CHEMISTRY
AN ASIAN JOURNAL
www.chemasianj.org

Title: Xantphos Doped POPs-PPh3 as Heterogeneous Ligand for Cobalt-Catalyzed Highly Regio- and Stereoselective Hydrosilylation of Alkynes

Authors: Ren-Hao Li, Guo-Liang Zhang, Jia-Xing Dong, Ding-Chang Li, Ying Yang, Ying-Ming Pan, Hai-Tao Tang, Li Chen, and Zhuang-Ping Zhan

To be cited as: *Chem. Asian J.* 10.1002/asia.201801241

Link to VoR: http://dx.doi.org/10.1002/asia.201801241

A Journal of
ACES
Asian Chemical Editorial Society

A sister journal of **Angewandte Chemie** and **Chemistry – A European Journal**

WILEY-VCH

Chemistry - An Asian Journal
10.1002/asia.201801241

Xantphos Doped POPs-PPh₃ as Heterogeneous Ligand for Cobalt-Catalyzed Highly Regio- and Stereoselective Hydrosilylation of Alkynes

Ren-Hao Li,[a] Guo-Liang Zhang,[a] Jia-Xing Dong,[a] Ding-Chang Li,[a] Ying Yang,[a] Ying-Ming Pan,[b] Hai-Tao Tang,*[b] Li Chen[a] and Zhuang-Ping Zhan*[a]

Dedication ((optional))

Abstract: A Co(acac)$_2$/POL-Xantphos@10PPh$_3$-catalyzed hydrosilylation of unsymmetrical internal alkynes with Ph$_2$SiH$_2$ have been firstly developed for the synthesis of highly selectivity *syn*-α-vinylsilane products. Furthermore, the terminal alkynes was also developed with excellent regioselectivity and wide functional group tolerance. Due to this porous organic polymer combines the selectivity and activity merits of Xantphos ligands with the stability advantage derived from the high concentration of PPh$_3$ ligands and Xantphos firmly coordinated with Co(acac)$_2$, the Co(acac)$_2$/POL-Xantphos@10PPh$_3$ can recycle multiple times without loss of activity and selectivity. This heterogeneous catalyst is expected to find promising applications in industrial synthesis.

Introduction

Vinylsilanes are versatile synthetic intermediates owing to their stability, non-toxicity and propensity to undergo a variety of transformations.[1] Alkyne hydrosilylation is the most efficient and atom-economic method to access such compounds. And for the preparation of vinylsilanes, transition-metal catalyzed hydrosilylation of alkynes is an ideal method. However, control of stereo- and regioselectivity is a serious issue hampering the widespread use of this method, since three possible products, (*E*)-β-, (*Z*)-β-, and α-vinylsilanes (Figure 1a), can be generated at least in terminal alkyne hydrosilylation. Besides, the hydrosilylation of an internal alkyne can also generate four possible products, *anti*-α-, *anti*-β-, *syn*-α- and *syn*-β-vinylsilanes (Figure 1b). Thus controlling the regio- and stereoselectivity is a key issue during the H–Si addition process. In addition to the regioselectivity and stereoselectivity issue, the side reaction of alkyne oligmerization and hydrogenation could complicate the catalytic system.

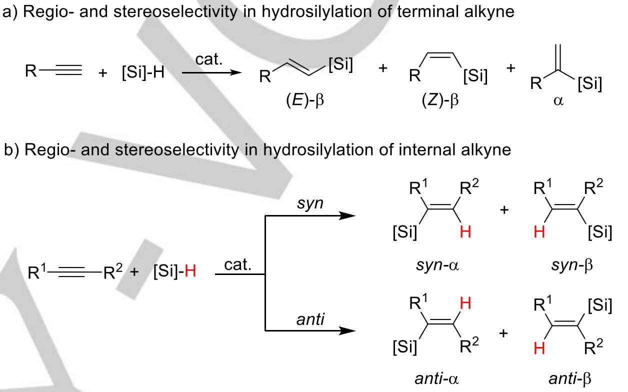


Figure 1. Regio- and stereoselectivity in hydrosilylation of terminal and internal alkyne

In the past decades, a series of noble metal-catalyzed hydrosilylation reactions have selectively formed (*E*)-β-vinylsilanes. Platinum-catalyzed hydrosilylation of alkenes is one of the most frequently conducted catalytic processes due to its effectiveness and high selectivity.[2] And a number of other noble metals, such as rhodium,[3] palladium,[4] iridium,[5] ruthenium,[6] thorium[7] and gold[8] have also been used for this transformation. Recently, the field of inexpensive metal catalysts for hydrosilylation have led to progress.[9] Several groups reported that non-noble metals cobalt could catalyze the hydrosilylation of terminal alkynes with (*E*)-β-selectivity. In 2014, Deng developed a carbine-coordinate cobalt(I) complex for terminal alkynes hydrosilylation with high (*E*)-β-selectivities (Figure 2b).[10] Thomas's group described a complex of the ^{Mes}BIPCoCl$_2$ and NaO^{t}Bu for stereoselective hydrosilylation of 1-octyne to give the moderate selectivity (*E*)-β-vinylsilanes.[11] Recently, Ge reported cobalt complexes of phosphine ligand for the highly (*E*)-β-selective hydrosilylation of terminal alkyne.[12]

As for internal alkynes without directing groups, cobalt-catalyzed hydrosilylation reactions is not an effective method to highly selectively generate *syn*-adducts. Butenschön et al. found that the cyclopentadienylcobalt(I) ethylene complex bearing an appended phosphine tether is an effective internal alkyne hydrosilylation catalyst. However, this cobalt(I) complex catalyzed unsymmetrical internal alkynes hydrosilylation suffers from poor regioselectivity (Figure 2a).[13] The reaction of an internal aryl alkyne exclusively provided the *syn*-addition products with Deng's carbine-coordinate cobalt(I) catalysts[10] or Huang's (^{tBu}PyBox)CoCl$_2$,[14] but the regioselectivity is poor (Figure 2b, 2c). Recetly, Lu's oxazoline iminopyridine cobalt complex[15] and Huang's (^{iPr}P^{C}NN^{iPr})CoCl$_2$[16] promoted the hydrosilylation of internal alkynes with moderate regioselectivity

