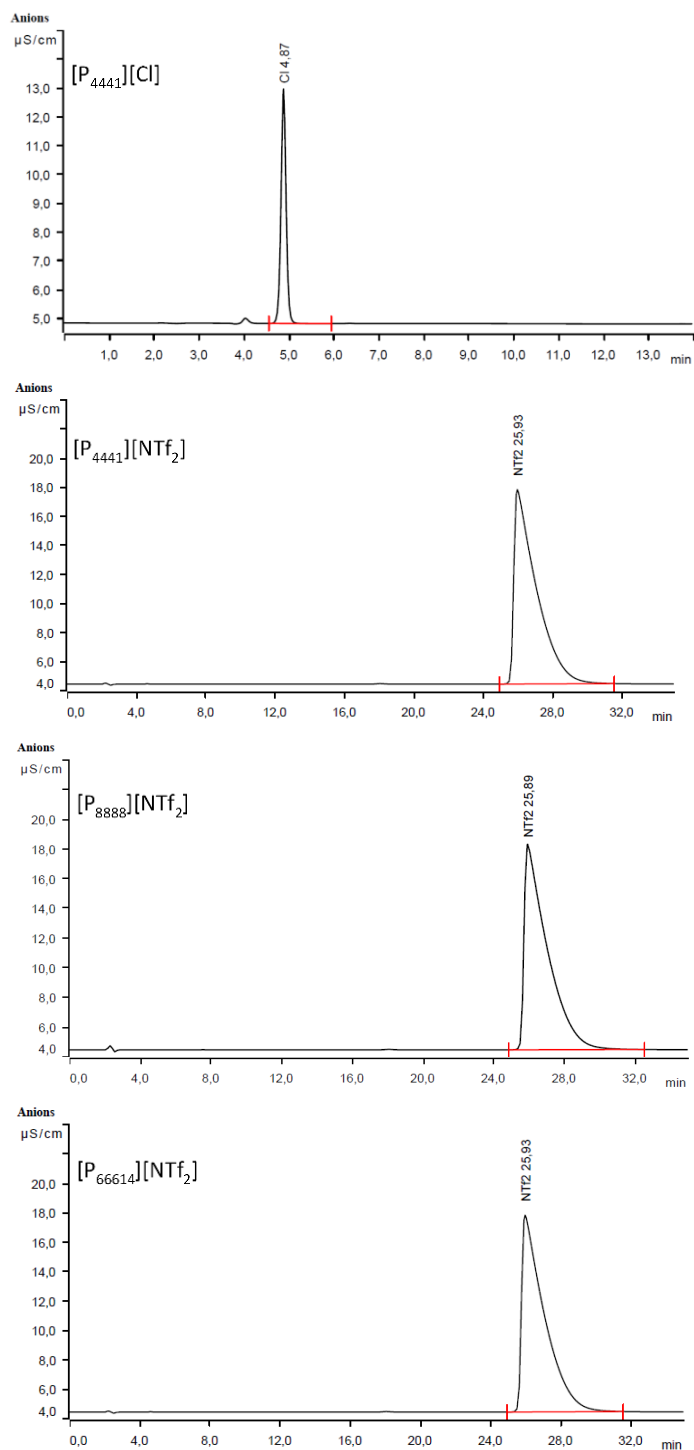


Figure S1. IC chromatograms of synthesized ILs with [NTf₂]⁻ anion from their chloride precursors. No peak observance at ~4.9 min means that [Cl]⁻ content in ionic liquid is below limit of detection.

ILs: tributylmethyl phosphonium bis(trifluoro-methylsulphonyl)imide [P₄₄₄₁][NTf₂], tetraoctylphosphonium bis(trifluoro-methylsulphonyl)imide [P₈₈₈₈][NTf₂], trihexyltetra-butyl phosphonium bis(trifluoromethylsulfonyl)imide [P₆₆₆₁₄][NTf₂] were synthesized by metathesis reaction from their halogen precursors as it was described in literature.² Purity of ILs was confirmed by ¹H NMR analysis and IC analysis (absence of halogen ion was observed, see Figure S1). Tributylmethylphosphonium methyl sulphate [P₄₄₄₁][MeSO₄], tributylmethylphosphonium chloride [P₄₄₄₁][Cl], tetraoctylphosphonium chloride [P₈₈₈₈][Cl] and trihexyltetradecyl phosphonium chloride [P₆₆₆₁₄][Cl] were purchased from Iolitec.

¹H NMR spectra were recorded on a Varian XL 300 NMR (300 MHz) using *d*6-DMSO as solvent with tetramethylsilane as the internal standard. Proton chemical shifts are shown in parts per million (δ ppm).

¹H NMR data for obtained salts:

[P₈₈₈₈][NTf₂]:

¹H NMR (300 MHz, DMSO): 2.17 (6H, m, P-CH₂-), 2.17 (8H, t, P-CH₂k), 1.27-1.47 (48H, m, -(CH₂)₆-), 0.87 (12H, t, -CH₃)

[P₄₄₄₁][MeSO₄]:

¹H NMR: (300 MHz, DMSO): 3.39 (3H, s, CH₃-SO₄⁻), 2.17 (6H, m, P-CH₂-), 1.80 (3H, s, P-CH₃), 1.43 (12H, m, -CH₂-CH₂-), 0.92 (9H, t, -CH₃)

[P₄₄₄₁][HSO₄]:

¹H NMR: (300 MHz, DMSO): 2.17 (6H, m, P-CH₂-), 1.80 (3H, s, P-CH₃), 1.43 (12H, m, -CH₂-CH₂-), 0.92 (9H, t, -CH₃)

[P₆₆₆₁₄][NTf₂]:

¹H NMR (300 MHz, DMSO): 2.18 (8H, t, P-CH₂-), 1.25-1.50 (48H, m, -(CH₂)_n-), 0.86-0.92 (12H, t, -CH₃)

[P₄₄₄₁][NTf₂]:

¹H NMR: (300 MHz, DMSO): 2.17 (6H, m, P-CH₂-), 1.80 (3H, s, P-CH₃), 1.43 (12H, m, -CH₂-CH₂-), 0.92 (9H, t, -CH₃)

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed on TGA Q50 Texas Instrument.

