

Recyclable and Convenient-to-Handle Pt/Ethylene Glycol Catalytic System – an Approach to Sustainable Hydrosilylation

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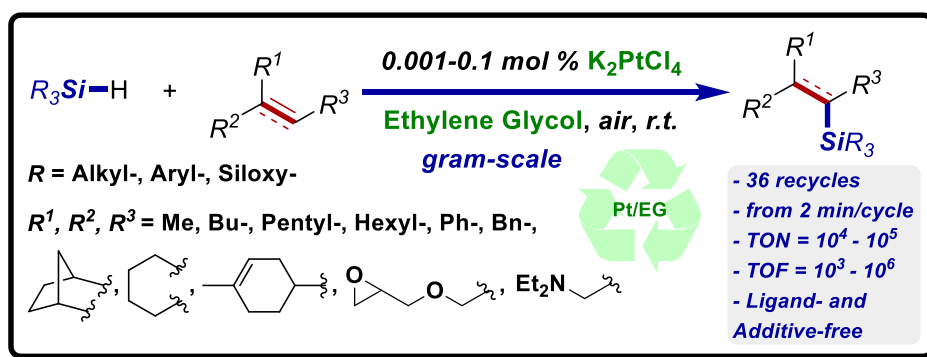
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Graphical Abstract



Abstract

This study presents a highly efficient and simple recyclable catalytic system for heterophase hydrosilylation. This catalytic system consisting of a commercially available platinum precatalyst, namely K_2PtCl_4 , and a cheap green solvent, namely ethylene glycol (EG), is easily prepared by dissolving K_2PtCl_4 in EG without employing ligands, additives, or an inert atmosphere, at *r.t.* The suggested method allows up to 45 recycles with quantitative conversion under air at *r.t.* to be performed. The high reaction rate (from 2 to 20 min per cycle) and low catalyst load (0.001 – 0.1 mol%) allow high values of TON (up to $\sim 10^4 - 10^5$) and TOF (up to $\sim 10^3 - 10^6$) to be reached. This approach is applicable to a wide range of unsaturated compounds, such as functional and nonfunctional terminal or internal alkenes, alkynes, and alkyl-, phenyl-, and siloxy-containing hydride silanes. Moreover, the heterophase catalytic system is suitable for the synthesis of linear and cross-linked polyorganosiloxanes. In most cases, the reaction provides high yields (up to 95-99%) and selectivity. It gives mostly *anti*-Markovnikov products which can be isolated from the catalytic system by simple decantation. The process is scalable to gram quantities.

30 **Keywords**

31 Hydrosilylation, heterophase catalysis, recycling and regeneration, hydride silanes,
32 unsaturated hydrocarbons, platinum, ethylene glycol, silicones, organosiloxanes

33

34 **1. Introduction**

35 Hydrosilylation, *i.e.*, addition of hydride silanes to unsaturated hydrocarbons, mainly
36 alkenes, is a key method for creating a Si–C-bond.¹ This reaction is used on the large
37 scale and presents the most successful example of homogeneous catalysis in industry.
38 Moreover, hydrosilylation opens a route to a wide variety of organosilicon products that
39 are widely used in nearly all fields of human activity, from aviation and space industries
40 to agriculture and medicine.²

41 This process was first mentioned in the middle of the 20th century, but a real
42 breakthrough in this field was made in 1957 in a work by Speier who was the first to
43 suggest the use of H_2PtCl_6 (in $i\text{-PrOH}$; Speier's catalyst) as a homogenous catalyst for
44 the *anti*-Markovnikov hydrosilylation of unsaturated compounds.³ The application of
45 Speier's catalyst made it possible to expand the capabilities of hydrosilylation
46 significantly and make it an industrial process. Later, a new and more efficient Pt-
47 catalyst type, namely $\text{Pt}_2(\text{dvtms})_3$, a complex of Pt^0 with the dvtms ligand (where dvtms
48 is divinyltetramethyldisiloxane), was developed and suggested by Karstedt in 1973.⁴
49 This catalyst is more active and well-soluble in organic solvents (and in siloxane
50 environments).⁴ In 2002, Marco presented a Pt-complex where one of the weakly
51 coordinating dvtms ligands in Karstedt's catalyst was replaced by a strongly
52 coordinating N-heterocyclic carbene (NHC), *i.e.*, $\text{Pt}(\text{dvtms})(\text{NHC})$.^{5a} The strong binding
53 of the Pt^0 -center by the NHC ligand prevents the formation of colloidal platinum which,
54 in addition to being able to catalyze a number of side reactions (reduction and
55 isomerization of alkenes), contaminates the reaction product. Studies on the synthesis
56 of new Pt-complexes are still continuing. Thus, in recent years, articles on the
57 development of new highly active and selective homogeneous Pt-catalysts of
58 hydrosilylation, in particular single-atom catalysts (SAC), were published.⁵ However,
59 Speier's and Karstedt's catalysts still hold their position as the main industrial
60 hydrosilylation catalysts.¹ Although these Pt-catalysts are efficient at rather low loads
61 (≤ 0.1 mol%), the industrial consumption of platinum is high. In 2007, the organosilicon
62 industry consumed about 5.6 tons of platinum.⁶

63 Given the growth of prices for platinum, its high consumption, and irretrievable
64 "scattering", the development of new approaches that can solve these problems, at
65 least partially, is an extremely urgent and practically important goal in the chemistry of
66 the 21st century.

