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COMMUNICATION

Functionalized Vinylsilanes Via Highly Efficient and Recyclable Pt-Nanoparticle Catalysed Hydrosilylation of Alkynes

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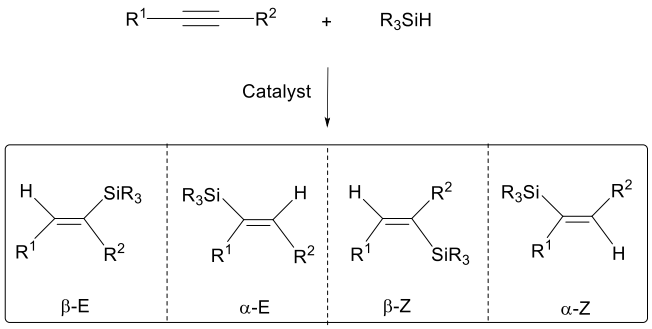
A mild, selective and facile synthesis of vinylsilanes via a recyclable platinum nanoparticle catalysed hydrosilylation of alkynes is reported. Various functionalized alkynes are selectively hydrosilylated to furnish functional β-E vinylsilanes in high yields. The catalytic effectiveness, ease of catalyst recovery and recyclability of polysiloxane stabilized Pt-nanoparticle catalyst are the major achievements of this work. Detailed in situ characterization using Electron Microscopy and controlled poisoning experiments supports the participation of Pt-nanoparticles as an active catalyst.

Vinylsilanes are versatile organosilicon family of compounds, which have found applications as important building blocks for the construction of novel organic/inorganic hybrid functional materials.[1-2] In last few decades, the utilization of this specific class of organometalloids in transition-metal catalysed cross-coupling reactions has grown tremendously due to their relatively low toxicity, high chemical stability and low molecular weight when compared with other organotin, organoboron, and organozinc counterparts.[3-9]

Metal complex catalysed hydrosilylation of alkynes has been investigated extensively because it can lead to variety of vinylsilanes with 100% atom efficiency (scheme 1). [10-21]

Platinum based catalysts have been most common and active catalysts for regio- and stereospecific hydrosilylation reactions. A large body of platinum catalysed hydrosilylation studies has been conducted under homogeneous conditions where expensive Pt-catalysts are not recyclable. Moreover, due to their extremely high reactivity, the handling of the catalysts often requires inert atmosphere compromising their utility for large scale production in industrial setting. On the other hand, their heterogeneous counterparts such as platinum-metal supported on titania,[14] silica,[19] and activated-carbon,[20] have provided benefits in terms of ease of catalyst recovery and recyclability, but the reactivity and selectivity of such catalysts are generally very low and often require stringent reaction condition to achieve 100% conversion.

Scheme 1: Hydrosilylation of alkynes with functional silanes



Efforts in our laboratory, have been directed towards creating heterogeneous platforms of selectively cross-linked polysiloxanes, in which the metal nanoparticles are nucleated in desired concentration and morphology. Using such catalysts, we have examined and reported highly efficient, mild and recyclable catalysts for hydrolytic oxidation of organosilane, hydrosilylation of olefin and polyolefins where the air-stable solid catalyst first forms a homogeneous/dispersed phase with the reactant molecules and separates out on the way to the end of reaction.[22-24]

To further extend our ongoing efforts towards the development of such hybrid-phase catalyst to produce industrially relevant building blocks, we wish to present herein a highly selective, mild and practical hydrosilylation reaction of functional alkynes with hydrosilanes to produce corresponding vinylsilanes in high yields. In this communication, catalytic performance of heterogeneous platinum nanoparticles powders in terms of activity, selectivity and recyclability is also examined. In

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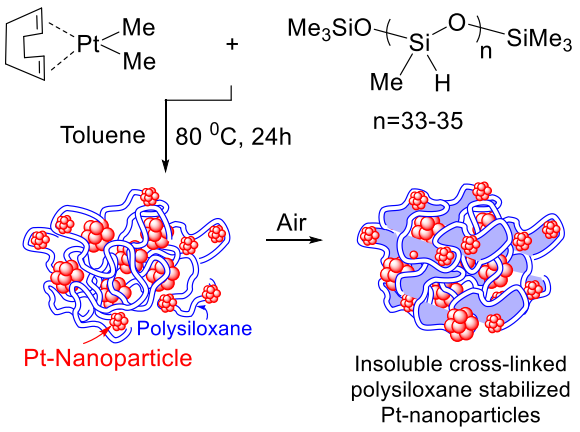
addition, the initial studies of the nature and surface reactions of polysiloxane stabilized Pt- nanoparticles is also reported.

The polysiloxane stabilized platinum nanoparticles were prepared according to the slightly modified procedure reported earlier by our group.[25] Briefly, the platinum complex, Me_2Pt (COD) (COD: 1,5 cyclo-octadiene) (0.25 mmol, 0.084 g), and polymethylhydrosiloxane (PMHS, average MW ~2000) (10.00 mmol, 0.60 mL) were mixed in 50 mL toluene in a 200-mL round bottom flask. The reaction mixture was stirred at 80 °C for 24 h under positive pressure of nitrogen. The reduction reaction of Me_2Pt (COD) to Pt-particles was monitored with UV-Vis spectroscopy, which revealed a gradual disappearance of intense absorption peak at ~320nm associated with the Me_2Pt (COD) leading to a featureless UV-Vis spectrum.

