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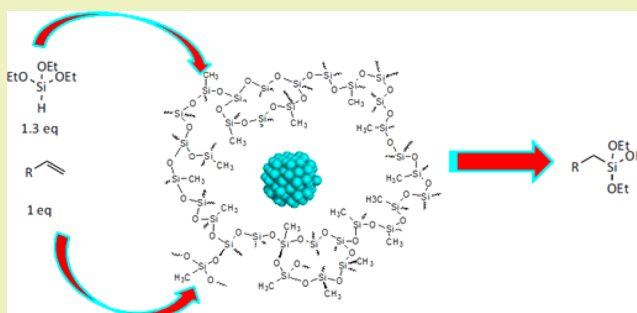
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## Closing the Organosilicon Synthetic Cycle: Efficient Heterogeneous Hydrosilylation of Alkenes over SiliaCat Pt(0)

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**ABSTRACT:** A modest 0.5–1 mol % amount of the sol–gel entrapped hybrid catalyst SiliaCat Pt(0) selectively mediates the hydrosilylation of different olefins under Ar atmosphere at room temperature or at 65 °C, depending on the substrate. Low levels of Pt leaching ensure minimal amounts of platinum residues in crude product and no plant contamination. Valued platinum nanoparticles remain entrapped within the organosilica xerogel that can thus be reused.

**KEYWORDS:** Hydrosilylation, Platinum, Immobilization, Heterogeneous, Sol–Gel, SiliaCat

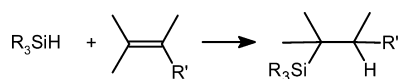


## ■ INTRODUCTION

Hydrosilylation is a reaction widely used in the silicone industry for the preparation of monomers containing silicon–carbon bonds and for cross-linking silicone polymers.<sup>1</sup> Organosilicon compounds<sup>2</sup> are the building blocks of silicones and hybrid inorganic–organic materials, namely, of Si polymers nowadays of fundamental relevance in industry and research. Silicones are currently used as coatings, sealants, preservatives, gels, foams, aerosols, adhesives, encapsulants, and hair/skin care and impression materials (dental applications). ORMOSILs (organically modified silicates) have now found practical application in fields as diverse as catalysis, chromatography, chemical analysis, biotechnology, advanced coatings, and many more.<sup>3</sup>

Since the 1957, introduction<sup>4</sup> of the chloroplatinic acid (Speier catalyst, H<sub>2</sub>PtCl<sub>6</sub>), catalysis of alkene hydrosilylation (or hydrosilation) using homogeneous Pt complexes, has been the fundamental method for the synthesis of organosilicon compounds both in industry and the laboratory. The method generally consists of the addition of Si–H bonds on unsaturated bonds like alkenes or alkynes promoted by a homogeneous or heterogeneous platinum group metal catalyst (Scheme 1) carried out at temperature above 60 °C.

**Scheme 1. Hydrosilation (or Hydrosilylation): Addition of H–Si Bond Across a Double Bond**



Originally, chloroplatinic acid was used as a hydrosilation catalyst. However the compound is a potent sensitizer and is hazardous to one's health.<sup>5</sup> Today platinum(0) compounds such as the silicone-soluble catalyst introduced by Karstedt in

1973 (a Pt(0) complex containing vinyl-siloxane ligands formed by the reaction of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane with chloroplatinic acid) and PtCl<sub>2</sub>(cyclooctadiene) are commonly used in place of H<sub>2</sub>PtCl<sub>6</sub>.<sup>6</sup>

The latter catalysts are active without an induction period. However, separation of the homogeneous catalyst from the solution after reaction is generally not possible as platinum colloids are formed at the end of the reaction.<sup>7</sup> One approach preventing the formation of platinum colloids byproducts makes use of platinum–carbene complexes.<sup>8</sup> Another approach, more desirable from a practical viewpoint, involves heterogeneous catalysis.<sup>9</sup>

