

# Synthesis of Single Atom Based Heterogeneous Platinum Catalysts: High Selectivity and Activity for Hydrosilylation Reactions

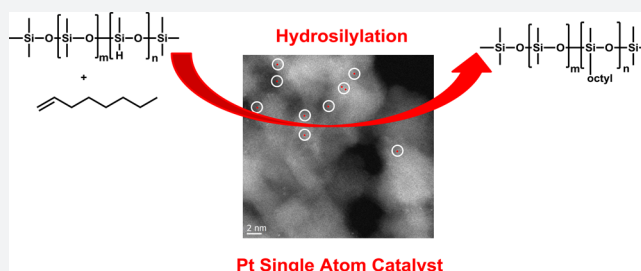
Xinjiang Cui,<sup>†</sup> Kathrin Junge,<sup>†</sup> Xingchao Dai,<sup>‡</sup> Carsten Kreyenschulte,<sup>†</sup> Marga-Martina Pohl,<sup>†</sup> Sebastian Wohlrab,<sup>†</sup> Feng Shi,<sup>‡</sup> Angelika Brückner,<sup>†</sup> and Matthias Beller<sup>\*,†</sup>

<sup>†</sup>Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein Straße 29a, Rostock, 18059, Germany

<sup>‡</sup>State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No. 18, Tianshui Middle Road, Lanzhou, 730000, China

## S Supporting Information

**ABSTRACT:** Catalytic hydrosilylation represents a straightforward and atom-efficient methodology for the creation of C–Si bonds. In general, the application of homogeneous platinum complexes prevails in industry and academia. Herein, we describe the first heterogeneous single atom catalysts (SACs), which are conveniently prepared by decorating alumina nanorods with platinum atoms. The resulting stable material efficiently catalyzes hydrosilylation of industrially relevant olefins with high TON ( $\approx 10^5$ ). A variety of substrates is selectively hydrosilylated including compounds with sensitive reducible and other functional groups (N, B, F, Cl). The single atom based catalyst shows significantly higher activity compared to related Pt nanoparticles.



Olefin hydrosilylation is an important process to form alkylsilanes by catalytic addition of Si–H bonds to olefins.<sup>1,2</sup> The resulting products find widespread application in the manufacture of silicone-based aerogels, surfactants, release coatings, lubricants, and adhesives.<sup>3,4</sup> Furthermore, organosilicon compounds are of interest for the design of novel catalysts, defense materials and life science products. In general, catalytic hydrosilylations are performed using molecularly defined (pre)catalysts containing mainly Pt,<sup>5,6</sup> but also Ru,<sup>7,8</sup> Pd,<sup>9</sup> and Rh.<sup>10,11</sup> In fact, some of these reactions constitute the largest-scale examples of homogeneous catalysis with noble metals. Nowadays, platinum-based complexes such as Speier's<sup>6</sup> and Karstedt's catalysts formed by reaction of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane with chloroplatinic acid and PtCl<sub>2</sub>(cyclooctadiene) are the most extensively used industrial catalysts, despite the cost of the precious metal. A disadvantage of these platinum catalysts in some applications is that they are trapped in the product and cannot be easily recovered due to the viscous morphology of them. Notably, catalyst costs might account for up to 30% of the cost of silicones.<sup>12</sup>

