Received: 19 January 2010

Revised: 24 March 2010

(www.interscience.com) DOI 10.1002/aoc.1662

Applied Organometallic

hemistry

Polymer-supported palladium complexes with C,N-ligands as efficient recoverable catalysts for the Heck reaction

Yu-xia Liu^{a,b}, Zhi-wei Ma^a, Jun Jia^a, Chuan-chuan Wang^a, Meng-lin Huang^a and Jing-chao Tao^a*

A series of new polymer-supported palladium complexes with C,N-ligands (1a-e and 2a-c) were easily synthesized. The synthesized catalysts could be applied as efficient heterogeneous catalysts for the Heck coupling reaction (turnover frequency up to 12 600 h⁻¹). Additionally, the catalysts could be recovered by a simple filtration progress and could be reused for at least five times with a slow progressive decrease in activity. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: Heck reaction; palladium complexes; recoverable catalysts

Introduction

Palladium-catalyzed coupling reactions provide an efficient and powerful method for the formation of carbon-carbon and carbon-heteroatom bonds.^[1-4] The Heck reaction has been noted due to its high tolerance of functional groups and general applicability.^[5-7] The reaction generally proceeds in the presence of palladium catalysts associated with phosphine ligands, which could stabilize the active palladium intermediates. However, most of the phosphine ligands are air- and moisture-sensitive. It is therefore not surprising that much effort has been devoted to the development of new catalytic systems for this reaction.^[8-16] From an economic point of view, the recovery and reuse of the noble metal catalysts are highly important. Therefore, supported Pd-catalysts have emerged in recent years as an alternative, with the advantages of heat stability and easy separation from the reaction systems compared with homogeneous catalysts.[17-29] However, recyclable, phosphine-free cyclopalladated complexes are rare.^[30,31]

In this paper, we report a simple method for the synthesis of polymer-supported cyclopalladated complexes (1a-e and 2a-c). Different methods of characterization, including elemental analysis and IR, were applied to obtain information about structural features. The catalytic performance of the resulting supported palladium complexes was studied in the Heck coupling reaction between aryl halides and butyl acrylate. Furthermore, the recoverability of synthesized catalysts was also tested.

Experimental

Materials and Methods

All chemicals were used as purchased unless otherwise noted. Solvents were dried and freshly distilled prior to use. Heck reactions were performed under a dry nitrogen atmosphere using Schlenk techniques. Elemental analyses of the products were obtained from a Carlo Erba 1106 elemental analyzer. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. The surface area was determined on a Carlo Erba model surface analyzer. Gas chromatographic analysis were carried out on an Agilent-5890, capillary column length 15 m, with helium in combination with a flame ionization detector. The products were identified by comparison of their GC and GC-MS features with those of authentic samples. Conversions and yields were calculated by GC using *n*-dodecane as internal standard. Chloromethylated P(S-DVB), 4% cross-linked, was obtained from Shanghai Resin Company.

Preparation of the Catalysts

The aminomethyl polystyrene was prepared from chloromethylated P(S-DVB) as reported in the literature.^[32,33] The supported cyclopalladated complexes were prepared in two steps as shown in Schemes 1 and 2.

Synthesis of the supported Schiff-bases La-e and L'a-c

A mixture of aldehydes (great excess) and aminomethyl polystyrene in pyridine was stirred at 110° C for 12 h under the protection of nitrogen. The products were isolated by filtration, washed with pyridine and methanol, then dried in the vacuum shelf dryer at 100° C overnight. The formation of the Schiff bases was confirmed by IR spectroscopy.

b Department of Material and Chemistry Engineering, Henan Institute of Engineering, Zhengzhou 450007, People's Republic of China

^{*} Correspondence to: Jing-chao Tao, Department of Chemistry, Zhengzhou University, Zhengzhou 450052, Public's Republic of China. E-mail: jctao@zzu.edu.cn

a Department of Chemistry, Zhengzhou University, Zhengzhou 450052, People's Republic of China



Scheme 1. Synthesis of polymer-supported Pd catalysts 1a-e.



Scheme 2. Synthesis of polymer-supported Pd catalysts 2a-c.

Synthesis of the supported cyclopalladated complexes 1a-e and 2a-c

The cyclopalladated complexes were synthesized as reported in the literature.^[35] To a solution of Li_2PdCl_4 (0.1 M) in methanol (15 ml), supported Schiff base **La**–**e** or **L'a**–**c** (1 g) and anhydrous sodium acetate were added. The mixture was stirred at room temperature for 12 h. Then the solid products were isolated by filtration, washed with methanol and dried in the vacuum shelf dryer overnight.

