CSIRO PUBLISHING

Aust. J. Chem. **2015**, *68*, 926–930
http://dx.doi.org/10.1071/CH14332

Full Paper

A Green Approach for Copper-Free Sonogashira Reaction of Aryl Halides with Phenylacetylene in the Presence of Nano-Pd/Phosphorylated Silica (SDPP/Pd^0)

Nasser Iranpoor,[A,B] *Habib Firouzabadi,*[A,B] *Somayeh Motevalli,*[A]
and Khashayar Rajabi[A]

[A]Department of Chemistry, Shiraz University, Shiraz, 71454, Iran.
[B]Corresponding authors. Email: iranpoor@susc.ac.ir; firouzabadi@susc.ac.ir

Silicadiphenyl phosphinite (SDPP) is used as the solid support for the generation of nano SDPP/Pd(0) from Pd^{II} as pre-catalyst. This nano catalyst was used for the efficient copper-free Sonogashira reaction of aryl halides in PEG-200 as a solvent. The nano Pd(0) that can be used as pre-prepared or as in situ-generated catalyst exhibited excellent reactivity and stability in the Sonogashira cross-coupling reactions with different aryl iodides, bromides, and also chlorides. This heterogeneous catalyst can be easily recovered and reused in several runs. The use of PEG as solvent and K_2CO_3 as inorganic base together with the heterogeneous nature of the reaction can be considered as green conditions for this reaction.

Manuscript received: 29 May 2014.
Manuscript accepted: 4 September 2014.

Introduction

One of the most straightforward methods for the preparation of aryl alkynes and conjugated enynes is the palladium-catalyzed coupling of terminal alkynes with aryl or alkenyl halides that was described for the first time by Sonogashira et al. in 1975.[1] The most common competitive pathway as side reaction that can affect the efficiency and yield of the Sonogashira coupling is homocoupling of the alkynes to diynes (Glaser-type coupling).[2] Hence, since 1992, for the cross-coupling reaction of alkynes with aryl- or vinyl-halides, several improvements have been reported. One of the most important solutions from industrial points of concern is efficient copper-free Sonogashira reaction in the presence of homogeneous catalytic systems.[3] CuI can induce homocoupling reactions of terminal alkynes to diynes in the presence of oxygen.[2] Though these examples contributed to the improvement of the Sonogashira reaction, the use of homogeneous Pd catalysts has several drawbacks, in particular, its limited thermal stability, the precipitation of palladium black, which limits the lifetime of the active species, and problems associated with catalyst recycling. This leads to a loss of expensive metal and ligands, formation of impurities in the products, and the need to remove residual metals.[4] To overcome these problems, heterogeneous catalysts have been developed for the Sonogashira cross-coupling reactions.[5] Chemists have made considerable achievements in heterogeneous catalysis and, recently, nanocatalysis.[6] Heterogeneous catalysts supported on a solid support, such as CNs,[7] metal oxides mainly silica,[8] clays,[9] organic polymers, such as polymeric *N*-heterocyclic carbene ligand-grafted silica,[10] and gelatin[11] and agarose as bioorganic supports,[12] have found considerable synthetic applications. In continuation of our studies on heterogeneous catalysis based on nano palladium supported on silica for C–C bond formation,[13] we herein report the excellent efficiency, stability, and recyclability of nano Pd(0)/SDPP catalyst in the Sonogashira cross coupling reaction with different aryl iodides, bromides, and also chlorides.

Results and Discussion

Preparation of the Catalyst

The Pd(0) metal complex of silicadiphenyl phosphinite (SDPP), Pd(0)$\{PPh_2O\text{-}SiO_2\}_n$, was prepared according to our previous report.[13] We have shown that P atoms are coordinated initially to the Pd^{II} centre, followed by the reduction to Pd(0) by another phosphinite group, and eventually the active Pd(0) catalyst as a black insoluble mass is obtained. According to inductively coupled plasma (ICP) analysis of several samples on the digested catalyst in refluxing aqueous HCl (37 %), a Pd content of 2.5–27 mmol per 1 g of Pd immobilized on SDPP was obtained. The scanning electron microscopy (SEM) image shows particles with diameters in the nanometer scale as presented in Fig. 1. Further information about the size of the Pd particles was obtained by transmission electron microscopy (TEM) analysis of the catalyst that showed that Pd nanoparticles (size: 7 nm) formed and dispersed in the silica matrix (Fig. 2). As observed from the X-ray diffraction (XRD) pattern, the Pd catalyst shows the (111), (200), (220), (311), and (222) crystallographic planes of the Pd(0) nanoparticles (Fig. 3). The Pd nanoparticle size from the XRD pattern was estimated to be 8 nm which is in good agreement with the results obtained from TEM (Fig. 2) and histogram (Fig. 4) analysis.

