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Recyclable and reusable K_2PtCl_4/Xphos-SO_3Na/PEG-400/H_2O system for highly regio- and stereoselective hydrosilylation of terminal alkynes

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K_2PtCl_4/Xphos-SO_3Na in a mixture of poly(ethylene glycol) (PEG-400) and water is shown to be a highly regio- and stereoselective catalyst for the hydrosilylation of terminal alkynes with hydrosilanes. The reaction could be conducted under mild conditions, yielding a variety of functionalized β-(*E*)-vinylsilanes in good to excellent yields with a total β-(*E*)-selectivity. The isolation of the products is readily performed by the extraction with cyclohexane and more importantly, both expensive K_2PtCl_4 and Xphos-SO_3Na in PEG-400/H_2O system could be easily recycled and reused at least eight times without any loss of catalytic activity.

Introduction

Vinylsilanes are especially valuable intermediates which can undergo a number of important chemical transformations such as Hiyama cross-couplings,[1] Friedel-Crafts reactions,[2] protodesilylation,[3] Diels-Alder reactions,[4] reduction of the double bond,[5] coupling with aldehydes,[6] and Heck-type couplings,[7] etc.. In general, vinylsilanes show reactivity similar to that of certain organometallic vinyl derivatives, but may

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offer some attractive advantages of low cost, low toxicity, high functionality tolerance and chemical stability. Transition-metal-catalyzed hydrosilylation of alkynes provides a simple and straightforward, atom-economical method for the preparation of vinylsilanes.[8] Since the first report of catalytic hydrosilylation of alkynes using Speier's catalyst,[9] a variety of transition metal catalysts have been developed for related transformations including Pt,[10] Rh,[11] Ru,[12] Ir,[13] Pd,[14] Au,[15] Co[16] and Cu.[17] Among these transition-metal catalysts, platinum complexes[18] and heterogeneous platinum catalysts [19] are by far the most well developed catalyst systems for the hydrosilylation of alkynes, providing the β-isomer, in the *E*-geometry as the major product. The main difficulty with the catalytic hydrosilylation of alkynes is control of the stereo- and regiochemistry of the vinylsilanes products since three isomeric products, α-, β-(*E*)-, and β-(*Z*)-isomers, may be formed with terminal alkynes. Generally, the selectivity is mainly affected by several factors including the nature of the hydrosilane, the alkyne, the metal species and the ligand, and reaction conditions. Industrial catalysts such as Speier's (H_2PtCl_6) and Karstedt's catalysts ($Pt_2(dvtms)_3$: dvtms = divinyltetramethyldisiloxane) can produce high catalyst turnovers; however, the regio- and stereoselectivities can be poor with terminal alkynes as substrates.[20]

The use of bulky trialkylphosphine ligands[21] or platinum *N*-heterocyclic carbene complexes[22] was reported to be an efficient solution to this problem. These sterically hindered platinum catalysts can impart high levels of selectivity on the reactions. Recently, a combination of Pt(II) salts and bulky Xphos[23] and platinum(0) olefin complexes of a bulky terphenylphosphine ligand[24] also proved to be efficient catalysts

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for the hydrosilylation of terminal alkynes with excellent regio- and stereoselectivities. Although these methods reported are highly efficient for construction of β-(*E*)-vinylsilanes, the use of a homogeneous catalytic system in organic solvents on an industrial scale is a challenge because both platinum and bulky phosphine ligands are highly expensive, cannot be recycled, and difficult to separate from the product. These problems are of particular economic and environmental concerns in industry. Moreover, in contemporary chemistry, the impact and consequence of reaction solvents on human health and environment needs to be carefully considered. Therefore, from the standpoint of green and sustainable chemistry,[25] the development of a recyclable and reusable catalyst system that allows for efficient synthesis of β-(*E*)-vinylsilanes via the highly regio- and stereoselective hydrosilylation of terminal alkynes in green solvents is worthwhile.

In order to address both recyclability and environmental concerns, a simple and efficient strategy is to immobilize the catalyst in a liquid phase by dissolving it into a nonvolatile and nonmixing liquid, such as ionic liquids[26] and poly(ethylene glycols) (PEGs). However, ionic liquids impart some disadvantages, such as a complicated procedure for the preparation of ionic liquids as well as their environmental safety, which is still being debated since the toxicity and environmental burden data are unknown for the most of them. It is well known that PEGs are readily available and inexpensive, thermally stable, recoverable, biodegradable and nontoxic compounds which serve as efficient media for environmentally friendly and safe chemical reactions.[27] In recent years, PEGs have been successfully utilized as reaction media for the