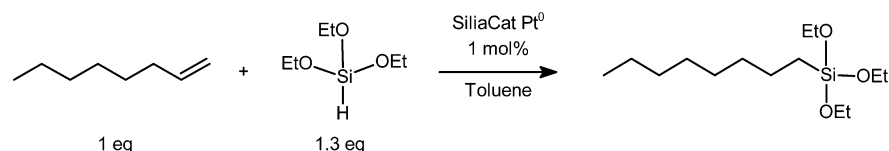
Conventional heterogeneous catalysts such as Pt/Al<sub>2</sub>O<sub>3</sub> or Pt/C, however, are not cost-effective as their typical large agglomerates of metal particles show a much lower level of catalytic activity in comparison to homogeneous catalysts. Remarkably, in 2003, a silica-supported Karstedt (Pt)-type catalyst was reported having high catalytic activity at room temperature under atmospheric pressure, while being reusable five times without any appreciable loss in the catalytic activity.<sup>10</sup> Research on the topic continues with recent advances including homogeneous catalysis by “self-dosing” PtO<sub>2</sub> releasing the soluble active species.<sup>11</sup>

Obviously, new efficient solid hydrosilylation catalysts are highly desirable. We report herein that the new SiliaCat Pt(0) catalyst can be effectively used for hydrosilylation reactions. SiliaCat Pt(0) is the trade name of a new series of commercial sol–gel-entrapped Pt nanocatalysts made of ultrasmall Pt nanoparticles (4–6 nm) encapsulated within a methyl-modified ORMOSIL porous matrix.<sup>12</sup> The catalyst was recently shown to

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Scheme 2. Hydrosilylation of 1-Octene Mediated by SiliaCat Pt(0)

Table 1. Hydrosilylation of Alkenes with Triethoxysilane Over SiliaCat Pt(0)<sup>a</sup>

entry	substrate	time (h)	T (°C)	conversion <sup>b</sup> (%)	selectivity <sup>c</sup> (%)
1	1-octene	5	22/60	88/99	98/99
2	1-decene	5	22/60	100/100	97/98
3	1-octadecene	5	22/60	95/98	56/83
4	4-vinyl aniline	5/24	60	47/80	96/96
5	3,3-diethoxy-prop-1-ene	5	22/60	94/100	93/81

<sup>a</sup>Experimental conditions: 2 mmol substrate and 30% molar excess of triethoxysilane in 15 mL toluene solvent (HPLC grade) and 1 mol % SiliaCat Pt(0) catalyst under Ar. Reaction temperature shown in Table 1. <sup>b</sup>Evaluated by GC/MS. <sup>c</sup>Evaluated by GC/MS.

promote the selective hydrogenation of nitroarenes.<sup>13</sup> At the same time, we published that given the broad applicability of Pt-based nanocatalysis to widely different chemical reactions these catalysts would find application in numerous domains of synthetic organic chemistry.

## EXPERIMENTAL SECTION

**Catalysts Preparation.** A mixture of methyltriethoxysilane, MTES (27 g, 30 mL, 151.4 mmol), 10 mL of 0.042 M HCl<sub>aq</sub> (0.42 mmol H<sup>+</sup>, and 555 mmol H<sub>2</sub>O) is stirred vigorously for 15 min (or until the solution is homogeneous). The resulting solution is concentrated on a rotavapor at 30 °C under reduced pressure to remove almost all ethanol. The alcohol-free sol thereby obtained was added with K<sub>2</sub>PtCl<sub>4</sub> (from 0.004 to 0.018 equiv) dissolved in H<sub>2</sub>O (from 5 to 10 mL) and 60 mL acetonitrile. In the resulting mixture, 1 M NaOH solution (from 0.023 to 0.053 equivalent) was added to favor gelation that indeed rapidly occurred. The resulting light-orange homogeneous and transparent gel was left to dry in air for 4 days. The dark-blue xerogel obtained was then reduced at room temperature with a solution of sodium borohydride in THF:H<sub>2</sub>O = 1:1, (Pt:NaBH<sub>4</sub> = 1:12 molar ratio; 180 mL), washed with H<sub>2</sub>O and THF, and left open to dry at room temperature.