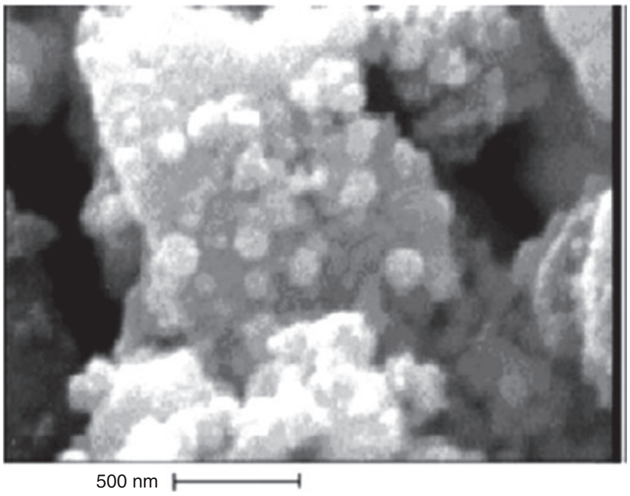


Fig. 1. Scanning electron microscopy (SEM) image of Pd-supported SDPP.[13]

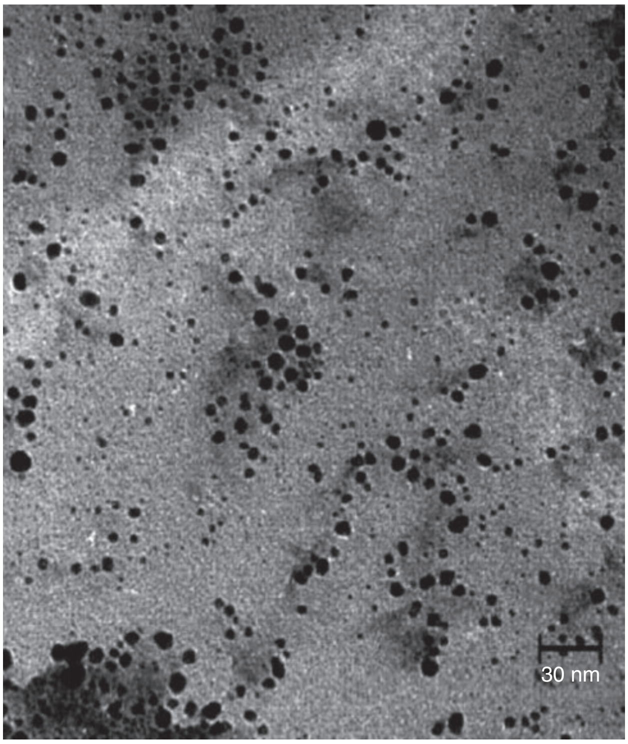


Fig. 2. Transmission electron microscopy (TEM) image of Pd-supported SDPP.[13]

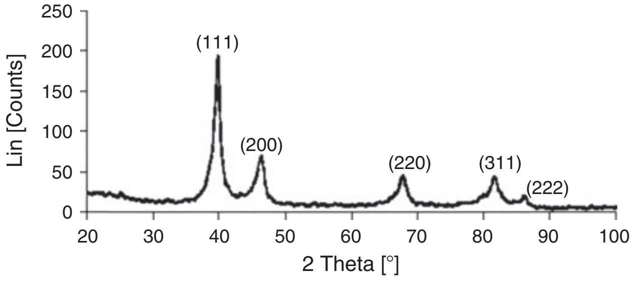


Fig. 3. X-Ray diffraction pattern of Pd-supported SDPP.[13]

