A novel Heck reaction catalyzed by Co hollow nanospheres in ligand-free condition†

Ping Zhou, Yingguang Li, Peipei Sun,* Jiahong Zhou and Jianchun Bao*

Heck reaction catalyzed by cobalt hollow nanospheres has been developed; the coupling of alkenes with aryl iodide or aryl bromide in the presence of potassium carbonate provides the corresponding products with moderate to good yields, which reveals obvious advantages such as low-cost catalyst, ligand-free condition, the recyclability of the catalyst and simple experimental operation.

The Heck reaction of aryl halides has recently been one of the most intensively studied transition-metal catalyzed C–C bond forming reactions.[1] The reaction has been applied to many areas, including natural products[2] and fine chemicals syntheses.[3] Usually aryl halides are reacted with alkenes in the presence of palladium and a suitable base. Soluble palladiums, generally phosphine palladium complexes are the most efficient catalysts for the Heck reaction. The main role of tertiary monophosphine ligands is to stabilize palladium(0) as the PdL_4 species, which can enter the catalytic cycle and consequently prevent the formation of inactive palladium black.[4] Although the phosphine–palladium catalysts are well established, providing excellent results in many respects, some obvious drawbacks of phosphine–palladium catalysts are that most phosphine ligands are expensive and also, generally toxic and unstable, *e.g.*, air- and moisture-sensitive. Efforts have recently been made to develop new catalysts to replace phosphine ligands, which also allow the use of other aryl derivatives. These new catalysts include palladacycles,[5] N-heterocyclic carbine (NHC)–palladium catalysts,[6] and a macrocyclic recoverable triolefin complex.[7] The Heck reaction on aryl iodides and bromides is best performed using very low loadings of palladium acetate[8] or with palladacycles[9] that show comparable reactivity. There are also some reports for the Heck reaction on aryl chlorides, in which palladium complexes based on bulky basic phosphine ligands or carbenes are the best choice.[10] A few cobalt(II) catalyzed Heck reactions have also been reported, these include the presence of phosphine ligands[11] or an electrochemical method.[12]

Transition-metal nanoparticles have attracted a great deal of attention in the last 10 years, especially for catalyzing the formation reaction of carbon–carbon bonds.[13] Their preparation, structure determination, and applications are topics of current interest. The smaller the cluster of atoms, the higher the percentage of atoms are on the surface, rendering nanoparticles very

interesting in catalysis.[14] Palladium hollow spheres with diameters of about 300 nm were prepared by using silica spheres as templates, and these showed good catalytic activities in Suzuki coupling reactions and could be reused several times by simple filtering and retrieving without loss of catalytic activity.[15] In our previous works, PdCo bimetallic hollow nanospheres were synthesized in poly(ethylene glycol) solution and applied successfully to catalyze the Sonogashira reaction.[16] The high surface area of the hollow spheres resulting from the nanoparticulate nature of the shell, which is much larger than that of dense spheres of the same diameter, is responsible for the high catalytic activity. In recent years, palladium nanoparticles of different origin have been utilized in the Heck arylation of unsubstituted acrylates and styrene with variable degrees of success.[13,17] Up to now, the catalysts for Heck reaction were mainly focused on costly palladium. To our knowledge, there is no report of the use of metallic cobalt as catalyst in Heck reaction.

In our recent research, cobalt hollow nanospheres were, for the first time, prepared by a wet chemical method and used to catalyze the Heck reaction with a good result (Scheme 1).

Fig. 1 shows the typical TEM image of cobalt hollow nanospheres prepared by reaction of $CoSO_4 \cdot 7H_2O$ with $NaBH_4$ in poly(ethylene glycol) solution. As can be seen from the image, the pale coloured regions in the central parts, in contrast to dark edges, imply a hollow spherical structure. The unchanged contrast
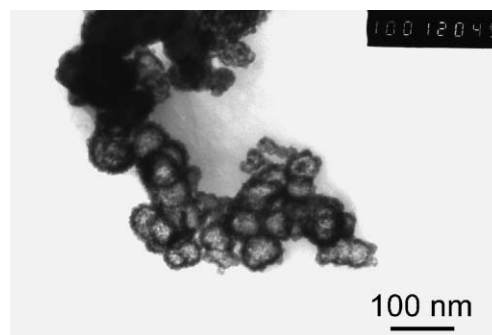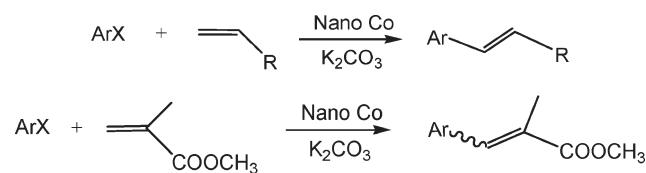

