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Pd(acac)₂/Xantphos: A highly efficient and readily available catalyst for regioselective hydrosilylation of allenes

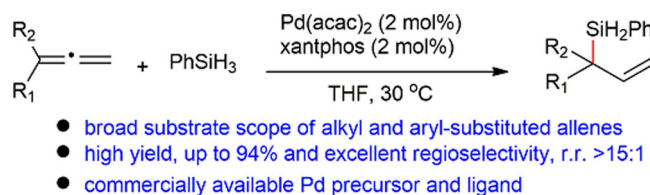
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ABSTRACT

A convenient and efficient Pd(acac)₂/Xantphos-catalyzed regioselective hydrosilylation of allenes has been developed. This convenient catalyst proved to be suitable for a broad range of allenes, offering a general and efficient route to branched allylsilanes in high yields with exceptional regioselectivity. A Pd(0) species involved mechanism is proposed.

GRAPHICAL ABSTRACT



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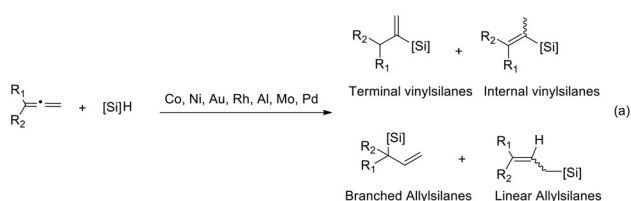
KEYWORDS

Hydrosilylation; allenes;
branched allylsilanes

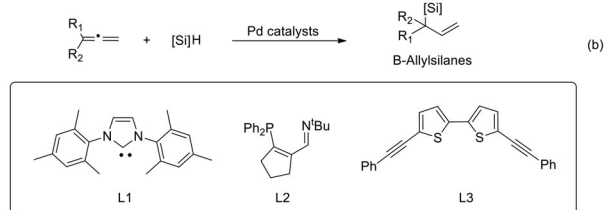
Catalytic hydrosilylation of C-C multiple bonds is a highly step- and atom-economical route to organosilicon compounds,^[1] which represent benign synthetic reagents in a wide variety of subsequent reactions,^[2] such as the allylsilanes and vinylsilanes are utilized in Hiyama^[3] and Sakurai reactions.^[4] In contrast to the extensive studies that have been reported on the hydrosilylation of alkene and alkyne,^[5] the research on hydrosilylation of allenes has started relatively late because the presence of two continuous orthogonal π bonds makes the hydrosilylation of allene more challenging in controlling the regio- and stereoselectivity.^[8k,9a] Besides, some side reactions such as hydrogenation^[6] and multiaddition^[5d,7] of allene can also complicate the catalytic system. In recent years, considerable efforts have been devoted to developing chemo-, regio-, and stereoselective hydrosilylation of allenes by transition metal catalysts (Scheme 1a).^[8,9] For example, in 2017, Ge et al. reported a Co-catalyzed hydrosilylation at the terminal C=C bonds of allenes that yielded linear allylsilanes,^[8a] and a synthetic route to internal vinylsilanes involving the hydrosilylation of allenes with supported Pd-Au alloy catalysts has been developed by Shishido group.^[8b] In 2013, the Montgomery group reported a Ni-catalyzed allene hydrosilylation for terminal vinylsilanes,^[9a] and they also first reported the palladium-catalyzed hydrosilylation of allene (L1) to access the branched allylsilanes (B-Allylsilanes).^[9a] Later, the Schmidt

group showed that employing a 3-iminophosphine ligand (L2) produces branched allylsilanes efficiently and regioselectively.^[9b] More recently, our group designed a bithiophene-alkyne-based ligand (L3) for the Pd-catalyzed regioselective allene hydrosilylation. It exhibits high selectivity and catalytic efficiency toward the production of branched allylsilanes.^[9c] But there are some inconveniences that they need to use glove box or synthesize the ligands (Scheme 1b). All the methods revealed that ligands are significant for controlling the regio- and stereoselectivity. Herein, we demonstrate a handy and efficient Palladium-catalyzed hydrosilylation of allenes, utilizing a commercially available Xantphos ligand to prepare branched-allylsilanes with excellent yield and regioselectivity (Scheme 1c).

