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Conjugated microporous polymer as recyclable heterogeneous ligand for highly efficient regioselective hydrosilylation of allenes

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Pyridines containing adjacent C≡C bonds was utilized as ligand units and integrated into the skeleton of conjugated microporous polymers. The resultant Pd-CMP-1 was first applied as a highly efficient heterogeneous catalytic system for the Pd-catalyzed allene hydrosilylation towards a wide range of allenes to produce branched allylsilanes with high regioselectivity. The ligand units of the polymer, along with the confinement effect of the porous structure, jointly regulated the regioselectivity. The parts-per-million (ppm) levels of Pd, coordinated with the recyclable heterogeneous ligand, shows promise for industrial application. This work opens a new front of using CMP as an intriguing platform for developing highly efficient catalysts in the control of the regioselectivities in allene hydrosilylation.

Compared with the homogeneous catalysis, the heterogeneous catalysis is an attractive approach for the achievement of recyclable catalysts in the chemistry of organic synthesis.[1] In homogeneous metal-catalyzed organic reactions, metals and ligands play a dominant role. As a result, the difficulty of separation would make it hard to recycle. In some organic reactions, the cost of ligands is more expensive than that of the corresponding metal catalysts.[2] Especially in the presence of noble metals, the cost of catalytic systems will be extremely high. From an economical and environmental viewpoint, the development of a highly efficient ligand that can be recycled and reduce the amount of noble metals is desirable and attractive.

The catalytic hydrosilylation of C–C unsaturated bonds has attracted great interest in recent years since the resulting products can be further utilized in a variety of transformations.[3,4] For example, allylsilanes are useful synthetic building blocks due to their use as coupling partners in Hiyama and Sakurai reactions.[4] Compared with traditional synthetic methods such as selective allylic substitution of allylic chlorides or allylic ethers,[5] catalytic hydrosilylation is the most direct and atom economical approaches to allylsilanes. Among those catalytic protocols, hydrosilylation of 1,3-dienes to afford allylsilanes is a versatile method,[6] meanwhile allene hydrosilylation is another effective approach to generate allylsilanes or vinylsilanes. However, various regioisomers may be generated to complex the reaction system (Figure 1), hence the key challenge in allene hydrosilylation is to regulate the regio- and stereoselectivity. Besides, some side reactions such as hydrogenation, multiaddition of allene can also complicate the catalytic system.

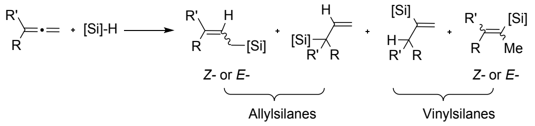

Figure 1. Different products of the allene hydrosilylation.

During the past years, the investigation of highly selective allene hydrosilylation has obtained great progress, a series of metal catalysts, such as Ni,[7] Au,[8] Cu,[9] Mo,[10] and Co,[11] have been successfully applied for linear (Z)-allylsilanes and terminal vinylsilanes (Figure 2a). In 2013, Montgomery' group reported a Pd catalyzed allene hydrosilylation for branched allylsilanes with an NHC ligand L9,[7a] and then they obtained terminal vinylsilanes with L10.[12] In 2015, Schmidt' group showed that employing a 3-iminophosphine ligand L11 produces branched allylsilanes efficiently and regioselectively (Figure 2b).[13] However, these methods still have limitations. The complex homogeneous ligands, and high amount (1-5 mol %) of noble metals, are difficult to separate and recycle. Therefore, the development of a highly efficient heterogeneous ligand that can be recycled and utmostly reduce the amount of noble metals will be challenging and significant.