**Hydrosilylation Reactions.** Reactions were carried out under argon on a 2 mmol scale in 15 mL anhydrous toluene reacting the triethoxysilane with different olefins. A 100 mL two neck dry round-bottomed flask equipped with a condenser and a rubber septum is filled with 1 mol % (relative to substrate) SiliaCat Pt(0) and degassed two times for 15 min was kept under argon conditions. The catalyst has a 0.05 mmol g<sup>-1</sup> Pt load determined from CAMECA SX100 equipped with an EPMA microanalyzer. The average size of the entrapped Pt crystallite is 2.9 nm.

The anhydrous solvent, silane (95% pure), and olefin (previously degassed for 15 min under argon) were added using a syringe. The reaction mixture was either stirred at room temperature or heated at 60 °C until the GC/MS analysis showed maximum conversion. Once the reaction was complete, the catalyst was filtered and washed extensively with toluene. The filtrate was concentrated to give a crude product. The conversion in the desired product was determined by GC/MS.

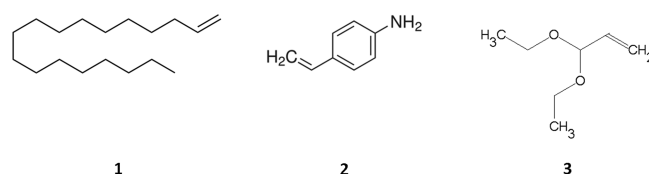
## RESULTS AND DISCUSSION

Preliminary investigation addressed a number of representative alkenes reacted with triethoxysilane over the solid catalyst under the conditions of Scheme 2.

Results show that nonfunctionalized alkenes such as 1-octene (entry 1 in Table 1) or 1-decene are smoothly converted into

the corresponding organo-alkoxysilanes at room temperature or faster at 60 °C.

Entry 3 shows that by rising the reaction temperature at 60 °C slightly enhances the conversion of 1-octadecene (**1**) from 95 to 98%, but it dramatically improves the selectivity, from 56 to 83%. We ascribe this finding to the enhanced rate of access and adsorption of the double moiety of this alpha-olefin to the entrapped Pt nanoparticles (see below).



A longer reaction time (24 h) and higher temperature (60 °C) were needed for converting 4-vinylaniline (**2**) with optimal 80% conversion and excellent 96% selectivity. As is often the case with amines undergoing heterogeneous catalytic conversion at the surface of Pt nanocrystals,<sup>14</sup> this may be due to the coordination of the nitrogen to the unsaturated Pt atoms. Finally, hydrosilylation of oxygenate molecule 3,3-diethoxy-1-propene (**3**) best requires room temperature to afford 94% conversion at optimal 93% selectivity.

**Reaction Optimization.** Aiming to optimize the reaction conditions, we studied the hydrosilylation of 1-octene (Scheme 2) mediated by SiliaCat Pt(0) under different reaction conditions. Reactions were thus carried out at different temperatures and using different catalyst amounts.

Table 2 shows that in general hydrosilylation ideally takes place over 0.5 mol % catalyst at 65 °C. Remarkably, both reactants, namely, the olefin and the silane, need to be added to the catalyst at the same time to optimize both reaction rate and selectivity (entry 6 vs entry 5, and entry 4 vs entry 3). This indeed avoids preliminary adsorption of the substrate within the sol-gel cages (ORMOSILs are chemical sponges) that is detrimental to the reaction rate.

Reaction at 90 °C is fast (entry 1, 5, and 6), but isomerization reactions that are detrimental to selectivity become increasingly more important with increasing temperature.