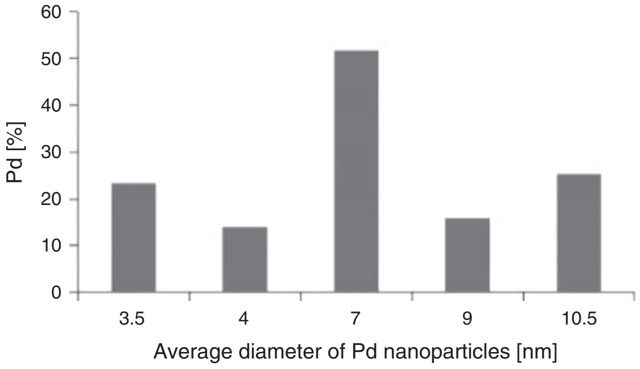


Fig. 4. Pd size histogram of Pd-doped SDPP based on the TEM image.[13]

Table 1. Study of different parameters on the reaction of iodobenzene and phenylacetylene[A]

Entry	Solvent	Base [mmol]	Temperature [°C]	Time [h]	Conversion [%][B]
1	None	n-Pr_3N	130	20	70
2	NMP	NaOH	130	6	75
3	NMP	K_2CO_3	130	4.25	100
4	NMP	NaOAc	130	5.5	100
5	NMP	Cs_2CO_3	130	2.5	100
6	NMP	Morpholine	130	4	100
7	NMP	Morpholine	80	20	95
8	TBAB	K_2CO_3	80	20	50
9	EtOH	K_2CO_3	80	20	80
10	PEG 200	K_2CO_3	80	20	90
11	PEG 200	NaOH	80	20	60
12	PEG 200	Morpholine	80	20	45
13	PEG 200	n-Pr_3N	80	20	73
14	PEG 200	K_2CO_3	100	3	100
15	PEG 200	Cs_2CO_3	100	20	70
16[C]	PEG 200	K_2CO_3	100	2	100
17[C]	PEG 200	K_2CO_3	100	1	100
18[D]	PEG 200	K_2CO_3	100	20	80

[A] Reaction conditions: iodobenzene (0.5 mmol), phenylacetylene (0.75 mmol), base (0.75 mmol), catalyst (0.001 mg, 0.5 mol-%), solvent (1 mL).
[B] Conversion based on gas chromatography analysis.
[C] The amounts of catalyst Pd(0)/SDPP used in entries 16 and 17 are 0.002 g (1 mol-%) and 0.003 (1.5 mol-%), respectively.
[D] Applied catalysts: Pd(0)/SDPP (0.001 g, 0.5 mol-%) and CuI (0.002 g).

Catalytic Activity of the Catalyst in C–C Coupling Reaction

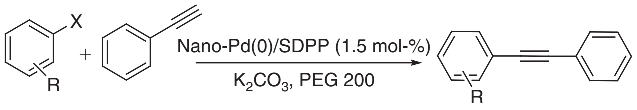
In order to examine the efficiency of SDPP-supported nanoparticles of palladium as the catalyst, we decided to further our studies on the Sonogashira reaction.

Preliminary screening was performed to compare different systems in the Sonogashira reaction using different solvents and bases as well as by changing the reaction temperature for the reaction of iodobenzene with phenylacetylene as a model reaction. Under solvent-free conditions, 130°C, and n-Pr_3N (n-tripropylamine) as an amine base, the reaction was not completed after 20 h and the conversion yield was only 70 % (Table 1, entry 1). Then, the effect of various solvents was investigated. In *N*-methylpyrrolidone (NMP), as a polar aprotic solvent, this reaction was examined in the presence of different inorganic and organic bases using 0.001 g Pd(0)/SDPP at 130°C. The results obtained in this solvent are shown in Table 1, entries