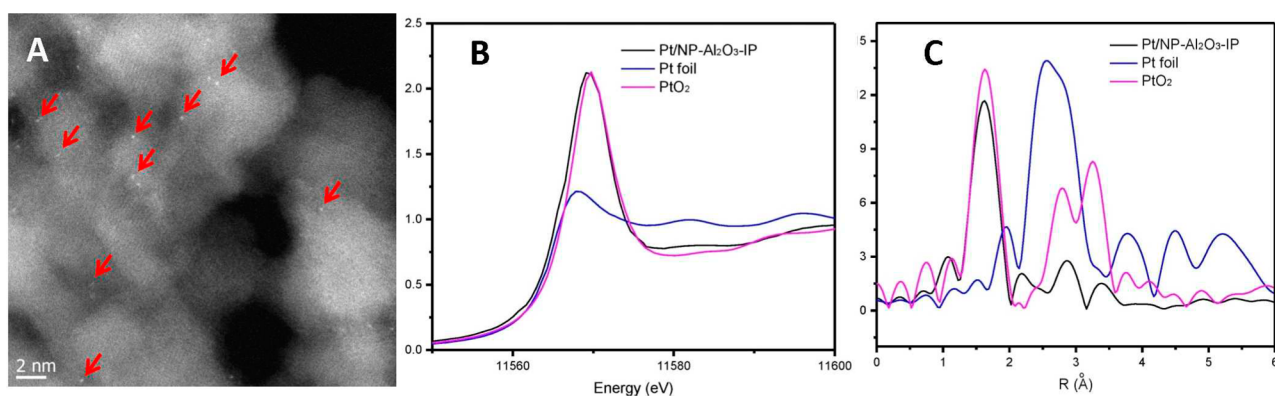
Hence, the development of less expensive catalysts is an important and ongoing goal for industrial and academic researchers. Apart from new developments based on common hydrosilylation metals,<sup>13,14</sup> in recent years the use of non-noble metals attracted significant interest. In this respect, Chirik and co-workers<sup>15</sup> showed that well-defined iron complexes are highly active for the selective anti-Markovnikov addition of silanes to alkenes under mild conditions. Since the original report in 2012, a series of catalysts based on Fe,<sup>15–17</sup> Co,<sup>12,17–20</sup> Ni,<sup>21–23</sup> and B<sup>24</sup> were successfully explored in hydrosilylation reactions.

An alternative approach to overcome the drawbacks (vide supra) is the development of highly active supported catalysts. However, most of the known heterogeneous materials are rather inactive. For example, Béland and Pagliaro<sup>25</sup> reported small Pt(0) nanoparticles (4–6 nm) encapsulated in a sol–gel derived porous matrix of methyltriethoxysilane for the hydrosilylation of different olefins with triethoxysilane in the presence of 1 mol % catalyst. Simple PtO<sub>2</sub> was studied in the hydrosilylation of heptamethyltrisiloxane with *n*-octene, which revealed that initially Pt(IV) is reduced during the reaction to form the active sites.<sup>26</sup> So far, only a silica-supported Karstedt Pt-type catalyst and crystalline Pt nanoparticles embedded into the walls of a mesostructured silica framework showed high catalytic activity on this reaction.<sup>27,28</sup> Thus, to the best of our knowledge general heterogeneous Pt-based catalysts with broad substrate scope, high regioselectivity, and high activity comparable to homogeneous systems do not exist.

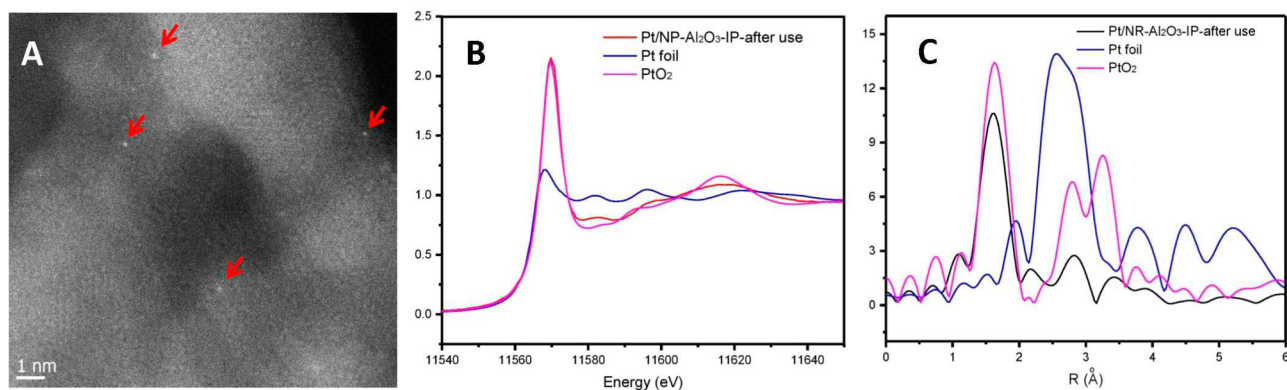
Recently, heterogeneous catalysts with atomically dispersed active sites were developed as model systems to understand as well as to design such materials at the molecular level and build a bridge between the catalysis subdisciplines.<sup>1,21,27,29</sup> In addition to recycling advantages for liquid products, such heterogeneous single atom catalysts (SACs) may display improved activity and selectivity compared to catalysts containing bulk metal or metal nanoparticles. Indeed, SACs based on Pt,<sup>22,30–36</sup> Pd,<sup>37,38</sup> Ir,<sup>39</sup> Rh,<sup>40</sup> Co,<sup>41–43</sup> and Fe<sup>44</sup> were presented in the past 5 years and displayed interesting activity, e.g., in hydrogenations and CO