Scheme 2: Synthesis of Cross-linked polysiloxane stabilized Pt-Nanoparticles

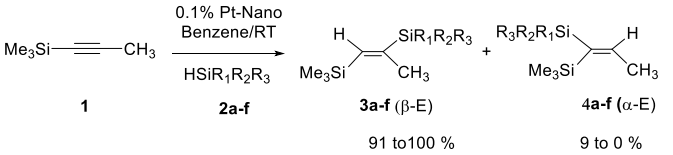


At this juncture, the TEM analysis was carried out to authenticate the formation of Pt-nanoparticles. The TEM analysis indicated presence of spherical metal nanoparticles with an average particle size of 2 nm. After verifying the presence of Pt-nanoparticles in the solution, the reaction flask was exposed to air. Further stirring of the solution in air yielded a black gummy solid. We assumed and later confirmed that this gummy solid was formed due to the oxidative coupling of the remaining silicon-hydrogen bonds in presence of oxygen to furnish cross-linked polysiloxane stabilized platinum nanoparticles in the powder form.

The resulting solid was thoroughly washed with benzene (100 mL) to remove any impurities. Air-drying of the solid furnished the polysiloxane conjugated Pt-nanoparticle catalyst as a black powder. The NMR, SEM and Elemental analyses of powder form of the catalyst have revealed that the material has a composition containing about 5% platinum metal uniformly dispersed in cross-linked polysiloxane. In the XPS spectra of the solid powder, two broad bands appear which correspond to the Pt4f7/2 and Pt4f5/2 levels. The Pt4f7/2 peaks were deconvoluted into two components and found to be at 72.75 and 75.5 eV respectively which is in good agreement with reported results for binding energy of Pt-Si bonds and in zero oxidation state of platinum.[26]

The initial investigations of catalytic activity of Pt-nanoparticles towards the hydrosilylation of alkyne were carried out using trimethylsilyl-1-propyne (Scheme 3). In the presence of catalytic amount of polysiloxane-platinum nanoparticles, the triethylsilane smoothly underwent hydrosilylation reaction with 1-trimethylsilyl propyne at room temperature affording a mixture of only two isomers in a ratio of 91: 9. We were surprised to encounter such a selective transformation because unsymmetrially disubstituted alkyne can give rise to four possible isomers (β-E, α-E, α-Z, β-Z and α-Z) depending upon the mode of addition of Si-H bond across the triple bond.

Scheme 3: Hydrosilylation of Trimehylsilyl-1-propyne (**1**) with functional silanes (**2a-f**).



Detailed NMR studies were carried out to establish the ratios of the isomers. In the ^1H NMR, the vinylic proton of the major product appeares as singlet peak at 6.05 ppm whereas for other isomer it was found to be a quartet at 6.8 ppm. Based on the spin-multiplicity analysis of these peaks, it was concluded that the major product was one of the β- isomers (i.e. β-E or β-Z) whereas the minor product was an α-isomers (i.e α-E or α-Z). To further distinguish the two isomers, the products were analysed by 1D NOE techniques. In the case of β-isomer a pronounced NOE effect was observed between the -Me and –$SiMe_3$ protons whereas no such effect was observed between the –Me and vinylic protons. Similarly, in case of the α-isomer a strong NOE was again observed between -Me and –$SiMe_3$ protons but no such effect was there between the –Me and -$SiEt_3$ proton. In order to show an NOE effect, both -Me and –$SiMe_3$ protons need to be within a close proximity which was only met in β-E and α-E isomers. These results confirmed the structure of major product as a β-E isomer and the minor product as α-E isomer.

A series of organosilanes containing different substituents on the silicon were employed as hydrosilylating agent for examining the scope of the preliminary findings. All reactions were carried out at room temperature using equimolar amount of silane and alkyne in presence 0.1 mol% with respect to alkyne. After completion of the reaction, the product was isolated from the catalyst by centrifugation while the precipitated catalyst was washed with hexane and re-used for next cycles of reaction. The identification of different isomers was made based on the analysis of spin-multiplicity, proton-proton coupling constant (J) values and Nuclear Overhauser effect (NOE) obtained from the ^1H NMR studies of the isolated product. The distribution of different isomers in the product was calculated using quantitative ^1H and ^{29}Si NMR spectroscopic techniques. Results are shown in Table 1.

The alkoxy- and chloro- substituted silanes (Entry 2b-f, Table 1) were reacted with trimethylsilyl-1-propyne under similar reaction conditions and molar ratios. The substitution of alkoxy and chloro groups on hydrosilane (**2b-f**) had a very positive impact on the selectivity towards β-E isomer. To our surprise reaction of trimehylsilyl-1-propyne (**1**) with hydrosilanes **2b-f** led to the quantitative formation of β-E isomer. Out of three other

possible isomers, no other isomer was observed. Such a selectivity with alkoxy- and chloro- functionalities bodes really well for vinyl silane application because these silanes can further undergo various transformation to produce intermediates and precursors to high end materials for various applications.

Table 1. Hydrosilylation of Trimethylsilyl-1-propyne (**1**) in presence of cross-linked polysiloxane stabilized platinum nanoparticles[a]

Silane	R_1	R_2	R_3	Isolated Yield (%)	Selectivity‡ β-E: α
2a	Et	Et	Et	98	**3a:4a** (91: 9)
2b	OEt	Me	Me	98	**3b:4b** (100: 0)
2c	OEt	OEt	OEt	97	**3c:4c** (100: 0)
2d	Cl	Me	Me	98	**3d:4d** (100: 0)
2e	Cl	Cl	Et	98	**3e:4e** (100: 0)
2f	Cl	Cl	Cl	95	**3f:4f** (100: 0)

[a]Trimethylsilyl-1-propyne (1.0 mmol), silane (1.0 mmol), polysiloxane stabilized Pt-nanoparticles (5 mg, 0.1 mol% of Pt), Benzene (2.0 ml) and r.t.; See ‡ for NMR data

To further explore the scope of the present catalysis, various functionalized alkynes were subjected to the hydrosilylation reaction. Unless mentioned otherwise, all reactions were carried out at RT using equimolar amounts of silane and alkyne in presence of 0.005 g of polysiloxane stabilized platinum nanoparticles (0.001 mmol of Pt, 0.1 mol% with respect to alkyne).