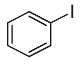
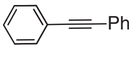
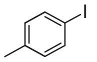
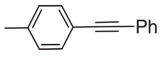
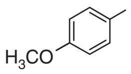
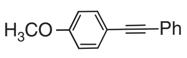
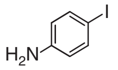
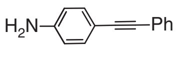
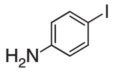
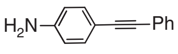
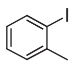
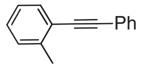
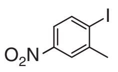
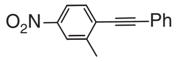
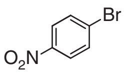
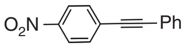
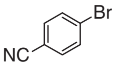
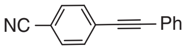
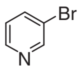
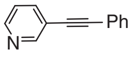
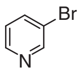
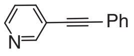
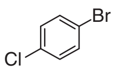
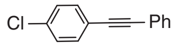
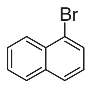
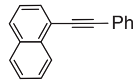
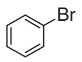
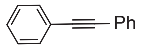
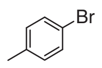
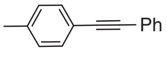
2–6. Decreasing the temperature from 130 to 80°C in the presence of morpholine as the base and NMP as the solvent, 95 % conversion of the starting material within 20 h was observed (Table 1, entry 7). The catalyst was inefficient when it was used in ethanol (EtOH) and/or molten tetrabutylammonium bromide (TBAB) using K_2CO_3 as a base at 80°C (Table 1, entries 8 and 9). The cross-coupling reaction was also screened in polyethylene glycol (PEG) by using different organic and inorganic bases at 80°C. According to the literature,[14] PEG is regarded as a green solvent because it has several benign characteristics, for example, low molecular weight liquid PEGs are non-volatile and the vapour density for such PEGs is greater than 1 relative to air according to available MSDS data, and is consistent with the industry standard for replacement of volatile organic solvents with PEG. [14] PEG also has low flammability and is biodegradable. In order to have green conditions for the reaction, PEG 200 was selected. The use of n-Pr_3N, morpholine, NaOH, and Cs_2CO_3 was less efficient in comparison with the use of K_2CO_3 as a base at 80°C (Table 1, entries 10–13, 15). We therefore selected K_2CO_3 as the most appropriate base. Hence, the reaction progressed very well at 100°C within 3 h (Table 1, entry 14). In all the above-performed reactions, the amount of palladium supported on SDPP was 0.001 g (0.5 mol-%). When the catalyst amount increased from 0.001 to 0.002 and 0.003 g, the reaction time decreased from 3 to 2 and 1 h, respectively (Table 1, entries 16, 17). The effect of CuI on the reaction was also investigated. When CuI was used as the co-catalyst in the Sonogashira reaction, the reaction proceeded achieving 80 % conversion after 20 h (Table 1, entry 18). Hopefully, the use of Pd(0)/SDPP provides a very suitable condition for conducting the reaction in the absence of copper by using K_2CO_3 as a cheap and available inorganic base in PEG as a green solvent.

Applying the optimized conditions i.e. 0.003 g (1.5 mol-%) Pd(0)/SDPP, 0.75 mmol phenylacetylene, 0.75 mmol K_2CO_3, 1.0 mL PEG 200, a variety of aryl iodides and activated aryl bromides at 100°C, and also less reactive and deactivated aryl bromides and chlorides at 120°C were examined. The results are illustrated in Table 2. Iodobenzene and iodobenzenes substituted with an electron-donating group at the *para*-position were applied in this cross-coupling reaction, and the starting materials were completely converted into the coupled products (Table 2, entries 1–3, 5). In the case of nitro compounds, the dehalogenated products were also observed in the mixture of the reaction. The product of cross-coupling of 2-iodo-5-nitrotoluene with phenylacetylene was obtained in moderate yields after 1.5 h. (Table 2, entry 7). Remarkably, the catalytic system was also efficient for the aryl bromides. The coupling of 1-bromo-4-nitrobenzene and 4-bromobenzonitrile with phenylacetylene produced the desired product within 5 and 2 h, respectively. Probably the elongation of the reaction time for 1-bromo-4-nitrobenzene relates to its reduced solubility in PEG 200 (Table 2, entries 8 and 9). Heterocyclic bromides, such as 3-bromopyridine and 3-bromothiophene, led to the corresponding bi-functionalized acetylene in desirable yields at 120°C (Table 2, entries 11 and 16). The Sonogashira reaction of 4-chlorobromobenzene produced the coupled product in good yields with high selectivity (Table 2, entry 12). The reaction between the sterically hindered 1-bromonaphthalene and phenylacetylene was not completed after 11 h and gave the desired product in 58 % yield (Table 2, entry 13). Complete conversion was obtained for the reaction of bromobenzene and 4-bromotoluene with phenylacetylene, affording good yields (Table 2, entries 14 and 15). The coupling reaction of *ortho*-substituted iodotoluene and