In order to determine decomposition temperature of examined ILs, the measurement were carried out as follows: samples between 8 – 15 mg were heated from 25°C to 100°C with heating rate of 10°C/min with a 10 min isotherm at 100°C under nitrogen atmosphere to remove water and possible volatile impurities present in the samples. Then samples were heating to 500°C with

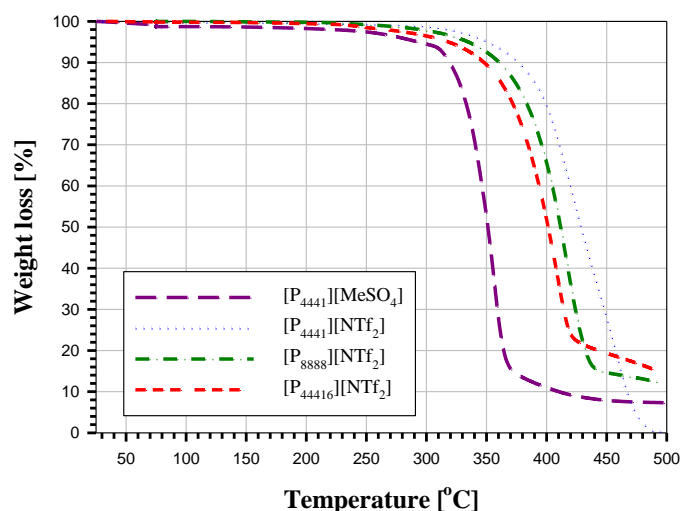


Figure S2. TGA curves of ILs used in SILP preparation.

heating rate of 10°C/min ([P₄₄₄₁][MeSO₄] were heating to 600°C). Results are presented in Figure S2 and Table S1.

Table S1. Onset decomposition temperature ($T_{d,onset}$) and 5% onset decomposition temperature ($T_{d,5\%onset}$) for the tested ILs and thermal stability of ILs at the temperature of 100°C, over the period of 10 h.

IL	$T_{d,onset}$ (°C)	$T_{d,5\%onset}$ (°C)	Loss of weight of ionic liquid [%]*
[P ₈₈₈₈][NTf ₂]	383	294	0.25
[P ₆₆₆₁₄][NTf ₂]	371	277	0.17
[P ₄₄₄₁][MeSO ₄]	334	284	0.21
[P ₄₄₄₁][NTf ₂]	384	318	0.40

In order to determine thermal stability of ILs at reaction temperature (100°C), the measurement were carried out as follows: samples between 8 – 15 mg were heated from 25°C to 100°C with heating rate of 10°C/min with a 10 hours isotherm at 100°C under nitrogen atmosphere. Despite the fact that we observed only loss of weight at a level of 0.4%, we did not determine either the onset temperature for decomposition of the first 5% of the sample ($T_{5\%onset}$) or the regular onset temperature for decomposition (T_{onset}) (Table S1).

Preparation of SILP materials

Silica support before impregnation was calcined (500°C, 24h) to decrease number of hydroxyl groups on silica support. In order to prepare supported ionic liquid on silica with rhodium catalyst (SILP from **A-L**) (to be later used in experiments at molar ratio 1-oct:HMTS:[Rh] 1:1:10⁻⁵) ionic liquid (0.2g) and rhodium catalyst ([Rh(PPh₃)₃Cl] – 0.68 mg, [RhCl(cod)}₂] – 0.18 mg and [Rh(cod)(μ-OSiMe₃)₂] – 0.53 mg) was dissolved in 20 ml dichloromethane. Subsequently mesoporous silica (High-purity grade Davisil Grade 62, Pore size 150 Å, 60-200 mesh, 1.15 cm³/g pore volume) (2 g) was added to a solution of IL in dichloromethane. In the next step the solution was stirred for 30 minutes at room temperature and after that the volatile solvent was very slowly evaporated, leaving a thin ionic liquid film on the surface of the support material. Then, SILP materials was dried under high vacuum at 40°C (48h).

In order to prepare supported ionic liquid on silica with rhodium catalyst (SILP (**L**), at lower rhodium concentration) (to be later used in experiments at molar ratio 1-oct:HMTS:[Rh] 1:1:10⁻⁷), ionic liquid (2 g) and rhodium catalyst [Rh(cod)(μ-OSiMe₃)₂] – 0.53 mg) was dissolved in 20 ml dichloromethane. Subsequently mesoporous silica (High-purity grade Davisil Grade 62, Pore size 150A, 60-200 mesh, 1.15 cm³/g pore volume) (20 g) was added to a solution of IL in dichloromethane. In the next step the solution was stirred for 30 minutes at room temperature and after that the volatile solvent was very slowly evaporated, leaving a thin ionic liquid film on the surface of the support material. Then, SILP materials was dried under high vacuum at 40°C (48h).

FT-IR spectra

FT-IR spectra were recorded in a Bruker Tensor 27 apparatus in the range 500–4000 cm⁻¹ of wave number. Solid samples (ca. 1 mg), were placed on a diamond window and then covered with a sapphire tip. Using OPUS 5.5 software, baseline and peak picking were carried out in order to determine the main peaks in the product.

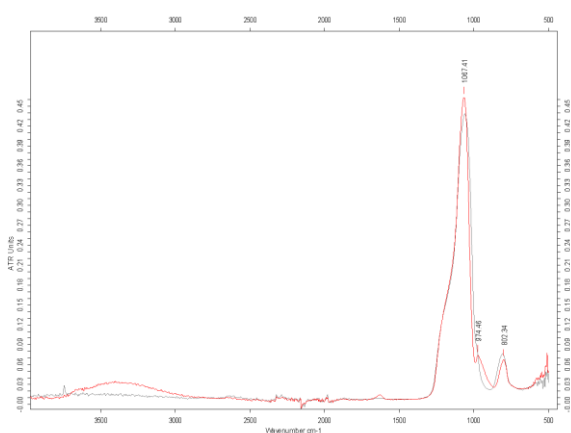


Figure S3. IR spectrum of silica support before (red) and after calcination (grey).

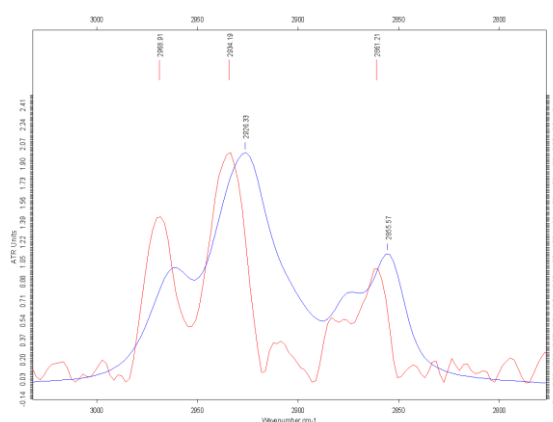


Figure S4. Part of an IR spectrum of (**J**) SILP material (red) and IL (blue).