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**Figure 1.** HRSTEM images of Pt/NR- $\text{Al}_2\text{O}_3$ -IP (A), Pt LIII edge XANES for Pt/NR- $\text{Al}_2\text{O}_3$ -IP (B), and  $k^3$ -weighted Fourier transform of Pt LIII edge EXAFS for Pt/NR- $\text{Al}_2\text{O}_3$ -IP (C).



**Figure 2.** HRSTEM images of Pt/NR- $\text{Al}_2\text{O}_3$ -IP after use (A), Pt LIII edge XANES for Pt/NR- $\text{Al}_2\text{O}_3$ -IP after use (B), and  $k^3$ -weighted Fourier transform of Pt LIII edge EXAFS for Pt/NR- $\text{Al}_2\text{O}_3$ -IP after use (C).

oxidation. Inspired by these works, we were curious if reducing the size of Pt nanoparticles to single atoms would create improved catalysts for alkene hydrosilylation chemistry. Herein, we present the first heterogeneous SAC for the selective hydrosilylation of all kinds of terminal olefins and show that supported Pt on the surface of specific aluminum oxide nanorods exhibits excellent activity.

To design SACs, it is crucial to select a support which allows creation of defined metal sites on the surface and inhibits the aggregation of the metal atoms toward nanoparticles. In this context, the use of an oxidic support is preferred due to the stronger interaction of unsaturated surface centers with the isolated metal species. Indeed, it has been demonstrated that ZnO,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  stabilize single noble metal atoms.<sup>27,39,40,45</sup> For our initial catalyst preparation,  $\text{Al}_2\text{O}_3$  nanorods (NR- $\text{Al}_2\text{O}_3$ )<sup>46</sup> were selected as carrier because of their high surface area ( $S_{\text{BET}} = 330 \text{ m}^2/\text{g}$ ) and controlled pore size ( $\approx 12 \text{ nm}$ ). Deposition of Pt (270 ppm, measured by ICP-AES) onto this support was performed by two different methods, namely, reductive precipitation (RP) and impregnation (IP) (see the Supporting Information).

When impregnation (IP) was used to deposit Pt on NR- $\text{Al}_2\text{O}_3$ , TEM images of the resulting material (Pt/NR- $\text{Al}_2\text{O}_3$ -IP) showed the rodlike morphology of the NR- $\text{Al}_2\text{O}_3$  support (Figure S1) and single Pt atoms (white dots in Figure 1A), which are formed exclusively. For comparison, reductive precipitation using  $\text{NaBH}_4$  led to the formation of uniform Pt nanoparticles (NPs) of 2–5 nm on NR- $\text{Al}_2\text{O}_3$  (Figures S2 and S3). The valence state and environment of Pt were analyzed by X-ray absorption

near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy at the Pt LIII edge. The white line peak of fresh Pt/NR- $\text{Al}_2\text{O}_3$ -IP in the XANES spectrum is similar to the  $\text{PtO}_2$  reference (Figure 1B), indicating the presence of oxidic platinum centers.