---

[a] Li, R. H., Zhang, G. L., Dong, J. X., Li, D. C., Yang, Y., Chen, L., Prof. Zhan, Z. P.
Department of Chemistry and Key Laboratory for Chemical Biology of Fujian Province, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
E-mail: zpzhan@xmu.edu.cn
[b] Pan, Y. M., Tang, H. T.
State Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, People's Republic of China
E-mail: httang@gxnu.edu.cn

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

(Figure 2d, 2e). Petit's group reported low-valent cobalt(I) $HCo(PMe_3)_4$ catalyzed unsymmetrical internal alkynes hydrosilylation suffers from good regioselectivity, but a series of internal alkynes have poor regioselectivity.[17]

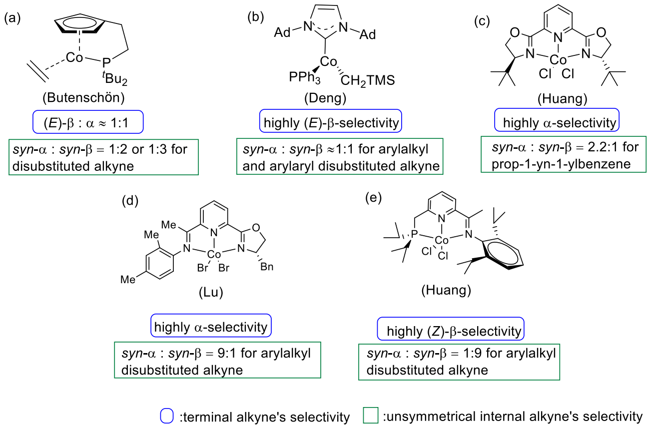


Figure 2. Cobalt complexs for catalytic hydrosilylation

Consequently, hydrosilylation of unsaturated hydrocarbon with homogeneous catalysts finds industrial applications including fluids, molding products, silicone-based surfactants and release coatings.[18] However, problems such as competing side reactions, catalyst activation, catalyst separation and regeneration have still persisted. Therefore, the development of heterogeneous ligands supported non-noble metals as recyclable catalysts capable of promoting highly selective Si-H additions to alkynes, remains to be greatly challenging and significant.

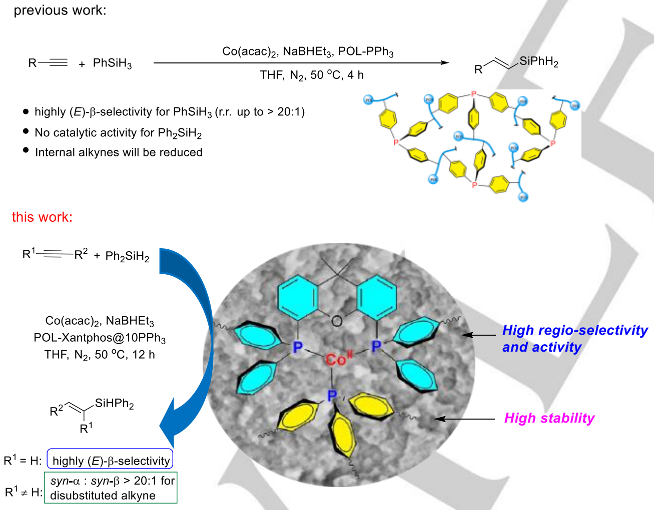


Figure 3. Cobalt/POPs complexes for catalytic hydrosilylation

Porous organic polymers (POPs), a class of highly crosslinked amorphous polymers, consist mainly of carbon, oxygen, nitrogen and phosphorus that are connected through strong covalent bonds. More importantly, Porous organic polymers can serve as a promising platform for incorporating homogeneous catalytic moieties into the framework.[19] Recently, our group reported a cobalt/POL-PPh_3 catalyzed (E)-selective hydrosilylation of alkynes with $PhSiH_3$ for the synthesis of (E)-β-vinylsilanes with high regio- and stereo-selectivity and wide functional group tolerance (Figure 3).[20] However, in this system, Cobalt not catalytic activity with Ph_2SiH_2 and internal alkynes will be reduced to alkenes or alkanes. Herein, we develop a highly regioselective hydrosilylation of terminal internal and terminal alkynes with Ph_2SiH_2 catalyzed by $Co(acac)_2$/POL-Xantphos@10PPh_3 which recycled multiple times without loss of activity and selectivity (Figure 3). This porous organic polymer combines the selectivity and activity merits of Xantphos ligands with the stability advantage derived from the high concentration of PPh_3 ligands and Xantphos firmly coordinated with $Co(acac)_2$.

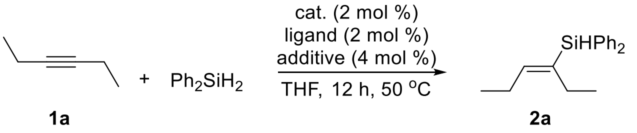
Results and Discussion

In our initial studies, the electronical unbiased hex-3-yne was investigated. We examined a variety of cobalt catalysts, ligands, and additive for this model reaction. The results are summarized in Table 1. The $Co(acac)_2$/Xantphos complex can catalyze the reaction of hex-3-yne with 1.1 equiv of Ph_2SiH_2 at 50 °C to selectively afford (E)-hex-3-en-3-yldiphenylsilane in 92% yield (Table 1, entry 1). Under the same reaction condition, Other cobalt catalysts such as $Co(OAc)_2$ and $CoCl_2$ were inactive for the hydrosilylation (Table 1, entries 2-3). It's noted that the reaction failed to afford the desired product using PPh_3 as the ligand. (Table 1, entry 4). Attempts to enhance the efficiency of product formation further by screening different kinds of bidentate phosphine ligands were unsuccessful (Table 1, entries 5-8). Additives were indispensable for promoting the efficacy. Without $NaBHEt_3$, the reaction did not yield any of the hydrosilylation product (Table 1, entry 9). And the MeMgBr as activator led to lower yield in comparison with $NaBHEt_3$ (Table 1, entry 10). The NaO^tBu as activator exhibited no activity in this reaction (Table 1, entry 11). Excitedly, the use of $Co(acac)_2$/POL-Xantphos as a heterogeneous catalyst afforded high yield and excellent selectivity. However, the heterogeneous catalyst led to lower yield after recycling three times (Table 1, entry 12). That showed the Cobalt in polymer has been washed off in recycle process.