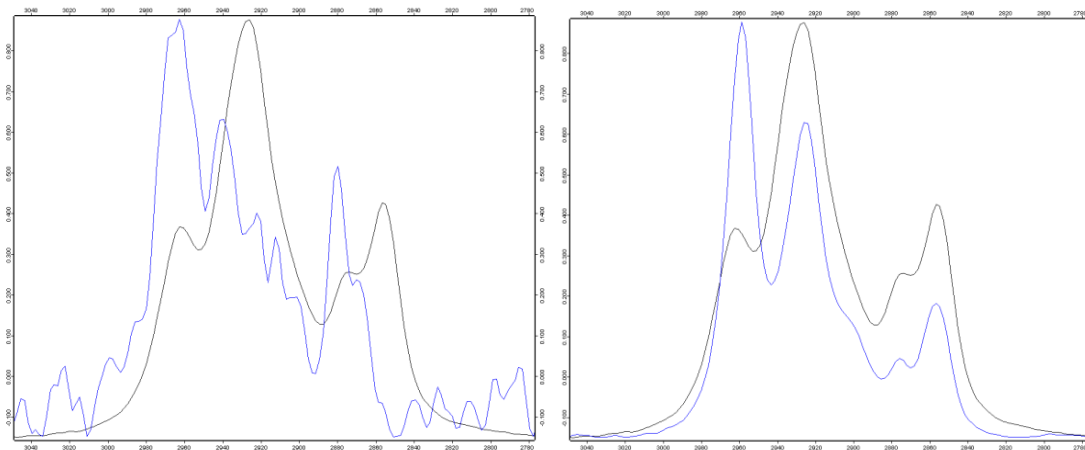


Figure S5. IR spectrum of IL [P4441][MeSO₄] (grey) and SILP (B) (blue) before hydrosilylation reaction (left) and after reaction (right).

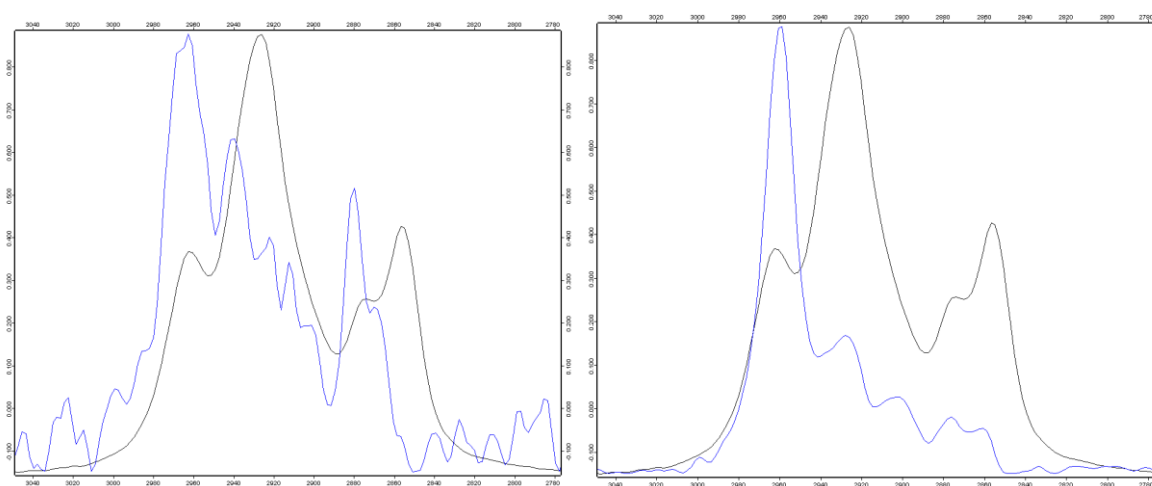


Figure S6. IR spectrum of IL [P4441][MeSO₄] (grey) and SILP (C) (blue) before hydrosilylation reaction (left) and after reaction (right).

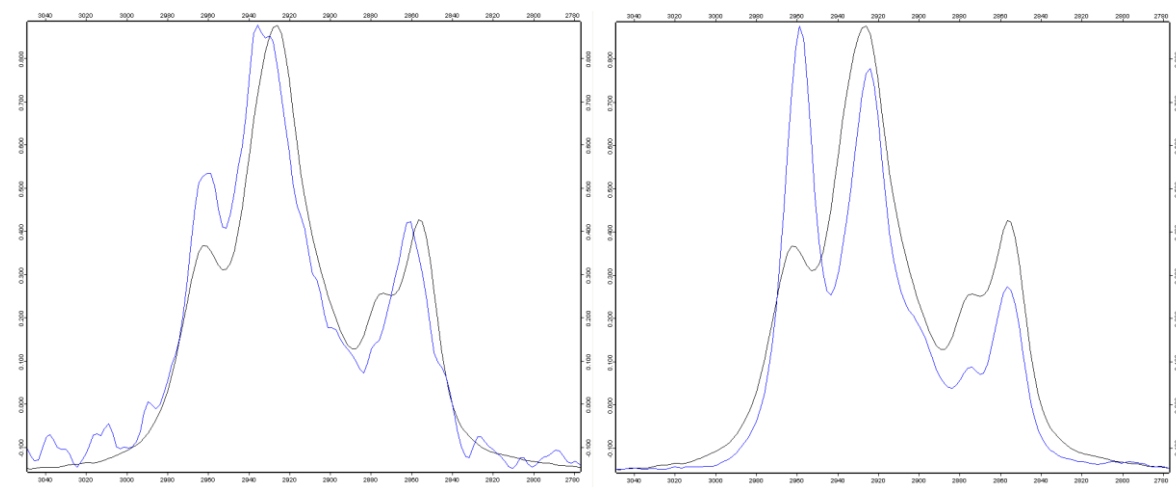


Figure S7. IR spectrum of IL [P4441][NTf₂] (grey) and SILP (D) (blue) before hydrosilylation reaction (left) and after reaction (right).

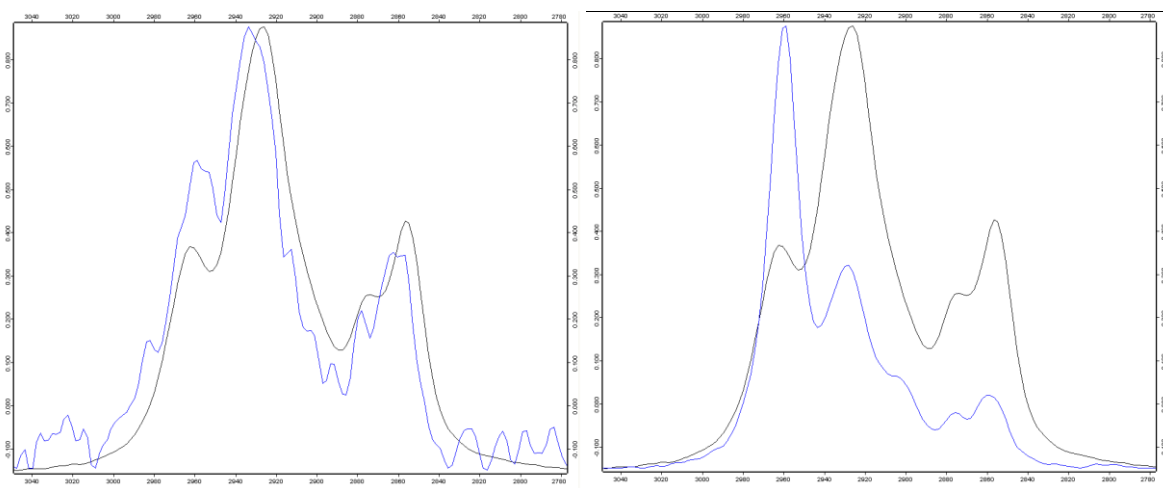


Figure S8. IR spectrum of IL [P₄₄₁][NTf₂] (grey) and SILP (E) (blue) before hydrosilylation reaction (left) and after reaction (right).