67 Though attempts to switch to catalysts based on cheaper and more accessible earth-
68 abundant transition metals⁷ made a significant scientific contribution to the development
69 and study of hydrosilylation reactions, they failed to find industrial application so far. Yet
70 another promising approach is the transition to heterogeneous⁸ or heterophase⁹
71 (biphase) recyclable catalysts. In recent years, studies were published on the
72 production of such catalysts that are not only recyclable^{8i,9d} but are also not inferior to
73 the most active homogeneous catalysts.^{5c-e}

74 The purpose of this study was to develop a recyclable hydrosilylation catalyst that would
75 be active under mild conditions, be air- and moisture-stable, require no special
76 preparation step, be convenient-to-handle and cost-effective.

77

78 **1. Results and Discussion**

79 One of the most promising approaches involves the development of heterophase
80 catalytic systems in which no ligands, substrates, various additives, or preliminary
81 stages of catalyst preparation are required. The most suitable media for heterophase
82 catalytic systems are alcohol derivatives, in particular one of the most accessible
83 polyols, ethylene glycol (EG).¹⁰ EG is an inexpensive, commercially available, low-toxic
84 and nonvolatile solvent.¹¹ Like other alcohols, it can reduce metal ions, including those
85 of platinum. An important feature of EG, like other polyols, is that it can act as a ligand
86 and stabilizer of M⁰-particles. The high polarity of EG can facilitate a separation of the
87 Pt-catalyst along with the solvent (EG) from the highly hydrophobic organosilicon
88 products, thus the regenerated Pt/EG-catalytic system can be used repeatedly.

89 **1.1. Pt/EG-Catalyzed Heterophase Recyclable Hydrosilylation**

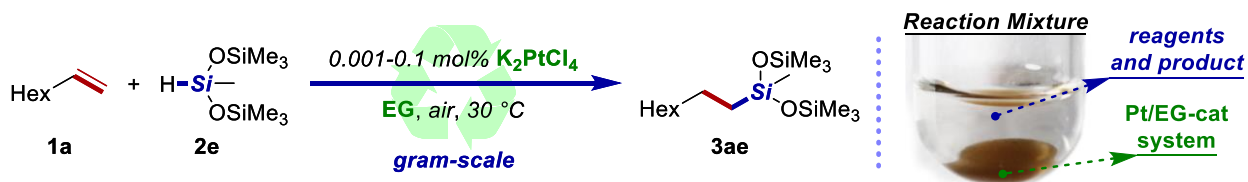
90 The hydrosilylation of 1-octene **1a** (1 eq., 0.45 mmol, 50.1 mg) with
91 bis(trimethylsiloxy)methylsilane **2e** (1 eq., 0.45 mmol, 100 mg) was chosen as the
92 model reaction. It was performed at room temperature (*r.t.*; 30 °C was used throughout
93 to unify the results), at atmospheric pressure and in the air, using commercially
94 available and easy-to-handle K₂PtCl₄ (which is stable in air and non-hygroscopic, unlike

95 H₂PtCl₆) dissolved in EG (**Table 1**) as the Pt-source. The Pt/EG-catalytic system was
96 prepared just prior to use by dissolving K₂PtCl₄ (0.1 mol% with respect to reagents **1a** /
97 **2e**, 0.19 mg) in EG (25 wt.% with respect to reaction mass, 43.81 mg) at *r.t.* without
98 adding any ligands, additives or creating an inert atmosphere. It was found that
99 hydrosilylation occurred efficiently under these conditions to selectively give *anti*-
100 Markovnikov addition product **3ae** with quantitative conversion (≥95%; entry 1, Table 1).
101 The reaction time is less than 10 min, which is comparable to that in the presence of
102 Karstedt's catalyst (neat, solvent-free).^{Ошибка! Закладка не определена.} It is important to note
103 that no side product of OH-group in EG silylation is formed. Unlike with Speier's catalyst
104 or K₂PtCl₄ (reaction under solvent-free conditions and in an organic aprotic polar or
105 nonpolar solvent; see Supp. Inf., Table S1), no induction period is observed in the
106 Pt/EG-catalytic system. It means that the catalytically active Pt⁰-form is generated
107 almost instantly upon mixing K₂PtCl₄ with EG.