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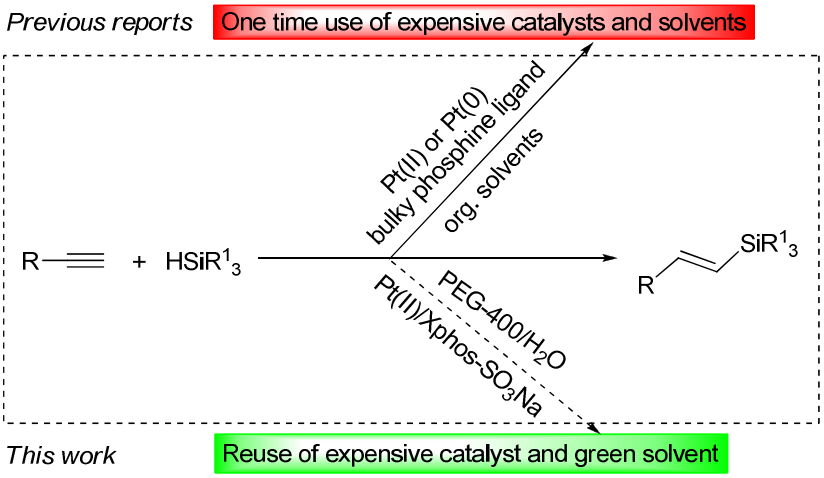
Pd-catalyzed cross-coupling reactions[28] and other transition metal-catalyzed organic transformations[29] with facile recyclability of solvents as well as catalysts. However, to the best of our knowledge, the platinum-catalyzed hydrosilylation of alkynes in PEGs have not been reported until now. We herein report the application of K_2PtCl_4/Xphos-SO_3Na/PEG-400/H_2O system as an extremely effective and reusable catalytic medium for the highly selective hydrosilylation of terminal alkynes leading to β-(*E*)-vinyl-silanes in good to excellent yields with a total β-(*E*)-selectivity (Scheme 1).



Scheme 1 Platinum-catalyzed highly selective synthesis of β-(*E*)-vinylsilanes

Results and discussion

Initially, the hydrosilylation of phenylacetylene **1a** with triethylsilane **2a** was chosen as a model reaction to determine the optimum conditions and the results are listed in Table 1. At first, the solvent effect was examined, and a significant solvent effect was observed. It is evident that the reaction proceeded slowly in H_2O at 25 or 60 ºC and the desired product **3a** was isolated in low yield (Table 1, entries 1 and 2). When

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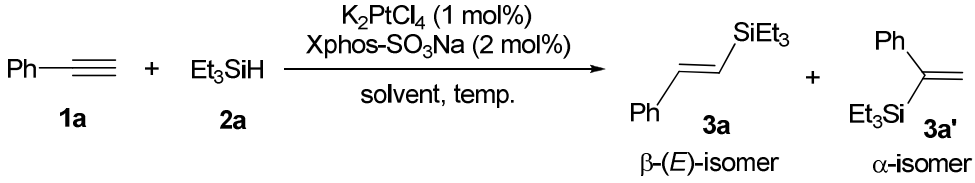
PEG-400 alone was used as solvent, the reaction at 60 ºC gave **3a** in only 62% yield (Table 1, entry 4). Although the conversion rate of phenylacetylene **1a** was low, a total β-(*E*)-selectivity could be observed with H_2O or PEG-400 alone as solvent due to the presence of Xphos-SO_3Na as the ligand. To our delight, a mixture of PEG-400 and H_2O was found to be more effective than PEG-400 or H_2O (Table 1, entries 5-9). The reaction run in PEG-400/H_2O (2:1) at 60 ºC gave **3a** in 94% yield (Table 1, entry 6). Our next studies focused on the effect of reaction temperature on the model reaction. Lowering reaction temperature to 25 °C resulted in a significant decrease in yield and a longer reaction time was needed (Table 1, entry 10). Raising reaction temperature to 80 °C could shorten reaction time, but did not improve the yield (Table 1, entry 11). Besides, the efficiency of various chain length PEGs on the model reaction was also examined under the same reaction conditions (Table 1, entries 12-15). PEG-400 was found to be superior to PEG-600 and PEG-1000. Finally, increasing the amounts of K_2PtCl_4 and Xphos-SO_3Na had no significant improvement in the yield of **3a**, whilst reducing the amounts of K_2PtCl_4 and Xphos-SO_3Na resulted in a decreased yield and a longer reaction time was required (Table 1, entries 16 and 17). Thus, the optimal catalytic system involved the use of K_2PtCl_4 (1 mol%), Xphos-SO_3Na (2 mol%) in PEG-400/H_2O (2:1) at 60 °C under Ar for 6 h (Table 1, entry 6).

Table 1 Optimization of platinum-catalyzed hydrosilylation of phenylacetylene with triethylsilane [a]



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Entry	Solvent (*v*/*v*)	Temp. (ºC)	α/β ratio[b]	Time (h)	Yield (%)[c]
1	H_2O	25	0:100	24	28
2	H_2O	60	0:100	12	35
3	PEG-400	25	0:100	24	37
4	PEG-400	60	0:100	12	62
5	PEG-400/H_2O (3:1)	60	0:100	7	90
6	PEG-400/H_2O (2:1)	60	0:100	6	94
7	PEG-400/H_2O (1:1)	60	0:100	7	86
8	PEG-400/H_2O (2:3)	60	0:100	7	79
9	PEG-400/H_2O (1:2)	60	0:100	10	71
10	PEG-400/H_2O (2:1)	25	0:100	24	52
11	PEG-400/H_2O (2:1)	80	0:100	4	93
12	PEG-600	60	0:100	12	58
13	PEG-600/H_2O (2:1)	60	0:100	6	87
14	PEG-1000	60	0:100	12	53
15	PEG-1000/H_2O (2:1)	60	0:100	6	84
16[d]	PEG-400/H_2O (2:1)	60	0:100	4	94
17[e]	PEG-400/H_2O (2:1)	60	0:100	12	79