**Scale-Up and Product Isolation.** In order to investigate the effect of scale-up and to assess the performance of the heterogeneous catalyst under synthetic conditions of relevance to industry, the hydrosilylation of 1-octene was performed

**Table 2. Hydrosilylation of 1-Octene with Triethoxysilane (TES) over SiliaCat Pt(0) under Different Reaction Conditions<sup>a</sup>**

entry	catalyst (mol %)	time (h)	T (°C)	conv. (%)	select. (%)	sequence of reagents addition
1	1	1	90	92	81	substrate at r.t. TES at 90 °C
		3		95	75	
		5		97	79	
2	0.5	3	50	—	—	substrate and TES at r.t.
		5		89	86	
		21		100	87	
3	0.5	1	65	54	86	substrate at r.t. TES at 65 °C
		3		70	85	
		5		75	81	
4	0.5	1	65	82	84	substrate and TES at 65 °C
		3		93	82	
		5		95	80	
5	0.5	1	90	76	79	substrate at room temp. TES at 90 °C
		3		86	81	
		5		87	79	
6	0.5	1	90	83	81	substrate and TES at 90 °C
		3		92	79	
		5		95	81	

<sup>a</sup>Experimental conditions: 2 mmol substrate and 30% molar excess of triethoxysilane in toluene solvent (HPLC grade, 0.5 M in substrate) under Ar. Catalyst amount and reaction temperature shown in Table 2.

starting from 50 and 100 mmol of olefin substrate (Table 3). The catalyst amount and reaction temperature were again fixed at 0.5 mol % at 65 °C, respectively.

At the end of the reaction, toluene was removed by vacuum evaporation, and the crude product isolated via vacuum fractional distillation.

Results in Table 3 show that practically pure octadecyl-triethoxysilane was eventually recovered with an overall 53% yield in isolated product. Considerable product loss occurs due to the nonoptimized product isolation method. This will be easily optimized in real industrial processes using state-of-the-art isolation techniques common in industry (alumina-column chromatography with dry solvent, for example). What is relevant here is that the process scaled up 50 times retains both the high selectivity and conversion degree (by GC-MS) observed under the 2 mmol scale.

**Scope of the Reaction.** Different substrate were therefore subjected to hydrosilylation under the optimized reaction conditions. Entries in Table 4 show that along with 1-octadecene (entry 1), acrolein diethyl acetal (entry 2), 5-hexen-2-one (entry 3), styrene (entry 4), and 1-decene (entry 5) were reacted with triethoxysilane over SiliaCat Pt(0). With the

exception of linear olefins, reactions proceed quickly with excellent selectivity and yield.

Again, hydrosilylation of linear olefins involves a certain degree of isomerization, namely, either shift of the double bond or even skeletal modification of the starting molecules. Hence, as shown by the case of 1-octadecene, in order to slow down isomerization and obtain a higher reaction rate, reaction is best carried out at 60 °C over 1 mol % catalyst amount (and not over 0.5 mol %, see entry 3 in Table 1).

**Leaching and Reusability.** Table 3 shows that the results of Pt leaching tests in the crude reaction product show very low levels of Pt (4–6 ppm). Higher leaching values were found only for molecules bearing functional groups able to coordinate the Pt nanoparticles, such as the chelating group in acrolein diethyl acetal (entry 2 in Table 3). It is of relevance here that in homogeneous hydrosilylation reactions conducted on a platinum catalyst commonly used in organic synthesis, robust metal scavenging agents need to be used that often make use of functionalized silica gels to bring the level of metal down to an acceptable level at relatively high temperature (80 °C is typical) and for prolonged time (several hours).<sup>15</sup> In addition, for comparison, leaching of Pt species in heterogeneous hydrosilylation from organic resin doped with Pt usually takes place affording dual catalytic processes:<sup>16</sup> hydrosilylation catalyzed by resin-immobilized Pt complexes and concurrent alkene isomerization due to leached soluble Pt species.

The catalyst was found to be reusable in three consecutive reaction runs using 1-octene as the representative substrate under the optimized conditions (Table 5). The catalyst selectivity was fully retained, whereas the decrease in conversion after the second run is owed to pore blockage following adsorption of the formed silane at the organosilica cages.