Determination of the Pd loading

Aqua regia (2.0–5.0 ml) was added to the heterogeneous catalyst (50–200 mg). The mixture was placed inside a high-pressure Teflon tube and leaching was carried out under microwave conditions (50, 600 and 450 W pulses, respectively, t = 30 min). After cooling to room temperature, the mixture was filtered through a 0.2 mm Teflon fiter and measured by ICP-OES ($\lambda = 340.458$ nm, ion line). The background was measured at $\Delta \lambda = \pm 0.0278$ nm.

Catalytic Reactions

A mixture of aryl halide (5 mmol), Et₃N (6 mmol), *n*-butyl acrylate (6 mmol) and supported Pd catalyst in DMF (1 ml) was stirred at the desired temperature until 100% conversion as monitored by GC analyses. Then the reaction mixture was cooled, added into 10 ml of diethyl ether and filtered. The filtrate was washed with with H₂O (3 ml × 3). The organic phase was separated, dried and analyzed by gas chromatography (*trans*-3-phenyl-*n*-butyl acrylate $t_r = 8.4$ min).

Reuse of the Recovered Catalyst

The supported Pd catalysts were recovered and reused by the following steps: the reaction mixture was cooled to room

Table 1.	Characterization	of	polymer-supported	Schiff-bases La-e
and L' a-	c			

		Eleme	ntal analy	IR (C=N)	
Ligand	R	С	Ν	Н	$v_{ m max}~ m cm^{-1}$
La	Н	85.92	5.58	7.05	1641
Lb	p-Cl	77.57	4.82	6.52	1641
Lc	p-N(CH ₃) ₂	81.78	8.20	7.73	1636
Ld	o-CH₃	84.52	4.39	8.12	1634
Le	m-NO ₂	77.86	8.07	6.72	1645
L′a	Н	73.96	5.16	6.44	1640
L′b	CH₃	75.49	4.77	6.88	1622
L′c	Ph	76.36	4.32	7.56	1618

temperature and filtered. The solid catalyst was washed with DMF, acetone and diethyl ether after filtration, dried at 80 $^\circ\text{C}$ under vacuum, and then reused in the next run without further treatment.

Determination of Pd Leaching

To determine the Pd content in the solution, the mixture of the catalytic reaction was filtered. Part of the filtrate was measured by ICP-OES (see determination of the Pd loading).

Results and Discussion

Synthesis and Characterization of the Supported Schiff Bases

The aminomethyl polymer was prepared from Merrifield resin as reported in the literature.^[32,33] The disappearance of absorption at 1265 cm⁻¹ for the C–Cl bonds indicated that the Merrifield resin

Table 2.Characterization of polymer-supported Pd catalysts 1a-eand 2a-c							
		Elemental analysis (%)			(C=N)		
Ligand	Surface area (m ² g ⁻¹) ^a	С	Ν	Н	$v_{\rm max}~{\rm cm}^{-1}$	mmol Pd g ⁻¹ resin	
1a	47.5	68.76	5.38	5.97	1633	0.40	
1b	48.8	66.88	4.78	5.43	1629	0.33	
1c	44.1	67.04	6.96	6.35	1628	0.44	
1d	46.7	70.70	4.67	6.13	1625	0.41	
1e	50.2	64.78	7.51	5.21	1640	0.29	
2a	56.3	73.56	4.07	6.05	1626	0.23	
2b	60.8	67.33	5.26	6.52	1611	0.21	
2c	68.5	71.28	6.34	7.25	1611	0.18	
^a Surface area of the support: Merrifield resin = 245.28 m ² g ⁻¹ .							

was successfully changed to the corresponding aminomethyl polystyrene. For the preparation of the Schiff bases, it is important to choose a suitable solvent to swell the resin. Pyridine was adopted as the best one in which the reaction could proceed smoothly. The formation of Schiff bases was demonstrated by the presence of the absorption peak at about 1618–1645 cm⁻¹ in the IR spectra. Elemental analysis and weight gain showed 1.38–1.86 mmol g⁻¹ ligand loading. The results are listed in Table 1.

Characterization of the Supported Cyclopalladated Complexes 1a-e and 2a-c

A decrease in surface area was found after immobilizing the ligands and the metal ions on the polymer support. It was might due to blocking of the pores after supporting the ligands

and the metal ions. Similar results were observed by the Ram group.^[36,37] All the supported catalysts were found to be thermo stable up to 150 °C and not sensitive to oxygen and moisture. The cyclopalladated complexs might be formed according to the literature.^[34,35] The metal center might be stabilized by the five-member ring. Formation of the cyclopalladated complexes was also proved by the C=N double bond in IR spectrum (shift to lower wave numbers) and the decreased percentage of C, H and N in the elemental analysis. The Pd loadings of the supported catalysts were determined by ICP-OES. The results showed that the Pd loading of the supported catalysts was 0.18–0.44 mmol g⁻¹. The results are listed in Table 2.