Recently, our and Ding's group jointly reported Xantphos doped Rh/POPs-PPh_3 catalysts appearing high activity, chemoselectivity and regioselectivity in the hydroformylation of long-chain olefins.[21] Based on our previous contributions,[22] and also inspired by the widely explored functional element (such as N, S, P, etc.) doped carbon materials which was generally applied in catalysis and electrochemistry,[23] we speculate the unique location of Co species dispersing on Xantphos doped POPs-PPh_3 materials may integrate the selectivity and activity merit of the Xantphos ligand with the stability advantages which contributed to PPh_3 matrix. Bearing these knowledge in mind, heterogeneous ligands with different proportions of Xantphos and PPh_3 were designed and employed in selective hydrosilylation reaction. Owing to easier synthesis of 2v-Xantphos than 4v-Xantphos, we used 2v-Xantphos as monomer to synthesize heterogeneous ligands through free-radical polymerization with different proportions of 3v-PPh_3. For comparison, the Xantphos doped POPs-DVB ligand was also synthesized (Figure 4). These reusability of porous organic polymers were examined for the hydrosilylation of hex-3-yne to obtain **2a** (Scheme 1). As can be seen, Co(acac)$_2$/POL-Xantphos@10PPh$_3$ was recycled seven times without loss of activity and selectivity, however, other polymers without PPh$_3$ as stabilizer (POL-Xantphos and POL-Xantphos@10DVB) were inactive after three times. The polymer synthesized with the 1:2 proportion of Xantphos and PPh$_3$ was also inactive after five times. Hence, the optimum conditions involved conducting the reaction in THF at 50 °C with Co(acac)$_2$ as catalyst, POL-Xantphos@10PPh$_3$ as ligand.

Concluded from the experimental results and our previous works, the high concentration of PPh$_3$ ligands played a key role in strengthening the stability of the catalysts, which can be attributed to the formation of multi-coordination bonds with Xantphos and at the same time will not affect Xantphos' catalytic activity and selectivity. The advantages of bidentate ligand (Xantphos) and the monodentate ligand (PPh$_3$) have been perfectly integrated in POL-Xantphos@10PPh$_3$ catalyst could be owning to the synergistic effect of the dispersed Co species and

Table 1. Optimization of the reaction conditions for hydrosilylation of 1-decyne and Ph$_2$SiH$_2$[a]



entry	cat.	ligand	additive	yield/%[b]
1	Co(acac)$_2$	Xantphos	NaBHEt$_3$	92
2	Co(OAc)$_2$	Xantphos	NaBHEt$_3$	53
3	CoCl$_2$	Xantphos	NaBHEt$_3$	62
4	Co(acac)$_2$	PPh$_3$	NaBHEt$_3$	0
5	Co(acac)$_2$	BINAP	NaBHEt$_3$	61
6	Co(acac)$_2$	dppe	NaBHEt$_3$	43
7	Co(acac)$_2$	dppb	NaBHEt$_3$	48
8	Co(acac)$_2$	dppf	NaBHEt$_3$	62
9	Co(acac)$_2$	Xantphos	-	0
10	Co(acac)$_2$	Xantphos	MeMgBr	36
11	Co(acac)$_2$	Xantphos	NaO^{t}Bu	0
12	Co(acac)$_2$	POL-Xantphos[c]	NaBHEt$_3$	89(42)[d]

[a] Reaction condition: hex-3-yne (1.0 mmol), diphenylsilane (1.1 mmol), cat. (2 mol %), ligand (2 mol %), additive (4 mol %), THF (2 mL), 50 °C, 12 h, N$_2$ atmosphere. [b] The yields were determined by ^{1}H NMR spectroscopy, the selectivity for **2a** (r.r. = *syn*-α-vinylsilane product / all other isomers) were > 20:1. [c] 13.6 mg POL-Xantphos. [d] recycle three times.

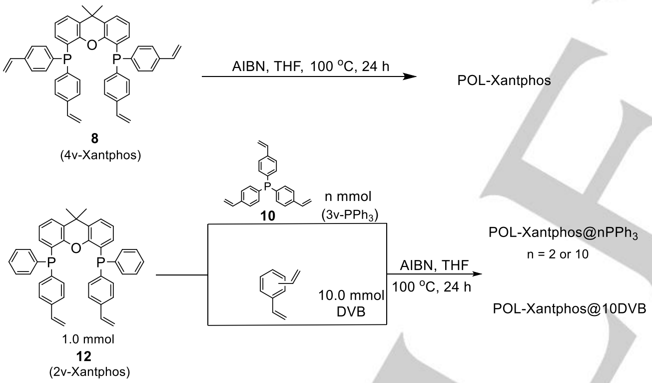
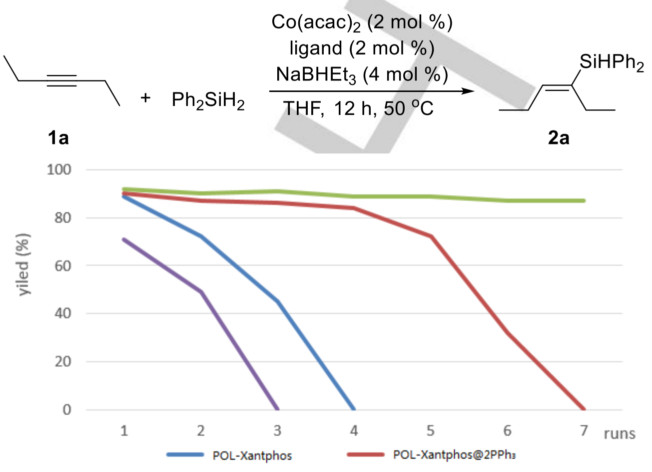