It is enough to sonicate the catalyst in CH<sub>2</sub>Cl<sub>2</sub> for 1 h to restore the original activity (for example in the conversion of 1-octene under the optimized conditions in Table 1).

In each reaction run, the amount of Pt in solution was <5 ppm, and in each case, it was not sufficient to promote homogeneous catalysis as shown by the lack of further conversion of the filtrate obtained by filtering the reaction mixture at 30% conversion.

Summarizing, SiliaCat Pt(0) is a versatile chemoselective hydrosilylation catalyst offering a suitable alternative to both homogeneous and heterogeneous conventional Pt catalysis. Isolation of the nanosized active Pt(0) particles within the inner porosity of a nanohybrid sol–gel ORMOSIL matrix results in isolated metallic nanophase (Figure 1) ensuring two concomitant advantages.

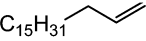

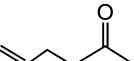
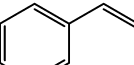
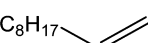
On one side, the strongly lipophilic nature of the ORMOSIL matrix dictates preferential access and adsorption of the electron-rich double bond moiety to the 2.9 nm ultrasmall Pt

**Table 3. Catalytic Hydrosilylation of 1-Octene with Triethoxysilane over SiliaCat Pt(0) at Different Reaction Scales<sup>a</sup>**

entry	substrate	solvent	time (h)	conv. (%)	select. (%)	yield by GC/MS (%)	isolated yield crude/purity
1	1-octene	toluene	1	82	84	69	—
	5 mmol	0.5 M	3	93	82	76	
			5	95	80	76	
2	1-octene	toluene	1	93	77	72	7.4 g/90%)
	50 mmol	0.5 M	3	99	81	80	yield:53%
3	1-octene	toluene	1	82	77	62	14.7 g/(95%)
	100 mmol	0.5 M	3	97	81	68	yield:53%

<sup>a</sup>Experimental conditions: mmol substrate as shown in Table 3, 30% molar excess of triethoxysilane in toluene solvent (HPLC grade, 0.5 M in substrate) under Ar, SiliaCat Pt(0) 0.5 mol %, T = 65 °C.

Table 4. Catalytic Hydrosilylation of Functionalised Alkenes with Triethoxysilane over SiliaCat Pt(0) under Different Reaction Conditions<sup>a</sup>

Entry	Substrate	Catalyst (mol%)	Solvent (M)	T (°C)	Time (h)	Conv. (%)	Select. (%)	Pt leaching (mg/kg) <sup>b</sup>
1		1	Toluene (0.5)	22	1	12	>95%	-
					2	26		
				3	35			
		40	1	88	ca. 65	-		
			2	100				
		65	1	100	ca. 65	6		
0.5	Toluene (0.5)	65	1	100	ca. 50	5		
							90	1
3	Toluene (2.0 )	40	1	3	85	97	ca. 80	-
2		1	Toluene (0.5)	65	1	100	100	25
		0.5						
3		0.5	Toluene (0.5)	65	3	100 <sup>#</sup>	100	-
		1	DCM (0.5)					
4		0.5	Toluene (0.5)	65	1	60	100	16
5		1	Toluene (0.5)	22	1	41	81	-
		3			45	85		
6		0.5	Toluene (0.5)	60	1	100	68	12
7		0.5	Toluene (0.5)	60	1	100	68	12

<sup>a</sup>Experimental conditions: 2 mmol substrate, 30% molar excess of triethoxysilane in toluene solvent (HPLC grade, 0.5 M in substrate) under Ar, SiliaCat Pt(0) amount as shown in Table 4,  $T = 65\text{ }^{\circ}\text{C}$ . <sup>b</sup>For the leaching test, after reaction completion, the reaction mixture was filtered and the solvent evaporated. The crude product was directly analyzed by ICP-OES to determine the leaching of Pt (1 g crude product in 10 mL DMF, 100 mg/mL concentration).