Table 2. Sonogashira reaction of phenylacetylene with selected organic halides[A]

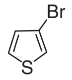
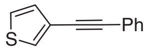
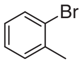
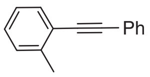
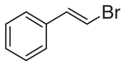
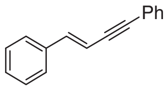
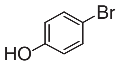
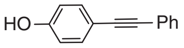
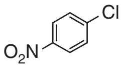
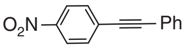
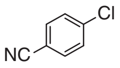
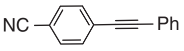
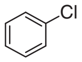
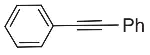
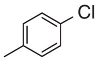
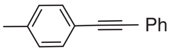


X: I, Br, Cl, CH:CH-Br (R: H)
R: H, OCH_3, CH_3, NO_2, OH, NH_2, Cl, CN

Entry	Substrate	Product	Temperature [°C]	Time [h]	Yield[B] [%]
1			100	1.5	95
2			100	2.5	91
3			100	2.5	91
4			100	20	53
5			120	5	73
6			100	4	90
7			100	1.5	65
8			100	5	81
9			100	2	58
10			100	28	49
11			120	4	83
12			120	5	78
13			120	11	58
14			120	3	72
15			120	6	72

(*Continued*)

Table 2. (Continued)

Entry	Substrate	Product	Temperature [°C]	Time [h]	Yield[B] [%]
16			120	6	71
17			120	7	72
18			120	5.5	64
19			120	4	70
20			120	7.5	75
21			120	15	51
22			120	15	83
23			120	15	74

[A] Reaction conditions: aryl halide (0.5 mmol), phenylacetylene (0.75 mmol), K_2CO_3 (0.75 mmol), Pd(0)/SDPP (1.5 mol-%, 0.003 g), PEG 200 (1.0 mL) at 100°C for aryl iodides and 120°C for aryl bromides and chlorides.

[B] Isolated yield.

[C] Products are known compounds.[14–23]

bromotoluene with phenylacetylene produced the desired products in excellent isolated yields (Table 2, entries 6 and 17). We applied our protocol for the reaction of β-bromostyrene, a vinylic bromide, and phenylacetylene under similar reaction conditions. The reaction proceeded well within 5.5 h (64 %) in PEG 200 (Table 2, entry 18). The catalytic system was efficient for the coupling reaction of 4-bromophenol and phenylacetylene at 120°C after 4 h to give the corresponding product in 70 % yield (Table 2, entry 19). The coupling reaction of 1-chloro-4-nitrobenzene with phenylacetylene gave the product in good yields (Table 2, entry 20). However, the reaction of 4-chlorobenzonitrile with phenylacetylene produced the desired product in moderate yields together with any unidentified side product (Table 2, entry 21). The coupling reaction of chlorobenzene and 4-chlorotoluene with phenylacetylene was performed at 120°C. The desired products were obtained in very good yields (Table 2, entries 22 and 23).

Heterogeneity Test and Catalyst Reusability Test

The recoverability of the catalyst was examined for the reaction of iodobenzene with phenylacetylene. After completion of the reaction, the catalyst was recovered and used in eight successive cycles. During this experiment, the Pd catalyst exhibited only a slight loss in activity and required a slightly longer time in the eighth run to achieve full conversion. The results are shown in Table 3. This investigation showed the excellent recyclability of the catalyst in the Sonogashira reaction.