To further verify that Pt was dispersed atomically on the support, EXAFS spectra were recorded (Figure 1C and Table S2). The strong peak between 1 and 2 Å is due to a Pt–O shell. No peak in the region of 2–3 Å, which is characteristic for a Pt–Pt shell, is observed, thus confirming the presence of isolated Pt atoms only. The Pt–O coordination number in Pt/NR- $\text{Al}_2\text{O}_3$ -IP was  $\approx 5.0$  considering the fitting error of EXAFS analysis (ca. 20%).

To evaluate the activity of the prepared single atom Pt catalyst and related materials, the hydrosilylation reaction of 1-octene and diethoxymethylsilane under solvent free conditions was chosen as a benchmark test. Obviously,  $\text{Al}_2\text{O}_3$  nanorods were not active in this reaction (Table 1, entry 1). Platinum nanoparticles (Pt/NR- $\text{Al}_2\text{O}_3$ -RP catalysts prepared by the reductive precipitation) showed low activity (entry 2). In contrast, the single atom platinum catalyst (SAC) prepared by the impregnation precipitation method showed under optimal conditions high activity achieving the desired product (3a) in 95% yield with  $2.06 \times 10^5$  TON (TON = turnover number, moles of product per mole of catalyst; entries 3 and 4). The benchmark reaction occurred with high anti-Markovnikov selectivity and low alkene isomerization compared with previously reported heterogeneous<sup>27</sup> and homogeneous<sup>6</sup> platinum catalysts. Notably, a commercial Pt/ $\text{Al}_2\text{O}_3$  catalyst showed no activity at all (entry

**Table 1. Hydrosilylation of 1-Octene in the Presence of Different Pt Catalysts<sup>a</sup>**

entry	catalyst	time (h)	yield (%)	TON (10 <sup>4</sup> ) <sup>b</sup>	TOF (10 <sup>4</sup> h <sup>-1</sup> ) <sup>b</sup>
1	Nr-Al <sub>2</sub> O <sub>3</sub>	2	0	0	0
2	Pt/Nr-Al <sub>2</sub> O <sub>3</sub> -RP <sup>c</sup>	2	33	7.1	3.6
3	Pt/Nr-Al <sub>2</sub> O <sub>3</sub> -IP	2	95	20.6	10.3
4	Pt/Nr-Al <sub>2</sub> O <sub>3</sub> -IP <sup>d</sup>	2	73	31.6	15.8
5	Pt/Nr-Al <sub>2</sub> O <sub>3</sub> -IP <sup>e</sup>	2	40	8.7	4.3
6	Pt/Nr-Al <sub>2</sub> O <sub>3</sub> -IP	1	41	8.9	4.5
7	Pt/Al <sub>2</sub> O <sub>3</sub> <sup>f</sup>	2	0	0	0
8	Pt/Al <sub>2</sub> O <sub>3</sub> -IP <sup>g</sup>	2	57	12.2	6.1
9	Pt/CeO <sub>2</sub> -IP	2	6	1.3	0.7
10	Pt/SiO <sub>2</sub> -IP	2	26	5.6	2.8
11	Pt/C-IP	2	6	2.6	1.3
12	Pt/MnO-IP	2	0	0	0
13	Pt/ZnO <sub>2</sub> -IP	2	0	0	0
14	H <sub>2</sub> PtCl <sub>6</sub>	2	46	10	5.0
15	Karstedt catalyst	2	96	20.6	10.3

<sup>a</sup>Reaction conditions: 3 mmol of olefin, 3 mmol of silane, 2 h, N<sub>2</sub> (10 bar), 100 °C, isolated yields. IP = impregnation precipitation.