[a] Reaction conditions: phenylacetylene **1a** (1.0 mmol), Et_3SiH **2a** (1.5 mmol), K_2PtCl_4 (1.0 mol%), Xphos-SO_3Na (2.0 mol%), solvent (1.0 mL) under Ar. [b] Determined by GC analysis and ^1H NMR in the crude reaction mixture. [c] Isolated yield of the mixture of **3a** and **3a'**. [d] K_2PtCl_4 (2.0 mol%) and Xphos-SO_3Na (4.0 mol%) were used. [e] K_2PtCl_4 (0.5 mol%) and Xphos-SO_3Na (1.0 mol%) were used.

With the optimized reaction conditions in hand, we began to examine the reaction with a wide range of substrates to determine the specificity and scope of substrates. Thus, a variety of substituted phenylacetylenes **1b-1k** were reacted with triethylsilane under the optimized conditions, and the results are listed in Table 2. As shown in Table 2, it is evident that most of the platinum-catalyzed hydrosilylation reactions

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proceeded smoothly under mild conditions in PEG-400/H_2O medium, affording the corresponding β-(*E*)-vinylsilanes in good to excellent yields with a 100% β-(*E*)-selectivity. In all cases, no other isomers were observed in the NMR spectra of the crude products. For example, both electron-rich phenylacetylenes **1b-1f** and electron-deficient phenylacetylenes **1g-1h** gave the desired β-(*E*)-vinylsilanes **3b-3h** in 72-93% yields. The results showed that the electronic properties of substituents on benzene ring have limited influence on the hydrosilylation reaction. Next, we evaluated the effect of *ortho* substituent groups on the reaction selectivity. When 2-methylphenylacetylene **1i** and 2-methoxyphenylacetylene **1j** were used as substrates, again a total β-regiocontrol was observed and the expected β-(*E*)-adducts **3i** and **3j** were produced in 80% and 92% yields, respectively, which indicating that the regioselectivity of the H–Si bond addition is governed by steric effects induced by Xphos-SO_3Na ligand rather than *ortho*-directing effect. To support this explanation, the hydrosilylation of 2-methylphenylacetylene **1i** with Et_3SiH was performed without Xphos-SO_3Na and formed a 35:65 ratio of α:β regioisomers. It is noteworthy that bulky 1-ethynylnaphthalene **1l** also underwent the hydrosilylation smoothly to afford the desired product **3l** in good yield with a 100% β-(*E*)-selectivity. Interestingly, although the reactivity of 2-ethynylpyridine **1m**, a heteroarylacetylene was lower than that of phenylacetylenes, the reaction also proceeded effectively at 80 ºC in the presence of K_2PtCl_4 (5 mol%), Xphos-SO_3Na (10 mol%) leading to a single β-(*E*)-vinylsilane **3m** in 68% yield. A conjugated enyne **1n** proved to be also suitable substrate and produced the desired β-(*E*)-adduct **3n** in 78% yield.

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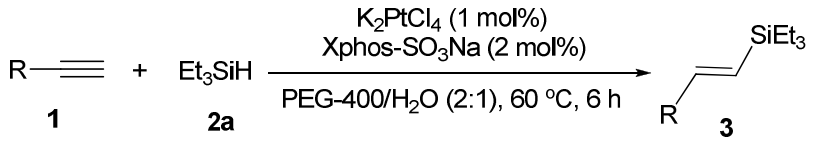
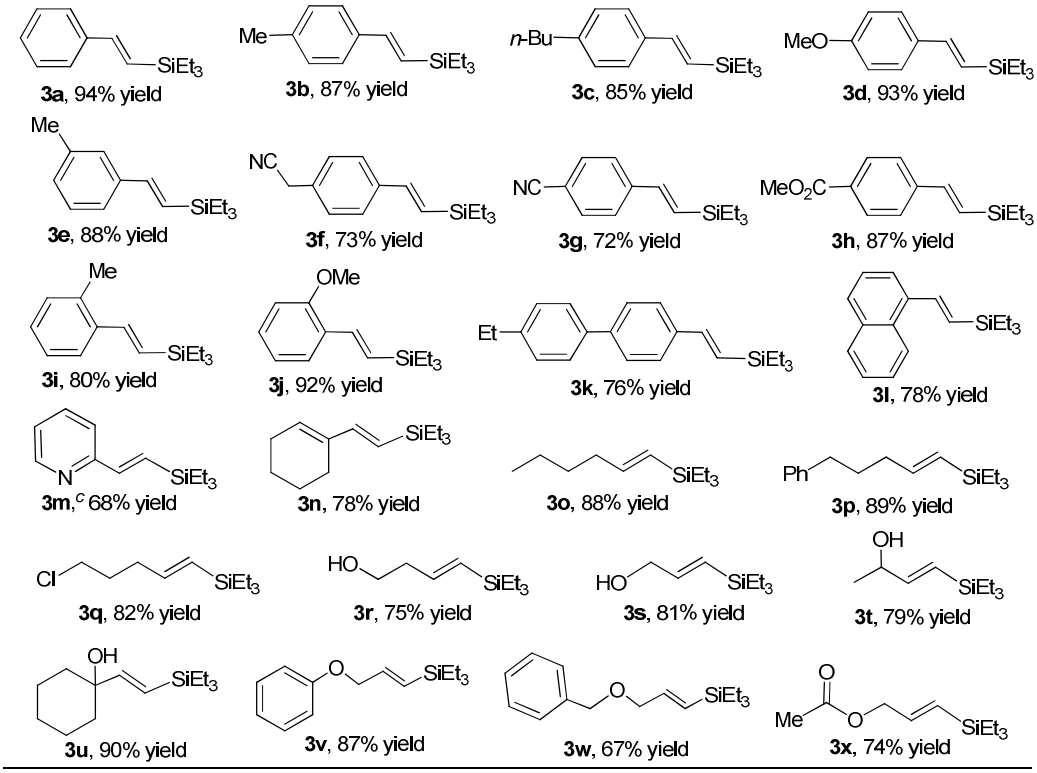
Table 2 Platinum-catalyzed hydrosilylation of terminal alkynes with triethylsilane in PEG-400/H_2O [a,b]