Over the past decades, conjugated microporous polymers (CMPs) have received increasing attention due to their high surface areas, excellent thermal and chemical stabilities, and tunable pore size distribution. For these reasons, CMP materials have been used in many fields such as energy storage,[14] sensing,[15] gas adsorption,[16] light emitting and harvesting.[17] More importantly, CMPs can serve as intriguing platforms for

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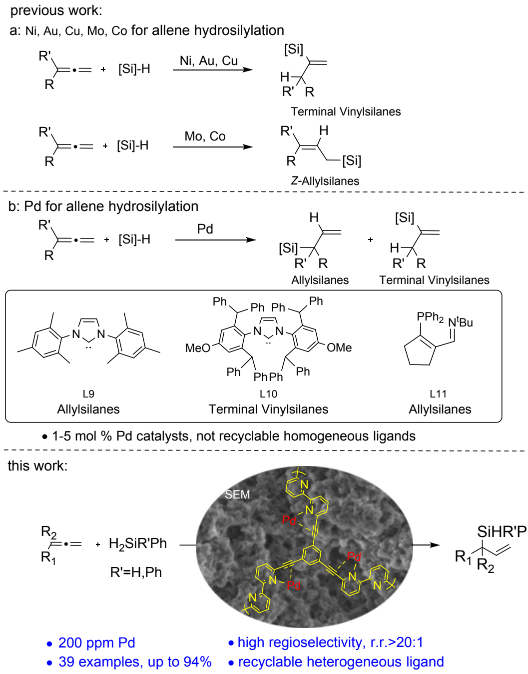
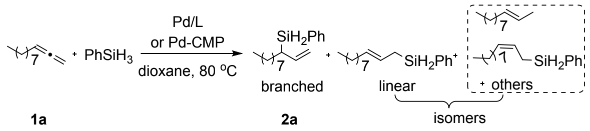
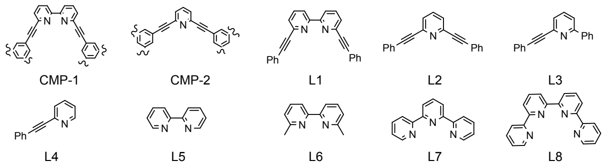


Figure 2. Hydrosilylation of allenes: previous work and our work.

Table 1. Optimization of Conditions for Hydrosilylation of 1-Octylallene and PhSiH$_3$^{a}



entry	Ligand	Yield^{b}	r.r.^{c}
1^{d}	CMP-1	95	> 20:1
2^{e}	CMP-1	92	> 20:1
3	CMP-2	76	> 20:1
4	L1	40	5:1
5^{f}	L1	----	----
6	L2	29	4:1
7	L3	27	2:1
8	L4	30	4:1
9	L5	n.d.	----
10	L6	39	6:1
11	L7	45	8:1
12	L8	31	3:1
13	--	45	4:1



^{a}Reaction conditions: 1-octylallene (0.25 mmol), phenylsilane (0.3 mmol), L (0.15 mol %), Pd(PPh$_3$)$_2$Cl$_2$ (0.05 mol %, 500 ppm), or 20 mg Pd-CMP (Pd, 0.05 mol %, 500 ppm), dioxane (2 mL), 80 °C, 5 h, N$_2$ atmosphere. ^{b}The yields of **2a** were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. ^{c}r.r. = **2a**/other isomers, determined by ^{1}H NMR spectroscopy or gas chromatography (GC) analysis. ^{d}0.5 h. ^{e}8 mg Pd-CMP-1 (Pd, 0.02 mol %, 200 ppm), 1 h. ^{f}L1 (0.15 mol %), without Pd(PPh$_3$)$_2$Cl$_2$.

incorporating homogeneous catalytic units into heterogeneous polymers. Recently CMPs are being increasingly applied in various organic reactions,[18] but the use of CMPs in the regulation of regioselective transformations has been rarely reported.[19]

Recently, we designed and synthesized a novel pyridine-alkyne-based CMP-1, which has been used as a heterogeneous ligand for the Pd-catalyzed oxidative Heck reaction with excellent linear selectivity.[19a] Polycondensation of 6, 6'-diiodo-2, 2'-bipyridine and 1, 3, 5-triethynylbenzene via Pd catalyzed Sonogashira cross-coupling strategy affords CMP-1 material (see the supporting information, Scheme S6). In our ongoing efforts to try the reactivity of CMPs, we surprisingly discovered that the newly synthesized CMP-1 can function as an active catalyst for the allene hydrosilylation without additional metals. Analysis of CMP-1 by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) showed that 0.27 wt % Pd was remained, which indicated that parts-per-million (ppm) levels of Pd (mol) was efficient in this allene hydrosilylation.