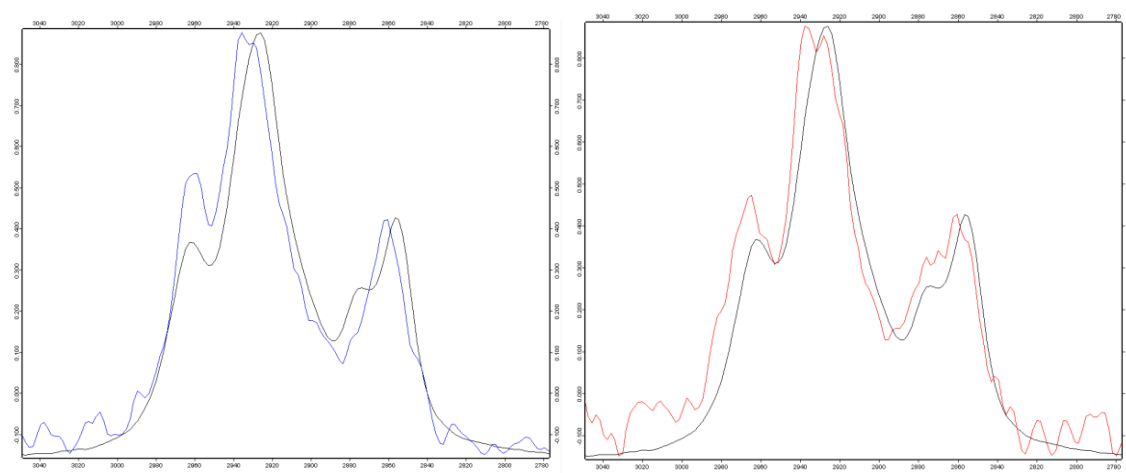


Figure S9. IR spectrum of IL [P₄₄₁][NTf₂] (grey) and SILP (F) (red) before hydrosilylation reaction (left) and after reaction (right).

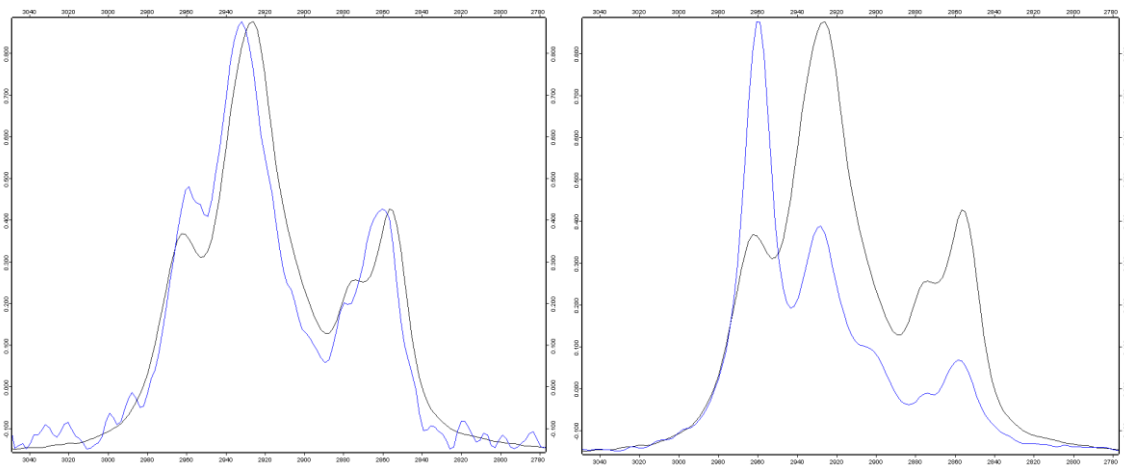


Figure S10. IR spectrum of IL [P₈₈₈][NTf₂] (grey) and SILP (g) (blue) before hydrosilylation reaction (left) and after reaction (right).

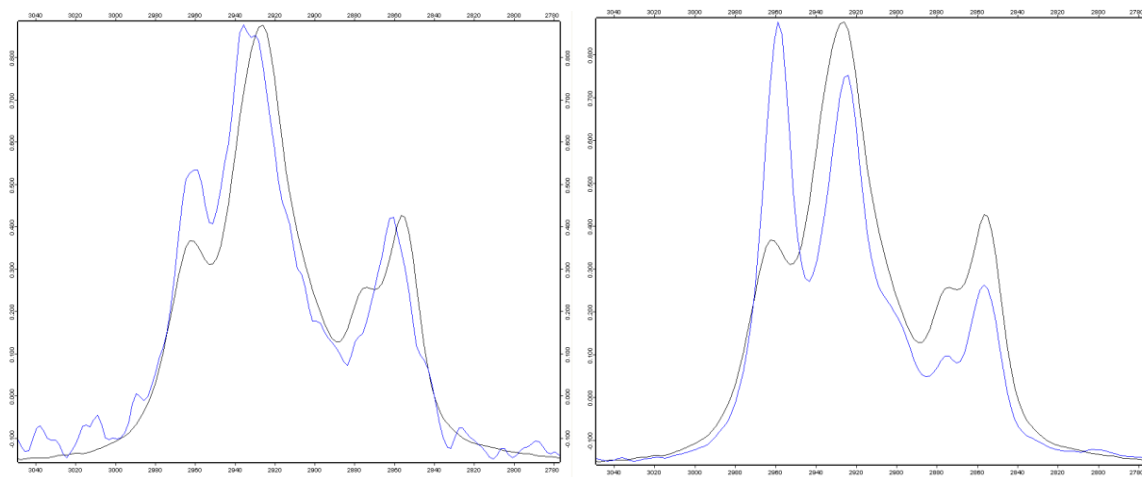


Figure S11. IR spectrum of IL $[P_{888}][NTf_2]$ (grey) and SILP (H) (blue) before hydrosilylation reaction (left) and after reaction (right).

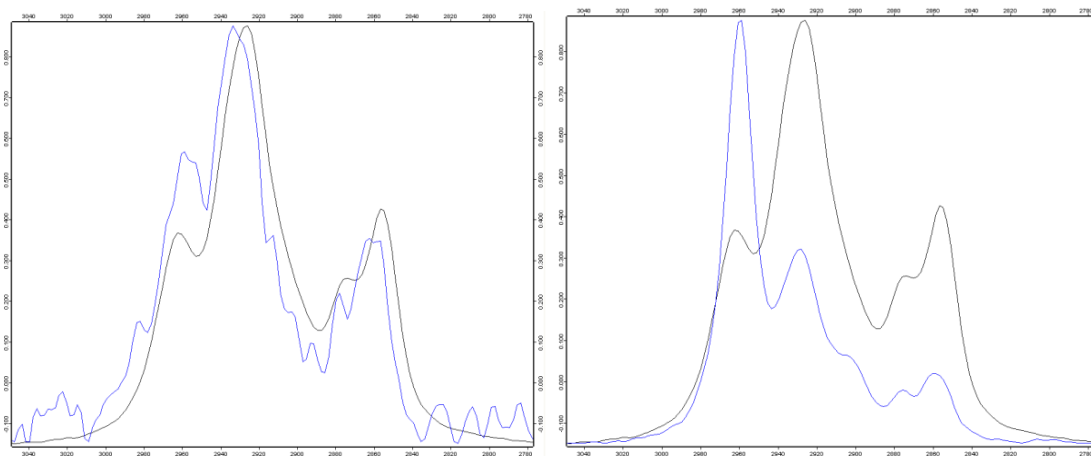


Figure S12. IR spectrum of IL $[P_{888}][NTf_2]$ (grey) and SILP (I) (blue) before hydrosilylation reaction (left) and after reaction (right).