Table 3. Recycling of Pd catalyst for the Sonogashira reaction of idobenzene and phenylacetylene[A]

Run	Time [h]	Isolated yield [%]	TON[B]	TOF[C] [min^{-1}]
1	1.5	95	61	0.7
2	1.5	95	61	0.7
3	1.5	93	60	0.66
4	1.6	92	59	0.61
5	1.6	93	60	0.63
6	1.8	90	58	0.53
7	2.2	87	56	0.42
8	2.5	74	47	0.31

[A] Reaction conditions: iodobenzene (0.5 mmol), phenylacetylene (0.75 mmol), K_2CO_3 (0.75 mmol), Pd(0)/SDPP (1.5 mol-%, 0.003 g), and PEG 200 (1 mL) at 100°C.

[B] TON (turn over number) = mmol of products/mmol of catalyst.

[C] TOF (turn over frequency) = TON/time.

Conclusions

In this work, SDPP (silicadiphenyl phosphinite) as the solid support for the generation of nano SDPP/Pd(0) from Pd^{II} has been used for the efficient copper-free Sonogashira reaction of aryl halides in PEG-200 as a green solvent. The obtained SDPP can be used as a stable solid to immobilize nanoparticles of Pd (0). The introduced catalyst can be used efficiently for the coupling of aryl iodides, bromides, and chlorides. The recyclability of the catalyst can also be regarded as an advantage of this method.

Experimental

X-Ray diffraction data were collected on D8 Advance Bruker AXS. TEM analyses were performed on a Philips CM 10 instrument. SEM images were obtained on a Philips XL-30 FEG scanning electron microscope operating at 20 kV. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX-250 MHz spectrometer using tetramethylsilane as internal standard. For gas chromatography analysis of the reaction mixture, *n*-heptane was used as internal reference to calculate the conversion yield.

Synthesis of Pd(0)/SDPP Nanocatalyst

The catalyst was prepared according to our previous report[13] with modification as follows. To a 50 mL round bottom flask, 56 mg (0.25 mmol) $Pd(OAc)_2$ and 0.1 g SDPP in 10 mL DMF were added, and the mixture was heated at 90–100°C for 2 h. The reaction mixture was allowed to cool and then centrifuged at 2.236 g for 5 min. The resulting black powder was washed with ethyl acetate (5 × 5 mL) and distilled water (5 × 5 mL) and centrifuged at 2.236 g for 5 min after each wash. Finally, it was dried under vacuum to give 0.12 g Pd(0)/SDPP catalyst. The content of palladium(0) was determined by ICP to be 2.6 mmol per 1 g.

General Procedure for the Sonogashira Coupling Reaction of Aryl Halides and Phenylacetyene in the Presence of Pd(0)/SDPP

A round-bottom flask was charged with phenylacetylene (0.75 mmol, 0.08 mL), K_2CO_3 (0.75 mmol, 100 mg), PEG 200 (1 mL), and aryl halide (0.5 mmol). To this mixture, Pd(0) nano-catalyst supported on SDPP (1.5 mol-%, 3.0 mg) prepared according to our previous report[13] was added. In the case of aryl iodides and activated aryl bromides, the reaction mixture was placed in a 100°C oil bath; and in the case of the less active and deactivated aryl bromides and chlorides, the reaction mixture was placed in a 120°C oil bath. After completion of the reaction, the catalyst was removed by centrifugation and the remaining mixture was extracted with ethyl acetate (3 × 10 mL) and water several times and dried over anhydrous Na_2SO_4. The organic layer was evaporated under reduced pressure, and then purified by column chromatography over silica gel 60 (230–240 mesh; Merck) using petroleum ether/ethyl acetate (5 : 1) as eluent to afford the product with high purity in 51–95 % yield. Note: This procedure can also be used, but the catalyst is prepared in situ by adding the appropriate amounts of SDPP and $Pd(OAc)_2$.

General Procedure for Recycling of the Catalyst

The reaction mixture of the Sonogashira reaction between iodobenzene and phenyl acetylene was cooled to room temperature, and water/ethyl acetate (1 : 1) was added to the reaction mixture. After centrifuging at 2.236 g for 5 min the reaction mixture and separating the upper phase, SDPP/Pd(0) catalyst remained at the bottom of the vessel. The obtained catalyst was washed with ethyl acetate to dissolve any residual organic materials. Then, the recovered catalyst was used in eight successive cycles.

Supplementary Material

Spectral data of the products are available on the Journal's website.