Herein, we demonstrate that the CMP materials with ppm levels of Pd can catalyze allene hydrosilylation efficiently and regioselectively. The CMP-1 was used as a recyclable heterogeneous ligand for highly efficient regioselective hydrosilylation of allenes. This Pd/CMP catalyst proved to be suitable for a broad scope of allenes. The very low amount of metal catalyst, coordinated by recyclable heterogeneous ligand, shows promise for industrial application.

In our initial screening experiments, the efficiency of different Pd-CMPs in hydrosilylation of 1-octylallene and PhSiH$_3$ was investigated. Pleasantly, the Pd-CMPs showed excellent regioselectivity and activity (Table 1, entries 1-3). With 500 ppm Pd (molar ratio), the use of Pd-CMP-1 as a heterogeneous catalyst gave the branched allylsilane product **2a** in 95% yield and excellent selectivity (Table 1, entry 1). When with 200 ppm Pd (molar ratio), the Pd-CMP-1 also obtained a high branched selectivity and 92% yield (Table 1, entry 2). And the homologous Pd-CMP-2 gave excellent selectivity of > 20:1 and 76% yield for branched allylsilane product **2a** (Table 1, entry 3). In contrast, a series of pyridine-type ligands were also investigated (Table 1, entries 4-12). Unfortunately, these ligands all led to low yields and moderate to poor selectivities. Without additional Pd, there was no reaction with only ligand L1 (Table 1, entry 5). Compared with CMP-1 and CMP-2, the corresponding homogeneous ligands L1 and L2 both resulted in low yields and poor selectivities. These experimental results indicated that porous polymer CMP-1 and CMP-2 outperformed the monomeric pyridine-type ligands L1 and L2 in controlling the regioselectivity (Table 1, entry 1 vs entry 4, entry 3 vs entry 6), which could be mainly attributed to the confinement effect of the porous structure of CMP materials, high ligand concentration and the spatial continuity of the Pd/CMP catalyst.[19a, 20]

In order to explore the structure properties, Pd-CMP-1 was characterized. Nitrogen adsorption-desorption analysis (Figure 3C) shows that Pd-CMP-1 possesses hierarchical porosity, which is further confirmed by SEM (Figure 3A) and TEM images (Figure 3B). The BET surface areas of Pd-CMP-1 is up to 415 m^2/g with a total pore volumes of 0.71 cm^3/g. Calculated from the method of non-local density functional theory (NLDFT), the pore sizes of

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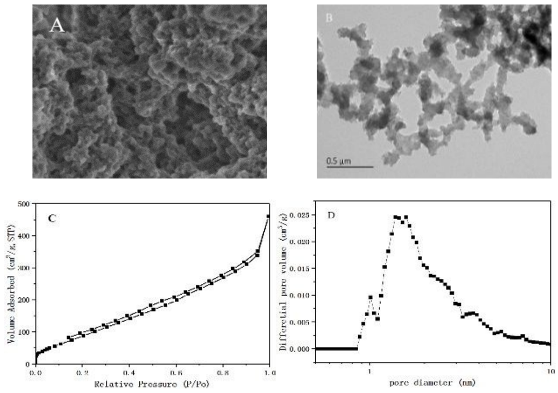
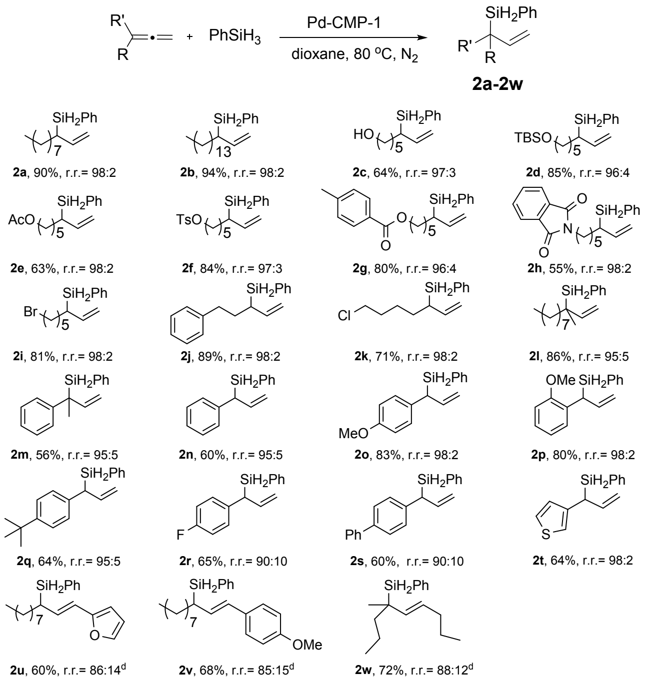