108 The isolation of the reaction product **3ae** and separation of the heterophase Pt/EG-
109 catalytic system were performed by ordinary decantation of the upper organosilicon
110 phase from the lower EG phase, or by a syringe in case of small loads. Since
111 separation of the organosilicon phase from the Pt/EG-catalytic system occurs without
112 mechanical losses and the conversion of reagents **1a** and **2e** to product **3ae** is
113 quantitative, the yield of target product **3ae** is also quantitative (≥95%; note a, **Table 1**).

114

Table 1. Pt/EG-Catalyzed Heterophase Recyclable Hydrosilylation



Entry	Cycle Number	Reaction Time Per Cycle	Conversion, ^a	TON ^b	TOF ^b , h ⁻¹
1	1	10-20 min	≥95%		
2	2-35	10-20 min	≥95%		
3	36	10-20 min	≥95%	3.42x10 ⁴	2.85x10 ³ – 5.7x10 ³
4	37	10-20 min 10-12 h	24% ≥95%		
5	38, 39	10-12 h	≥95%		
6	40	10-12 h	≥95%	3.8x10 ⁴	6.33x10 ² – 8.26x10 ²
7	41	10-12 h 1-3 days	29% ≥95%		
8	42-44	1-3 days	≥95%		
9	45	1-3 days	≥95%	4.27x10 ⁴	1.02x10 ² – 2.57x10 ²
10	1-5 ^c	10-20 min	≥95%		
11	1 ^d	10-20 min	≥95%		
12	2-5 ^d	10-20 min	≥95%		
13	6 ^d	10-20 min	≥95%	5.7x10 ⁴	2.85x10 ⁴ – 5.7x10 ⁴
14	1 ^e	10-20 min	≥95%		
15	2 ^e	10-20 min	≥95%	1.9x10 ⁵	2.85x10 ⁵ – 5.7x10 ⁵
16	1 ^f	2 min	≥95%		2.85x10 ⁴
17	1 ^{d,f}	5 min	≥95%		1.14x10 ⁵
18	1 ^{e,f}	7 min	≥95%		8.14x10 ⁵

117 Reaction conditions: A mixture of **1a** (0.45 mmol, 0.0501 g, 1 eq) and **2e** (0.45 mmol, 0.1 g, 1 eq) was
 118 added to the Pt/EG catalytic system (44 mg, 0.2 wt.% Pt in EG, prepared by mixing K_2PtCl_4 [0.1 mol%
 119 with respect to reagents **1a** / **2e**, 0.19 mg] and EG [25 wt.% with respect to the mass of the reaction
 120 mixture, 43.81 mg]); the resulting two-phase system was stirred at 30 °C under air for 10 min in the first
 121 cycle. The reaction mixture was analyzed using GLC and ¹H NMR. After reaching ≥95% conversion, the
 122 upper layer (organosilicon products) was decanted, and another portion of **1a** (0.45 mmol, 0.0501 g, 1 eq)
 123 and **2e** (0.45 mmol, 0.1 g, 1 eq) was added to the remaining catalytic system. *Notes:* (a) conversion
 124 corresponds to the yield of **3ae**; (b) the total value of TON for the corresponding number of recycles, TON
 125 = (cycle number • product amount [mol]) / catalyst load [mol]; the total value of TOF for the corresponding
 126 number of recycles taking into account the total process time (for the corresponding number of recycles),
 127 TOF = TON / total process time (Table S4, Supp. Inf.); (c) 10-times process scaling, at 0.1 mol% K_2PtCl_6 ;
 128 (d) 0.01 mol% K_2PtCl_6 (0.019 mg); (e) 0.001 mol% K_2PtCl_6 (0.0019 mg); (f) TOF for the 1st cycle.

129 The possibility of using the heterophase Pt/EG-catalytic system more than once was
130 studied. It was shown in subsequent experiments with the Pt/EG-catalytic system that
131 36 recycles could be performed with quantitative conversion to product **3ae** and a time
132 of 10-20 min per recycle (entries 1-3, **Table 1**). This allowed high total values of TON
133 (Turnover Number $\sim 3.42 \times 10^4$, note *b*, **Table 1**), as well as TOF (Turnover Frequency \sim
134 $2.85 \times 10^3 - 5.7 \times 10^3 \text{ h}^{-1}$, note *b*, **Table 1**) to be reached (the total process time from
135 recycle 1 to recycle 36 is 6-12 h; Table S4, Supp. Inf.).

