

Conjugated Microporous Polymer as Heterogeneous Ligand for Highly Selective Oxidative Heck Reaction

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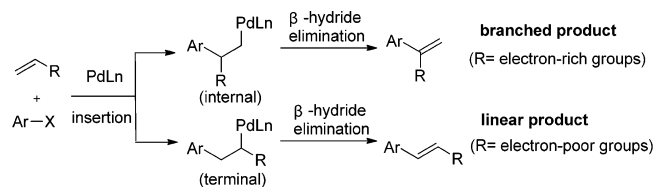
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S Supporting Information

ABSTRACT: A series of pyridine-type ligands containing C≡C bonds were designed and synthesized for selective oxidative Heck reaction. These ligands were utilized as functional units and integrated into the skeleton of conjugated microporous polymers. 6,6'-diiodo-2,2'-bipyridine and 1,3,5-triethynylbenzene were polycondensed via Sonogashira cross-coupling strategy to afford CMP-1 material. The resultant CMP-1 was used as a heterogeneous catalytic ligand for the Pd^{II}-catalyzed oxidative Heck reaction with high linear selectivity. The linear selectivity of CMP-1 is about 30 times higher than that of bipyridine-based monomer ligand. This work opens a new front of using CMP as an intriguing platform for developing highly efficient catalysts in controlling the regioselectivity in organic reactions.

The Heck–Mizoroki reaction is one of the most powerful transformations for the construction of C–C bonds.¹ A key issue remains to be solved is to control the position where aryl groups insert into olefins. For electronically biased olefins such as styrene, vinyl ethers and acrylates, high regioselectivity can be achieved easily. Typically, electron-rich alkenes favor coupling at the internal site to deliver the branched products,² whereas electron-poor alkenes favor coupling at the terminal site to give the linear products (Scheme 1).³ However, the development of

Scheme 1. Two Different Products of Heck Reaction



regioselective Heck reactions using electronically unbiased alkenes, especially for aliphatic olefins, as substrates in a catalytic manner is a formidable challenge.⁴ In the past few years, several groups have focused on homogeneous catalyst-controlled highly selective oxidative Heck reaction of electronically unbiased alkenes. For example, Sigman and co-workers demonstrated that high linear-selectivity could be achieved by submitting electron-

cally unbiased alkene substrates to a catalytic system incorporating a carbene ligand (Figure 1, L1).⁵ Stahl's group also

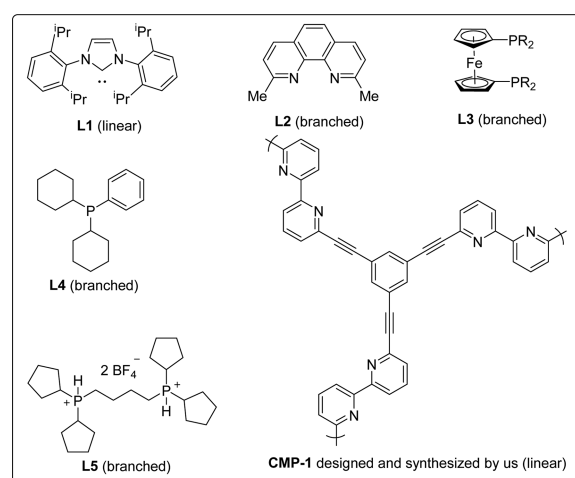


Figure 1. Ligands for selective Heck reaction.

demonstrated high regioselectivity in oxidative Heck synthesis of branched conjugated dienes, using the catalyst derived from palladium and phenanthroline-type ligand (Figure 1, L2).⁶ Meanwhile, the homogeneous catalyst-controlled selective Heck reaction of electronically unbiased alkenes have been made some progress. With bulky biphosphine ligands (Figure 1, L3), Zhou and co-workers developed Pd⁰-catalyzed branched-selective Heck reaction of electronically unbiased alkenes.⁷ Furthermore, Jamison and co-workers reported Heck-coupling reactions between benzyl chlorides and electronically unbiased alkenes using [Ni(cod)₂] and PCy₂Ph (Figure 1, L4),⁸ providing a regioselective access to branched alkene products. Subsequently, Jamison expanded the Ni⁰-catalyzed regioselective Heck-type reaction to include widely used aryl electrophiles as substrates by using a bidentate phosphine ligand (Figure 1, L5).⁹ In all of these approaches, the ligands play a crucial role in controlling the regioselectivity for the Heck reaction. Nevertheless, to the best of our knowledge, there have been no reports

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of heterogeneous ligand capable of promoting selective Heck reactions of electronically unbiased alkenes.