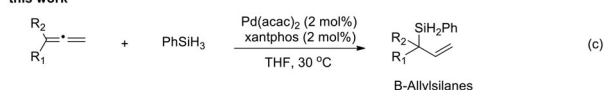
In our initial screening experiments, we examined different Pd catalysts and phosphorus ligands (Table 1). The 1-octylallene and PhSiH₃ were used as model substrates. We first tried the Pd(acac)₂ and PPh₃, getting the branched allylsilanes in low yield with poor selectivity (Table 1, entry 1). Then, we screened a series of bidentate phosphine ligands. The dppm, dppbz, and dppf were inefficient for allene hydrosilylation (Table 1, entries 2–4). However, the reaction afforded the branched allylsilanes in high isolated yield with excellent selectivity when we used the dpephos or Xantphos as ligand (Table 1, entries 5–6). Decreasing the catalyst loading to 1 mol% resulted in obvious reduction of yield (Table 1, entry 7). Other palladium sources, such as Pd(OAc)₂, PdCl₂, and



Pd catalyzed allene hydrosilylation for branched allylsilanes



this work



- broad scope for alkyl and aryl-substituted allenes
- high yield and regioselectivity
- commercially available Pd precursor and ligand

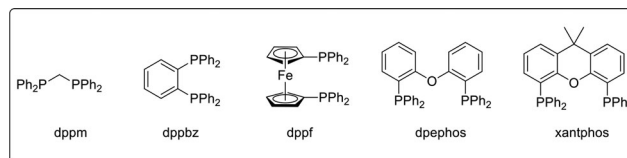
Scheme 1. Hydrosilylation of allenes: previous work and our work.

Table 1. Optimization of conditions for hydrosilylation of 1-octyllallene and $PhSiH_3$.^a

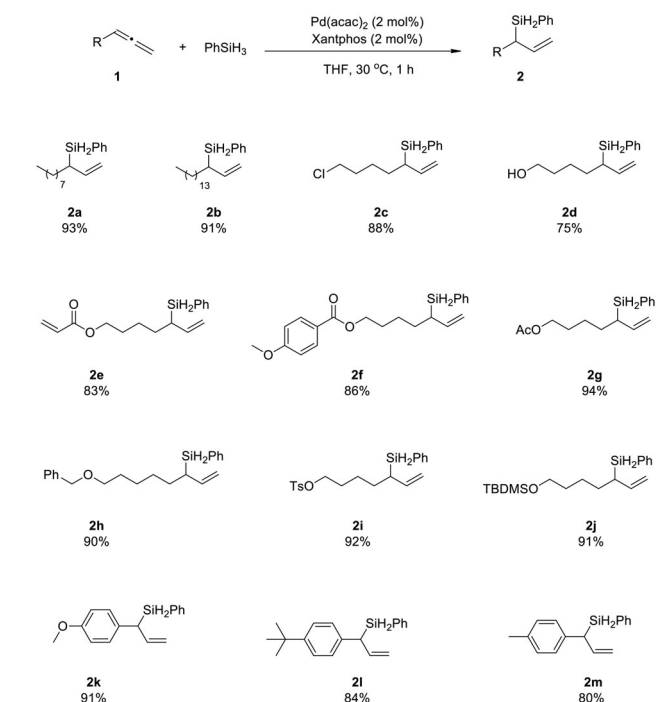
Entry	cat	Ligand	2a/yield% ^b	r.r. ^c
1	$Pd(acac)_2$	PPh_3	46	1:1
2	$Pd(acac)_2$	Dppm	25	1:2
3	$Pd(acac)_2$	Dppbz	15	1:3
4	$Pd(acac)_2$	Dppf	trace	–
5	$Pd(acac)_2$	dpphos	90	30:1
6	$Pd(acac)_2$	xantphos	96	32:1
7 ^d	$Pd(acac)_2$	xantphos	65	13:1
8	$Pd(OAc)_2$	xantphos	44	3:1
9	$PdCl_2$	xantphos	trace	–
10	$Pd(MeCN)_2Cl_2$	xantphos	trace	–

^aReaction conditions: 1-octyllallene (0.25 mmol), phenylsilane (0.3 mmol), L (2 mol%), Pd source (2 mol%), THF (1 mL), 30 °C, 1 h, N_2 atmosphere. ^bThe yields of **2a** were determined by 1H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. ^cr.r. = **2a**/other isomers, determined by 1H NMR spectroscopy.