Acknowledgements

We would like to acknowledge the support of this work by Shiraz University Research Council and a grant from Iran National Elite Foundation.

References

[1] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467. doi:10.1016/S0040-4039(00)91094-3

[2] P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2632. doi:10.1002/1521-3773(20000804)39:15<2632::AID-ANIE2632>3.0.CO;2-F

[3] (a) A. Jutand, S. Ńegri, A. Principaud, *Eur. J. Inorg. Chem.* **2005**, 631. doi:10.1002/EJIC.200400413
(b) B. Liang, M. Dai, J. Chen, Z. Yang, *J. Org. Chem.* **2005**, *70*, 391. doi:10.1021/JO048599Z
(c) M. Alami, F. Ferri, G. Linstrumelle, *Tetrahedron Lett.* **1993**, *34*, 6403. doi:10.1016/0040-4039(93)85056-3
(d) V. P. W. Böhm, W. A. Herrmann, *Eur. J. Org. Chem.* **2000**, 3679. doi:10.1002/1099-0690(200011)2000:22<3679::AID-EJOC3679>3.0.CO;2-X
(e) M. Pal, K. Parasuraman, S. Gupta, K. R. Yeleswarapu, *Synlett.* **2002**, 1976. doi:10.1055/S-2002-35587
(f) X. Fu, S. Zhang, Y. Yin, D. Schumacher, *Tetrahedron Lett.* **2002**, *43*, 6673. doi:10.1016/S0040-4039(02)01447-8
(g) D. A. Alonso, C. Ńajera, M. C. Pacheco, *Tetrahedron Lett.* **2002**, *43*, 9365. doi:10.1016/S0040-4039(02)02335-3
(h) D. A. Alonso, C. Ńajera, M. C. Pacheco, *Adv. Synth. Catal.* **2003**, *345*, 1146. doi:10.1002/ADSC.200303067
(i) N. Sakai, K. Annaka, T. Konakahara, *Org. Lett.* **2004**, *6*, 1527. doi:10.1021/OL036499U
(j) G. Zhang, *Synlett* **2005**, 619. doi:10.1055/S-2005-863720

[4] L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133. doi:10.1021/CR0505674

[5] (a) M.-J. Jin, D.-H. Lee, *Angew. Chem., Int. Ed.* **2010**, *49*, 1119. doi:10.1002/ANIE.200905626
(b) M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet, F.-X. Felpin, *Adv. Synth. Catal.* **2010**, *352*, 33. doi:10.1002/ADSC.200900765
(c) B.-N. Lin, S.-H. Huang, W.-Y. Wu, C.-Y. Mou, F.-Y. Tsai, *Molecules* **2010**, *15*, 9157. doi:10.3390/MOLECULES15129157

[6] (a) V. Ponec, G. C. Bond, *Catalysis by Metals and Alloys*, in Studies in Surface Science and Catalysis (Ed. G. Centi) **1995** Vol. 95 (Elsevier: Amsterdam).
(b) G. C. Bond, *Heterogeneous Catalysis: Principles and Applications* **1987** (Oxford Science Publications, Clarendon Press: Oxford).
(c) *Handbook of Heterogeneous Catalysis* (Eds G. Ertl, H. Knözinger, J. Weitkamp) **1997** (Wiley-VCH: Weinheim).
(d) R. J. Farauto, C. H. Bartholomew, *Fundamentals of Industrial Catalytic Processes* **1997** (Blackie Academic and Professional: London).
(e) J. M. Thomas, W. J. Thomas, *Principle and Practice of Heterogeneous Catalysis* **1997** (Wiley-VCH: Weinheim).
(f) C. R. Henry, *Appl. Surf. Sci.* **2000**, *164*, 252. doi:10.1016/S0169-4332(00)00344-5
(g) T. P. St Clair, D. W. Goodman, *Top. Catal.* **2000**, *13*, 5. doi:10.1023/A:1009020502894
(h) M. Bowker, R. A. Bennet, A. Dickinson, D. James, R. Smith, P. Stone, *Stud. Surf. Sci. Catal.* **2001**, *133*, 3. doi:10.1016/S0167-2991(01)81946-7
(i) M. Králik, A. Biffis, *J. Mol. Catal. A: Chem.* **2001**, *177*, 113. doi:10.1016/S1381-1169(01)00313-2
(j) J. Thomas, R. Raja, *Chem. Rec.* **2001**, *1*, 448. doi:10.1002/TCR.10003
(k) C. Mohr, P. Claus, *Sci. Prog.* **2001**, *84*, 311. doi:10.3184/003685001783238925
(l) J. M. Thomas, B. F. G. Johnson, R. Raja, G. Sankar, P. A. Migley, *Acc. Chem. Res.* **2003**, *36*, 20. doi:10.1021/AR990017Q
(m) O. Alexeev, B. C. Gates, *Ind. Eng. Chem. Res.* **2003**, *42*, 1571. doi:10.1021/IE020351H