All alkynes underwent Pt-nanoparticle catalyzed hydrosilylation at room temperature to selectively produce corresponding β-E and α-E isomers in 96-98% yield (Scheme 4). Formation of other two possible isomers (Scheme 1) was not detected in any of the hydrosilylation reactions. In most cases, relatively higher selectivity towards β-E over the α–E/α isomer was observed. Since, the hydrosilylation with triethylsilanes is known to be sluggish and produce mixtures, the hydrosilylation reactions of triethylsilane with disubstitutedacetylenes were examined to access the efficacy and selectivity of present catalyst.

In order to elucidate the electronic and steric implications of the substituent present on alkyne moiety, disubstituted alkynes with four possible combination of substituents including -$SiMe_3$ /-C_6H_5 (entry 5a, Table 2), -$SiMe_3$/1-Cyclohexenyl (entry 5b), -$SiMe_3$/1-Cyclopropyl (entry 5c), and -C_6H_5/-Me (entry 5d,) were subjected to hydrosilylation reaction under the present catalytic conditions. It was quite interesting to note that whereas all the substituents combination smoothly underwent selective hydrosilylation, the alkyne containing -$SiMe_3$/1-Cyclohexenyl substituents (5b) did not show any reactivity towards the present catalytic system. As is evident from the table 2, in most cases a mixture of β-E and α-E isomers was observed. In most cases, except entry 5d, the regioselectivity is favored towards formation of β-E isomer.

Scheme 4: Hydrosilylation of disubstituted alkyne using Triethyl silane.

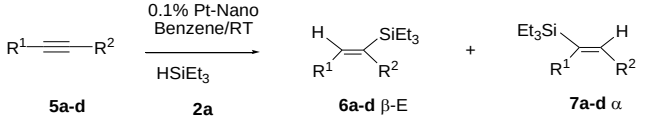


Table 2: Hydrosilylation of disubstituted alkyne using Triethyl silane[a]

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Alkyne	R^1	R^2	Isolated Yield (%)	Selectivity‡ β-E: α-E
5a	$SiMe_3$	C_6H_5	96	**6a:7a** (85:15)
5b	$SiMe_3$	1-Cyclohexenyl	NR	-
5c	$SiMe_3$	Cyclopropyl	97	**6c:7c** (87:13)
5d	C_6H_5	Me	98	**6d:7d** (54:46)

[a]Alkyne (1.0 mmol), silane (1.0 mmol), polysiloxane stabilized Pt-nanoparticles (5 mg, 0.1 mol% of Pt), Benzene (2.0 ml), RT; See ‡ for NMR data.

Since, it is well known that the silanes bearing electron-withdrawing groups undergo oxidative addition more efficiently than those bearing electron-donating groups, an electron withdrawing group substituted silane dimethylchlorosilane **2d** was investigated as reactant. As we expected, the hydrosilylation reactions of acetylenes 5a-d, produced β-E isomer in more than 90 % yield. The same trend was observed, when disubstituted acetylenes **5a** and **5b**, were subjected to hydrosilylation reaction with dimethylchlorosilane **2d**. Exclusive formation of β-E isomer was observed in quantitative yield. (table 3).

Scheme 5: Hydrosilylation of disubstituted alkyne using Dimethylchlorosilane.

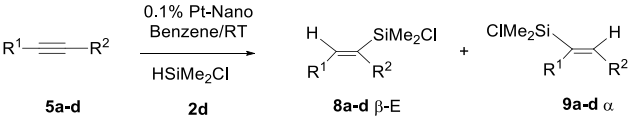

Table 3: Hydrosilylation of disubstituted alkyne using Dimethylchlorosilane.

Alkyne	R1	R2	Isolated Yield (%)	Selectivity ‡ β-E: α
5a	$SiMe_3$	C_6H_5	96	**8a:9a** (100:0)
5b	$SiMe_3$	1-Cyclohexenyl	98	**8b:9b** (100:0)
5c	$SiMe_3$	Cyclopropyl	98	**8c:9c** (98:02)
5d	C_6H_5	Me	98	**8d:9d** (92:08)

[a]Alkyne (1.0 mmol), silane (1.0 mmol), polysiloxane stabilized Pt-nanoparticles (5 mg, 0.1 mol% of Pt), Benzene (2.0 ml), RT; See ‡ for NMR data.

Similar effects were also noticed while performing the hydrosilylation of phenylacetylene with functional silanes (Scheme 6). In these cases, the selectivity towards β-E isomer was improved from 87% upto 100% when a chlorosilane was used (2d, 2f, Table 4). It is worthwhile mentioning that hydrosilylation of phenylacetylene was reported to give polyphenylacetylene as undesired side-product,[19] whereas under the present catalytic conditions the phenylacetyne was selectively converted to corresponding vinylsilane without the formation of any side-product. From synthetic perspective, the predictable selectivity, moderate reaction conditions and functional group tolerance are quite notable features of this catalysis.