The Catalytic Heck Reaction between Idiobenzene and Butyl Arcylate

First, the Heck reactions of iodobenzene with *n*-butyl acrylate catalyzed by catalysts 1 or 2 were examined in a number of solvents, such as DMF, CH₃CN, 1,4-dioxane, toluene, THF, etc. Of all solvents tested, DMF was found to be the best one. In the catalyzed coupling reaction of iodonenzene with *n*-butyl acrylate, all of the tested catalysts showed good activities. The results are listed in Table 3. It was found that the catalysts with the electron-donating group had the higher catalytic activity (entries 1-5, 1c > 1d > 1a> 1b > 1e). The catalysts 2 with ferrocene group showed much better catalytic effect than the catalysts 1. Especially for 2b and 2c (entries 7 and 8), their turnover frequencies (TOF) were increased to 12600 and 10600, respectively. This was probably because of the high electron atmosphere of the ferrocene. In addition, the performance of the recovered catalyst was also evaluated after a simple separation from the reaction mixture without any further treatment. The catalytic results using recovered catalyst indicated that the synthesized catalysts could be re-used at least five times, although the catalytic reactivity decreased gradually (entries 9–13). This obvious decrease in catalytic performance may

		$I + CH_2 = CHCO_2C_4H_9 - \frac{Et_3N,DMF}{Cat.}$		O₂C₄H ₉	
Entry	Catalyst	Catalyst loading (10 ⁻⁴ mmol)	<i>t</i> (h)	Conversion (%) ^b	TOF ^c
1	1a	2.31	7	95	3000
2	1b	3.40	10	93	1400
3	1c	2.63	5	100	3800
4	1d	2.23	7	100	3300
5	1e	3.31	15	100	1000
6	2a	0.92	7	100	5400
7	2b	0.53	7.5	100	12600
8	2c	0.43	11	100	10600
9	Entry 3 cycle 1	2.63	7	100	2700
10	cycle 2	2.63	19	100	1000
11	cycle 3	2.63	26	100	730
12	cycle 4	2.63	32	100	590
13	cycle 5	2.63	55	100	350

Reaction conditions: Phl (5 mmol), Et₃N (6 mmol), *n*-butyl acrylate (6 mmol), DMF (1 ml).

^b Determined by GC.

^c TOF, turnover frequency (mol product per mol catalyst h⁻¹).

Table 4.	Fable 4. Heck reaction of anyl bromide with butyl acrylates in DMF catalyzed by 2b ^a					
	Br + CH ₂ =CHCO ₂ Bu	Et ₃ N DMF Cat 140°C	► R H H CO ₂ Bu			
Entry	Catalyst (10 ⁻² mmol Pd)	R	<i>t</i> (h)	Conversion (%) ^b		
1	2b (1.8)	Н	24	81		
2	2b (1.8)	o-NO ₂	24	92		
3	2b (1.2)	m-NO ₂	24	88		
4	2b (1.6)	p-NO ₂	24	83		
5	2b (2.0)	p-CH ₃	24	55		
^a Reactio ^b Determ	n conditions: aryl bromide (5 mmol), Et ₃ N (6 mmol), <i>n</i> -butyl acry iined by GC.	late (6 mmol), D	DMF (1 ml).			

be due to the loss of the active Pd species. After five cycles, 5.2 wt% of the overall Pd loss was observed.

In order to increase the range of substrates, we investigated the catalytic activity of **2b** for the Heck reaction between aryl bromide and butyl acrylate. The results are listed in Table 4. It shows that, in the presence of **2b**, the Heck reaction between aryl bromide and butyl acrylate could proceed smoothly. However, the catalytic activity was lower compared with the reaction between iodobenzene and *n*-butyl acrylate.

Conclusion

In conclusion, new kinds of supported palladium catalysts have been synthesized for the Heck coupling reaction. The synthesized catalysts exhibited excellent activity in the Heck reactions between iodobenzene and *n*-butyl arcylate with TOF numbers up to $12600 h^{-1}$. It was found that high electron atmosphere could increase the catalytic activiy. The resulting catalyst **2b** could catalyze the reaction between aryl bromide and butyl arcylate efficiently. Moreover, the catalysts could be recovered by a simple filtration progress. They could also be reused for at least five times with a slow progressive decrease in activity.

Acknowledgments

We are grateful for the financial support from the National Natural Science Foundation of China (grant 20372059) and the Doctoral Foundation of Henan Institute of Engineering (D09002). We also thank Zong-Pei Zhang for the element analysis.