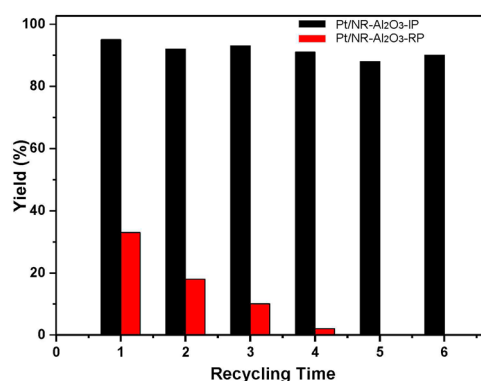
<sup>b</sup>Calculated for the total Pt content. <sup>c</sup>RP = reductive precipitation.

<sup>d</sup>30 mmol of olefin, 30 mmol of silane, 5.0 × 10<sup>-6</sup> mmol of Pt. <sup>e</sup>100 °C. <sup>f</sup>Commercial 5 wt % Pt/Al<sub>2</sub>O<sub>3</sub>, 30 mmol of olefin, 30 mmol of silane, 1.02 × 10<sup>-5</sup> mmol of Pt. <sup>g</sup>Commercial Al<sub>2</sub>O<sub>3</sub>. TON = mol product/mol Pt. TOF = TON/reaction time.

7). Meanwhile, the material prepared using commercial Al<sub>2</sub>O<sub>3</sub> instead of Al<sub>2</sub>O<sub>3</sub> nanorods showed significantly lower activity (entry 8). Platinum immobilized on SiO<sub>2</sub>, CeO<sub>2</sub>, carbon black (Vulcan XC72), MnO, and ZnO<sub>2</sub> formed catalysts, which gave the desired product in no or only low yields (0–26%; entries 9–13). TEM images for Pt/CeO<sub>2</sub>-IP, Pt/SiO<sub>2</sub>-IP, and Pt/C showed the formation of Pt nanoparticles on the surface of these materials. These results clearly indicate that the NR-Al<sub>2</sub>O<sub>3</sub> plays a crucial role for the formation of single platinum sites with high activity for the hydrosilylation process. Notably, in terms of activity our Pt/Nr-Al<sub>2</sub>O<sub>3</sub>-IP is at least comparable to homogeneous state-of-the-art catalysts such as H<sub>2</sub>PtCl<sub>6</sub> and Karstedt's system (entries 14 and 15).

Next, we investigated the stability and recyclability of selected catalysts, which are important factors for potential applications in industrial processes. For this purpose, we compared the Pt-SAC and supported Pt-NPs, which both were recycled by centrifugation and reused six times without any reactivation. Gratifyingly, when Pt/Nr-Al<sub>2</sub>O<sub>3</sub>-IP was used after the sixth recycling, still 92% yield (total TONs of 1.18 × 10<sup>6</sup>) was achieved (Figure 3). In contrast, a significantly lower activity was observed in the presence of Pt/Nr-Al<sub>2</sub>O<sub>3</sub>-RP, where almost no product was obtained after the third recycling. These results demonstrate the higher activity of Pt-SAC—which can be anticipated due to the better dispersion of active catalyst centers—compared to Pt nanoparticles. However, contrary to expectations, the former catalyst also showed an improved stability at least on a shorter time scale.

To prove the stability of the SAC, a sample of the recycled material (after 6 runs) was characterized by STEM, XANES, and EXAFS and compared to the fresh one. As shown in Figure 2, no

**Figure 3.** Recyclability of Pt/Nr-Al<sub>2</sub>O<sub>3</sub>-IP and Pt/Nr-Al<sub>2</sub>O<sub>3</sub>-RP in the hydrosilylation of 1a and 2a.

significant differences were observed. For example, the Pt–O coordination number in fresh Pt/Nr-Al<sub>2</sub>O<sub>3</sub>-IP was ≈5.0 and did not change much after catalysis (Table S2). Hence, we conclude that single Pt atoms on NR-Al<sub>2</sub>O<sub>3</sub> are stable during the hydrosilylation reactions.