Scheme 6: Hydrosilylation of phenylacetylene with various functional silane

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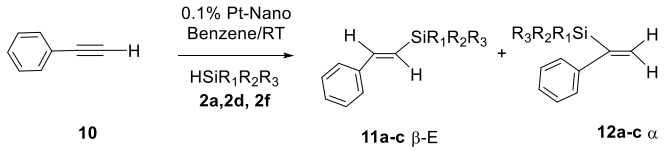


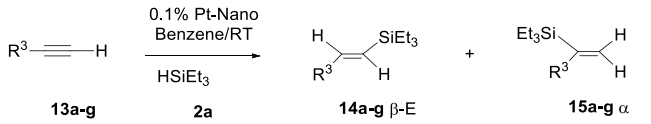
Table 4: Hydrosilylation of phenylacetylene with various functional silane[a]

Silane	R_1	R_2	R_3	Isolated Yield (%)	Selectivity ‡ β-E: α
2a	Et	Et	Et	98	11a:12a (87: 13)
2d	Cl	Me	Me	98	11b:12b (100:0)
3f	Cl	Cl	Cl	98	11c:12c (100:0)

[a]Alkyne (1.0 mmol), silane (1.0 mmol), polysiloxane stabilized Pt-nanoparticles (5 mg, 0.1 mol% of Pt), Benzene (2.0 ml) and RT; See ‡ for details and NMR data.

In order to further scrutinize the scope and new opportunities for generating functionalized vinly silanes the hydrosilylation reactions of various functional acetylenes were performed. In these investigations, one of the sluggishly reacting silane was used for all the transformation. First experiments were carried out with aromatic acetylenes (R^3=*para*-X-C_6H_4-) bearing a substituent at *para*-position of the aryl ring (Scheme 7).

Scheme 7: Hydrosilylation of functional monosubstituted alkyne with Triethylsilane



In this series of acetylenes, we observed that the β-E: α ratio was only slightly influenced by the nature of the substituents at the para position of the aromatic ring. For example, an electron withdrawing -OMe group at the para position of aryl ring furnished 88% selectivity towards β-E isomer whereas the electron-donating -Me and $-NH_2$ groups were found to be 84% and 85% selective toward β-E isomer (Table 5).

Similar observations were also noted in the case of hydrosilylation of terminal aliphatic alkyne possessing different functional moieties. Thus, the hydrosilylation of 5-cyanopentyne (13e, Table 5) produced corresponding β-E isomer with 87% selectivity whereas the diethylamino 2-propyne afforded β-E isomer with 92% selectivity (13e, Table 5).

It is worth noting that the only exception in all the acetylenes, which were studied, was the hydrosilylation studies of the propiolic acid (13g, table 5). In this case our catalysts showed inverse selectivity by furnishing the sterically unfavorable α isomer over the β-E isomer (Entry 15, Table 5). It is also noteworthy that no dehydrocoupling reaction involving the silane and carboxylic acid moiety was detected during the hydrosilylation of the propiolic acid. It is important to mention that though almost all the alkynes underwent room temperature hydrosilylation reaction under the present nanoparticle catalysis, some alkynes especially those functionalized with a coordinating group such as $-(CH_2)_4CN$, $-C_6H_4NH_2$, $-CH_2NEt_2$ and –COOH required heating at 70 °C for a little bit longer reaction time (20h) to provide 100% conversion.

Table 5: Hydrosilylation of functional monosubstituted alkyne with Triethylsilane

Acetylene	R^3	Isolated Yield (%)	Selectivity‡ β-E: α-E
13a	4-C_6H_4F	95	**14a:15a** (85:15)
13b	4- C_6H_4(OMe)	98	**14b:15b** (88:12)
13c	4- C_6H_4Me	98	**14c:15c** (84:16)
13d[c]	4- $C_6H_4NH_2$	96	**14d:15d** (85:15)
13e[c]	$CH_2CH_2CH_2CN$	96	**14e:15e** (89:11)
13f[c]	CH_2NEt_2	96	**14f:15f** (92:08)
13g[c]	COOH	96	**14g:15g** (30:70)

[a]Alkyne (1.0 mmol), silane (1.0 mmol), polysiloxane stabilized Pt-nanoparticles (5 mg, 0.1 mol% of Pt), Benzene (2.0 ml) and r.t.; See ‡ for NMR data

One of the important feature of the present catalysis is the recyclability of the nanoparticle catalysts. In order to scope and study the limitation, hydrosilylation of 4-methylphenyl acetylene with triethylsilane was examined under standard reaction protocols (see supplementary materials). To our delight, quantitative conversion was recorded in the hydrosilylation of 4-methylphenyl acetylene with triethylsilane using recycled a platinum nanoparticle catalyst up to five consecutive runs with no significant loss in the catalytic activity. The in-situ UV-vis experiment for all the catalyst cycles resulted in a featureless spectra indicating the fact that Pt-nanoparticles were involved in each cycle of the catalysis. It was also evident from the ICP analysis of hydrosilylated products that the amount of leachable platinum found in the product was in the range between 0.01-0.5 ppm.

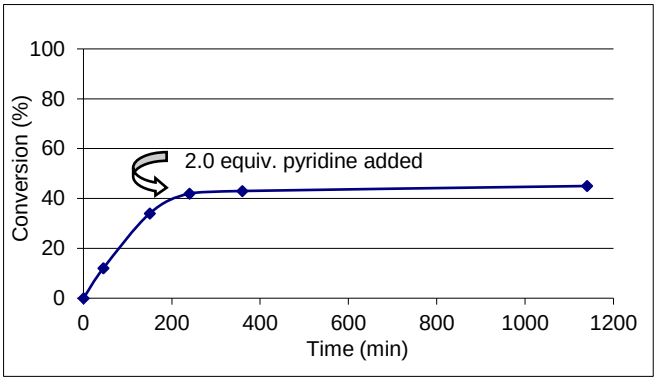
In view of extending the present protocol towards the large scale applications the above reaction was tested in various solvents including benzene, toluene, xylene and hexane where no change in reactivity as well as selectivity was detected.