[a] Reaction conditions: terminal alkyne (1.0 mmol), Et_3SiH (1.5 mmol), K_2PtCl_4 (1.0 mol%), Xphos-SO_3Na (2.0 mol%), PEG-400/H_2O (2:1, 1.0 mL) at 60 ºC under Ar for 6 h. [b] Isolated yield. [c] K_2PtCl_4 (5 mol%) and Xphos-SO_3Na (10 mol%) were used at 80 ºC for 12 h.

After completion of investigation of functionalized terminal arylalkynes, further examination showed that the K_2PtCl_4/Xphos-SO_3Na/PEG-400/H_2O system efficiently catalyzes the hydrosilylation of terminal aliphatic alkynes. For instance, the reactions of hex-1-yne **1o** and 5-phenylpent-1-yne **1p** with Et_3SiH afforded exclusively their corresponding β-(*E*)-vinylsilanes **3o** and **3p** in high yields, respectively. The reaction

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worked equally well with aliphatic terminal alkynes bearing functional groups. 5-Chloropent-1-yne **1q** and 4-hydroxybut-1-yne **1r** could undergo the hydrosilylation with Et_3SiH effectively to furnish the desired β-(*E*)-adducts **3q** and **3r** in good yields. In addition to aromatic and aliphatic terminal alkynes, we were also pleased to observe that the K_2PtCl_4/Xphos-SO_3Na/PEG-400/H_2O system was still efficient with propargylic alcohols, propargylic ethers and propargylic esters. For example, the reactions of propargylic alcohols **1s-1u**, regardless of primary, secondary and tertiary alcohols, produced the corresponding vinylsilanes **3s-3u** in 79-90% yields with a 100% β-(*E*)-selectivity. Propargylic ethers **1v** and **1w** could give the desired β-(*E*)-adducts **3v** and **3w** in good yields. Interestingly, the reaction of prop-2-yn-1-yl acetate **1x** with Et_3SiH also gave exclusively the expected β-(*E*)-vinylsilane **3x** in 74% yield. In all cases, no other isomers could be observed prior to purification.

Encouraged by the above results, we next investigated the reaction of terminal alkynes with dimethyl(phenyl)silane **2b** under the reaction conditions optimized for triethylsilane **2a** and the results are listed in Table 3. We were pleased to find that the standard conditions were compatible with a variety of terminal alkynes. It was found that electron-neutral, electron-rich and electron-deficient aromatic terminal alkynes underwent the hydrosilylation reaction with dimethyl(phenyl)silane **2b** efficiently and generated the corresponding vinylsilanes **4a-4c** in excellent yields with a 100% β-(*E*) -selectivity. The reaction of conjugated 1-ethynylcyclohex-1-ene with **2b** also worked well under the standard reaction conditions to afford the desired β-(*E*)-adduct **4d** in 78% yield. The reactions of aliphatic terminal alkynes such as 6-hydroxyhex-1-yne,