Figure 4. Synthesis of porous organic polymers

Scheme 1. Reuse of porous organic polymers towards hydrosilylation[a]



[a] Reaction condition: hex-3-yne (1.0 mmol), diphenylsilane (1.1 mmol), NaBHEt$_3$ (4 mol %), THF (2 mL), 50 °C, 12 h, N$_2$ atmosphere, Co(acac)$_2$ (5.1 mg), POL-Xantphos (13.6 mg, synthesized from 13.6 mg **8**), POL-Xantphos@2PPh$_3$ (26.2 mg, synthesized from 0.02 mmol **12** and 0.04 mmol **10**), POL-Xantphos@10PPh$_3$ (80.6 mg, synthesized from 0.02 mmol **12** and 0.2 mmol **10**), POL-Xantphos@10DVB (38.6 mg, synthesized from 0.02 mmol **12** and 0.2 mmol DVB).

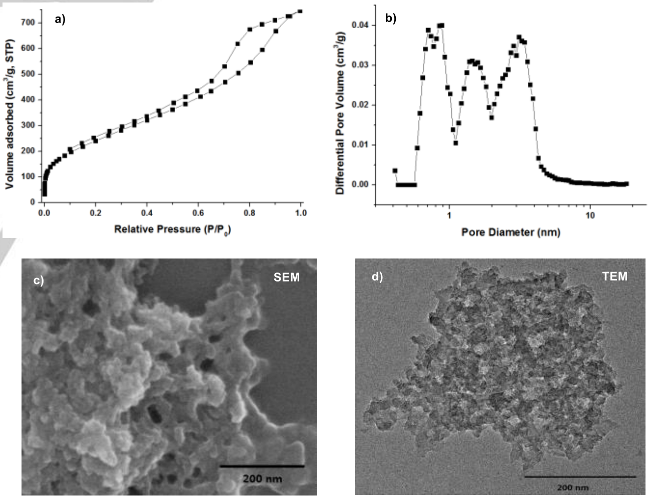


Figure 5. a) N$_2$ adsorption–desorption analysis of POL-Xantphos@10PPh$_3$, b) N$_2$ adsorption–desorption analysis of POL-Xantphos@10PPh$_3$, c) scanning electron microscopy of POL-Xantphos@10PPh$_3$, d) transmission electron microscopy of POL-Xantphos@10PPh$_3$

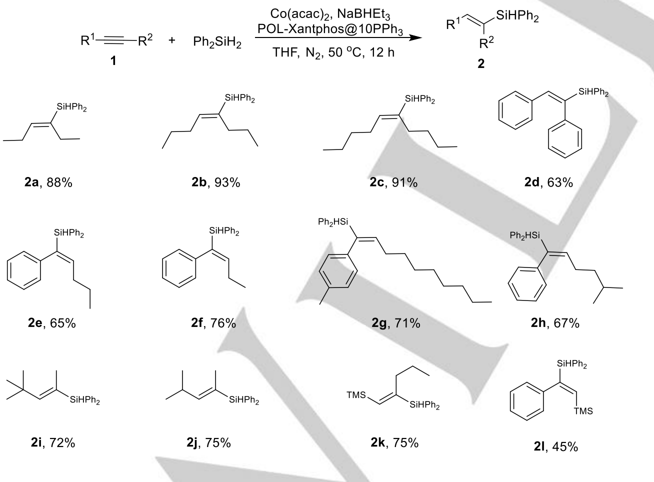
the synchronous coordination of both of ligands. The Xantphos ligand takes the role of controlling selectivity and activity while the PPh_3 ligand plays the roles of maintaining high stability (Figure 3).

In an effort to explore the structure–activity relationship, the POL-Xantphos@10PPh_3 was characterized by thermo-gravimetry (TG), N_2 adsorption–desorption analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The TG shows that POL-Xantphos@10PPh_3 remains intact at temperatures up to 410 ^{o}C, indicating its superior thermal stability (Supporting Information, Figure S3). Nitrogen adsorption–desorption analysis (Figure 5a) shows that POL-Xantphos@10PPh_3 gave a type IV isotherm with a significant hysteresis loop in the high pressure region. This result indicates the presence of mesopores in this polymer. Furthermore, a large number of nitrogen uptake is observed in the low pressure region (below 0.1 bar), suggesting the presence of sufficient amount of micropores in POL-Xantphos@10PPh_3. As seen from Figure 5a that POL-Xantphos@10PPh_3 possesses very favorable hierarchical pore size distributions, which is further confirmed by SEM (Figure 5c) and TEM (Figure 5d) images. The pore sizes were mainly distributed at 0.6-1.0 nm and 1.2- 4.0 nm which was calculated by the method of non-local density functional theory (NLDFT) (Figure 5b). The BET surface areas and total pore volumes of POL-PPh_3 are up to 880 m^2/g and 1.10 cm^3/g, respectively. The hierarchical pore structure, which allows for easy accessibility of the P coordination sites, is very favorable for the mass transfer.

To evaluate the scope of the Cobalt/POL-Xantphos@10PPh_3 catalyzed alkyne hydrosilylation, reactions with a series of internal alkynes and a variety of functionalized terminal alkynes were carried out using Ph_2SiH_2 as the silicon source. The results are summarized in Scheme 2 and Scheme 3, respectively. The hydrosilylation of symmetric dialkyl-substituted alkynes (Scheme 2, products **2a**-**2c**) and diaryl-substituted alkyne (Scheme 2, product **2d**) occurred to form the *syn*-addition products in good yields and selectivity. Then, we turned our attention to the more challenging unsymmetrical internal alkynes.