References

- [1] A. M. Trzeciak, J. J. Zió3kowski, Coord. Chem. Rev. 2005, 249, 2308.
- [2] J. G. deVries, Dalton Trans. 2006, 421.
- [3] N. T.S. Phan, M. V.D. Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609.
- [4] V. Polshettiwar, Á. Molnár, Tetrahedron 2007, 63, 6949.
- [5] I. P. Beletskaya, A. V. Cheprakov, Chem. Rev. 2000, 100, 3009.
- [6] A. B. Donnay, L. E. Overman, Chem. Rev. 2003, 103, 2945.

- [7] F. Alonso, I. P. Beletskaya, M. Yus, Tetrahedron 2005, 61, 11771.
- [8] C. S. Consorti, M. L. Zanini, S. Leal, G. Ebeling, J. Dupont, Org. Lett. 2003, 5, 983.
- [9] T. Schultz, N. Schmees, A. Pfaltz, Appl. Organomet. Chem. 2004, 18, 595.
- [10] Z. C. Xiong, N. D. Wang, M. J. Dai, A. Li, J. H. Chen, Z. Yang, Org. Lett. 2004, 6, 3337.
- [11] K. Takenaka, Y. Uozumi, Adv. Synth. Catal. 2004, 346, 1693.
- [12] T. Mino, Y. Shirae, Y. Sasai, M. Sakamoto, T. Fujita, *J. Org. Chem.* **2006**, *71*, 6834.
- [13] S. Li, Y. J. Lin, H. B. Xie, S. B. Zhang, J. N. Xu, Org. Lett. **2006**, *8*, 391.
- [14] W. X. Chen, C. J. Xi, K. Yang, Appl. Organomet. Chem. 2007, 21, 641.
- [15] H. Li, Y. J. Wu, C. Xu, R. Q. Tian, *Polyhedron* **2007**, *26*, 4389.
- [16] A. A. Bello da Silva, A. L.F. de Souza, O. A.C. Antunes, Appl. Organomet. Chem. 2008, 22, 2.
- [17] F. Y. Zhao, B. M. Bhanage, M. Shirai, M. Arai, Chem. Eur. J. 2000, 5, 6.
- [18] A. Biffis, M. Zecca, M. Basato, J. Mol. Catal. A. 2001, 173, 249.
- [19] Y. Uozumi, Y. Nakai, Org. Lett. **2002**, *4*, 2997.
- [20] A. Dahan, M. Portnoy, Org. Lett. 2003, 5, 1197.
- [21] A. Datta, K. Ebert, H. Plenio, Organometallics 2003, 22, 4685.
- [22] Y. Cui, L. Zhang Y. Li, Polym. Adv. Technol. 2005, 16, 633.
- [23] Y. Kobayashi, D. Tanaka, H. Danjo, Y. Uozumi, Adv. Synth. Catal. 2006, 348, 1561.
- [24] L. X. Yin, J. Liebscher, Chem. Rev. 2007, 107, 133.
- [25] G. Z. Fan, S. Q. Cheng, M. F. Zhu, X. L. Gao, Appl. Organomet. Chem. 2007, 21, 670.
- [26] S. Schweizer, J. M. Becht, C. Le Drian, Org. Lett. 2007, 9, 3777.
- [27] S. M. Sarkar, M. N. Alam, M. R. Miah, React. Kinet. Catal. Lett. 2009, 96. 175.
- [28] M. N. Alam, S. M. Sarkar, M. R. Miah, React. Kinet. Catal. Lett. 2009, 98, 383.
- [29] A. F. Grandsirea, C. Labordeb, F. Lamatyb, A. Mehdia, Appl. Organomet. Chem. 2009, DOI: 10.1002/aoc.1566.
- [30] R. B. Bedford, C. S.J. Cazin, M. B. Hursthouse, M. E. Light, K. J. Pike, S. Wimperis, J. Organomet. Chem. 2001, 633, 173.
- [31] A. Corma, D. Das, H. García, A. Leyva, J. Catal. 2005, 229, 322.
- [32] J. M.J. Frechet, G. Pelle, J. Chem. Soc. 1975, 225.
- [33] G. M. Blackburn, M. J. Brown, M. P. Harris, J. Chem. Soc. 1969, 676.
- [34] Y. J. Wu, S. Q. Huo, J. F. Gong, X. L. Cui, K. L. Ding, C. X. Du, Y. H. Liu,
- M. P. Song, J. Organomet. Chem. **2001**, 637-639, 27. [35] Y. J. Wu, J. J. Hou, H. Y. Yun, X. L. Cui, R. J. Yuan, J. Organomet. Chem.
- 2001, 637-639, 793. [36] D. T. Gokak, B. V. Kamath,; R. N. Ram, J. Appl. Polym. Sci. 1988, 35,
- 1523. [37] D. R. Patel,; M. K Dalal.; R. N. Ram, J. Mol. Cat. A: Chem. **1996**, 109, 141.