The exact nature of the catalyst was established via controlled poisoning experiments where a series of hydrosilylation reactions were performed in the presence of a ligand that is capable of forming strong coordination bond with the metallic surface preventing the reactant molecules to approach nanoparticle surface. Various coordinating ligands have been reported to be used as an effective surface stabilizing agents for the synthesis of stable metal nanoparticles.[27-28]

In order to investigate the nature of the catalyst during the catalysis, hydrosilylation of trimethylsilyl-1-propyne with triethylsilane (scheme 2) was selected as standard reaction. Thus, under standard reaction conditions, transmission Electron Microscopic (TEM) and UV-vis studies were performed in combination with quantitative poisoning studies. Thus, during the catalysis (silane 2a, scheme 2) one drop of crude reaction mixture was deposited on formvar/carbon-coated copper grid and analyzed by TEM, which showed the presence of Pt-nanoparticle in the size regime of 2-3 nm. The reaction was also monitored by UV-visible spectroscopy at regular intervals and showed featureless spectra, a characteristic of Pt-nanoclusters.[5d]

Additional poisoning experiments were performed to further support the nanoparticle catalysis where a series of hydrosilylation reactions were performed in the presence of a coordinating ligand such as pyridine that is capable of forming strong coordination bond with the metallic surface preventing the reactant molecules to approach nanoparticle surface. In a typical procedure, a standard hydrosilylation (entry 13c, table 5) was performed in three different schlenk tubes in presence of different amounts of pyridine (0.0005 mmol, 0.001 mmol and 0.002 mmol). The reaction mixtures were monitored using ^{1}HNMR; while we observed significant retardation of catalysis with 0.5 and 1.0 equivalent of pyridine (0.0005 mmol and 0.001 mmol) and complete retardation was observed with 2.0 equivalent of pyridine (0.002 mmol). An additional poisoning experiment was performed adding pyridine (0.002 mmol) after ~40 % conversion of the reaction; no reaction was observed thereafter (figure 1).

Figure 1. Catalyst Poisoning During The Catalysis Using Pyridine.



Conclusions

In this paper, a mild, predictable, facile and widely applicable Pt-based recyclable platinum nanoparticle catalyzed selective hydrosilylation of mono- and di-substituted alkynes is reported. A variety of hydrosilanes were selectively reacted with alkynes containing diverse functionality including –Me, –C_6H_5, *para* -C_6H_4Me, *para*-$C_6H_4(OMe)$, -$SiMe_3$, -$(CH_2)_4CN$, -$C_6H_4NH_2$, -CH_2NEt_2 and -COOH to furnish corresponding vinylsilanes in high yields. In situ characterization using UV-vis, Electron Microscopy and controlled poisoning experiments during the reaction has revealed the participation of Pt-nanoparticles as an active catalyst. Whereas, the regio and stereo selectivity of the present nanoparticles catalyst were not very different for the hydrosilylation of certain alkynes reported previously, significant improvement in terms of catalytic efficiency, ease of catalyst recovery and recyclability over other platinum-based catalysts were achieved using polysiloxane stabilized Pt-nanoparticle catalysis. Thus, excellent yields of various functionalized vinylsilanes (>95%) can be achieved by using polysiloxane stabilized Pt-nanoparticles providing a significant cost advantage over homogeneous platinum complexes. Further research to expand the substrate scope of the present catalysis is underway.

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Notes and references

‡ **Typical procedure for Pt-nanoparticle catalyzed hydrosilylation of alkyne**. A Schlenk tube was charged with Pt-nanoparticle catalyst (0.005g, 0.001 mmol of Pt) and flushed thoroughly with nitrogen. To this solid catalyst, benzene (2 ml), alkyne (1 mmol) and silane (1.0 mmol) were added consecutively and the resulting mixture was stirred at room temperature. Within a period of 30 minutes the solid catalyst was gradually disperse into the reaction mixture resulting in an almost homogeneous solution. After the completion of the reaction (10 hours), the catalyst was precipitated and isolated by centrifuging the reaction mixture at about 2000 rpm. On evaporation of the solvent from the supernatant products were obtained in high yields. The isolated products were characterized by ^{1}H, ^{13}C and ^{29}Si NMR techniques. Spectral signatures of the vinyl silane products reported in this paper are given below.

3a. δH(600MHz; $CDCl_3$;$CHCl_3$) 0.21 (9H, s, SiMe_3), 0.68 (6H,q, *J*=7.4 Hz, SiCH_2), 0.96 (9H, t, *J*=7.4 Hz,$SiCH_2CH_3$), 1.95 (3H,s,CH_3), 6.05 (1H,s,C=C*H*$SiMe_3$). δC(150MHz; $CDCl_3$; $CHCl_3$) 0.3, 1.5, 7.4, 21.7, 142.5, 157.5. δSi(120MHz; $CDCl_3$)-11.95, 1.98.

4a. δH (600MHz; $CDCl_3$;$CHCl_3$)0.25 (9H, s, SiMe_3), 0.72 (6H, q, *J*=7.4 Hz, SiCH_2), 0.99 (9H, t, *J*=7.4 Hz, $SiCH_2CH_3$), 2.01 (3H, d, *J*=6.7 Hz, CH_3), 6.80 (1H, q, *J*=6.7 Hz, C=C*H*Me).

3b. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.05 (9H, s, SiMe_3), 0.28 (6H, s, SiMe_2OEt), 1.04 (3H, t, *J*=6.9 Hz, OCH_2CH_3), 2.78 (3H, s,CH_3), 3.49 (2H, q, *J*=6.9 Hz, SiCH_2CH_3), 6.0 (1H, s, C=C*H*$SiMe_3$). δC(150MHz; $CDCl_3$; $CHCl_3$) -2.9, -0.07, 18.3, 20.2, 58.2, 142.7, 157.8. δSi(120MHz;$CDCl_3$)-11.31, 5.58.