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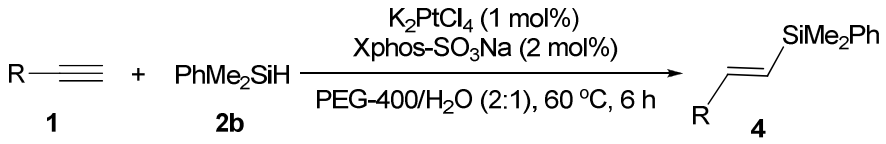
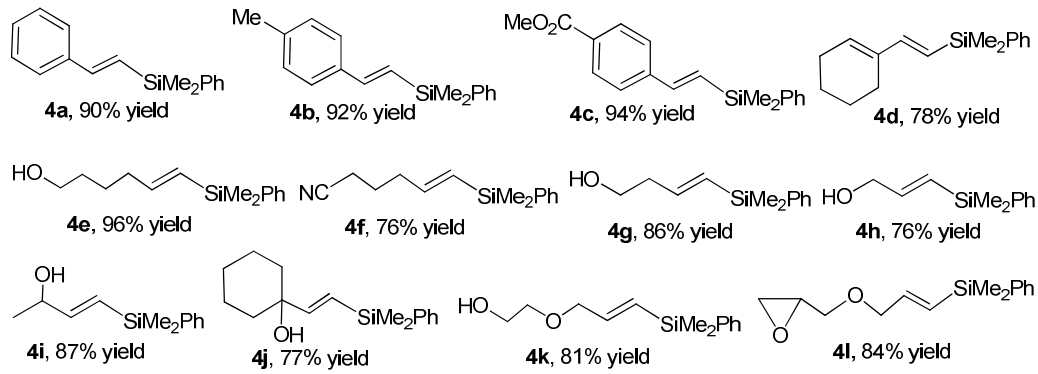
5-cyanopent-1-yne, and 4-hydroxybut-1-yne with **2b** could proceed smoothly to give the corresponding β-(*E*)-vinylsilanes **4e-4g** in good to excellent yields. In addition, both propargylic alcohols and propargylic ethers also proved to be good substrates. For example, the reactions of propargylic alcohols **1s-1u** with **2b** produced the corresponding β-(*E*)-adducts **4h-4j** in 76-87% yields. The reactions of 2-(prop-2-yn-1-yloxy)ethanol and 2-((prop-2-yn-1-yloxy)methyl)oxirane with **2b** could afford the desired vinylsilanes **4k** and **4l** in high yields, respectively. Also, in all cases no other isomers were observed in the NMR spectra of the crude products. A wide range of functional groups such as methyl, methoxy, chloro, cyano, hydroxy, epoxy and ester were well tolerated in present catalytic system.

Table 3 Platinum-catalyzed hydrosilylation of terminal alkynes with dimethyl(phenyl)silane in PEG-400/H_2O [a,b]





[a] Reaction conditions: terminal alkyne (1.0 mmol), $PhMe_2SiH$ (1.5 mmol), K_2PtCl_4 (1.0 mol%), Xphos-SO_3Na (2.0 mol%), PEG-400/H_2O (2:1, 1.0 mL) at 60 °C under Ar for 6 h. [b] Isolated yield.

Table 4 Platinum-catalyzed hydrosilylation of internal alkynes with triethylsilane or dimethyl(phenyl)silane in PEG-400/H_2O [a,b]

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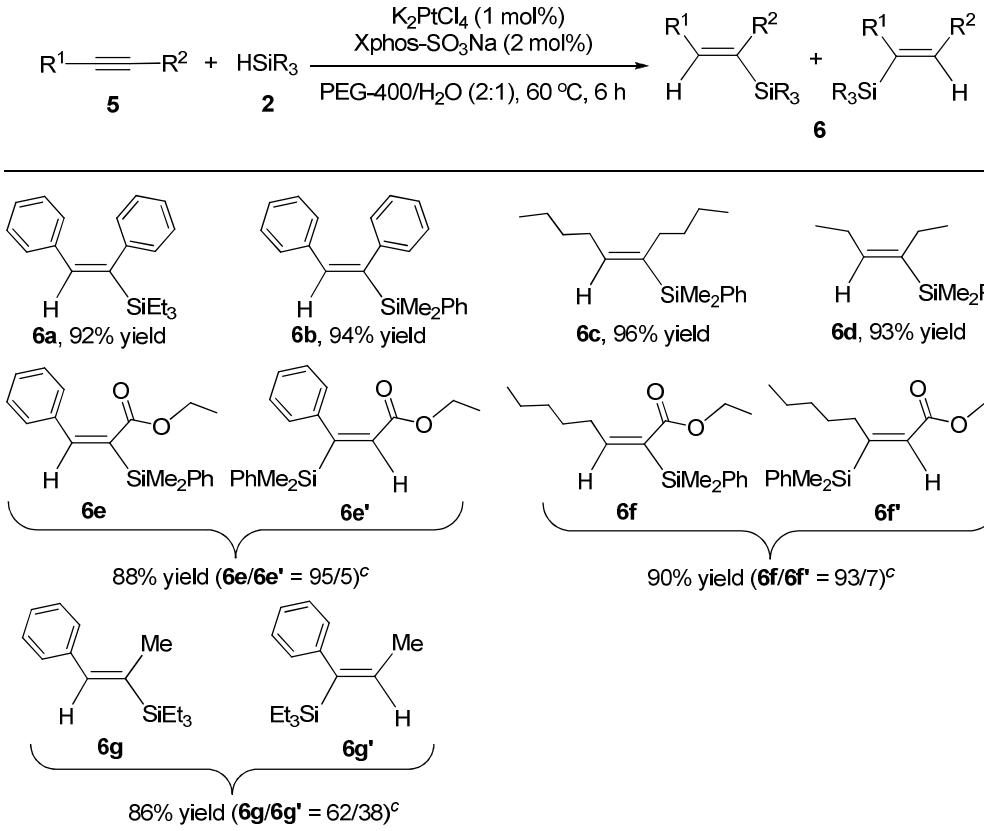

[a] Reaction conditions: internal alkyne (1.0 mmol), Et_3SiH or $PhMe_2SiH$ (1.5 mmol), K_2PtCl_4 (1.0 mol%), Xphos-SO_3Na (2.0 mol%), PEG-400/H_2O (2:1, 1.0 mL) at 60 ºC under Ar for 6 h. [b] Isolated yield. [c] Regioselectivty was determined by ^1H NMR.