To demonstrate the general synthetic applicability of this single atom catalyst, we explored the hydrosilylation of 1-octene with a variety of tertiary silanes. In all cases we used the active platinum in neat olefin and obtained excellent to quantitative yields of the desired linear products. Hence, hydrosilylations with dimethylphenylsilane (1b) as well as with multisilicon containing compounds proceeded smoothly (Table 2). Reaction with 1c is

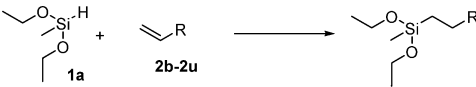
**Table 2. Single Atom Pt Catalyzed Selective Hydrosilylation of 1-Octene with Various Tertiary Silanes<sup>a</sup>**





















entry	substrate	T (°C)	yield (%)	TON (10 <sup>5</sup> )
1	Me(EtO) <sub>2</sub> SiH (1a)	100	95	2.06
2	PhMe <sub>2</sub> SiH (1b)	120	94	2.04
3	HSi(Me) <sub>2</sub> OSi(Me) <sub>3</sub> (1c)	100	95	2.06
4	HSi(Me) <sub>2</sub> O(Me) <sub>2</sub> SiH (1d)	100	94 <sup>b</sup>	1.36
5	HSi(Me) <sub>2</sub> OSi(Me) <sub>2</sub> O(Me) <sub>2</sub> SiH (1e)	120	93 <sup>b</sup>	1.35
6	HSi(Me)NH(Me) <sub>2</sub> SiH (1f)	120	92 <sup>b</sup>	1.33
7	TDMSS (1g)	120	96 <sup>c</sup>	0.70

<sup>a</sup>Reaction conditions: 3 mmol of 1-octene, 3 mmol of silane, 2 h, 10 mg of Pt/Nr-Al<sub>2</sub>O<sub>3</sub>-IP, N<sub>2</sub> (10 bar), isolated yields. TON = mol product/mol Pt. <sup>b</sup>4 mmol of 1-octene, 2 mmol of silane. <sup>c</sup>4 mmol of 1-octene, 1 mmol of silane, TDMSS = tetrakis(dimethylsilyloxy)silane. TON = mol product/mol Pt.

of special interest because the hydrosilylated products have been widely applied in both inorganic chemistry and organic syntheses.<sup>2</sup> In addition, hydrosilylations of the benchmark alkene with silanes containing two Si–H bonds were accomplished, and again, excellent yields were obtained using 1d–1g as starting materials (entries 4–7). In all cases, no side products were observed and the single atom Pt possessed catalytic performance with high turnover numbers.

Furthermore, we tested the hydrosilylation of diverse alkenes using the Pt-SAC. Simple linear and branched aliphatic olefins gave very good yields of the corresponding silylated products (Table 3, entries 1 and 2). More challenging and sensitive oxygen-containing allylic compounds, such as cyclohexyl vinyl

**Table 3. Single Atom Pt Catalyzed Selective Hydrosilylation of Various Olefins with 1a<sup>a</sup>**


Entry	Substrate	Temp. [°C]	T (h)	Yield	TON (10 <sup>5</sup> )
1	 (2b)	100	2	93	2.03
2	 (2c)	100	2	88	1.92
3	 (2d)	120	2	97	2.11
4	 (2e)	120	4	96	2.09
5	 (2f)	100	2	97	2.11
6	 (2g)	100	2	96	2.11
7	 (2h)	100	4	94	2.04
8	 (2i)	120	2	97	2.11
9	 (2j)	120	2	96	2.11
10	 (2k)	120	6	73	1.58
11	 (2l)	120	4	91	1.97
12	 (2m)	100	3	95	2.06
13	 (2n)	100	2	95	2.06
14	 (2o)	100	2	93	2.03
15	 (2p)	120	2	87	1.89
16	 (2q)	120	3	83	1.81
17	 (2r)	120	4	94	2.04
18	 (2s)	120	4	93	2.03
19	 (2t)	120	4	94	2.04
20	 (2u)	120	5	93	2.03

<sup>a</sup>Reaction conditions: 3 mmol of olefin, 3 mmol of silane, 2 h, 10 mgPt/NR-Al<sub>2</sub>O<sub>3</sub>-IP, N<sub>2</sub> (10 bar), isolated yields. TON = mol product/mol Pt.