Figure 3. (A) Scanning electron microscope (SEM) of Pd-CMP-1. (B) Transmission electron microscope (TEM) of Pd-CMP-1. (C) Nitrogen sorption isotherms of Pd-CMP-1. (D) Pore size distribution of Pd-CMP-1.

Pd-CMP-1 are mainly distributed between 1 and 4 nm (Figure 3D), indicating that the hierarchical porous Pd-CMP-1 mainly consists of micropores and mesopores. We suggest that the confinement effect of these porous space plays a crucial role in regulating the regioselectivity for allene hydrosilylation.

Scheme 1. Scope of allene hydrosilylation with $PhSiH_3$[a, b, c]

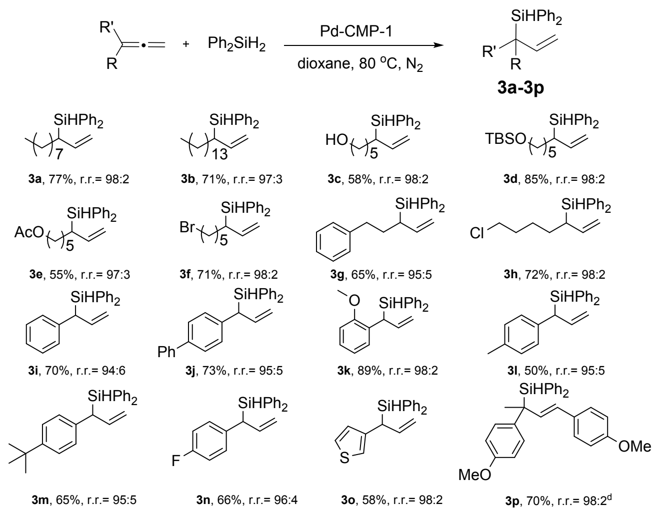


[a]Reaction conditions: allenes (0.25 mmol), $PhSiH_3$ (0.3 mmol), 8 mg Pd-CMP-1 (Pd, 0.02 mol %, 200 ppm), dioxane (2 mL), 80 °C, 0.5-5 h, N_2 atmosphere. [b]Yields of isolated products. [c]The selectivity of product (r.r. = branched allylsilane product/all other isomers) was determined by ^1H NMR spectroscopy. [d]Internal allenes.

The catalytic efficiency of the Pd-CMP-1 was evaluated using a variety of allenes with $PhSiH_3$ (Scheme 1). In general, a variety of allenes reacted to produce the desired branched allylsilanes (**2a-2w**) in moderate to high yields (55-94%) with excellent regioselectivities. The straight-chain aliphatic allenes gave the corresponding products **2a**, **2b**. The catalyst was compatible with aliphatic allenes bearing various functional groups and reactive groups, including hydroxyl (**2c**), bromo (**2i**), chloro (**2k**), ester (**2g**), and imide (**2h**). Aliphatic allenes containing protecting groups, such as silyl ether, acetylate, and tosylate (**2d-f**), afforded the expected products in moderate to high yields. A variety of aromatic allenes bearing electron-donating , neutral substituents and thiophene gave the corresponding hydrosilylation products (**2m-2q, 2t**) in moderate to good yields and excellent regioselectivities. The aromatic allenes containing 4-F (**2r**), 4-phenyl (**2s**) led to slightly lower selectivities and yields. Importantly, disubstituted terminal allenes could afford the hydrosilylation products containing quaternary carbon stereogenic centers (**2l**, **2m**). The internal allenes afforded the products **2u**, **2v**, **2w** in good yields and slightly decreased selectivities.