Over the past decade, conjugated microporous polymers (CMPs) with extended π -conjugation have attracted much attention as an important porous organic material platform. Various microporous CMPs with high surface areas have been synthesized via proper selection of cross-linking strategies and building blocks. Compared with materials such as covalent organic frameworks (COFs) and metal–organic frameworks (MOFs), the CMPs usually have good thermal and chemical stability. Remarkably, CMPs possess cross-linked 3D molecular skeletons that can be finely tuned in many aspects such as specific surface areas and pore size distributions. Therefore, CMP materials have been applied in many areas such as energy storage,¹⁰ gas adsorption,¹¹ sensing,¹² light emitting¹³ and light harvesting.¹⁴ More importantly, CMPs can serve as an intriguing platform for incorporating homogeneous catalytic sites into heterogeneous polymeric systems.¹⁵ For example, an iron(III) porphyrin-based CMP (FeP-CMP) showed excellent catalytic activity for the oxidation of thiols^{15b} and the epoxidation of olefins under mild conditions.^{15g} A cyclometalated Ir(III) complex-contained CMP was found to be highly active for reductive amination reaction.^{15c} However, CMP catalysts have not been used for regioselective reactions. We speculated that the rigid porous structures of CMPs might have a positive effect on controlling the regioselectivity of organic reactions. Herein, a new type of organic conjugated microporous polymer (Figure 1, CMP-1) used as ligand for heterogeneous catalysis was designed and synthesized, which shows high selectivity for the Pd^{II}-catalyzed linear-selective oxidative Heck reaction.

To design rational framework of CMP for selective oxidative Heck reaction, proper functional units should be first selected. Over the past decades, various bidentate nitrogen ligands in complex with palladium have been successfully applied to the Heck coupling reactions.¹⁶ On the other hand, several groups have demonstrated that a Pd^{II} center could coordinate with the N atom and the C \equiv C bond simultaneously.¹⁷ Bearing these knowledge in mind, several pyridine-type ligands containing C \equiv C bonds (Figure 2, L6–L10) were designed and employed in selective oxidative Heck reaction.

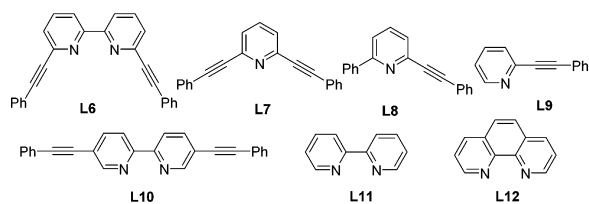


Figure 2. Ligands designed or selected for selective Heck reaction.

In our initial screening experiments, the efficiency of different nitrogen ligands in promoting the coupling of phenylboronic ester and 1-octene was investigated (Table 1). To our delight, the pyridine-type ligands containing acetylene bond (L6–L9) showed good yields, ln/br selectivities and moderate regioisomeric ratios (Table 1, entries 1–4). A decrease in ln/br selectivity was observed with the pyridine-type ligand L10 in which the C \equiv C bonds are too far from the N sites to coordinate to the palladium center (Table 1, entry 5). For comparison, we then screened commercially available nitrogen ligands. Both bipyridine and phenanthroline led to very low regioisomeric ratio of the desired product despite high conversions (Table 1, entries 6

Table 1. Impact of Different Ligands on Selective Oxidative Heck^a

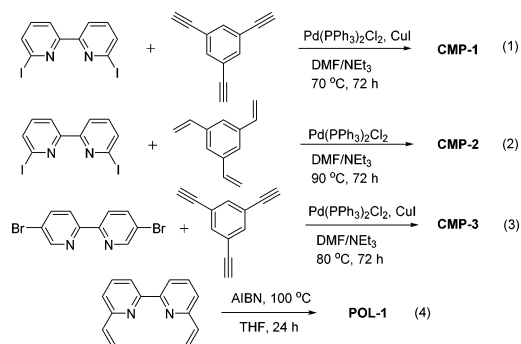
entry	ligand	yield ^b	ln:br ^c	r.r. ^d
1	L6	41%	12:1	2.1:1
2	L7	65%	15:1	3.9:1
3	L8	84%	20:1	4.4:1
4	L9	65%	21:1	4.3:1
5	L10	88%	2.5:1	1.3:1
6	L11	91%	2.1:1	0.6:1
7	L12	92%	2.5:1	0.8:1
8		95%	6:1	0.2:1
9	CMP-1	76%	70:1	30:1
10	CMP-2	81%	7:1	2.7:1
11	CMP-3	52%	10:1	2.1:1
12	CMP-4	57%	14:1	4.9:1
13	POL-1	48%	12:1	2.9:1