ether (2d), 1,2-epoxy-4-vinylcyclohexane (2e), and allyl glycidyl ether (2f), were also hydrosilylated with the single atom catalyst to form the corresponding products in high yields (entries 3–5). Notably, the catalyst system even tolerates epoxy rings in allyl glycidyl ether, which is susceptible to various ring-opening

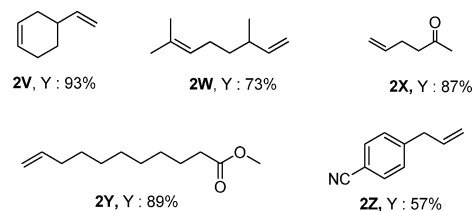
reactions. Furthermore, the reaction of 6-chloro-1-hexene (2g) with 1a yielded the desired product and no dehalogenated side product was observed (entry 6). Hydrosilylations of allylbenzene (2h), allyl phenyl ether (2i), and allyl benzyl ether (2j) with 1a also afforded the corresponding hydrosilylated products in quantitative isolated yields with high selectivity (entries 7–9).

N-Allylaniline (2k) and allylpentafluorobenzene (2l) were hydrosilylated smoothly to the desired products in 73% and 91% yields, respectively (entries 10 and 11). Moreover, we performed the hydrosilylation of 1a with vinylsiloxanes such as triethoxyvinylsilane (2m), allyltrimethylsilane (2n), vinyltrimethylsilane (2o), and 1,3-divinyltetramethyldisiloxane (2p) and formed the corresponding products in high yields selectively (entries 12–15). For the first time, the boron-containing alkene (2q) was transformed successfully to the hydrosilylated product in 83% yield, which might be interesting for applications in material sciences (entry 16). Moreover, the single atom catalyst showed high activity for the hydrosilylation of renewable substrates with 1a. In this respect, lignin-derived alkenes such as eugenol (2r), 4-allylanisole (2s), 4-allyl-1,2-dimethoxybenzene (2t), and methyl 5-allyl-3-methoxysalicylate (2u) reacted in excellent yields (entries 17–20).

In general, hydrosilylation reactions allow controlling the hydrophilicity/hydrophobicity of a given material/surface. In this respect, such transformations offer interesting possibilities for innovations and find increasing interest for the development of consumer and life science products such as elastic skin.<sup>47,48</sup>

Hence, selective Si–C bond formation in the presence of different functional groups is of increasing concern. For this purpose, the chemoselectivity of the single atom catalyst was tested with substrates including other reducible groups. As shown in Scheme 1, the hydrosilylation of 4-vinyl-1-cyclohexene

### Scheme 1. Selective Hydrosilylation of Alkenes with Other Functional Groups

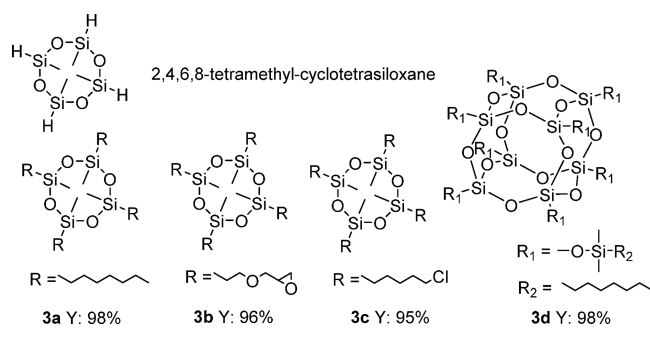


(2v) took place selectively at the terminal position without hydrosilylation of the internal cyclohexyl group or hydrogenation of the C=C bonds. Furthermore, (+)-β-citronellene (2w) underwent selective hydrosilylation retaining the internal C=C bond in the substrate. In the case of 5-hexen-2-one (2x), the desired product was obtained in 87% yield without touching the ketone, which easily occurred in the presence of homogeneous Pt and other metal catalysts. In addition, the single site Pt catalyst exhibited good activity in the hydrosilylation of an unsaturated ester affording an ester group tagged silane in 89% yield. Finally, the reaction of 4-allylbenzonitrile (2z) with 1a gave the corresponding nitrile in 57%.