We also performed hydrosilylation reaction of internal alkynes with triethylsilane **2a** or dimethyl(phenyl)silane **2b** under the reaction conditions optimized for terminal alkynes and the results are summarized in Table 4. Aromatic or aliphatic symmetrical internal alkynes **5a-c** could undergo the *cis*-hydrosilylation with **2a** or **2b** smoothly to afford exclusively the corresponding (*E*)-vinylsilanes **6a-6d** in excellent yields. For unsymmetrical internal alkynes, the hydrosilylation reactions also proceeded highly stereoselectively to give the expected *syn* adducts, but the regioselectivity depended on the nature of the internal alkynes. For example, electron-deficient unsymmetrical internal alkynes, ethyl 3-phenylpropiolate **5d** and ethyl oct-2-ynoate **5e** underwent the

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cis-hydrosilylation with **2b** effectively to furnish the corresponding (*E*)-ethyl 2-(dimethyl(phenyl)silyl)-3-phenylacrylate **6e** and (*E*)-ethyl 2-(dimethyl(phenyl)silyl)-oct-2-enoate **6f** in high yields with high regioselectivities (93-95%) due to the strong electron-withdrawing nature of ester. However, when 1-phenylprop-1-yne **5f** was used as substrate, despite the different steric hindrances between phenyl and methyl, the hydrosilylation reaction with **2a** afforded a poor regioselectivity (**6g**/**6g'** = 62/38).

In order to show the consistency of this protocol we moved towards exploration of this methodology on the gram scale level (Scheme 2). Under the optimized reaction conditions, 1.02 g (10 mmol) of **1a** and 1.16 g (10 mmol) of **1b** were taken as starting substrates and 1.99 g (91%) of **3a** and 2.27 g (90%) of **4b** were observed respectively. Recently, Alami and Cook reported a platinum-catalyzed hydrosilylation of terminal alkynes and propargylic alcohols by using a $PtCl_2$/Xphos catalyst system in THF.[23] Although a variety of β-(*E*)-vinylsilanes were obtained in high yields with excellent regio- and steroselectivities, expensive platinum catalyst and Xphos ligand could not be separated from the reaction mixture and recycled, which limiting its applications on a large scale. To examine the reusability of the solvent, the catalyst as well as the ligand, the hydrosilylation reaction of phenylacetylene **1a** (1.0 mmol) with Et_3SiH **2a** (1.5 mmol) was evaluated in the presence of K_2PtCl_4 (1.0 mol%) and Xphos-SO_3Na (2.0 mol%) in PEG-400/H_2O (2:1, 1.0 mL) at 60 ºC under Ar for 6 h. The observations of recyclability are demonstrated in Fig. 1, before the light brown color reaction mixture **1** was observed, while after the completion of the reaction the color changed to orange **2**. With cooling of the reaction mixture at room temperature, 5 mL of

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cyclohexane was added and shaken, the two layers **3** were generated. The upper layer of cyclohexane contains the product directly used for purification and the lower layer contains PEG/H_2O with a catalytic system. The PEG/H_2O layer was heated to 60 ºC in vacuum for 20 min to remove the residual cyclohexane. The cooled PEG/H_2O-catalytic system was used for the next cycle by charging with the same substrates (phenylacetylene **1a** and Et_3SiH **2a**) without the addition of K_2PtCl_4 and Xphos-SO_3Na. We were pleased to observe that the K_2PtCl_4/Xphos-SO_3Na/PEG-400/H_2O system could be recycled and reused eight times without any loss of activity. The results of eight runs within an average reaction time of 7 h showed that they were almost consistent in yields (94%, 93%, 94%, 94%, 93%, 92%, 93%, and 92%, respectively) (Fig. 2).

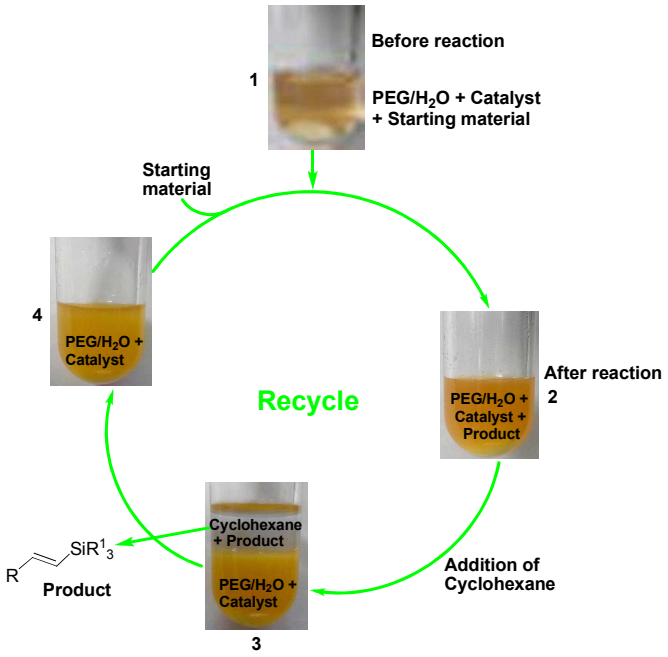

Fig. 1 Procedure for reuse of the catalyst and the solvent system.