^aReaction conditions: 1-octene (0.4 mmol), phenylboronic ester (1.2 mmol), Pd(OAc)₂ (6 mol %), Cu(OTf)₂ (20 mol %), L6–L12 (20 mol %), CMP-1, CMP-2, CMP-3, CMP-4 or POL-1 (35 mg), DMA (4 mL), 40 °C, O₂ (1 atm), 48 h. ^bIsolated yield. ^cDetermined by ¹H NMR spectroscopy. ^dRatio of linear/other isomers, as determined by GC analysis.

and 7). These results were similar to those in the absence of a ligand (Table 1, entry 8). On the basis of the above results, we selected L9 (a bifunctional ligand consists of C \equiv C and pyridine-N sites with proper coordination geometric angle) as a functional unit and further integrated into the skeleton of CMP to serve as a heterogeneous catalytic ligand.

CMP-1 was synthesized by Sonogashira coupling of 6,6'-diiodo-2,2'-bipyridine and 1,3,5-triethynylbenzene in the presence of PdCl₂(PPh₃)₂ and CuI (Scheme 2, eq 1). For comparison,

Scheme 2. Synthesis of Porous Polymers



other bipyridine-containing polymers CMP-2, CMP-3, POL-1 (Scheme 2, eqs 2–4) and CMP-4 (see SI) were also synthesized. In the presence of CMP-2 or POL-1, good or moderate yield and low regioisomeric ratios were obtained (Table 1, entries 10 and 13). Compared with L10 monomer, polymer CMP-3 provided some improvement in regioisomeric ratios (Table 1, entry 11 vs entry 5). Excitedly, the use of CMP-1 as a heterogeneous ligand furnished the desired alkene in 76% yield, excellent ln/br selectivity of 70:1 and high regioisomeric ratio of 30:1 (Table 1, entry 9). These impressive experimental results indicated these porous polymer, such as CMP-1 and CMP-3, outperformed the monomeric pyridine-type ligands L6 and L10 in controlling the

regioselectivity (Table 1, entry 9 vs entry 1, entry 11 vs entry 5), which can be largely attributed to the confinement effect of the porous structure of CMP materials.

To explore the structure–activity relationship, CMP-1 and related prepared Pd(OAc)₂/CMP-1 were characterized by thermogravimetry (TG), N₂ adsorption–desorption analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The TG shows that CMP-1 remains intact at temperatures up to 400 °C, even with only about 15% weight loss at 800 °C, indicating its good thermal stability (see the Supporting Information, Figure S1). Nitrogen adsorption–desorption analysis (Figure S2a) demonstrates that CMP-1 possesses hierarchical porosity, which is further confirmed by SEM (Figure 3A) and TEM images (Figure S5). The BET surface areas and

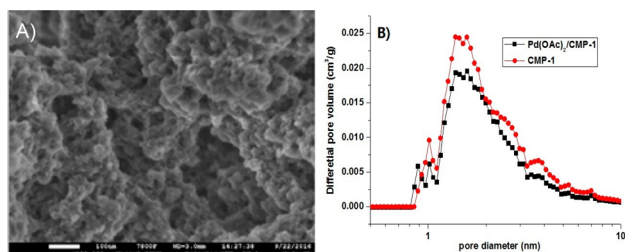


Figure 3. (A) SEM of CMP-1. (B) Pore size distribution curves.

total pore volumes of CMP-1 are up to 415 m²/g and 0.71 cm³/g, respectively. The pore sizes of CMP-1 are mainly distributed between 1 and 4 nm, which was calculated from the method of nonlocal density functional theory (NLDFT), indicating that the hierarchical porous CMP-1 mainly consists of micropores and mesopores. We suggest that the confinement effect of these porous space plays an important role in controlling the regioselectivity for the Heck reaction. No obvious change in the pore size distribution emerged between CMP-1 and Pd(OAc)₂/CMP-1 (Figure 3B). Despite the slight decrease in specific surface area, Pd(OAc)₂/CMP-1 is still significantly microporous (Table S2). Furthermore, XPS confirmed the coordination of palladium with pyridyl nitrogen (Figure S3).