136 However, subsequent recyclizations from 37 to 40 cycles were accompanied by an
137 abrupt decrease in the activity of the Pt/EG-catalytic system, so more time, up to 10-12
138 h, was required for the quantitative conversion (entries 4-6, **Table 1**). Four additional
139 recycles could be additionally performed in this mode to give a total of 40 recycles. In
140 this case, the total TON value amounted to 3.8×10^4 (in recycles 1 through 40), the total
141 value of TOF decreased to $6.33 \times 10^2 - 8.26 \times 10^2 \text{ h}^{-1}$ (the total process time of recycles 1
142 through 40 was 46-60 h; Table S4, Supp. Inf.) due to a considerable increase in the
143 duration of recycles 37 to 40. In the subsequent recycles, from 41 to 45, the Pt/EG-
144 catalytic system also manifested activity but much more time, 1-3 days, was required for
145 the quantitative conversion (entries 7-9, **Table 1**).

146 Furthermore, we also showed the suggested reaction to be scalable. Upscaling the
147 reaction 10-fold showed that the Pt/EG-catalytic system also worked efficiently: the
148 reaction time did not increase (10-20 min was quite enough to achieve the quantitative
149 conversion). Moreover, the subsequent recyclization with the Pt/EG-catalytic system
150 occurred without any loss of activity and selectivity, as shown by the example of 5
151 recyclizations (entry 10, note *c*, **Table 1**).

152 We studied whether the precatalyst (K_2PtCl_4) loading can be diminished from 0.1 mol%
153 (0.19 mg) to 0.01 mol% (0.019 mg) or 0.001 mol% (0.0019 mg) without altering the
154 amount of EG. A K_2PtCl_4 load of 0.01 mol% (entries 11-13, note *d*, **Table 1**) or 0.001
155 mol% (entries 14-15, note *e*, **Table 1**) made it possible to perform 6 or 2 recycles,
156 respectively, with a quantitative conversion to product **3ae** and a time of 10-20 min per
157 recycle. At a K_2PtCl_4 load of 0.01 mol%, the total values of TON $\sim 5.7 \times 10^4$ and TOF \sim
158 $2.85 \times 10^4 - 5.7 \times 10^4 \text{ h}^{-1}$ were achieved (Table S4, Supp. Inf.). In the case of a K_2PtCl_4
159 load of 0.001 mol%, even larger total values of TON $\sim 1.9 \times 10^5$ and TOF $\sim 2.85 \times 10^5 -$
160 $5.7 \times 10^5 \text{ h}^{-1}$ were reached (Table S4, Supp. Inf.).

161 In fact, the reported TON and TOF values could have been even higher if the specified
162 10-20 min per cycle had not included the times of analysis and product isolation. In
163 order to determine the real reaction time required for the quantitative formation of
164 product **3ae**, two recycles, each with three different Pt-catalyst loads, were performed
165 (Tables S2-S4, Supp. Inf.).

166 With 0.1 mol% of the Pt-catalyst (entry 16, **Table 1**), the reaction occurred with
167 quantitative conversion into product **3ae** at the 1st and 2nd cycles in 2 min each, which
168 allowed a TOF $\sim 2.85 \times 10^4 \text{ h}^{-1}$ to be reached (for the 1st cycle, 2 min). If the catalyst load
169 was decreased to 0.01 mol% (entry 17, **Table 1**), the reaction at the 1st and 2nd cycles
170 required 5 min each to complete, with TOF $\sim 1.14 \times 10^5 \text{ h}^{-1}$ (for the 1st cycle, 5 min). At
171 0.001 mol% of the Pt-catalyst (entry 18, **Table 1**), the reaction required 7 and 10 min at
172 the 1st and 2nd cycles, respectively, and TOF became $8.14 \times 10^5 \text{ h}^{-1}$ (for the 1st cycle, 7
173 min). Taking the TON and TOF values obtained into account, we believe that these are
174 not the maximum values.

175

1.2. Scope of Pt/EG-Catalyzed Heterophase Hydrosilylation

The applicability of the Pt/EG-catalytic system for the hydrosilylation of functional or nonfunctional terminal and internal alkenes as well as alkynes with tertiary silanes of various nature was studied (**Figure 1**; Supp. Inf., Figure S1). To estimate the efficiency of the suggested Pt/EG-catalytic system for hydrosilylation, comparative experiments were also performed with Karstedt's catalyst that is most widely used industrially and is commercially available (notes *a* and *b*, **Figure 1**). The qualitative and quantitative composition of the products was studied using 1D и 2D ^1H , ^{13}C and ^{29}Si NMR spectroscopy after the reaction was carried out for 24 h at *r.t.*