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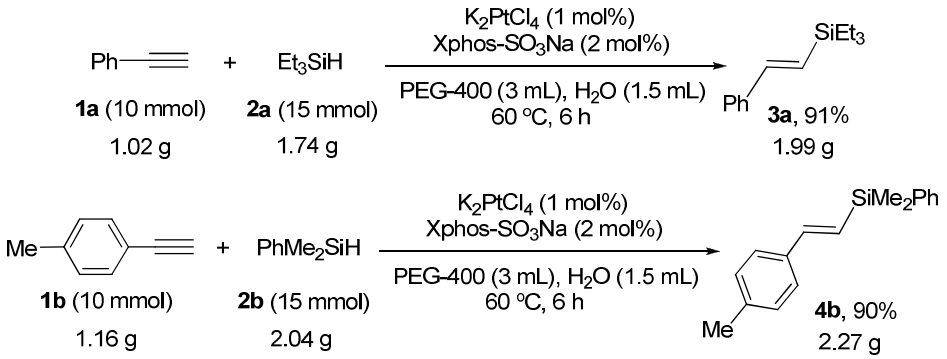

Scheme 2 Gram scale synthesis of (*E*)-vinylsilanes **3a** and **4b**.

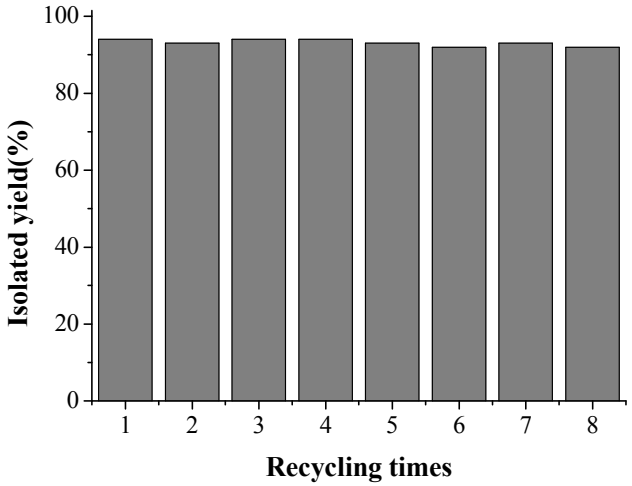

Fig. 2 Recycle of the catalytic system.

The hydrosilylation of terminal alkyne **1** with hydrosilane **2** catalyzed by K_2PtCl_4/Xphos-SO_3Na catalyst system in PEG-400/H_2O may proceed through a mechanism analogous to that proposed for the $PtCl_2$/Xphos catalyst system in THF (Scheme 3).[23] First, the reaction of K_2PtCl_4 with Xphos-SO_3Na ligand produces the $PtCl_2L_2$ (L = Xphos-SO_3Na) complex, which is then reduced with hydrosilane **2** to the platinum(0) catalyst, associated with one or two Xphos-SO_3Na ligands. Subsequently, oxidative addition of hydrosilane **2** to the platinum(0) catalyst generates the platinum(II) complex **A** or **B** and a further coordination with terminal alkyne **1** would give intermediate