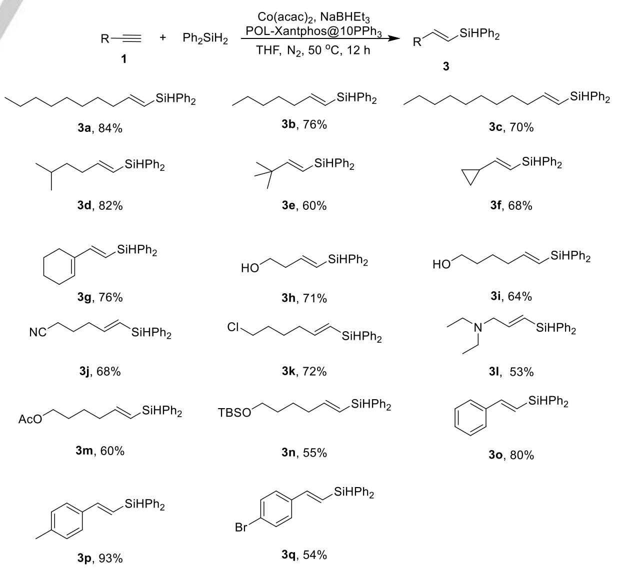
As for unsymmetrical internal alkynes without directing groups, cobalt-catalyzed hydrosilylation reactions generate highly selective *syn*-adduct products difficultly.[13-17] Herein, we firstly reported a highly *syn*-adducts-selective hydrosilylation of unsymmetrical internal alkynes with Ph_2SiH_2 using heterocatalysis system. All reactions were excellently selective for the formation of the *syn*-α-vinylsilane products (r.r. > 20:1, *syn*-α-vinylsilane product/all other isomers). The reaction of arylalkyl disubstituted alkynes (Scheme 2, products **2e-h**) gave the products in 65-76% yields. The unsymmetrical disubstituted alkynes with different steric properties, such as 4,4-dimethylpent-2-yne and 4-methylpent-2-yne, were suitable for the selective hydrosilylation, producing the *syn*-addition products **2i** and **2j** with the incorporation of the silyl group into the less sterically demanding *sp*-hybridised carbon. To our delight, the reactions of the unsymmetrical internal alkynes that bearing a trimethylsilyl (TMS) group could give exclusively *syn*-adducts in the form of (*E*)-α,β-disilylalkenes(Scheme 2, products **2k-l**).

Scheme 2. Scope of internal alkynes for the $Co(acac)_2$/POL-Xantphos@10PPh_3-Catalyzed *anti*-Markovnikov Hydrosilylation with Ph_2SiH_2[a,b]



[a] Reaction conditions: internal alkynes (1.0 mmol), Ph_2SiH_2 (1.1 mmol), $Co(acac)_2$ (2 mol %), POL-Xantphos@10PPh_3 (80.6 mg), $NaBHEt_3$ (4 mol %), THF (2 mL), 50 ^{o}C, N_2, 12 h, yields of isolated products. [b] The selectivity for all products (r.r. = *syn*-α-vinylsilane product/all other isomers) were > 20:1, Determined by ^{1}H NMR spectroscopy.

Scheme 3. Scope of terminal alkynes for the $Co(acac)_2$/POL-Xantphos@10PPh_3-Catalyzed *anti*-Markovnikov Hydrosilylation with Ph_2SiH_2[a,b]



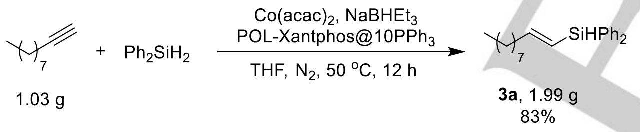
[a] Reaction conditions: terminal alkynes (1.0 mmol), Ph_2SiH_2 (1.1 mmol), $Co(acac)_2$ (2 mol %),Xantphos@10PPh_3 (80.6 mg), $NaBHEt_3$ (4 mol %), THF (2 mL), 50 ^{o}C, N_2, 12 h, yields of isolated products. [b] The selectivity for all

products (r.r. = (*E*)-β-vinylsilane product / all other isomers) were > 20:1, Determined by ^{1}H NMR spectroscopy.

For terminal alkyne substrates, all reactions were highly selective for the formation of the (*E*)-β-vinylsilane products (r.r. > 20:1, r.r. = (*E*)-β-vinylsilane product/all other isomers). The straight-chain terminal alkynes and branched-chain terminal alkyne gave the corresponding products **3a**-**3e** in moderate-to-high isolated yields. Alkynes containing cyclopropyl (Scheme 3, product **3f**) and cyclohexeyl (Scheme 3, product **3g**) groups reacted with moderate to good isolated yields. This Co(acac)$_2$/Xantphos-catalyzed hydrosilylation of aliphatic alkynes shows high functional groups tolerance. A wide range of functional groups, including hydroxyl (Scheme 3, products **3h**, **3i**), nitrile(Scheme 3, product **3j**), chloride (Scheme 3, product **3k**) and tertiary amine (Scheme 3, product **3l**), were compatible with the reaction condition. Aliphatic alkynes containing protecting groups, such as acetylate (Scheme 3, product **3m**) and silylether (Scheme 3, product **3n**), afforded the desired products in useful yields. Additionally, aryl alkynes also reacted smoothly with moderate-to-high yields (Scheme 3, product **3o**-**3q**).