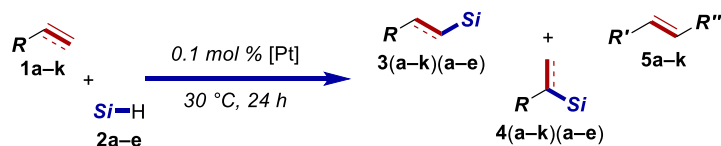
The applicability of the method to various hydride silanes was studied using the reactions of alkyl-, phenyl-, and siloxy-containing hydride silanes **2a-e** with 1-octene **1a** as an example (**Figure 1, A**). The reaction of di(methyl)phenylsilane **2a** in the presence of both catalysts results in the quantitative conversion to the corresponding *anti*-Markovnikov product **3aa**. In the case of a more sterically hindered hydride silane, methyldi(phenyl)silane **2b**, the conversion to product **3ab** occurs quantitatively if the Pt/EG-catalytic system is used. With Karstedt's catalyst, product **3ab** is formed in 78% yield, along with 14% of internal alkenes **5a**, *i.e.*, isomerization products of 1-octene **1a**. Mono(siloxy)di(methyl)silanes **2c,d** and bis(siloxy)methylsilane **2e** are quantitatively converted to *anti*-Markovnikov addition products **3ac,ad,ae** in the reaction with 1-octene **1a**, both in the presence of the Pt/EG-catalytic system and Karstedt's catalyst. However, the Pt/EG-catalytic system is not applicable to hydride-containing alkoxy- and chlorosilanes (see Supp. Inf., Figure S2). It can be explained by side reactions, namely, (trans)esterification or hydrolysis of the Si–OEt- and Si–Cl-groups followed by removal of the corresponding hydride silanes from the reaction zone.

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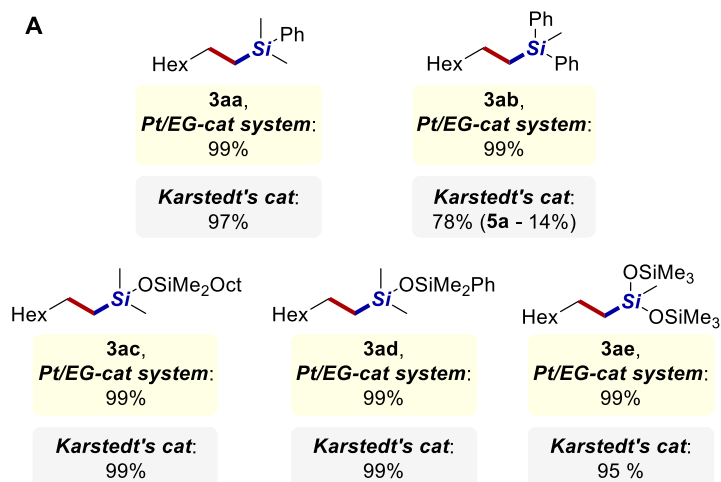
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Figure 1. Scope of Pt/EG-Catalyzed Heterophase Hydrosilylation.

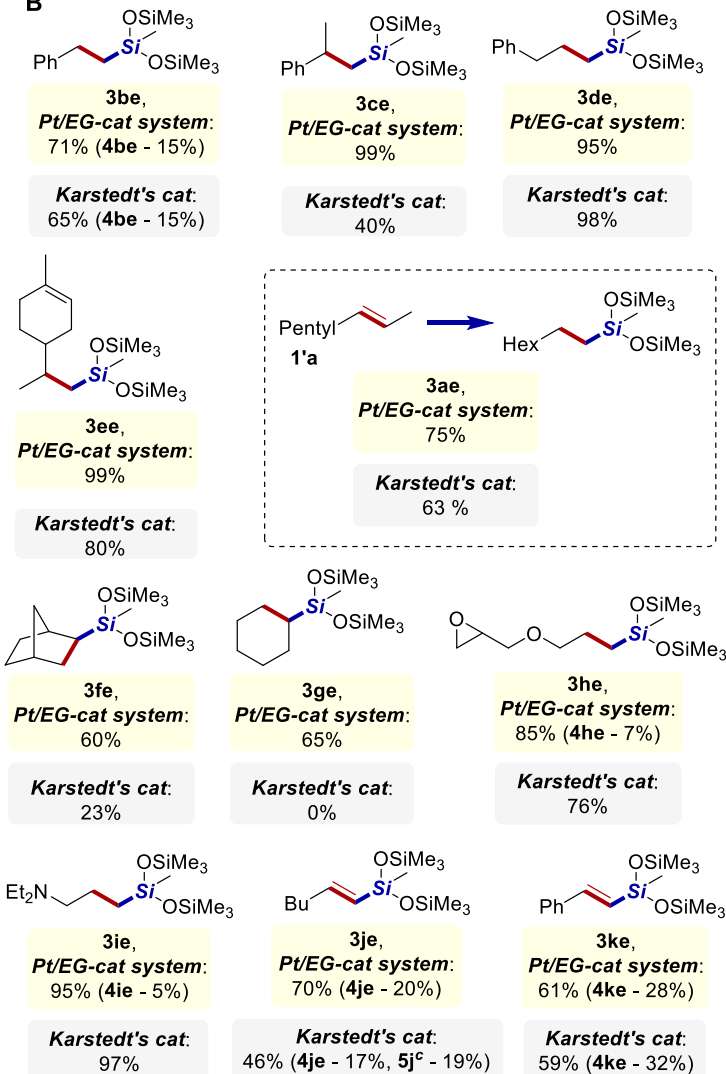
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Comparison of the Pt/EG catalytic System^a with Karstedt's catalyst^b