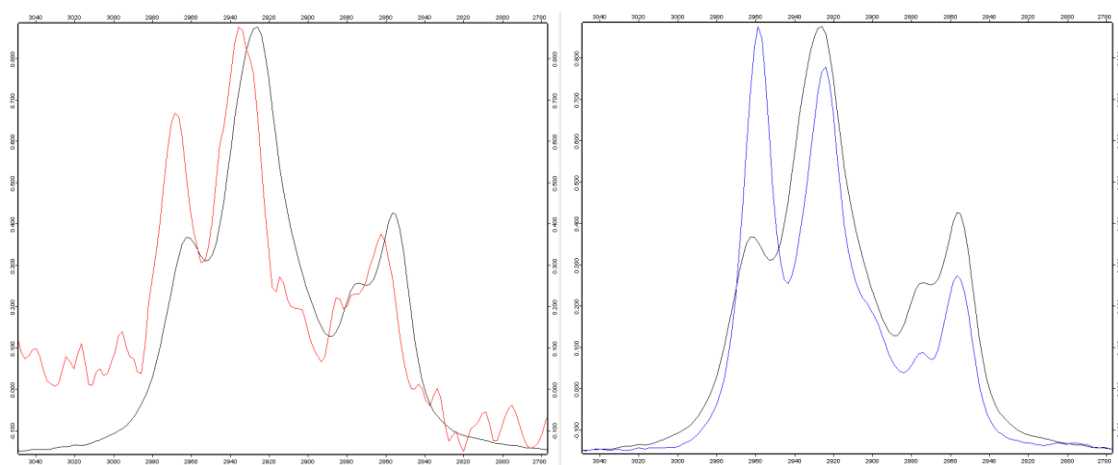


Figure S13. IR spectrum of IL $[P_{44416}][NTf_2]$ and (grey) and SILP (J) (red, blue) before hydrosilylation reaction (left) and after reaction (right).

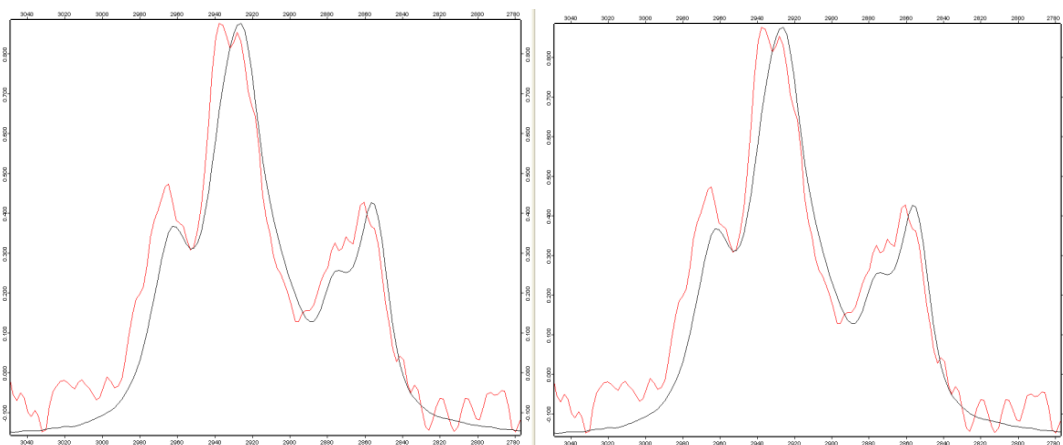


Figure S14. IR spectrum of IL [P₄₄₁₆][NTf₂] (grey) and SILP (**K**) (red) before hydrosilylation reaction (left) and after reaction (right).

Determination of surface area, pore volume and pore diameter

The Brunauer-Emmet-Teller (BET) surface areas were determined by N₂ adsorption at 77K using a Micromeritics ASAP 2010 sorptometer. Total pore volume and average pore diameter were determined

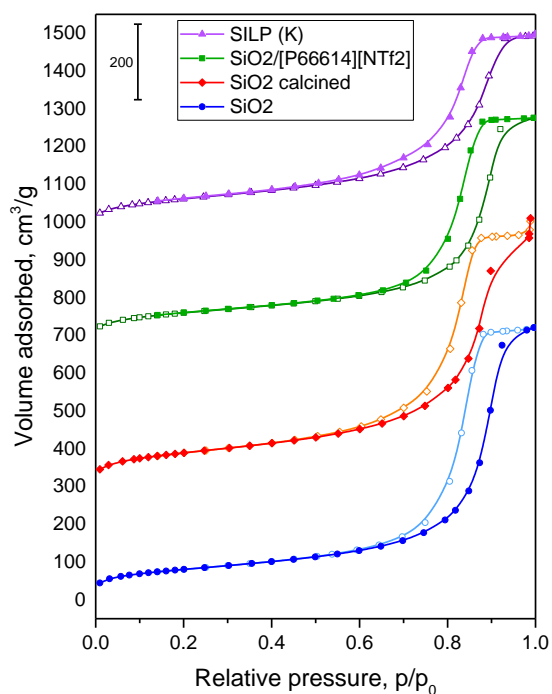


Figure S15. Exemplary adsorption/desorption isotherms of SiO₂, SiO₂ after calcination, SiO₂ with impregnated IL [P₆₆₆₁₄][NTf₂] and SILP (**K**).

by applying the Barrett-Joyner-Halenda (BJH) method to the isotherm desorption branch. Prior to the measurements of adsorption/desorption isotherms, the samples were outgassed at 393K for 20h.

All obtained low temperature nitrogen adsorption/desorption isotherms belong to Type IVa (according to the IUPAC classification) with a clearly marked hysteresis loop characteristic of mesoporous materials. Average pore diameters for SiO₂, calcined SiO₂, SiO₂/IL and SILP materials are similar (~10-15 nm).