Scheme 1

Fig. 1   TEM image of cobalt hollow nanospheres.

College of Chemistry and Environmental Science, Nanjing Normal University, Nanjing, 210097, P. R. China.
E-mail: sunpeipei@njnu.edu.cn; baojianchun@njnu.du.cn;
Fax: +86 25 83598280
† Electronic supplementary information (ESI) available: Details of experimental procedures and spectra data of the products. See DOI: 10.1039/b617556b
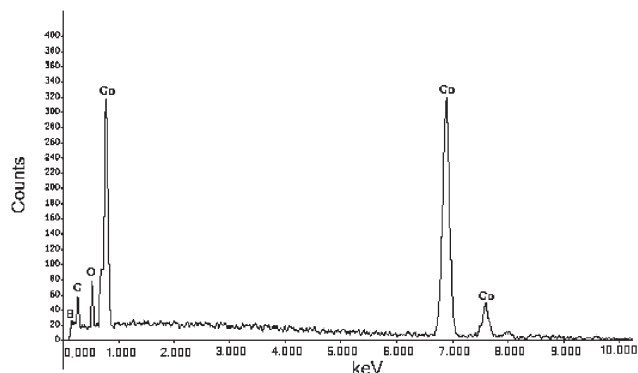
Fig. 2 EDS image of cobalt hollow nanospheres.

difference between the center and edge in the TEM image of one sphere obtained when the sample grid is rotated by different degrees further proves their hollow structures. The average diameter of the hollow spheres is about 50 nm with this mainly ranging from 50 to 60 nm, and the shell thickness is about 10 nm. The corresponding electron diffraction analysis of the hollow nanospheres was carried out indicating that they are noncrystalline. Further evidence comes from the analysis of XRD of the sample, which shows that the sample is poorly crystalline or amorphous.

In order to further identify the samples, energy-dispersive spectrometry (EDS, Fig. 2) analysis was also carried out. This revealed that the hollow spheres are composed of cobalt and minor amount of boron which came from BH_4^- during the reduction of Co^{2+} ions. Also, carbon and oxygen were found in the EDS analysis, meaning a small amount of poly(ethylene glycol) existing in the sample. To the best of our knowledge, this is the first example of Co hollow spheres prepared using a wet chemical method (such hollow nanostructures have not been reported previously). It is noteworthy that, according to TEM observation, the amount of the hollow nanospheres in the nanoparticles is more than 70% under the typical reaction conditions using the present simple, rapid and economical method.

The results of the cobalt hollow nanospheres catalyzed Heck reaction are shown in Table 1. The most obvious advantage of this method is that no ligand was needed. This metallic cobalt catalyzed reaction gave the corresponding products with moderate to good yields. The experiment indicated that 2 mol% of catalyst could catalyze the reaction sufficiently. Solvents such as *p*-xylene, *N*,*N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) were employed as reaction media. The results showed that the nonpolar solvent *p*-xylene was not effective to this reaction. In DMF, it gave a low yield while in NMP the best results were achieved. The appropriate temperature was 130 °C. A basic environment was also important for the Heck reaction: almost all reports and our experiment showed this feature. As general bases, Na_2CO_3, K_2CO_3, NaOH and KOH were tested and K_2CO_3 was found to be the best, and was therefore selected as the base for our research. The catalyst showed high activity in the Heck coupling of iodoarenes as well as bromoarenes. Aromatic chloro compounds were found to be of low activity for the reaction (entry 3) but high regioselectivity could be achieved with the reactants such as 1-chloro-4-iodobenzene and 1-chloro-2-iodobenzene. For the reaction of monosubstituted olefins

Table 1 The couplings of aryl halides with alkenes[a]