Among the industrially applied silanes, there is a substantial interest in the reaction of 2,4,6,8-tetramethylcyclotetrasiloxane: The derived products find widespread applications in cosmetic ingredients due to their excellent spreading, lubrication properties, and unique volatility characteristics. Thus, the hydrosilylation of different alkenes such as 1-octene, allyl glycidyl ether, and 6-chloro-1-hexene with 2,4,6,8-tetramethylcyclotetrasilox-

ane was done in the presence of the single atom Pt catalyst (Scheme 2).

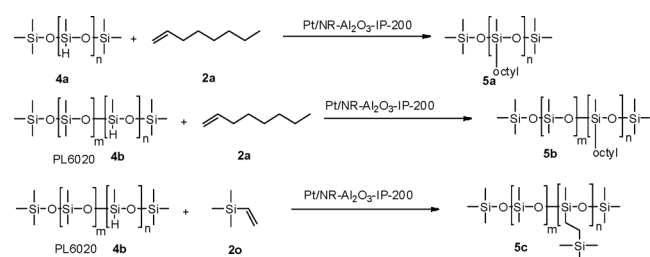
### Scheme 2. Selective Hydrosilylation of Cyclotetrasiloxane and POSS Derivatives



To our delight, in all experiments the products were obtained in good yields as colorless fluids with high selectivity and low alkene isomerization. Furthermore, polyhedral oligomeric silsesquioxanes (POSS) have attracted attention as precursors to ceramic materials and nanocomposites. Traditionally, substituted POSS derivatives are prepared by hydrolysis of organotrichlorosilanes where large amounts of HCl are formed. Complementarily, the cross-coupling of 1-octene and POSS-SiH proceeded in the presence of Pt-SAC with excellent yield.

To demonstrate the utility of our catalyst, two industrially relevant reactions of polysilanes with olefins were studied. The resulting materials exhibit distinctive optical and electrical properties, and some of them constitute important precursors for novel materials such as nanostructured silicon carbide.<sup>49</sup> Hence, the hydrosilylation of 1-octene with PMHS and PL6020 proceeded smoothly in the presence of the single atom Pt catalyst (Scheme 3). Finally, the cross-coupling of PL6020 and vinyl-trimethylsilane gave 5c, which represents an example for cross-linked silicone polymers.

### Scheme 3. Cross-Linked Silicone Fluids Prepared Using Single Atom Pt Catalyst<sup>a</sup>



<sup>a</sup>270 mg of PMHS (Sigma-Aldrich, MFCD00084478), 3 mmol of 1-octene. 270 mg of PL6020 (Sigma-Aldrich, MFCD01325013), 2 mmol of olefin.

In summary, we present the first heterogeneous single atom Pt catalyst, which allows for efficient and selective Si–C bond formation. Contrary to all previously known heterogenized catalysts for hydrosilylation, the prepared Pt/NR–Al<sub>2</sub>O<sub>3</sub>–IP offers high activity as well as wide substrate scope and excellent chemoselectivity. In a more general sense, this example demonstrates the superiority of SAC compared to more common heterogenized nanoparticles.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.7b00105.

Extended data about optimization of reaction conditions, preparation and characterization of catalyst, and synthesis and spectroscopic data of products (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: matthias.beller@catalysis.de.

### ORCID

Feng Shi: 0000-0001-5665-4933

Angelika Brückner: 0000-0003-4647-1273

Matthias Beller: 0000-0001-5709-0965

### Author Contributions

M.B. designed the method and coordinated the project. X.C. and K.J. conducted the experiments and developed the project. We thank S.W. for his kind support on the preparation of SAC. X.D., C.K., and M.-M.P. helped to characterize the SACs. We thank F.S. and A.B. for their kind suggestions and improvements on this project. M.B., X.C., and K.J. wrote the manuscript.

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### Notes

The authors declare no competing financial interest.

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