3c. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.08 (9H, s, SiMe_3), 1.17 (9H, t, *J*=6.9 Hz, OCH_2CH_3), 1.86 (3H, s, CH_3), 3.77 (6H, q, *J*=6.9 Hz, OCH_2CH_3), 6.32 (1H, s, C=C*H*$SiMe_3$). δC(150MHz; $CDCl_3$; $CHCl_3$)-0.1, 18.2, 20.7, 58.5, 147.3, 150.2.

3d. δH(600MHz; $CDCl_3$;$CHCl_3$) 0.14 (9H, s, SiMe_3), 0.38 (6H, s, SiMe_2Cl), 1.90 (3H, s,CH_3), 6.13 (1H, s, C=C*H*$SiMe_3$).

3e. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.13 (9H, s, SiMe_3), 1.02 (3H, t, *J*=7.0 Hz, $SiCH_2CH_3$), 1.06 (2H, q, *J*=7.0 Hz, SiCH_2CH_3), 1.95 (3H, s, CH_3), 6.38 (1H, s, C=C*H*$SiMe_3$). δC(150MHz; $CDCl_3$; $CHCl_3$)-2.7, 6.3, 11.3, 19.3, 148.4, 150.6. δSi(120MHz;$CDCl_3$)-9.27, 17.25.

3f. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.01 (9H, s, SiMe_3), 1.88 (3H, s, CH_3), 6.53 (1H, s, C=C*H*$SiMe_3$).). δC(150MHz; $CDCl_3$; $CHCl_3$)-0.4, 18.5, 147.9, 151.4. δSi(120MHz;$CDCl_3$)-8.19, -4.17.

6a. δH (600MHz; $CDCl_3$;$CHCl_3$) -0.31 (9H, s, SiMe_3), 0.47 (6H, q, *J*=7.6 Hz, SiCH_2CH_3), 0.78 (9H, t, *J*=7.6 Hz, $SiCH_2CH_3$), 6.1 (1H, s, C=C*H*$SiMe_3$) 6.99-7.25 (5H, m, C_6H_5). δC(150MHz; $CDCl_3$; $CHCl_3$) 0.1, 2.8, 7.3, 125.6, 127.0, 127.7, 132.2, 145.9, 163.6.

7a. δH(600MHz; $CDCl_3$;$CHCl_3$) 0.06 (9H, s, SiMe_3), 0.16 (6H, q, *J*=7.6 Hz, SiCH_2CH_3), 0.59 (9H, t, *J*=7.6 Hz, $SiCH_2CH_3$), 6.99 -7.25 (5H, m, C_6H_5), 7.65 (1H, s, C=C*H*C_6H_5).

6c. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.13 (9H, s, SiMe_3), 0.44 (4H, m, CH_2CH_2), 0.54 (6H, q, *J*=7.9 Hz, SiCH_2CH_3), 0.88 (9H, t, *J*=7.9 Hz, $SiCH_2CH_3$), 1.74 (1H, m, C*H*), 5.85 (1H, s, C=C*H*$SiMe_3$). δC(150MHz; $CDCl_3$; $CHCl_3$) 0.22, 2.58, 4.16, 7.53, 21.81, 128.33, 142.5.

7c. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.18 (9H, s, Si*Me*$_3$), 0.44 (4H, m, *CH*$_2$*CH*$_2$), 0.45 (6H, q, *J*=7.9 Hz, Si*CH*$_2$CH$_3$), 0.84 (9H, t, *J*=7.9 Hz, SiCH$_2$*CH*$_3$), 1.19 (1H, m, C*H*), 5.73 (1H, d, *J*= 9.8 Hz, C=C*H*SiMe$_3$).

6d. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.61 (6H, q, *J*=7.6 Hz, Si*CH*$_2$CH$_3$), 0.95 (9H, t, *J*=7.6 Hz, SiCH$_2$*CH*$_3$), 1.60 (3H, s, C=C*CH*$_3$C$_6$H$_5$), 6.85 (1H, s, C=C*H*C$_6$H$_5$), 6.97-7.32 (5H, m, *C*$_6$*H*$_5$).

7d. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.73 (6H, q, *J*=7.6 Hz, Si*CH*$_2$CH$_3$), 0.95 (6H, t, *J*=7.6 Hz, SiCH$_2$*CH*$_3$), 2.00 (3H, d, , *J*=2.8 Hz, C=CH*CH*$_3$), 6.10 (1H, q, *J*=2.8 Hz, C=C*H*CH$_3$), 6.97-7.32 (5H, m, C$_6$H$_5$).

8a. δH (600MHz; $CDCl_3$;$CHCl_3$) -0.19 (9H, s, Si*Me*$_3$), 0.42 (6H, s, Si*Me*$_2$Cl), 6.58 (1H, s, C=C*H*SiMe$_3$), 6.99-7.25 (5H, m, *C*$_6$*H*$_5$). δC(150MHz; $CDCl_3$; $CHCl_3$) -0.2, 1.3, 126.4, 127.7, 128.8, 142.7, 148.0, 160.8. δSi(120MHz; $CDCl_3$) -8.31, 17.05.

8b. δH (600MHz; $CDCl_3$;$CHCl_3$) -0.01 (9H, s, Si*Me*$_3$), 0.30 (6H, s, Si*Me*$_2$Cl), 1.48 (4H, m, C=CH*CH*$_2$CH$_2$), 1.93 (4H, m, C=CHCH$_2$*CH*$_2$), 5.16 (1H, s, C=C*H*SiMe$_3$), 6.09 (1H, m, C=C*H*CH$_2$CH$_2$).