Similarly, secondary hydrosilanes like Ph_2SiH_2 also reacted smoothly with various allenes (Scheme 2). Aliphatic and aromatic allenes were well hydrosilylated (**3a–3p**). A variety of reactive groups, such as hydroxyl (**3c**), siloxy (**3d**), bromo (**3f**), chloro (**3h**), fluoro (**3n**), and acetal (**3e**), were tolerated under the standard reaction conditions. Aromatic allenes bearing electron-donating, electron-withdrawing groups and thiophene were also compatible to yield the corresponding hydrosilylation products (**3i-3o**) in good yields and excellent regioselectivities. The trisubstituted internal allene got the hydrosilylation products **3p** in high yield and excellent selectivity.

Scheme 2. Scope of allene hydrosilylation with Ph_2SiH_2[a, b, c]



[a]Reaction conditions: allenes (0.25 mmol), Ph_2SiH_2 (0.3 mmol), 8 mg Pd-CMP-1 (Pd, 0.02 mol %, 200 ppm), dioxane (2 mL), 80 °C, 1-5 h, N_2 atmosphere. [b]Yields of isolated products. [c]The selectivity of product (r.r. = branched allylsilane product/all other isomers) was determined by ^1H NMR spectroscopy. [d]Internal allenes.

The reusability of CMP-1 was examined for the hydrosilylation of 1-Octylallene and $PhSiH_3$ to obtain **2a**. After each reaction, the CMP-1 was separated from centrifugation. Next run, the recycled CMP-1 and $Pd(PPh_3)_2Cl_2$ (0.02 mol %) was added as a catalytic system. After five runs, the Pd/CMP-1 worked without loss of activity and selectivity (Figure 4), demonstrating the good reusability of CMP-1.

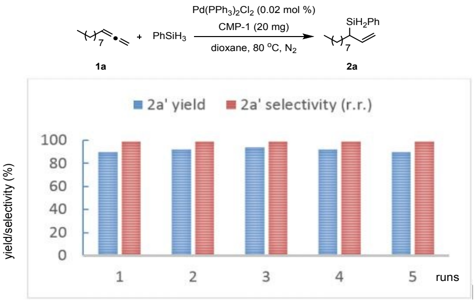


Figure 4. Studies on recycling of CMP-1 for the Hydrosilylation of 1-Octylallene and $PhSiH_3$.

Conclusions

In summary, we have developed a conjugated microporous polymer with pyridines containing adjacent C≡C bonds as the ligand unit. The resultant Pd-CMP-1 was first applied as a highly efficient heterogeneous catalytic system for the Pd-catalyzed regioselective allene hydrosilylation towards a wide scope of allenes to produce branched allylsilanes. The ligand units of the polymer, along with the confinement effect of the porous structure, jointly regulated the regioselectivity. The parts-per-million (ppm) levels of Pd, coordinated with the recyclable heterogeneous ligand, shows promise for industrial application. This work opens a new front of using CMP as an intriguing platform for developing highly efficient catalysts in the control of the regioselectivities in allene hydrosilylation.

Conflicts of interest

There are no conflicts to declare.

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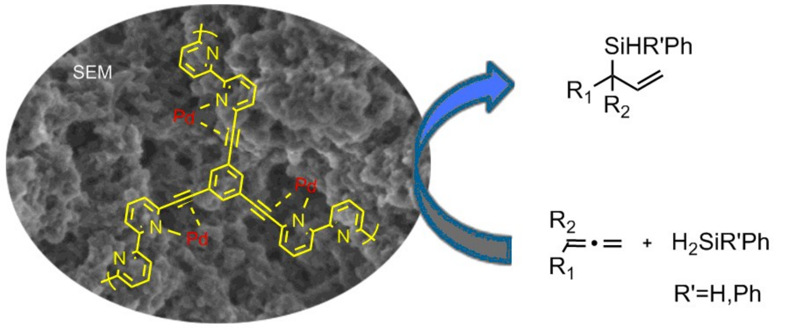

- 200 ppm Pd
- 39 examples, up to 94%
- recyclable heterogeneous ligand
- high regioselectivity, r.r.>20:1