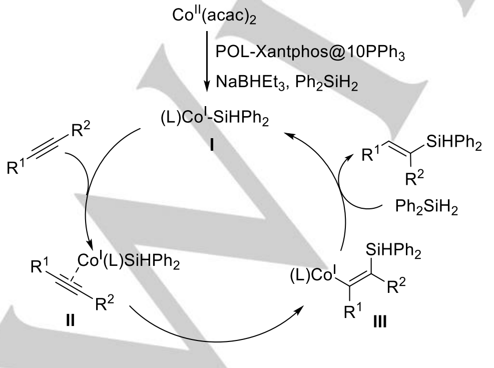
The scalability of (*E*)-dec-1-en-1-yldiphenylsilane (**3a**) synthesis was evaluated by performing the hydrosilylation of 1-decyne on a gram scale. The reaction furnished the desired product in 83% yields, similar to that obtained on smaller scales (Scheme 4).

Scheme 4. Reaction carried out on the gram scale



A proposed mechanism accounting for the formation of vinylsilane is presented in Scheme 5. On the basis of the precedents of previous work,[19] we propose that the low-valent Co(I) silyl intermediate **I** play important role in catalytic cycle. Once intermediate **I** formed, the alkenyl metal species **III** will be produced through migratory insertion of the silyl moiety to the C≡C triple bond in **II**. Complex **III** could further react with Ph$_2$SiH$_2$ to yield the hydrosilylation product vinylsilane and regenerate **I**. Other possible pathways cannot be ruled out, such as cobalt hydride species as important active role.

Scheme 5. Proposed mechanism



Conclusions

In summary, we have developed a highly regioselective Co(acac)$_2$/POL-Xantphos@10PPh$_3$ catalyzed hydrosilylation of unsymmetrical internal alkynes method for the synthesis of *syn*-α-vinylsilane products in heterocatalysis. Furthermore, an excellent regioselective cobalt-catalyzed hydrosilylation of terminal alkynes with Ph$_2$SiH$_2$ to produce vinylsilanes has also been developed. Various functionalized groups, such as hydroxyl, nitrile, chloride and tertiary amine, are tolerated to increase the possibility for future applications and late-stage derivatizations. The Co(acac)$_2$/POL-Xantphos@10PPh$_3$ recycled multiple times without loss of activity and selectivity. This porous organic polymer could integrate the selectivity and activity merits of Xantphos ligands with the stability advantage derived from the high concentration of PPh$_3$ ligands and Xantphos firmly coordinated with Co(acac)$_2$. This heterogeneous catalyst is expected to find promising applications in industrial synthesis.

Experimental Section

General procedure for synthesis 2, 3: In a nitrogen filled schlenk tube, Co(acac)$_2$ (2 mol %), POL-Xantphos@10PPh$_3$ (80.6 mg), NaBHEt$_3$ (4 mol %) and THF (2 mL) were added then stirred at room temperature for 10 minutes, then alkyne (1.0 mmol), diphenylsilane (1.1 mmol) were added under N$_2$. The reaction mixture was stirred at 50 ºC. Upon completion, the solvent was removed by vacuum and the crude residue was purified by silica gel column chromatography to afford the corresponding products **2**, **3** (eluent: petroleum ether/EtOAc = 100/1).

General procedure for recycling experiment：In a nitrogen filled schlenk tube, Co(acac)$_2$ (2 mol %), polymer (POL-Xantphos: 13.6 mg, POL-Xantphos@2PPh$_3$: 26.2 mg, POL-Xantphos@10PPh$_3$: 80.6 mg or POL-Xantphos@10DVB: 38.6 mg), NaBHEt$_3$ (4 mol %) and THF (2 mL) were added and stirred at room temperature for 10 minutes, then alkyne (1.0 mmol), diphenylsilane (1.1 mmol) were added under N$_2$. The reaction mixture was stirred at 50 ºC. Upon completion, the catalyst was separated through centrifugation, diethyl phthalate was added to the supernatant liquid as an internal standard, and the mixture was filtered under vacuum, the yield was determined by NMR and the catalyst was washed by Et$_2$O, dried, and reused in a next run.

Preparation of POL-Xantphos：9.9-dimethylxanthene (**4**, 5 g, 24 mmol), TMEDA (9 mL, 60 mmol) and Et$_2$O (40 mL) was charged in a flask. Then *n*-BuLi (24 mL of 2.5 M solution in hexane, 60 mmol) was added dropwise at 0 ºC, followed by stirring overnight at room temperature. 60 mmol of ClP(NEt$_2$)$_2$ dissolved in 10 mL of Et$_2$O was added dropwise at -78 ºC and the afforded mixture was stirred at room temperature overnight. After removal of the precipitate and the solvent under vacuum, compound **6** 1,1'-(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(N,N,N',N'-

tetraethylphosphanedi-amine) (white powder) was afforded. The obtained white powder **6** was dissolved in 250 mL of dry hexane, dry HCl gas was passed through the solution at room temperature for 0.5 h. Then the precipitate was removed, and the solvent was removed under vacuum. Thus compound **7** (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(dichlorophosphane) was afforded. 4.03 g of 4-bromostyrene (22 mmol) was dissolved in 40 ml of tetrahydrofuran, *n*-BuLi (8.8 mL of 2.5 M solution in hexane, 22 mmol) was added dropwise at -78 ºC, followed by stirring for 2 h at -78 ºC. Then compound **7** dissolved in 20 mL of tetrahydrofuran was added dropwise in the mixture at -78 ºC. After stirring for 2 h, the mixture was quenching with aq. NH_4Cl, and extracted with ethyl acetate. The organic layer was washed with water, dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography (20:1 hexane/EtOAc) to give compound **8** (9,9-dimethyl-9*H*-xanthene-4,5-diyl)bis(bis(4-vinylphenyl)phosphane) as the white solid (1.1 g, 7 % total yield). Under nitrogen, **8** (1.0 g) was dissolved in THF (5 mL), followed by the addition of AIBN (0.1 g) at room temperature. Next, the mixture was transferred into a sealing tube at 100 ºC for 24 h. After evaporation of THF under vacuum, a white solid POL-Xantphos was obtained.