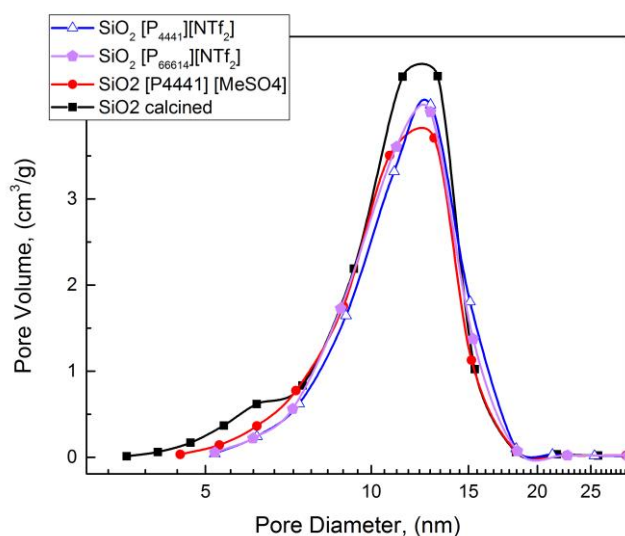


Figure S16. Dependence between pore volume distribution and pore diameter

Reaction progress monitored *in situ*

The progress of each of the hydrosilylation reaction was monitored and controlled by using a real time *in situ* IR spectrometer (React15 by Mettler Toledo). The conversion of Si-H bond was calculated from the decreasing area of band (calculated from the area band describing the vibration of Si-H - around 915 cm⁻¹).

Catalysis in homogenous system

To a two-necked flask, 1 ml HMTS (3.7 mmol), 0.58 ml 1-oct (3.7 mmol) and the rhodium catalyst ([Rh(PPh₃)₃Cl], [{Rh(μ-Cl)(cod)}₂] or [{Rh(cod)(μ-OSiMe₃)₂]) dissolved in hexane (concentration in hexane 10%) were added and heated to 100 °C while stirring. Molar ratio of 1-oct:HMTS:[Rh] was set to 1:1:10⁻⁴. Experiments with lower amount of catalyst were not carried out due to the problems with precise metering and dosing volume of catalysts dissolved in hexane. The reaction was carried out for 30 minutes. After collection and after cooling to room temperature, the samples were examined by GC in order to calculate the reaction conversion.

Catalysis in biphasic system

Reactions in biphasic liquid-liquid system were carried out as it was described by Jankowska-Wajda et al.³ using 0.58 ml of 1-octene and 1.0 ml of 1,1,1,3,5,5,5-heptamethyltrisiloxane as substrate and ILs ($[P_{4441}][NTf_2]$, $[P_{8888}][NTf_2]$, $[P_{66614}][NTf_2]$ or $[P_{4441}][MeSO_4]$) with dissolved catalyst ($[Rh(PPh_3)_3Cl]$, $[Rh(\mu-Cl)(cod)_2]$ or $[Rh(cod)(\mu-OSiMe_3)_2]$). Molar ratio of 1-oct:HMTS:[Rh] was set to 1:1:10⁻⁴, IL loading 10%. Reaction was carried out by 30 minutes at 100°C. After reaction product was characterized by GC and GC/MS/ to confirm selectivity.

Reactions with using SILP materials

The reaction system was composed of a glass reactor of 2 ml capacity and a side neck for substrate introduction, equipped with a magnetic stirrer and reflux condenser. The reactor was charged with the SILP material (in 0.1g of SILP material is amount of catalyst corresponding to 10⁻⁵ mole of Rh per 1 mole of substrates or in 0.01g of SILP material is amount of catalyst corresponding to 10⁻⁷ mole of Rh per 1 mole of substrates) and then the substrates 0.58 ml of 1-octene and 1 ml of 1,1,1,3,5,5,5-heptamethyltrisiloxane (1 : 1 molar ratio) were added to the reactor (molar ratio of 1-oct:HMTS:[Rh] was set to 1:1:10⁻⁵ or molar ratio of 1-oct:HMTS:[Rh] was set to 1:1:10⁻⁷). The whole mixture was stirred and heated at 100°C for 30 minutes. Subsequently system was cooled to room temperature and liquid phase was separated from solid SILP material. Product phase was then analyzed by GC (Figure S17) and GC/MS/MS to confirm selectivity (Figure S18-S20) and SILP material was reused to next reaction cycle.

GC analysis

The yield of the reaction was analysed using an Varian CP 3800 Gas Chromatograph with FactorFour VF-5ms column with decane as internal standard . Additional experiments to confirm the selectivity of the reactions were performed using a Varian 400 GC/MS/MS instrument.

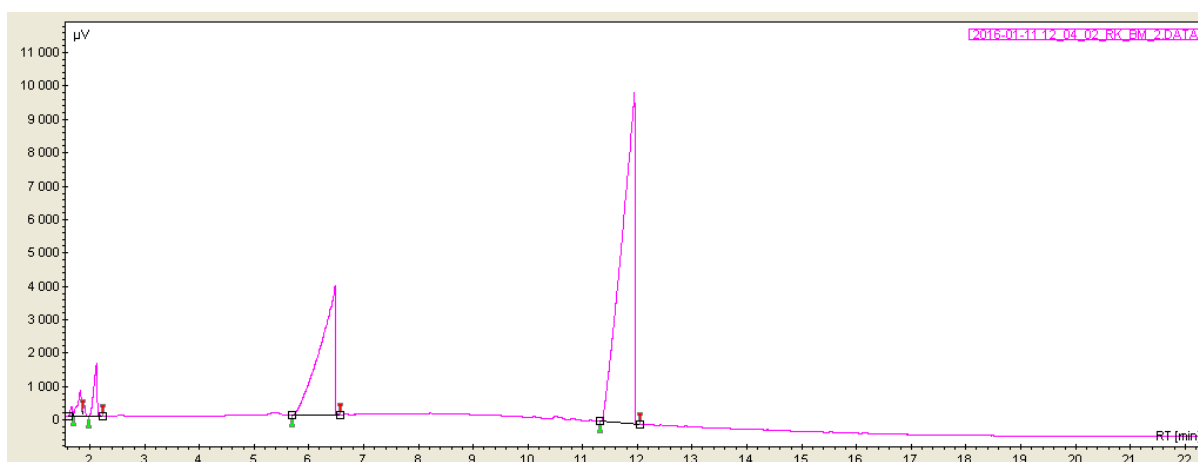


Figure S17. GC chromatograms of post reaction mixture obtained from reaction using SILP (A); retention times 1.5-2.0 min – substrates (1-octene, HMTS), 6.4 min – decane (internal standard), 11.7 min – product (octyloheptamethyltrisiloxane)