8c. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.09 (9H, s, Si*Me*$_3$), 0.45 (6H, s, Si*Me*$_2$Cl), 0.74 (4H, m, *CH*$_2$*CH*$_2$), 1.66(1H, m, C*H*), 6.32 (1H, s, C=C*H*SiMe$_3$). δC(150MHz; $CDCl_3$; $CHCl_3$) 0.0, 3.0, 7.2, 16.9, 147.0, 160.0.

8d. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.55 (6H, s, Si*Me*$_2$Cl), 1.99 (3H, s, C=C*CH*$_3$), 6.86 (s, 1H, C=C*H*C$_6$H$_5$), 7.20-7.32 (5H, m, C$_6$H$_5$).

9d. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.40 (6H, s, Si*Me*$_2$Cl), 1.58 (3H, d, *J*=6.9 Hz, C=CH*CH*$_3$), 6.34 (1H, q, *J*=6.9 Hz, C=C*H*CH$_3$), 7.20-7.32 (5H, m, *C*$_6$*H*$_5$).

11a. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.58 (6H, q, *J*=8.0 Hz, Si*CH*$_2$CH$_3$), 0.91 (9H, t, *J*=8.0 Hz, SiCH$_2$*CH*$_3$), 6.35 (1H, d, *J*=19.7 Hz, C=C*H*Si) 6.80 (1H, d, *J*=19.7 Hz, C=C*H*C$_6$H$_5$), 7.00-7.36 (5H, m, C$_6$H$_5$).

12a. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.53 (6H, q, *J*=8.0 Hz, Si*CH*$_2$CH$_3$), 0.85 (9H, t, *J*=8.0 Hz, SiCH$_2$*CH*$_3$), 5.47 (1H, d, *J*=2.9 Hz, C=C*H*H) 5.77 (1H, d, *J*=2.9 Hz, C=CH*H*), 7.01-7.35 (5H, m, C$_6$H$_5$).

11b. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.63 (6H, s, SiMe$_2$Cl), 6.50 (1H, d, *J*=19.2 Hz, C=C*H*Si) 7.11 (1H, d, *J*=19.2 Hz, C=C*H*C$_6$H$_5$), 7.30-7.50 (5H, m, *C*$_6$*H*$_5$). δC(150MHz; $CDCl_3$; $CHCl_3$) 2.0, 124.5, 126.8, 128.5, 128.8, 137.1, 146.5. δSi(120MHz; $CDCl_3$) 19.47.

11c. δH (600MHz; $CDCl_3$;$CHCl_3$) 6.00 (1H, d, *J*=18.6 Hz, C=C*H*Si), 6.72 (1H, d, *J*=18.6 Hz, C=C*H*C$_6$H$_5$), 7.10-7.42 (5H, m, C$_6$H$_5$).

14a. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.83 (6H, q, *J*=7.8Hz, Si*CH*$_2$CH$_3$), 1.15 (9H, t, *J*=7.8Hz, SiCH$_2$*CH*$_3$), 6.48 (1H,d, *J*=19.2Hz, C=C*H*Si), 7.10 (1H, d, *J*=19.2Hz, C=C*H*C$_6$H$_4$), 7.25-7.55 (4H, m, *C*$_6$*H*$_4$). δSi(120MHz; $CDCl_3$) 0.42.

14b. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.51 (6H, q, *J*=7.6 Hz, Si*CH*$_2$CH$_3$), 0.83 (9H, t, J=7.6 Hz, SiCH$_2$*CH*$_3$), 3.62 (3H, s, C$_6$H$_4$O*Me*), 6.07 (1H, d, *J*=19.6 Hz, C=C*H*Si), 6.69 (1H, d, *J*=19.6 Hz, C=C*H*C$_6$H$_4$), 6.67 (2H, d, *J*=8.4Hz, *C*$_6$*H*$_4$), 7.20 (2H, d, *J*=8.4Hz, *C*$_6$*H*$_4$).

15b. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.47 (6H, q, *J*=7.6 Hz, Si*CH*$_2$CH$_3$), 0.77 (9H, t, J=7.6 Hz, SiCH$_2$*CH*$_3$), 3.62 (3H, s, C$_6$H$_4$O*Me*), 5.35 (1H,d, *J*=3.1 Hz, C=C*H*H), 5.70 (1H, d, *J*=3.1 Hz, C=CH*H*), 6.93 (2H, d, *J*=8.4Hz, *C*$_6$*H*$_4$), 7.05 (2H, d, *J*=8.4Hz, *C*$_6$*H*$_4$).

14c. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.95 (6H, q, *J*=8.0 Hz, Si*CH*$_2$CH$_3$), 1.26 (9H, t, *J*=8.0 Hz, SiCH$_2$*CH*$_3$), 2.59 (3H, s, C$_6$H$_4$*Me*), 6.63 (1H, d, *J*=18.8 Hz, C=C*H*Si), 7.15 (1H, d, *J*=18.8 Hz, C=C*H*C$_6$H$_4$), 7.38 (2H, d, *J*=8.4Hz, *C*$_6$*H*$_4$), 7.60 (2H, d, *J*=8.4Hz, *C*$_6$*H*$_4$).

15c. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.93 (6H, q, *J*=7.6 Hz, Si*CH*$_2$CH$_3$), 1.20 (9H, t, J=7.6 Hz, SiCH$_2$*CH*$_3$), 2.59 (3H, s, C$_6$H$_4$*Me*), 5.82 (1H, d, *J*=2.8 Hz, C=C*H*H), 6.14 (1H, d, *J*=2.8 Hz, C=CH*H*), 7.13-7.38 (4H, m, *C*$_6$*H*$_4$).