A



B



203

204 Note: (a) **1a-k** (0.45 mmol, 1 eq), **2a-e** (0.45 mmol, 1 eq) and K₂PtCl₄ solution in EG system (44 mg, 0.2
205 wt.% Pt in EG) prepared by mixing K₂PtCl₄ [0.1 mol% reagents **1a-k** / **2a-e**, 0.19 mg] and EG [43.81 mg]
206 were stirred for 24 h at 30 °C under air. (b) **1a-k** (0.45 mmol, 1 eq), **2a-e** (0.45 mmol, 1 eq) and Karstedt's
207 catalyst (5 μL, 2 wt.% Pt solution in xylene; commercially available form) were stirred for 24 h at 30 °C
208 under Ar. (c) **5j** is a product of **3je** isomerization.

209

210 The applicability of the Pt/EG-catalytic system for the hydrosilylation of unsaturated
211 hydrocarbons with diverse structures **1b-k** with hydride silane **2e** was studied (**Figure 1,**
212 **B**). The hydrosilylation of styrene **1b** results in a major *anti*-Markovnikov (**3be**) and
213 minor Markovnikov (**4be**) products in a ratio of **3be/4be** – 71%/15% with the Pt/EG-
214 catalytic system or 65%/15% with Karstedt's catalyst. The hydrosilylation of α-
215 methylstyrene **1c** with the Pt/EG-catalytic system results in the quantitative conversion
216 to the *anti*-Markovnikov product **3ce**, but only 40% of product **3ce** is formed in the
217 presence of Karstedt's catalyst. The hydrosilylation of allylbenzene **1d** in the presence
218 of the Pt/EG-catalytic system or Karstedt's catalyst also leads to the selective formation
219 of *anti*-Markovnikov product **3de** with quantitative conversion. The hydrosilylation of
220 limonene, which has both internal and terminal double bonds, occurs selectively at the
221 terminal position to give the *anti*-Markovnikov product **3ee** with quantitative conversion
222 in the case of the Pt/EG-catalytic system or 80% conversion with Karstedt's catalyst.

223 It was found that internal alkenes could also undergo hydrosilylation with the Pt/EG-
224 catalytic system (**Figure 1, B**). The reaction of hydride silane **2e** with an acyclic internal
225 alkene, 2-octene **1'a**, occurs as isomerization-hydrosilylation to give product **3ae** with
226 75% or 63% conversion in the presence of the Pt/EG-catalytic system or Karstedt's
227 catalyst, respectively. In the case of cyclic internal alkenes (**1f,g**), the difference
228 between the catalytic activity of the Pt/EG-catalytic system and Karstedt's catalyst
229 becomes more evident. In fact, hydrosilylation of norbornene **1f** results in product **3fe** in
230 the presence of the Pt/EG-catalytic system with 60% conversion, while with Karstedt's
231 catalyst, the conversion is 23%. In the case of cyclohexene **1g**, the formation of product
232 **3ge** with 65% conversion is observed in the presence of the Pt/EG-catalytic system,
233 whereas the product is not formed at all with Karstedt's catalyst.

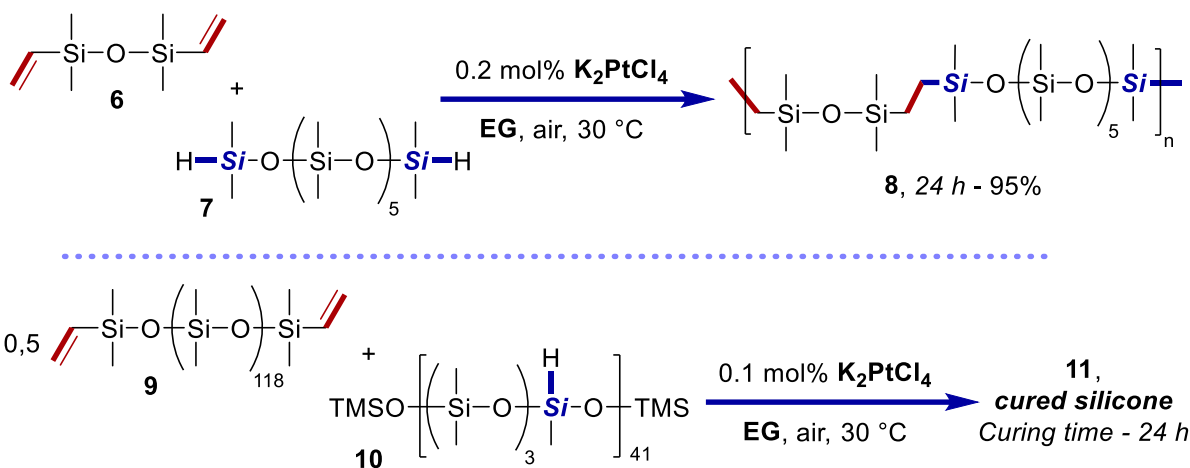
234 The reaction of allylglycidyl ether **1h** with hydride silane **2e** in the presence of the
235 Pt/EG-catalytic system gives a major *anti*-Markovnikov product **3he** with 85%
236 conversion and a minor Markovnikov product **4he** with 7% conversion; in the case of
237 Karstedt's catalyst, product **3he** is formed with 76% conversion.