Preparation of tris(4-vinylphenyl)phosphane： Mg turnings (2.40g, 100 mmol) was added to a round bottom flask under nitrogen, and were activated by treatment with a grain of I_2 in THF (80 mL). *p*-bromostyrene (14.64g, 80 mmol) was slowly added to the flask, and the mixture was stirred for 1 h at room temperature. Next, PCl_3 (3.43g, 25 mmol) was slowly added to the solution in the ice water bath over 30 min followed by stirring at room temperature for 4 h. The reaction was quenched by aq.NH_4Cl, and the mixture was extracted with ethyl acetate. The organic layer was washed by H_2O twice, dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford tris(4-vinylphenyl)phosphane (**10**, 5.45 g, 64% yield).

Preparation of POL-Xantphos@10PPh$_3$： Mg turnings (1.75g, 72 mmol) was added to a round bottom flask under nitrogen, and were activated by treatment with a grain of I_2 in THF (50 mL). *p*-bromostyrene (10.98g, 60 mmol) was slowly added to the flask, and the mixture was stirred for 1 h at room temperature. Next, $PhPCl_2$ (4.83 g, 27 mmol) was slowly added to the solution in -78 ºC over 30 min followed by stirring overnight at room temperature. The compound **11** chloro(phenyl)(4-vinylphenyl)phosphane was afforded. 9.9-dimethylxanthene (**4**, 2.52 g, 12 mmol), TMEDA (3.25 g, 28 mmol) and Et_2O (20 mL) was charged in a flask. Then *n*-BuLi (11.2 mL of 2.5 M solution in hexane, 60 mmol) was added dropwise at 0 ºC, followed by stirring overnight at room temperature. Then compound **11** dissolved in 20 mL of tetrahydrofuran was added dropwise in the mixture at -78 ºC. After stirring for 2 h, the mixture was quenching with aq. NH_4Cl, and extracted with ethyl acetate. The organic layer was washed with water, dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography (20:1 hexane/EtOAc) to give compound **12** (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(phenyl(4-vinylphenyl)phosphane) as the white solid (2.19 g, 29 % total yield). Under nitrogen, **12** (630 mg) and **10** (3.40 g) was dissolved in THF (15 mL), followed by the addition of AIBN (403 mg) at room temperature. Next, the mixture was transferred into a sealing tube at 100 ºC for 24 h. After evaporation of THF under vacuum, a white solid POL-Xantphos@10PPh$_3$ was obtained.

Acknowledgements ((optional))

We are grateful to the National Natural Science Foundation of China (No. 21772166) and NFFTBS (No. J1310024).

Keywords: hydrosilylation • porous organic polymer • cobalt • alkynes • heterocatalysis

[1] a) E. Rémond, C. Martin, J. Martinez, F. Cavelier, *Chem. Rev.* **2016**, *116*, 11654-11684. b) S. Bracegirdle, E. A. Anderson, *Chem. Soc. Rev*., **2010**, *39*, 4114-4129. c) E. Langkopf, D. Schinzer, *Chem. Rev*. **1995**, *95*, 1375-1408. d) T. A. Blumenkopf, L. E. Overman, *Chem. Rev*. **1986**, *86*, 857-873.

[2] a) R. Cano, M. Yus, D. J. Ramón, *ACS Catal.* **2012**, *2*, 1070-1078. b) H. Kinoshita, R. Uemura, D. Fukuda, K. Miura, *Org. Lett*. **2013**, *15*, 5538-5541. c) M. G. McLaughlin, M. J. Cook, *Chem. Commun*. **2011**, *47*, 11104-11106. d) C. A. McAdam, M. G. McLaughlin, A. J. S. Johnston, J. Chen, M. W. Walter, M. J. Cook, *Org. Biomol. Chem*., **2013**, *11*, 4488-4502.

[3] a) J. P. Morales-Cerón, P. Lara, J. López-Serrano, L. L. Santos, V. Salazar, E. Álvarez, A. Suárez, *Organometallics* **2017**, *36*, 2460-2469. b) A. J. Huckaba, T. K. Hollis, T. O. Howell, H. U. Valle, Y. Wu, *Organometallics* **2013**, *32*, 63-69.

[4] a) J. W. Zhang, G. P. Lu, C. Cai, *Green Chem*., **2017**, *19*, 2535-2540. b) H. Yamashita, Y. Uchimaru, *Chem. Commun*., **1999**, 1763-1764.

[5] L. D. Field, A. J. Ward, *J. Organomet. Chem*., **2003**. *681*. 91-97.

[6] a) R. Gao, D. R. Pahls, T. R. Cundari, C. S. Yi, *Organometallics* **2014**, *33*, 6937-6944. b) M. Zaranek, B. Marciniec, P. Pawluć, *Org. Chem. Front.*, **2016**, *3*, 1337-1344.

[7] a) T. Andrea. M. S. Eisen. *Chem. Soc. Rev*., **2008**, *37*, 550-567. b) A. K. Dash, I. Gourevich, J. Q. Wang, J. Wang, M. Kapon, M. S. Eisen, *Organometallics* **2001**, *20*, 5084-5104.

[8] a) A. Corma, C. González-Arellano, M. Iglesias, F. Sanchez, *Angew. Chem. Int. Ed.* **2007**, *46*, 7820-7822. b) Y. Ishikawa, Y. Yamamoto, N. Asao, *Catal. Sci. Technol*., **2013**, *3*, 2902-2905.

[9] a) J. Sun, L. Deng, *ACS Catal.* **2016**, *6*, 290-300. b) T. M. Porter, G. B. Hall, T. L. Groy, R. J. Trovitch, *Dalton Trans.* **2013**, *42*, 14689-14692. Alkene hydrosilylation reaction: c) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, *science*, **2012**, *335*, 567-570. d) A. D. Ibrahim, S. W. Entsminger, L. Zhu, A. R. Fout, *ACS Catal.* **2016**, *6*, 3589-3593. e) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, *J. Am. Chem. Soc*. **2015**, *137*, 13244-13247. f) Y. Liu, L. Deng, *J. Am. Chem. Soc.* **2017**, *139*, 1798-1801.