14d. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.56 (6H, q, *J*=8.0 Hz, Si*CH*$_2$CH$_3$), 0.87 (9H, t, *J*=8.0 Hz, SiCH$_2$*CH*$_3$), 3.46 (2H, br, *NH*$_2$), 6.05 (1H, d, *J*=19.2 Hz, C=C*H*Si), 6.47 (2H, d, *J*=8.4 Hz, *C*$_6$*H*$_4$), 6.68 (1H, d, *J*=19.2 Hz, C=C*H*C$_6$H$_4$), 7.15 (2H, d, *J*=8.4Hz, *C*$_6$*H*$_4$). δC(150MHz; $CDCl_3$; $CHCl_3$) 3.5, 7.3, 114.7, 120.5, 127.3, 133.2, 144.5, 146.3. δSi(120MHz;$CDCl_3$) 0.14.

15d. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.54 (6H, q, *J*=8.0 Hz, Si*CH*$_2$CH$_3$), 0.83 (9H, t, *J*=8.0 Hz, SiCH$_2$*CH*$_3$), 3.46 (2H, br, *NH*$_2$), 5.36 (1H, d, *J*=3.2 Hz, C=C*H*H), 5.74 (1H, d, *J*=3.2 Hz, C=CH*H*), 6.46 (2H, d, *J*=8.4 Hz, *C*$_6$*H*$_4$), 6.89 (2H, d, *J*=8.4 Hz, *C*$_6$*H*$_4$).

14e. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.53 (6H, q, *J*=7.9 Hz, Si*CH*$_2$CH$_3$), 0.90 (9H, t, *J*=7.9 Hz, SiCH$_2$*CH*$_3$), 1.76 (2H, quintet, *J*=7.2 Hz, C=CHCH$_2$*CH*$_2$), 2.25 (2H, dt, *J*=7.2 Hz, *J*=6.3 Hz, CH*CH*$_2$CH$_2$), 2.30 (2H, t, *J*=7.2 Hz, *CH*$_2$CN), 5.63 (1H, d, *J*=18.7 Hz, Si*CH*=CHCH$_2$), 5.92 (1H, dt, *J*=18.7 Hz, *J*=6.3 Hz, SiCH=*CH*CH$_2$). δC(150MHz; $CDCl_3$; $CHCl_3$) 3.3, 7.2, 16.2, 24.3, 35.4, 119.5, 128.7, 145.0. δSi(120MHz;$CDCl_3$) -1.04.

15e. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.58 (6H, q, *J*=7.9 Hz, Si*CH*$_2$CH$_3$), 0.90 (9H, t, *J*=7.9 Hz, SiCH$_2$*CH*$_3$), 1.76 (2H, quintet, *J*=7.2 Hz, CH$_2$*CH*$_2$CH$_2$CN), 2.21 (2H, t, *J*=7.2 Hz, *CH*$_2$CH$_2$CH$_2$CN), 2.30 (t, 2H, *J*=7.2 Hz, CH$_2$CH$_2$*CH*$_2$CN), 5.36 (1H, d, *J*=2.5 Hz, C=C*H*H), 5.60 (1H, d, *J*=2.5 Hz, C=CH*H*).

14f. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.73 (6H, q, *J*=7.9 Hz, Si*CH*$_2$CH$_3$), 1.08 (9H, t, *J*=7.9 Hz, SiCH$_2$*CH*$_3$), 1.15 (6H, t, *J*=7.2 Hz, NCH$_2$*CH*$_3$), 2.69 (4H, q, *J*=7.2 Hz, N*CH*$_2$CH$_3$), 3.33 (2H, d, *J*=5.8 Hz, C=CH*CH*$_2$N), 5.90 (1H, d, *J*=18.6 Hz, C=C*H*Si), 6.25 (1H, dt, *J*=18.6 Hz, *J*=5.8 Hz, C=C*H*CH$_2$N). δC(150MHz; $CDCl_3$; $CHCl_3$) 3.4, 7.3, 11.6, 46.7, 59.3, 128.9, 145.5.

15f. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.78 (6H, q, *J*=7.9 Hz, Si*CH*$_2$CH$_3$), 1.12 (9H, t, *J*=7.9 Hz, SiCH$_2$*CH*$_3$), 1.19 (6H, t, *J*=7.2 Hz, NCH$_2$*CH*$_3$), 2.56 (q, 4H, *J*=7.2 Hz, N*CH*$_2$CH$_3$), 3.17 (2H,s, N*CH*$_2$C=C), 5.50 (1H, d, *J*=3.5 Hz,C=C*H*H), 5.95 (1H, d, *J*=3.5 Hz, C=CH*H*).

14g. δH (600MHz; $CDCl_3$;$CHCl_3$) 0.51(6H, q, *J*=7.0 Hz, Si*CH*$_2$CH$_3$), 0.92 (9H, t, *J*=7.0 Hz, SiCH$_2$*CH*$_3$), 6.27 (1H, d, *J*=19.1 Hz, C=C*H*Si), 7.36 (1H, d, *J*=19.1 Hz, SiC=C*H*COOH), 12.10 (1H, br, COO*H*)

15g. δH (600MHz; $CDCl_3$;$CHCl_3$) δ 0.73(6H, q, *J*=7.0 Hz, Si*CH*$_2$CH$_3$), 0.92 (9H, t, *J*=7.0 Hz, SiCH$_2$*CH*$_3$), 6.09 (1H, d, *J*=2.6 Hz, C=C*H*H), 6.95 (1H, d, *J*=2.6 Hz, C=CH*H*), 12.10 (1H, br, COO*H*).

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