GC/MS/MS chromatograms

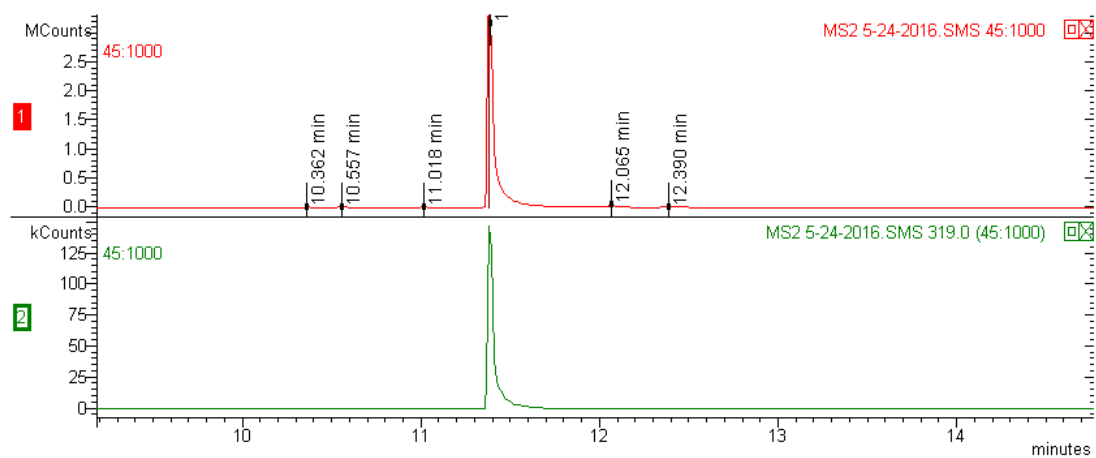


Figure S18. GC-MS chromatogram of octyloheptamethyltrisiloxane obtained from batch reaction using SILP (A); 1- TIC chromatogram, 2- 319M/z chromatogram

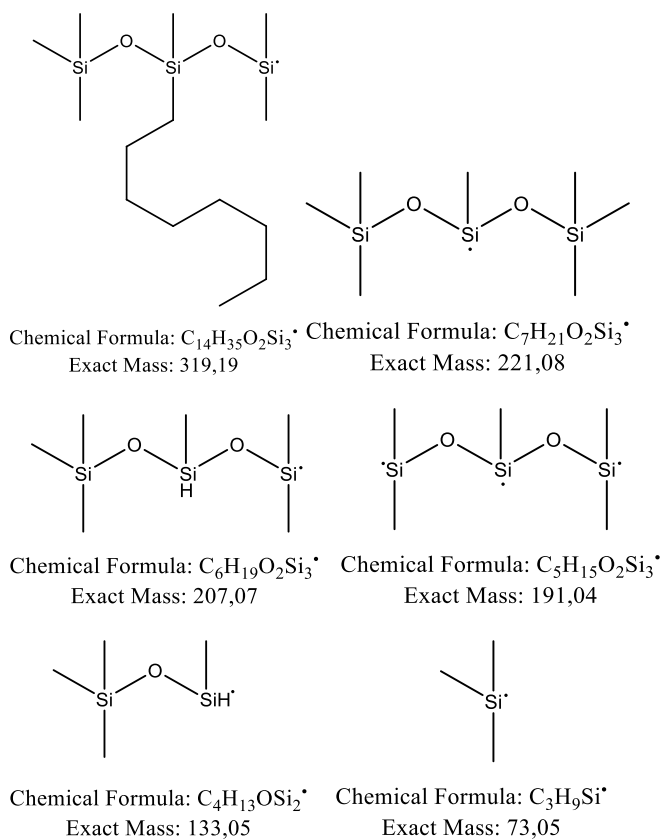


Figure S19. MS spectra of octyloheptamethyltrisiloxane (product) at the retention time 11.38 min obtained from reaction using SILP (A)

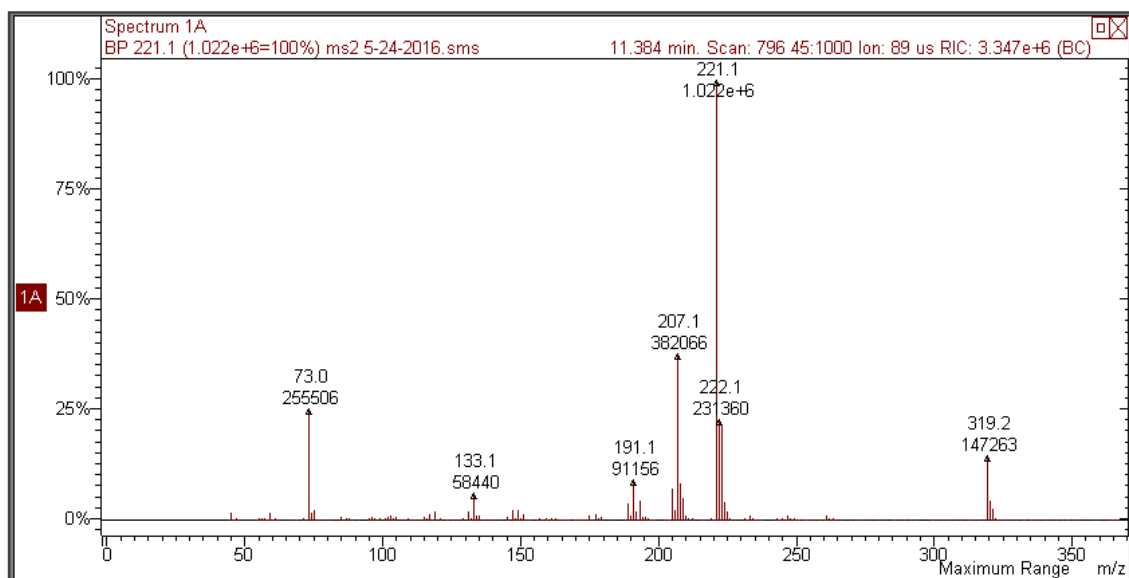


Figure S20. Proposed fragmentation of MS spectra of octyloheptamethyltrisiloxane as observed for the peak from GC-MS measurements at the retention time 11.38 min

³¹P NMR

³¹P NMR spectra were recorded on a Bruker Ascend™ (600 MHz) using CDCl₃ as solvent. Phosphorus chemical shifts are shown in parts per million (δ ppm).

Leaching ionic liquid from SILP material experiments

The ³¹P NMR spectrum was measured on the [P₄₄₄₁][MeSO₄] to identify the signal from the substituted phosphorus atom. Then, the given ionic liquid was dissolved in CDCl₃ (0.5 ml) and a number of samples with a varying concentration of the IL in CDCl₃ were prepared: 0.005 mg/0.5 ml, 0.025 mg/0.5 ml, 0.05 mg/0.5 ml and 0.5 mg/0.5 ml respectively) to check limit of detection. Peak from ILs in all concentration, with exception of 0.005 mg/0.5 ml, were observed in NMR spectra. Then, for each of the reaction with using SILP material, after the first reaction cycle, 10% of the volume of post reaction mixture (0.158 ml) was separated and evaporated on high vacuum (60°C, 24h). Amount of ILs examined in ³¹P NMR studies correspond to 1%, 5%, 10% and 100% of mass of IL in post reaction mixture sample (0.158 ml of post reaction mixture, max amount of IL in sample on the assumption that 100% of IL leached from SILP material – 0.5 mg).