^d $Pd(acac)_2$ (1 mol%), xantphos (1 mol%).

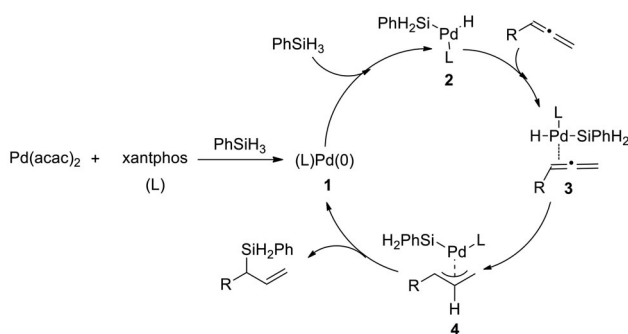


$Pd(MeCN)_2Cl_2$, were also tried, but these results were inferior to that of $Pd(acac)_2$ (Table 1, entries 8–10). So we identified the optimum conditions: hydrosilylation of allenes was performed with 2 mol% $Pd(acac)_2$ and Xantphos as the catalyst system at 30 °C.



Scheme 2. Scope of allene hydrosilylation with $PhSiH_3$.^{a,b,c,a} Reaction conditions: allenes (1 mmol), $PhSiH_3$ (1.2 mmol), $Pd(acac)_2$ (2 mol%), xantphos (2 mol%), THF (2 mL), 30 °C, 0.5–3 h, N_2 atmosphere. ^bYields of isolated products. ^cThe selectivity of product (r.r. = branched allylsilane product/all other isomers) was > 15:1, determined by 1H NMR spectroscopy.

Under the identified conditions (Table 1, entry 6), we explored the substrate scope of a variety of allenes with primary phenylsilane and the results are summarized in Scheme 2. In general, a variety of allenes reacted to produce



Scheme 3. Proposed mechanism.

the desired branched allylsilanes (**2a–2m**) in high yields (75%–94%) with excellent regioselectivities. The heteroatom-free straight-chain aliphatic allenes gave the target products in high yields (**2a**, **2b**). This reaction also showed good functional group tolerance with a range of reactive groups, such as chloro (**2c**), hydroxyl (**2d**), ester (**2e**, **2f**), and ether (**2h**). Furthermore, the allene showed a higher reactivity than the alkene as demonstrated by the isolation of **2e** in a high yield with an exclusive chemoselectivity toward the allene unit. Aliphatic allenes containing protecting groups, including acetate (**2g**), tosylate (**2i**), and silyl ether (**2j**), were also compatible with the reaction conditions to afford the expected products in decent yields with high selectivities. In addition, we also used Aryl-substituted allenes to evaluate this catalytic system. Aromatic allenes bearing electron-donating and neutral groups proceeded smoothly to afford the branched allylsilanes in good yields with high selectivities (**2k–2m**).

According to our previous investigation^[9c] and related literatures,^[8g,9a] we proposed a rationale for the palladium-catalyzed hydrosilylation of allenes as shown in **Scheme 3**. Firstly, $\text{Pd}(\text{acac})_2$ was reduced to form the $\text{Pd}(0)$ catalyst, and oxidative addition of hydrosilane to $\text{Pd}(0)$ generated the complex **[2]**. Then, hydrometalation of the allene complex intermediate **[3]** formed an allylpalladium intermediate **[4]**. Finally, C–Si reductive elimination of **[4]** would afford allylsilane product with return of the active $\text{Pd}(0)$ catalyst into the cycle. Further detailed mechanistic studies are ongoing to establish unambiguously the real mechanistic nature of the reaction.