238 Hydrosilylation of allyldi(ethyl)amine **1i** in the presence of the Pt/EG-catalytic system
239 also results in a major *anti*-Markovnikov (**3ie**) and a minor Markovnikov product (**4ie**)
240 with a ratio **3ie/4ie** – 95%/5%; the reaction in the presence of Karstedt's catalyst gives
241 product **3ie** with 97% conversion.

242 In addition to alkenes, the possibility of hydrosilylation of alkynes **1j,k** to give vinylsilane
243 derivatives was studied (**Figure 1, B**). The reaction of 1-hexyne **1j** with hydride silane
244 **2e** under Pt/EG-catalytic system conditions gives a mixture of *anti*-Markovnikov (**3je**,
245 major) and Markovnikov (**4je**, minor) addition products with a **3je/4je** ratio of 70%/20%.
246 If Karstedt's catalyst is used, in addition to a mixture of products **3je** and **4je** with a
247 **3je/4je** ratio of 46%/17%, migration of the double bond in vinylsilane **3je** to give a
248 mixture of isomeric products **5j** with up to 19% conversion is also observed (note c,
249 **Figure 1**). The hydrosilylation of phenylacetylene **1k** with both the Pt/EG-catalytic
250 system and Karstedt's catalyst produced a mixture of products of *anti*-Markovnikov
251 (**3ke**, major) and Markovnikov (**4ke**, minor) addition products with **3ke/4ke** ratios of
252 61%/28% and 59%/32%, respectively.

253 It can be summarized that the suggested Pt/EG-catalytic system is not only as efficient
254 as the industrially important Karstedt's catalyst, but is superior to the latter in some
255 cases (**Figure 1**). For example, the Pt/EG-catalytic system is less sensitive to the steric
256 environment of a hydride silane (**2b**) or alkene (**1c,e,f,g**) and does not catalyze the
257 isomerization of alkene derivatives into their internal derivatives (**5j**), unlike Karstedt's
258 catalyst. However, the Pt/EG-catalytic system operates slightly less selectively in the
259 case of allyl alcohol and amine derivatives than Karstedt's catalyst. The limitations of
260 the Pt/EG catalytic system include its inapplicability to chloro- and alkoxy-hydride
261 silanes.

262 Furthermore, we studied the prospects of the Pt/EG-catalytic system in the synthesis of
263 linear (**8**) and cross-linked (**11**) organosiloxane polymers (**Figure 2**).



265

266 Note: (a) **6** (0.225 mmol, 0.042 g, 1 eq), **7** (0.225 mmol, 0.11 g, 1 eq) and K_2PtCl_4 solution in ethylene
 267 glycol (44 mg, 0.2 wt.% Pt in EG, was prepared by mixing K_2PtCl_4 [0.2 mol% to reagents **6** / **7**, 0.19 mg]
 268 and EG [43.81 mg]) and stirring for 24 h at 30 °C under air. The reaction mixture was analyzed using ^1H
 269 NMR and GPC. After reaching $\geq 95\%$ conversion, the mixture was separated by centrifugation and
 270 decantation of the upper layer (organosilicon products). (b) **9** (0.0113 mmol, 0.1 g, 1 eq), **10** (0.0226
 271 mmol, 0.006 g, 2 eq of $[(\text{Me}_2\text{SiO})_3\text{Si}(\text{Me})\text{H}]$ -units), and K_2PtCl_4 solution in ethylene glycol (2.2 mg, 0.2
 272 wt.% Pt in EG, was prepared by mixing K_2PtCl_4 [0.1 mol% to reagent **10**, 0.0095 mg] and EG [2.19 mg])
 273 and stirring for 24 h at 30 °C under air.