Entry	Aryl halide	Alkene	Time/h	Yield[b] (%)
1	⟨phenyl⟩–I	$COOC_2H_5$	14	78
2	⟨phenyl⟩–Br	$COOC_2H_5$	16	68
3	⟨phenyl⟩–Cl	$COOC_2H_5$	20	20
4	H_3C–⟨phenyl⟩–I	$COOC_2H_5$	10	85 (83, 85, 82)[c]
5	H_3C–⟨phenyl⟩–Br	$COOC_2H_5$	12	70
6	H_3C–⟨phenyl, meta⟩–I	$COOC_2H_5$	12	82
7	⟨phenyl, ortho-CH_3⟩–I	$COOC_2H_5$	14	84
8	Cl–⟨phenyl⟩–I	$COOC_2H_5$	10	83
9	⟨phenyl, ortho-Cl⟩–I	$COOC_2H_5$	14	78
10	⟨phenyl⟩–I	$COOCH_3$	16	73
11	H_3C–⟨phenyl⟩–I	$COOCH_3$	11	77
12	H_3C–⟨phenyl, meta⟩–I	$COOCH_3$	14	80
13	Cl–⟨phenyl⟩–I	$COOCH_3$	12	76
14	H_3C–⟨phenyl⟩–I	$COOCH_3$, CH_3	13	75
15	H_3C–⟨phenyl, meta⟩–I	$COOCH_3$, CH_3	15	74

[a] Aryl halide (1 mmol), alkene (1.3 mmol), K_2CO_3 (0. 6 mmol), Co (0.02 mmol) in 2 mL NMP at 130 °C with stirring for an appropriate time. [b] Isolated yields. [c] The catalyst was reused three times.

(acrylates), complete *E* configuration was observed; while in the arylation of 1,1-disubstituted olefin (methacrylate, entries 14, 15), only internal olefins were separated, different from the palladium catalyzed reaction reported by Calo *et al.*[17a] in which isomerized products were generated. Aryl halides with both electron-donating and electron-withdrawing groups showed no obvious difference in reactivity.

Recovery and catalyst reuse are important issues in the Heck coupling. Easy catalyst separation and recycling in successive batch operations can greatly increase the efficiency of the reaction. Thus we studied the reuse possibility of this catalyst and it was shown that the stability of this catalyst makes the recycling process feasible. The catalyst could be reused after being centrifuged and separated from the solution and washed sufficiently with methanol and diethyl ether. After reuse for three times, the catalytic activity

did not decrease obviously. In these processes, there is no obvious agglomeration of the nanoparticles.

In conclusion, we have prepared hollow cobalt nanospheres for the first time by using a direct solution-phase approach and successfully used this catalyst in the Heck coupling of iodo and bromoarenes with olefins. More importantly, the catalyst is cheaper compared to the palladium catalysts and no ligand was needed. The application of this new catalyst in organic synthesis will be expanded. Such work is under way in our laboratory.

Notes and references

1 (a) R. F. Heck, *Acc. Chem. Res.*, 1979, **12**, 146; (b) R. F. Heck, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 4, p. 833; (c) W. A. Herrmann, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinhem, 1996, p. 712; (d) W. Cabri and I. Candiani, *Acc. Chem. Res.*, 1995, **28**, 2; (e) I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009.

2 For examples, see: (a) J.-M. Gaudin, *Tetrahedron Lett.*, 1991, **32**, 6113; (b) L. E. Overman, D. J. Ricca and V. D. Tran, *J. Am. Chem. Soc.*, 1993, **115**, 2042; (c) L. F. Tietze and W. Buhr, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1366.

3 For examples, see: (a) R. R. Bader, P. Baumeister and H. U. Blaser, *Chimia*, 1996, **50**, 99; (b) T. C. Wu, *US Pat.*, 5536870, 1996; (c) A. Eisenstadt, in *Catalysis of Organic Reactions*, ed. F. E. Herkes, Marcel Dekker, New York, 1998.

4 (a) T. Mino, Y. Shirae, Y. Sasai, M. Sakamoto and T. Fujita, *J. Org. Chem.*, 2006, **71**, 6834; (b) G. Zou, W. Huang, W. J. Xiao and J. Tang, *New J. Chem.*, 2006, **30**, 803.