In conclusion, we have developed a convenient and efficient palladium-catalyzed regioselective allene-hydrosilylation method for the synthesis of branched allylsilanes.¹ The catalyst is readily available and stable, and a wide range of allenes bearing a variety of synthetically useful functional groups could be tolerated, affording the corresponding products in high yields with excellent regioselectivities. Further investigations including

mechanistic studies and synthetic applications of the allylsilane products have been pursued in our lab.

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References

- [1] Marcinić, B.; Maciejewski, Pietraszuk, H.; Pawluc, C. P. *Hydrosilylation: A Comprehensive Review on Recent Advances*; Marcinić, B., Ed.; Springer: Berlin, **2009**.
- [2] (a) Fleming, I.; Barbero, A.; Walter, D. Stereochemical Control in Organic Synthesis using Silicon-Containing Compounds. *Chem. Rev.* **1997**, *97*, 2063–2192. DOI: [10.1021/cr941074u](https://doi.org/10.1021/cr941074u). (b) Denmark, S. E.; Liu, J. H.-C. Silicon-Based Cross-Coupling Reactions in the Total Synthesis of Natural Products. *Angew. Chem. Int. Ed.* **2010**, *49*, 2978–2986. DOI: [10.1002/anie.200905657](https://doi.org/10.1002/anie.200905657). (c) Barbero, A.; Pulido, F. J. Allylsilanes and Vinylsilanes from Silylcupration of Carbon–Carbon Multiple Bonds: Scope and Synthetic Applications. *Acc. Chem. Res.* **2004**, *37*, 817–825. DOI: [10.1021/ar0400490](https://doi.org/10.1021/ar0400490).
- [3] (a) Hatanaka, Y.; Hiyama, T. Cross-Coupling of Organosilanes with Organic Halides Mediated by Palladium Catalyst and Tri(diethylamino)sulfonium Difluorotrimethylsilane. *J. Org. Chem.* **1988**, *53*, 918–920. DOI: [10.1021/jo00239a056](https://doi.org/10.1021/jo00239a056). (b) Nakao, Y.; Hiyama, T. Silicon-Based Cross-Coupling Reaction: An Environmentally Benign Version. *Chem. Soc. Rev.* **2011**, *40*, 4893–4901. DOI: [10.1039/C1CS15122C](https://doi.org/10.1039/C1CS15122C).
- [4] (a) Sellars, J. D.; Steel, P. G.; Turner, M. J. Hosomi-Sakurai Reactions of Silacyclic Allyl Silanes. *Chem. Commun.* **2006**, *37*, 2385–2387. DOI: [10.1039/B602642G](https://doi.org/10.1039/B602642G). (b) Momiyama, N.; Nishimoto, H.; Terada, M. Chiral Brønsted Acid Catalysis for Enantioselective Hosomi-Sakurai Reaction of Imines with Allyltrimethylsilane. *Org. Lett.* **2011**, *13*, 2126–2129. DOI: [10.1021/ol200595b](https://doi.org/10.1021/ol200595b). (c) Ollevier, T.; Li, Z. The First Catalytic Sakurai Reaction of N-Alkoxy-carbonylamino Sulfones with Allyltrimethylsilane. *Org. Biomol. Chem.* **2006**, *4*, 4440–4443. DOI: [10.1039/B613331B](https://doi.org/10.1039/B613331B). (d) Cao, Z.-Y.; Jiang, J.-S.; Zhou, J. A Highly Enantioselective Hg(II)-Catalyzed Sakurai-Hosomi Reaction of Isatins with Allyltrimethylsilanes. *Org. Biomol. Chem.* **2016**, *14*, 5500–5504. DOI: [10.1039/C5OB02582F](https://doi.org/10.1039/C5OB02582F).
- [5] For selected reviews on transition-metal-catalyzed hydrosilylation of alkenes and alkynes: (a) Trost, B. M.; Ball, Z. T. Addition of Metalloid Hydrides to Alkynes: Hydrometalation with Boron, Silicon, and Tin. *Synthesis* **2005**, *2005*, 853–887. DOI: [10.1055/s-2005-861874](https://doi.org/10.1055/s-2005-861874). (b) Sun, J.; Deng, L. Cobalt Complex-Catalyzed Hydrosilylation of Alkenes and Alkynes. *ACS Catal.* **2016**, *6*, 290–300. DOI: [10.1021/acscatal.5b02308](https://doi.org/10.1021/acscatal.5b02308). (c) Zaranek, M.; Pawluc, P. Markovnikov Hydrosilylation of Alkenes: How an Oddity becomes the Goal. *ACS Catal.* **2018**, *8*, 9865–9876. DOI: [10.1021/acscatal.8b03104](https://doi.org/10.1021/acscatal.8b03104). (d) Du, X.; Huang, Z. Advances in Base-Metal-Catalyzed Alkene Hydrosilylation. *ACS Catal.* **2017**, *7*, 1227–1243. DOI: [10.1021/acscatal.6b02990](https://doi.org/10.1021/acscatal.6b02990).
- [6] Enthaler, Haberberger, S.; Irran, M. E. Highly Selective Iron-Catalyzed Synthesis of Alkenes by the Reduction of Alkynes. *Chem. Asian J.* **2011**, *6*, 1613–1623. DOI: [10.1002/asia.201000941](https://doi.org/10.1002/asia.201000941).
- [7] (a) McLaughlin, M. G.; Cook, M. J. $\text{PtCl}_2/\text{XPhos}$: A Highly Efficient and Readily Available Catalyst for the Hydrosilylation of Propargylic Alcohols. *Chem. Commun.* **2011**, *47*, 11104–11106. DOI: [10.1039/C1CC14433B](https://doi.org/10.1039/C1CC14433B). (b) Wu, C.; Teo, W. J.; Ge, S. Cobalt-Catalyzed (E)-Selective Anti-Markovnikov Hydrosilylation of Terminal Alkynes. *ACS Catal.* **2018**, *8*, 5896–5900. DOI: [10.1021/acscatal.8b01410](https://doi.org/10.1021/acscatal.8b01410).