Table 5. Consecutive Catalytic Hydrosilylation of 1-Octene with Triethoxysilane over SiliaCat Pt(0)<sup>a</sup>

reaction run	time (h)	conv. <sup>b</sup> (%)	select. <sup>b</sup> (%)	yield <sup>b</sup> (%)
1	3	99	81	80
2	3	92	81	80
3	3	47	100	47

<sup>a</sup>Experimental conditions: 2 mmol substrate, 30% molar excess of triethoxysilane in toluene solvent (HPLC grade, 0.5 M in substrate) under Ar, SiliaCat Pt(0) 0.5 mol %,  $T = 65\text{ }^{\circ}\text{C}$ . <sup>b</sup>From GC-MS analysis.

nanoparticles curved surface where hydrosilylation takes place; whereas interaction with other substituents of the alkene moiety (taking place in large metal particles and flat surfaces) is minimized (Figure 1).<sup>17</sup> On the other, the very same sol-gel encapsulation within the sol-gel cages ensures physical and chemical stabilization of the isolated Pt nanoensembles<sup>18</sup> and thus prolonged activity of the catalyst.

In conclusion, we have discovered that a modest 0.5–1 mol % amount of SiliaCat Pt(0) selectively mediates the hydrosilylation of different olefins under Ar atmosphere at room

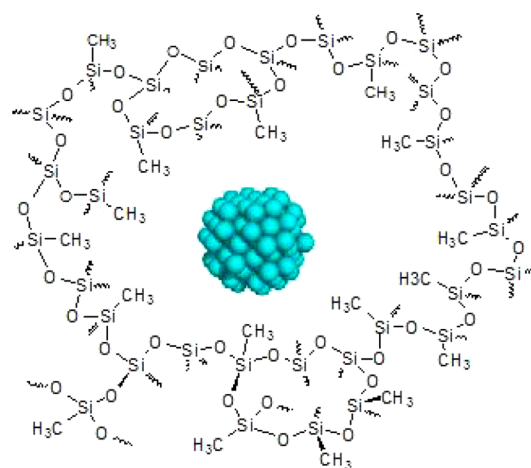


Figure 1. Schematic representation of the bare Pt nanoparticle entrapped in the methyl-modified cage of the SiliaCat Pt(0) catalyst.

temperature or at  $65\text{ }^{\circ}\text{C}$ , depending on the substrate. Ultralow leaching of Pt ensures very low levels of Pt in crude product and no plant contamination as platinum remains entrapped



within the organosilica xerogel. The organosilica organic–inorganic catalysts of the SiliaCat series do not swell or stick to the reactor surface and can be easily filtered and handled showing no tendency to ignite upon exposure to air (a feature of most Pt/C catalysts), while being reusable upon a mild treatment to reopen the partly clogged pores.

Catalytic hydrosilylation is the most important application of platinum in homogeneous catalysis,<sup>19</sup> but it is not the most important application of platinum in heterogeneous catalysis. Industry, in turn, remains highly interested in the reduction of precious platinum consumption through catalyst recycling and increasing the TOF values so as to lead to modest amounts of catalyst employed.<sup>20</sup> Hopefully, this highly selective new catalyst and its advantageous features mentioned above will extend the applicability of platinum nanocatalysis also to the important hydrosilylation conversion. To conclude, one may notice how catalytic hydrosilylation by SiliaCat Pt(0) closes a synthetic loop, namely, the catalyst is obtained by entrapment of Pt nanoparticles via sol–gel polycondensation of methyltriethoxysilane (MTES). The latter organosilane and many others can now be synthesized over the SiliaCat Pt(0) organosilica catalyst obtained from MTES itself, eliminating altogether the use of costly and unstable conventional Pt catalysts.<sup>21</sup>

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### Notes

The authors declare no competing financial interest.

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