The limit of detection ionic liquid in the conditions of conducting experiment in the samples was 1% of mass of IL in SILP material (0.01 mg). Subsequently sample was dissolved in 0.5 ml of CDCl₃ and the ³¹P NMR spectrum was performed. ³¹P NMR spectra were recorded on a Bruker Ascend™ (600 MHz) using CDCl₃ as solvent. Phosphorus chemical shifts are shown in parts per million (δ ppm).

ICP analysis

Attempts to determine the rhodium content were performed using an ICP-OES (Quantima).

Three-phase test

The reaction system was composed of a glass reactor of 2 ml capacity and a side neck for substrate introduction, equipped with a magnetic stirrer and reflux condenser. The reactor was charged with the SILP (C) material (in 0.1g of SILP material where the amount of catalyst corresponds to 10⁻⁵ mol of Rh) and then the substrates 0.58 ml of 1-octene and 1 ml of 1,1,1,3,5,5,5-heptamethyltrisiloxane (1 : 1 molar ratio) were added to the reactor (molar ratio of 1-oct:HMTS:[Rh] was set to 1:1:10⁻⁵). The whole mixture was stirred and heated at 100°C for 30 minutes. Subsequently system was cooled to room temperature and liquid phase was separated from solid SILP (C) material. Product phase was then analyzed by GC (Figure S17) to determine Si-H conversion and yield and SILP (C) material was reused in the next reaction cycle. To each product phase, separated from SILP after subsequent cycle, additional portion of substrates (0.58 ml of 1-octene and 1 ml of 1,1,1,3,5,5,5-heptamethyltrisiloxane) was added without new portion of catalyst. The mixture was heated at 100°C for 30 minutes. In the next step system was cooled to room temperature and analyzed by GC.

Catalytic activity

Table S2. Comparison of data obtained from GC and *in situ* IR (conversion of Si-H bond, in percent) for the reaction between HMTS and 1-octene (SILP (A)).

T, conc. of the catalyst [°C; 1-oct:HMTS:[Rh]]	conversion of Si-H bond [%]							
	1 min		10 min		20 min		30 min	
	GC	IR	GC	IR	GC	IR	GC	IR
100°C, 1:1:10 ⁻⁵	69	66	99	99	99	99	>99	99
100°C, 1:1:10 ⁻⁶	70	68	93	93	96	96	>99	99
100°C, 1:1:10 ⁻⁷	11	4	20	19	21	18	20	20

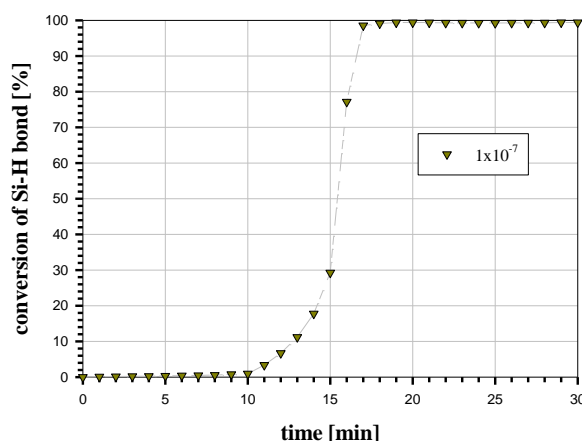


Figure S21. Conversion of Si-H monitored *in situ* on example on SILP (L) between 1-oct and HMTS in molar ratio of 1-oct:HMTS:[Rh] 1:1:10⁻⁷ at 100°C.

Determination of isolated yields

The isolated yields for product, octylheptamethyltrisiloxane, obtained in reaction using SILP (A), (D) and (G) were determined. Product, after synthesis described according to procedure in section “Reactions with using SILP materials” was isolated as follows.

To remove possible traces of ionic liquid, product phase was shaken vigorously using funnel separator with acetonitrile and then separated from organic solvent. To remove residues of solvent and other volatile impurities, including substrates 1-octene and HMTS, product was kept under high vacuum (40°C, 48h). Then, HNMR, GC and GC/MS/MS analysis were performed to confirm structure and selectivity of product.

As it is shown in chromatograms, only one peak is presented from product (11.7 min, Figure S17 and S18). Moreover, fragmentation of product at retention time (11.4) confirms structure of octylheptamethyltrisiloxane (Figure S19 and S20). Also, HNMR analysis confirms purity of obtained product. Isolated yields and ¹HNMR data are presented below:

Reaction with SILP (A)

octylheptamethyltrisiloxane

isolated yield 96%

δH (CDCl_3 , 298K, 300 MHz) = 0.21 (s, 18H), 0.26 (s, 3H), 0.70 (t, 2H), 0.99 (t, 3H), 1.32 (t, 12H), 1.38 (m, 2H)

Reaction with SILP (D)

octylheptamethyltrisiloxane

isolated yield 92%

δH (CDCl_3 , 298K, 300 MHz) = 0.21 (s, 18H), 0.26 (s, 3H), 0.70 (t, 2H), 0.99 (t, 3H), 1.32 (t, 12H), 1.38 (m, 2H)

Reaction with SILP (G)

octylheptamethyltrisiloxane

isolated yield 93%

δH (CDCl_3 , 298K, 300 MHz) = 0.21 (s, 18H), 0.26 (s, 3H), 0.70 (t, 2H), 0.99 (t, 3H), 1.32 (t, 12H), 1.38 (m, 2H)

Hot filtration tests

The reaction system was composed of a glass reactor of 2 ml capacity and a side neck for substrate introduction, equipped with a magnetic stirrer and reflux condenser. The reactor was charged with the SILP (L) material (in 0.1g of SILP material is amount of catalyst corresponding to 10^{-5} mole of Rh per 1 mole of substrates) and then the substrates 0.58 ml of 1-octene and 1 ml of 1,1,1,3,5,5,5-heptamethyltrisiloxane (1 : 1 molar ratio) were added to the reactor (molar ratio of 1-oct:HMTS:[Rh] was set to 1:1: 10^{-5}). The entire mixture was stirred at 100°C for 30 minutes. After this time, the hot mixture of SILP (L) and product was separated using filters. Product phase was then cooled to room temperature.

Transmission electron microscopy (TEM) measurements

Both, SILP (L) catalyst which was dried under high vacuum (40°C, 48h) and product phase after hot filtration tests were examined via Transmission electron microscopy (TEM) HRTEM Jeol ARM 200F.

Mercury poisoning test

One drop of mercury was added to the reagents followed by addition of the SILP (L) catalyst. Then, mixture was stirred at 100°C for 30 minutes. After this time, the solution was decanted from the mercury and SILP (L) catalyst and product phase was then analyzed by GC. Product was obtained with 99% yield (the same yield as in experiments without mercury).

References

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- (2) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, 2008, DOI 10.1002/9783527621194.
- (3) Jankowska-Wajda, M.; Kukawka, R.; Smiglak, M.; Maciejewski, H. The effect of the catalyst and the type of ionic liquid on the hydrosilylation process under batch and continuous reaction conditions. *New J. Chem.* **2018**, *42* (7), 5229-5236, DOI 10.1039/C7NJ04396A.