¹General procedure for hydrosilylation of allenes: In a nitrogen-filled Schlenk tube, $\text{Pd}(\text{acac})_2$ (6 mg, 2 mmol%), Xantphos (12 mg, 2 mol%) were added to THF (1 mL), followed by the addition of allene (1 mmol) and PhSiH_3 (130 mg, 1.2 mmol) in THF (1 mL) under nitrogen. The reaction mixture was stirred at 30 °C. When the reaction was completed (0.5–3 h, monitored by TLC), the solvent was removed in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product. The Supplemental Materials contains sample ^1H and ^{13}C NMR spectra of the products **2** (Figures S1 – S13).

- [8] For selected transition-metal-catalyzed hydrosilylation of allene, see: (a) Wang, C.; Teo, W. J.; Ge, S. Access to Stereodefined (Z)-Allylsilanes and (Z)-Allylic Alcohols via Cobalt-Catalyzed Regioselective Hydrosilylation of Allenes. *Nat. Commun.* **2017**, *8*, 2258. DOI: [10.1038/s41467-017-02382-7](https://doi.org/10.1038/s41467-017-02382-7). (b) Miura, H.; Sasaki, S.; Ogawa, R.; Shishido, T. Hydrosilylation of Allenes over Palladium-Gold Alloy Catalysts: Enhancing Activity and Switching Selectivity by the Incorporation of Palladium into Gold Nanoparticles. *Eur. J. Org. Chem.* **2018**, *2018*, 1858–1862. DOI: [10.1002/ejoc.201800224](https://doi.org/10.1002/ejoc.201800224). (c) Yang, Z.; Peng, D.; Du, X.; Huang, Z.; Ma, S. Identifying A Cobalt Catalyst for Highly Selective Hydrosilylation of Allenes. *Org. Chem. Front.* **2017**, *4*, 1829–1832. DOI: [10.1039/C7QO00497D](https://doi.org/10.1039/C7QO00497D). (d) Asako, S.; Ishikawa, S.; Takai, K. Synthesis of Linear Allylsilanes via Molybdenum-Catalyzed Regioselective Hydrosilylation of Allenes. *ACS Catal.* **2016**, *6*, 3387–3395. DOI: [10.1021/acscatal.6b00627](https://doi.org/10.1021/acscatal.6b00627). (e) Jiang, Y.-N.; Zeng, J.-H.; Yang, Y.; Liu, Z.-K.; Chen, J.-J.; Li, D.-C.; Chen, L.; Zhan, Z.-P. A Conjugated Microporous Polymer as A Recyclable Heterogeneous Ligand for Highly Efficient Regioselective Hydrosilylation of Allenes. *Chem. Commun.* **2020**, *56*, 1597–1600. DOI: [10.1039/C9CC09387G](https://doi.org/10.1039/C9CC09387G). (f) Zeng, J.-H.; Chen, J.-J.; Chen, L.; Zhan, Z.-P. Access to Branched Allylsilanes by Nickel-Catalyzed Regioselective Hydrosilylation of Allenes. *Org. Chem. Front.