[7] M. Navidi, N. Rezaei, B. Movassagh, *J. Organomet. Chem.* **2013**, *743*, 63. doi:10.1016/J.JORGANCHEM.2013.06.021

[8] P. Veerakumar, M. Velayudham, K.-L. Lu, S. Rajagopal, *Appl. Catal., A* **2013**, *455*, 247. doi:10.1016/J.APCATA.2013.01.021

[9] V. Singh, R. Ratti, S. Kaur, *J. Mol. Catal. Chem.* **2011**, *334*, 13. doi:10.1016/J.MOLCATA.2010.10.015

[10] B. Tamami, F. Farjadian, S. Ghasemi, H. Allahyari, *New J. Chem.* **2013**, *37*, 2011. doi:10.1039/C3NJ41137K

[11] H. Firouzabadi, N. Iranpoor, A. Ghaderi, *Org. Biomol. Chem.* **2011**, *9*, 865. doi:10.1039/C0OB00253D

[12] H. Firouzabadi, N. Iranpoor, F. Kazemi, M. Gholinejad, *J. Mol. Catal. Chem.* **2012**, *357*, 154. doi:10.1016/J.MOLCATA.2012.02.006

[13] N. Iranpoor, H. Firouzabadi, S. Motevalli, M. Talebi, *J. Organomet. Chem.* **2012**, *708–709*, 118. doi:10.1016/J.JORGANCHEM.2012.03.006

[14] J. Chen, S. K. Spear, J. G. Huddleston, R. D. Rogers, *Green Chem.* **2005**, *7*, 64. doi:10.1039/B413546F

[15] M. Carril, A. Correa, C. Bolm, *Angew. Chem., Int. Ed.* **2008**, *47*, 4862. doi:10.1002/ANIE.200801539

[16] N. Satish Kumar, K. P. Kumar, K. V. P. P. Kumar, P. Kommana, J. J. Vittal, K. C. K. Swamy, *J. Org. Chem.* **2004**, *69*, 1880. doi:10.1021/JO035634D

[17] F. Yang, X. Cui, Y.-N. Li, J. Zhang, G.-R. Ren, Y. Wu, *Tetrahedron* **2007**, *63*, 1963. doi:10.1016/J.TET.2006.12.064

[18] H. Kawanami, K. Matsushima, M. Sato, Y. Ikushima, *Angew. Chem., Int. Ed.* **2007**, *46*, 5129. doi:10.1002/ANIE.200700611

[19] J.-C. Hierso, J. Boudon, M. Picquet, P. Meunier, *Eur. J. Org. Chem.* **2007**, 583. doi:10.1002/EJOC.200600976

[20] J. Gil-Moltó, C. Nájera, *Adv. Synth. Catal.* **2006**, *348*, 1874. doi:10.1002/ADSC.200606033

[21] M. Feuerstein, H. Doucet, M. Santelli, *J. Mol. Catal. Chem.* **2006**, *256*, 75. doi:10.1016/J.MOLCATA.2006.04.059

[22] P. Sun, H. Yan, L. Lu, D. Liu, G. Rong, J. Mao, *Tetrahedron* **2013**, *69*, 6969. doi:10.1016/J.TET.2013.06.063

[23] M. Hosseini-Sarvari, Z. Razmi, M. M. Doroodmand, *Appl. Catal., A* **2014**, *475*, 477. doi:10.1016/J.APCATA.2014.02.002