The catalytic efficiency of the Pd(OAc)₂/CMP-1 system was evaluated using a variety of electronically unbiased alkenes and arylboronic esters (Table 2). This oxidative Heck reaction favors formation of the (*E*)-linear product and was proved to be tolerant of various functional groups. For example, the olefins bearing a ketone (Table 2, entry 6), an ester (Table 2, entry 7) or a silyl ether (Table 2, entry 13) all proceed with good yields and excellent regio- and *E*:*Z* stereoselectivities. Moreover, the catalyst Pd(OAc)₂/CMP-1 promoted the cross-coupling of a doubly protected allylic amine with a broad range of arylboronic esters to afford the linear products with excellent yields and selectivity (Table 2, entries 1–5). It should be pointed out that good yield and excellent selectivity were observed for an allyl ester, a type of substrate which is prone to undergo oxidative addition in the presence of a palladium catalyst (Table 2, entry 8).¹⁸ Substrates containing an acetyl or TBS-protected homoallylic alcohol also afforded high selectivities and moderate yields with a range of arylboronic esters (Table 2, entries 9–11). Alkenyl epoxides usually suffered from nucleophilic attack by organoboron compounds.¹⁹ However, the alkene containing an oxirane group was a suitable substrate for the oxidative Heck reaction in the presence of Pd(OAc)₂/CMP-1, delivering the desired product with good yield and selectivity (Table 2, entry 12).

Table 2. Substrate Scope of Oxidative Heck^a

R'CH=CH2 + R-C6H4-B(OAc)2 >> R'CH=CH-C6H4-R
 Reaction conditions: 6 mol% Pd(OAc)₂/CMP-1, 20 mol% Cu(OTf)₂, DMA, O₂, 40 °C

entry	product	% yield ^b (% yield ^c)	linear : branched ^d
1		91	100:1
2		89 (7)	>100:1
3		83	>100:1
4		90	100:1
5		63 (33)	100:1
6		66 (26)	37:1
7		69 (20)	40:1
8		55 (38)	55:1
9		65 (25)	20:1
10		54 (42)	90:1
11		55 (41)	30:1
12		68 (23)	25:1
13		70 (23)	17:1
14		69 (25)	20:1
15		76 (16)	70:1
16		77	30:1
17		86	50:1
18		91	60:1
19		71 (15)	25:1
20		76	10:1
21		74 (14)	40:1
22		93	43:1
23		87	45:1
24		81	25:1
25		71 (20)	60:1

^aReaction conditions: olefins (0.4 mmol), arylboronic esters (1.2 mmol), Pd(OAc)₂ (6 mol %), Cu(OTf)₂ (20 mol %), CMP-1 (35 mg), DMA (4 mL), 40 °C, O₂ (1 atm), 48 h. The selectivity (r.r.) for desired product was >10:1. ^bIsolated yield. ^cRecovered starting material. ^dDetermined by ¹H NMR spectroscopy.

Owing to the lack of chelation and inductive effects, the heteroatom-free substrates such as aliphatic olefins are usually challenging substrates for selective Heck reaction. Highly branched-selective Heck reactions of aliphatic olefins have been made much progress in recent years.^{6–9} However, less attention has been paid to linear-selective Heck reactions of aliphatic olefins. Several methods were developed for Heck-type reactions that delivered only a maximum selectivity of 10:1 for (*E*)-linear product using aliphatic olefin substrate.^{5,20} Of note, in the presence of CMP-1, aliphatic olefins were converted smoothly to the (*E*)-linear products in good yields with excellent ln/br selectivity (>25:1 ratio in most cases) (Table 2, entries 15–24), which provided strong evidence that the selectivity obtained is catalyst-controlled rather than chelate-controlled.^{20a}

To know more mechanistic study about the selectivity in a homogeneous system, DFT calculations have been performed to

explore the pathways of 1-octene inserting into a Pd^{II}-phenyl species chelated by L8 (Figure S8). The coordination of 1-octene to Pd^{II} gives rise to two lowest-energy isomers I^{pro-R} and I^{pro-S}. They are followed by the two most favorable alkene insertion transition states TS^{linear(pro-R)} and TS^{branched(pro-S)} that lead correspondingly to the linear and branched products. Note that TS^{linear(pro-R)} is lower than TS^{branched(pro-S)} by 4 kcal/mol in free energy. Thus, formation of linear regioisomer is much more preferable than that of branched isomer both kinetically and thermodynamically, in sharp contrast to the reversed regioselectivity in the neocuproine-ligated Pd^{II}-catalyzed Heck reaction.⁶ The heterogeneous system is more complex, and further study is underway to uncover the detailed mechanism of the excellent selectivity in heterogeneous system.

In conclusion, we have developed a highly linear-selective oxidative Heck reaction of simple olefins by employing CMP materials as a ligand. Because of the beneficial confinement effect of the porous structure in CMP materials and the bifunctional ligand feature (consists of C≡C and pyridine-N sites with proper coordination geometric angle), this heterogeneous ligand displayed very high selectivity toward a broad range of electronically unbiased alkenes. The linear selectivity of CMP-1 is about 30 times higher than that of bipyridine-based monomer ligand. This work opens a new front of using CMP as an intriguing platform for developing highly efficient catalysts in controlling the regioselectivity of organic reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b00643.

Experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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