* **2020**, *7*, 1132–1136. DOI: [10.1039/D0QO00156B](https://doi.org/10.1039/D0QO00156B). (g) Miller, Z. D.; Dorel, R.; Montgomery, J. Regiodivergent and Stereoselective Hydrosilylation of 1,3-Disubstituted Allenes. *Angew. Chem., Int. Ed.* **2015**, *54*, 9088–9091. DOI: [10.1002/anie.201503521](https://doi.org/10.1002/anie.201503521). (h) Kidonakis, M.; Stratakis, M. Ligandless Regioselective Hydrosilylation of Allenes catalyzed by Gold Nanoparticles. *Org. Lett.* **2015**, *17*, 4538–4541. DOI: [10.1021/acs.orglett.5b02236](https://doi.org/10.1021/acs.orglett.5b02236). (i) Miller, Z. D.; Montgomery, J. Regioselective Allene Hydroarylation via One-Pot Allene Hydrosilylation/Pd-Catalyzed Cross-Coupling. *Org. Lett.* **2014**, *16*, 5486–5489. DOI: [10.1021/ol502766q](https://doi.org/10.1021/ol502766q). (j) Kang, S.; Hong, Y.; Lee, J.; Kim, W.; Lee, I.; Yu, C. Silylative Carbocyclization of Allenyl-Carbonyl Units with Et₃SiH Catalyzed by Rhodium: Cis-Stereoselective Synthesis of Homoallylic Cycloalkanols. *Org. Lett.* **2003**, *5*, 2813–2816. DOI: [10.1021/ol034787k](https://doi.org/10.1021/ol034787k). (k) Sudo, T.; Asao, N.; Gevorgyan, V.; Yamamoto, Y. Lewis Acid catalyzed Highly Regio- and Stereocontrolled Trans-Hydrosilylation of Alkynes and Allenes. *J. Org. Chem.* **1999**, *64*, 2494–2499. DOI: [10.1021/jo9824293](https://doi.org/10.1021/jo9824293).
- [9] (a) Miller, Z. D.; Li, W.; Belderrain, T. R.; Montgomery, J. Regioselective Allene Hydrosilylation catalyzed by N-Heterocyclic Carbene Complexes of Nickel and Palladium. *J. Am. Chem. Soc.* **2013**, *135*, 15282–15285. DOI: [10.1021/ja407749w](https://doi.org/10.1021/ja407749w). (b) Tafazolian, H.; Schmidt, J. A. R. Highly Efficient Regioselective Hydrosilylation of Allenes using a [(3IP)Pd(allyl)]OTf Catalyst; First Example of Allene Hydrosilylation with Phenyl- and Diphenylsilane. *Chem Commun.* **2015**, *51*, 5943–5946. DOI: [10.1039/C4CC09804H](https://doi.org/10.1039/C4CC09804H). (c) Chen, J.-J.; Zeng, J.-H.; Yang, Y.; Liu, Z.-K.; Jiang, Y.-N.; Li, M.-R.; Chen, L.; Zhan, Z.-P. A Bithiophene-Promoted ppm Level Palladium-Catalyzed Highly Regioselective Hydrosilylation of Terminal Allenes. *Adv. Synth. Catal.* **2020**, *362*, 2360–2366. DOI: [10.1002/adsc.201901552](https://doi.org/10.1002/adsc.201901552).