5 (a) J. Dupont, M. Pfeffer and J. Spencer, *Eur. J. Inorg. Chem.*, 2001, 1917; (b) R. B. Bedford, *Chem. Commun.*, 2003, 1787.

6 (a) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (b) R. B. Bedford, C. S. J. Cazin and D. Holder, *Coord. Chem. Rev.*, 2004, **248**, 2283; (c) D. J. Nielsen, K. J. Cavell, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 2006, **359**, 1855; (d) C. Tubaro, A. Biffis, C. Gonzato, M. Zecca and M. Basato, *J. Mol. Catal. A: Chem.*, 2006, **248**, 93; (e) R. Wang, B. Twamley and J. M. Shreeve, *J. Org. Chem.*, 2006, **71**, 426.

7 J. Masllorens, M. Moreno-Manas, A. Pla-Quintana and A. Roglans, *Org. Lett.*, 2003, **5**, 1559.

8 (a) M. T. Reetz, E. Westermann, R. Lohmer and G. Lohmer, *Tetrahedron Lett.*, 1998, **39**, 8449; (b) M. T. Reetz, G. Lohmer and R. Schwickardi, *Angew. Chem., Int. Ed.*, 1998, **37**, 481; (c) A. H. M. de Vries, J. M. C. A. Mulders, J. H. M. Mommers, H. J. W. Henderickx and J. G. de Vries, *Org. Lett.*, 2003, **5**, 3285; (d) N. E. Leadbeater, *Chem. Commun.*, 2005, 2881.

9 (a) G. D. Frey and W. A. Herrmann, *J. Organomet. Chem.*, 2005, **690**, 5876; (b) G. D. Frey, J. Schutz, E. Herdtweek and W. A. Herrmann, *Organometallics*, 2005, **24**, 4416; (c) C. Najera and L. Botella, *Tetrahedron*, 2005, **61**, 9688; (d) C. M. Frech, L. J. W. Shimon and D. Milstein, *Angew. Chem., Int. Ed.*, 2005, **44**, 1709.

10 (a) A. F. Littke and G. C. Fu, *J. Org. Chem.*, 1999, **64**, 10; (b) K. Selvakumar, A. Zapf and M. Beller, *Org. Lett.*, 2002, **4**, 3031; (c) D. Gelman and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2003, **42**, 5993.

11 (a) W. Affo, H. Ohmiya, T. Fujioka, Y. Ikeda, T. Nakamura, H. Yorimitsu, K. Oshima, Y. Imamura, T. Mizuta and K. Miyosh, *J. Am. Chem. Soc.*, 2006, **128**, 8068; (b) Y. Ikeda, T. Nakamura, H. Yorimitsu and K. Oshima, *J. Am. Chem. Soc.*, 2002, **124**, 6514.

12 (a) P. Gomes, C. Gosmini, J. Y. Nedelec and J. Perichon, *Tetrahedron Lett.*, 2002, **43**, 5901; (b) P. Gomes, C. Gosmini and J. Perichon, *Tetrahedron*, 2003, **59**, 2999.

13 M. Moreno-Manas and R. Pleixats, *Acc. Chem. Res.*, 2003, **36**, 638.

14 A. Roucoux, J. Schulz and H. Patin, *Chem. Rev.*, 2002, **102**, 3757.

15 S. W. Kim, M. Kim, W. Y. Lee and T. Hyeon, *J. Am. Chem. Soc.*, 2002, **124**, 7642.

16 Y. G. Li, P. Zhou, Z. H. Dai, Z. X. Hu, P. P. Sun and J. C. Bao, *New J. Chem.*, 2006, **30**, 832.

17 (a) V. Calo, A. Nacci, A. Monopoli, A. Detomaso and P. Iliade, *Organometallics*, 2003, **22**, 4193; (b) M. A. R. Meier, M. Filali, J. F. Gohy and U. S. Schubert, *J. Mater. Chem.*, 2006, **16**, 3001; (c) L. K. Yeung and R. M. Crooks, *Nano Lett.*, 2001, **1**, 14; (d) K. R. Gopidas, J. K. Whitesell and M. A. Fox, *Nano Lett.*, 2003, **3**, 1757.