274 The use of readily separable and regenerable catalytic systems to produce such
 275 polymeric organosiloxanes and the corresponding silicone materials based on these is
 276 an extremely important practical goal. As mentioned above, this will not only reduce
 277 platinum emission/losses, regenerate and recycle it and thus solve economic and
 278 environmental problems, but also minimize the contamination of polysiloxanes with
 279 colloidal platinum that adversely affects the performance characteristics of such
 280 materials. *Ошибка! Залкадка не определена.* The point is that the purification of high-molecular-
 281 weight silicone products from platinum is much more difficult than that of low-molecular-
 282 weight organosiloxanes that can be purified by distillation. For example, the reaction of
 283 tetra(methyl)di(vinyl)disiloxane **6** and oligomeric siloxane with terminal Si-H-groups **7**
 284 gives linear organosiloxane **8** with 95% conversion of Si-H-/Si-Vin-groups in 24 h (GPC
 285 data: $M_n = 9\,000$, $M_w = 15\,500$, $\text{PDI} = 1.7$). Cross-linked polymers – the basis for RTV
 286 (Room-Temperature-Vulcanizing) silicone compositions¹² – were also obtained using
 287 the Pt/EG-catalytic system in the reaction of a polymeric siloxane with terminal Si-Vin-
 288 groups **9** and a siloxane with internal Si-H-groups **10** as an example. The example of
 289 product **8** shows the possibility of separating a catalytic system from the reaction
 290 product. Due to the high viscosity of polysiloxane **8**, it was difficult to separate the

291 product from the catalytic system by simple decantation, but this task was easily
292 accomplished by centrifugation.

293

294 **2. Conclusion**

295 Thus, a regenerable and recyclable heterophase Pt/EG-catalytic system for
296 hydrosilylation based on K_2PtCl_4 , a commercially available Pt-precatalyst, and ethylene
297 glycol (EG), a cheap, commercially available and green heterophase medium, was
298 suggested. The developed catalytic system makes it possible to perform up to 36 cycles
299 with quantitative conversion, no induction period, no loss of activity, a reaction time of 2-
300 20 min (per cycle) and low Pt-catalyst loading (0.001 – 0.1 mol%), under air at *r.t.* High
301 total values of TON up to $\sim 10^4$ – 10^5 and TOF up to $\sim 10^3$ – 10^6 were achieved using
302 the Pt/EG-catalytic system. The reaction product is isolated by simple decantation from
303 the catalytic system in a quantitative yield ($\geq 95\%$). This method is well scalable to gram
304 quantities without loss of catalytic activity.

305 This approach is applicable to a wide range of compounds, such as functional and
306 nonfunctional terminal or internal alkenes, alkynes, as well as alkyl-, phenyl-, and siloxy-
307 containing hydride silanes. In most cases, the reaction provides high yields (up to 95-
308 99%) and selectivity, giving mostly *anti*-Markovnikov products. The method also makes
309 it possible to obtain linear and cross-linked polyorganosiloxanes that form the basis of
310 silicone materials, with the possibility of separating the Pt-containing catalytic system
311 from the final material, which is one of the practically important procedures in the
312 silicone industry. It should be noted that the suggested Pt/EG-catalytic system is not
313 only as efficient as Karstedt's industrial catalyst, but is superior in some cases. One of
314 the limitations of the Pt/EG-catalytic system is that it is not applicable to chloro- and
315 alkoxy-hydride silanes.

316 Though the suggested Pt/EG-catalytic system is inferior to certain homogeneous,^{5c-e}
317 heterogeneous^{8l} and heterophase^{9d} catalysts in terms of the TON and TOF values, it is
318 unsophisticated, reliable, and easy to accomplish.

319 **Experimental section**

320 Catalyst preparation: K_2PtCl_4 (2 mg, 0.0048 mmol, 0.939 mg Pt-atoms) and ethylene
321 glycol (468 mg) were stirred at 30 °C for 10-15 minutes until total dissolution. A clear
322 transparent solution of the Pt/EG catalytic system (0.2 wt.% Pt-atoms) was thus
323 obtained and used at once after preparation. 44 mg of the Pt/EG catalytic system was
324 transferred into a Schott culture tube and used in the reaction.

325 General procedure: A mixture of **1a-k** (0.45 mmol, 1 eq) and **2a-e** (0.45 mmol, 1 eq)
326 was added to a K_2PtCl_4 solution in ethylene glycol (44 mg of solution: 0.2 wt.% Pt, 0.001
327 eq Pt). The resulting two-phase system was stirred in a Schott culture tube at 30 °C.
328 The reaction mixture was analyzed using GLC, 1H , ^{13}C and ^{29}Si NMR.

329

330 **Supporting Information**

331 Supp.Inf.: optimization, methods of synthesis, characterization data (PDF).

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