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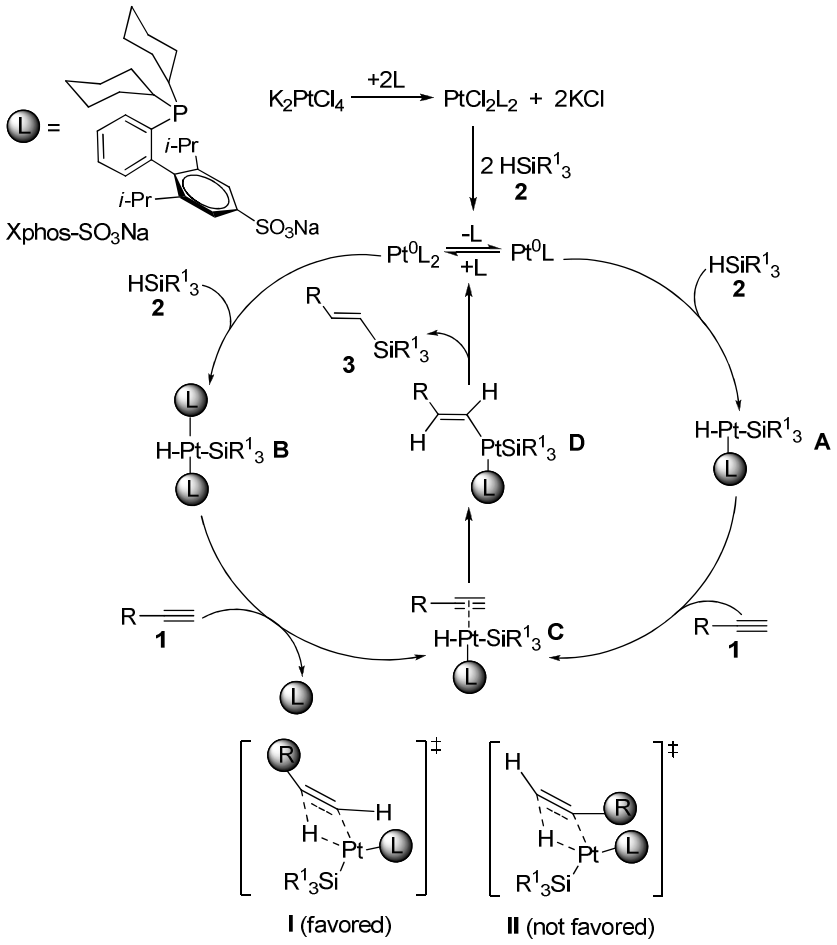
C. Then terminal alkyne **1** would insert into the Pt–H bond (Chalk-Harrod mechanism) rather than Pt–Si bond as was suggested by ab initio molecular orbital and Møller-Plesset perturbation theory calculations.[30] In the presence of Xphos-SO_3Na ligand, the 100% selectivity for the β-(*E*)-isomer **3** can be rationalized by the formation of the transition state **I** as it would be sterically less demanding and constitutes the unique pathway to give the vinylplatinum(II) complex **D**, while the transition state **II**, is more congested due to steric repulsion between the R substituent and the sterically hindered Xphos-SO_3Na ligand. Finally, reductive elimination of intermediate **D** affords the desired β-(*E*)-vinylsilane **3** and regenerates the platinum(0) catalyst to complete the catalytic cycle.



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Scheme 3 Proposed catalytic cycle.

Conclusions

In conclusion, a highly efficient and reusable K_2PtCl_4/Xphos-SO_3Na/PEG-400/H_2O system for the highly regio- and stereoselective hydrosilylation of terminal alkynes with hydrosilanes has been developed. In the presence of K_2PtCl_4 (1.0 mol%) and Xphos-SO_3Na (2.0 mol%), the hydrosilylation reactions of a variety of functionalized terminal arylalkynes as well as aliphatic alkynes with hydrosilanes such as Et_3SiH and $PhMe_2SiH$ proceeded smoothly and efficiently at 60 °C in a mixture of PEG-400 and water to afford the desired β-(*E*)-vinylsilanes in good to excellent yields with a total β-(*E*)-selectivity. In addition, under the same reaction conditions symmetrical internal alkynes underwent the hydrosilylation smoothly to afford exclusively (*E*)-vinylsilanes in excellent yields and the hydrosilylation reaction of electron-deficient substituted ethyl propiolates also worked well to give the corresponding (*E*)-α-ethoxycarbonyl-vinylsilanes in high yields with high regio- and stereoselectivities. Furthermore, the K_2PtCl_4/Xphos-SO_3Na/PEG-400/H_2O system can be recycled and reused eight times without any loss of catalytic activity. This protocol will serve as an efficient, practical and green way to prepare a variety of valuable functionalized β-(*E*)-vinylsilanes.

Experimental

Under an argon atmosphere, a mixture of K_2PtCl_4 (0.01 mmol), Xphos-SO_3Na (0.02

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mmol), PEG-400 (0.67 mL) and H_2O (0.33 mL) was stirred at 60 ºC for 30 min. Then, terminal alkyne **1** (1.0 mmol) and hydrosilane **2** (1.5 mmol) were successively added via syringe and the resulting mixture was stirred at 60 ºC for 6 h. After being cooled to room temperature, the mixture was extracted three times with cyclohexane (3 × 5 mL). The combined cyclohexane phase was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (light petroleum ether or light petroleum ether–ethyl acetate) to afford the desired product **3** or **4**.

The residue of the extraction was heated to 60 ºC in vacuum for 20 min to remove the residual cyclohexane, and then subjected to a second run of the hydrosilylation reaction by charging with the same substrates (terminal alkyne **1** and hydrosilane **2**) under the same conditions without further addition of K_2PtCl_4 and Xphos-SO_3Na.

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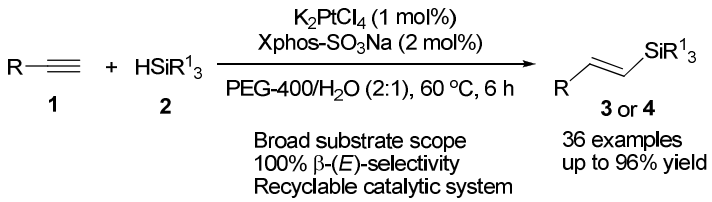
Graphical contents entry

Recyclable and reusable K_2PtCl_4/Xphos-SO_3Na/PEG-400/H_2O system for highly regio- and stereoselective hydrosilylation of terminal alkynes



Caifeng Xu, Bin Huang, Tao Yan, Mingzhong Cai*

Recyclable K_2PtCl_4/Xphos-SO_3Na/PEG-400/H_2O system has been developed for highly regio- and stereoselective hydrosilylation of terminal alkynes leading to β-(*E*)-vinylsilanes exclusively.