[10] Z. B. Mo, J. Xiao, Y. F. Gao, L. Deng, *J. Am. Chem. Soc.* **2014**, *136*, 17414-17417.

[11] J. H. Docherty, J. Y. Peng, A. P. Dominey, S. P. Thomas, *Nat. Chem*. **2017**, *9*, 595-600.

[12] C. Wu, W. J. Teo, S. Ge, *ACS Catal*. **2018**, *8*, 5896-5900. During our preparation for submitting, this paper was published. Ge's group only studied terminal alkynes' hydrosilylation but did not conduct in-depth research in internal alkynes.

[13] L. Yong, K. Kirleis, Holger. Butenschön, *Adv. Synth. Catal.* **2006**, *348*, 833-836.

[14] Z. Zuo, J. Yang, Z. Huang, *Angew. Chem. Int. Ed.* **2016**, *55*, 10839-10843.

[15] J. Guo, Z. Lu, *Angew. Chem. Int. Ed.* **2016**, *55*, 10835-10838.

[16] X. Du, W. Hou, Y. Zhang, Z. Huang, *Org. Chem. Front.*, **2017**, *4*, 1517-1521.

[17] A. Rivera-Hernández, B. J. Fallon, S. Ventre, C Simon, M. –H. Tremblay, G. Gontard, E. Derat, M. Amatore, C. Aubert, M. Petit, *Org. Lett.* **2016**, *18*, 4242−4245

[18] I. Ojima, Z. Li, J. Zhu, The chemistry of organic silicon compounds, Patai, S. Rappoport, Z. Eds. Wiley Interscience, New York, **1989**, p 1687-1792.

[19] a) R. Gomes, P. Bhanja, A. Bhaumik, *J. Mol. Catal. A: Chem.* **2016**, *411*, 110-116. b) R. Gomes, A. Bhaumik, *J. Solid State Chem.* **2015**, *222*, 7-11.

[20] R. H. Li, X. M. An, Y. Yang, D. C. Li, Z. L. Hu, Z. P. Zhan, *Org. Lett.* **2018**, *20*, 5023.

[21] C. Li, K. Sun, W. Wang, L. Yan, X. Sun, Y. Wang, K. Xiong, Z. P. Zhan, Z. Jiang, Y. J. Ding, *J. Catal.* **2017**, *353*, 123-132.

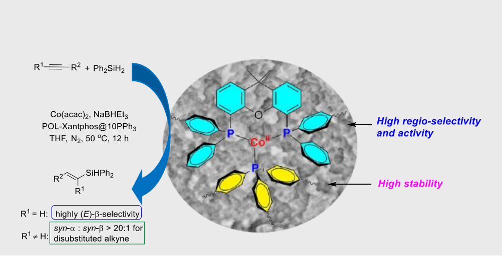
[22] a) Y. B. Zhou, Y. Q. Wang, L. C. Ning, Z. C. Ding, W. L. Wang, C. K. Ding, R. H. Li, J. J. Chen, X. Lu, Y. J. Ding, Z. P. Zhan, *J. Am. Chem. Soc*. **2017**, *139*, 3966-3969. b) R. H. Li, Z. C. Ding, C. Y. Li, J. J. Chen, Y. B. Zhou, X. M. An, Y. J. Ding, Z. P. Zhan, *Org. Lett.* **2017**, *19*, 4432-4435. c) Y. B. Zhou, C. Y. Li, M. Lin, Y. J. Ding, Z. P. Zhan, *Adv. Synth. Catal.* **2015**, *357*, 2503-2508. d) Z. C. Ding, C. Y. Li, J. J. Chen, J. H. Zeng, H. T. Tang, Y. J. Ding, Z. P. Zhan, *Adv. Synth. Catal.* **2017**, *359*, 2280-2287.

[23] a) Y. B. Zhou, Z. P. Zhan, *Chem. Asian J.* **2018**, *13*, 9-19. b) J. Jiang, C. Wang, A. Laybourn, T. Hasell, R. Clowes, Y. Z. Khimyak, J. Xiao, S. J. Higgins, D. J. Adams, A. I. Cooper, *Angew. Chem., Int. Ed*. **2011**, *50*, 1072-1075. c) Y. Zhang, S. N. Riduan, *Chem. Soc. Rev.* **2012**, *41*, 2083-2094. d) X. Wang, X. Li, L. Zhang, Y. Yoon, P.K. Weber, H. Wang, J. Guo, H. Dai, *Science* **2009**, *324*, 768-771. e) F. Cheng, W.-C. Li, J.-N. Zhu, W.-P. Zhang, A.-H. Lu, *Nano Energy* **2016**, *19*, 486-494. f) X. Chen, D. Deng, X. Pan, Y. Hu, X. Bao, *Chem. Commun*. **2015**, *51*, 217-220. g) A. Manthiram, Y. Fu, S.-H. Chung, C. Zu, Y.-S. Su, *Chem. Rev*. **2014**, *114*, 11751-11787. h) B. He, W.-C. Li, C. Yang, S.-Q. Wang, A.-H. Lu, *ACS Nano* **2016**, *10*, 1633-1639.

Entry for the Table of Contents (Please choose one layout)

FULL PAPER

Text for Table of Contents



Ren-Hao Li, Guo-Liang Zhang, Jia-Xing Dong, Ding-Chang Li, Ying Yang, Ying-Ming Pan, Hai-Tao Tang, Li Chen and Zhuang-Ping Zhan**

Page No. – Page No.

Xantphos Doped POPs-PPh_3 as Heterogeneous Ligand for Cobalt-Catalyzed Highly Regio- and Stereoselective Hydrosilylation of Alkynes

For internal use, please do not delete. Submitted_Manuscript