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Pd(II) salen complex covalently anchored to multi-walled carbon nanotubes as a heterogeneous and reusable precatalyst for Mizoroki–Heck and Hiyama cross-coupling reactions†

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A Pd(II) salen complex anchored to multi-walled carbon nanotubes showed excellent catalytic activity and stability for the Mizoroki–Heck and Hiyama cross-couplings of aryl halides with olefins and phenylsiloxanes. Furthermore, the heterogeneous catalyst could be reused up to four times with the catalytic activity being recovered easily after simple manipulations. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: cross-coupling reactions; Mizoroki–Heck reaction; Hiyama reaction; palladium salen complex; heterogeneous catalysis

Introduction

The use of Schiff base complexes containing transition metal ions is of significant importance due to their catalytic and biological properties.[1] Recently, there has been considerable interest in exploring the catalytic activities of transition metals covalently anchored to carbon nanotubes (CNTs) owing to their specific catalytic applications compared to homogeneous complexes. Also, functionalization of CNTs is an effective way to enhance their physical and chemical properties, and improve the solubility. Metal nanoparticles and various transition metal complexes such as porphyrins and polymers have been used for the functionalization of CNTs.[2] Transition metal Schiff base complexes have shown excellent catalytic activity when grafted on CNTs.[3]

Transition metal-catalysed cross-coupling reactions to form a new carbon–carbon (C_{sp2}–C_{sp2}) bond have been recognized as powerful synthetic tools and a major area of interest in multiple organic transformations for academic and industrial processes.[4] The palladium-catalysed coupling of aryl halides with olefins (the Mizoroki–Heck reaction) or aryltrialkoxysilanes (Hiyama cross-coupling) is a powerful tool for the preparation of various substituted olefins and biaryls. The former reaction has been used in the synthesis of natural products, agrochemicals and pharmaceuticals,[5] and the products of the latter reaction have found widespread applications as organocatalysts,[6] agrochemicals,[6] organic materials for organic light-emitting diodes[6] and pharmaceutically active compounds.[6] Unlike other carbon–carbon coupling reactions, the Mizoroki–Heck reaction has the ability to tolerate a variety of functional groups such as ketone, aldehyde, amino, cyano, carbonyl, hydroxyl, ester, or nitro groups, thus avoiding the need for protection and deprotection of functional groups during organic transformations.[4,7] The catalytic system for an efficient Heck reaction consists of a palladium source, ligand, base and solvent. Usually, phosphane[8] and phosphorus[9] ligands are used in the Mizoroki–Heck reaction, as they play an important role in stabilization and *in situ* generation of Pd(0) species from Pd(II) complexes. Because of the high cost, toxicity and thermal instability of phosphine ligands, various phosphane-free catalytic systems[10] have been introduced as less complicated and environmentally more desirable alternatives to the original Pd–phosphane catalysts. However most of them show poor efficiency and reusability in palladium-catalysed Mizoroki–Heck reactions.[11] Moreover, a major restriction on palladium-catalysed coupling processes has been the poor reactivity of cheaper and more readily available aryl bromides and chlorides in comparison with more active aryl iodides. Therefore, the search for efficient catalysts for the cross-coupling of olefins with deactivated aryl bromides and, eventually, activated aryl chlorides is under way.

The most efficient methodologies for the construction of biaryls are the palladium-catalysed cross-coupling transformations between aryl halides and organometallic species. Among the various organometallic coupling reagents, the organoboranes (Suzuki–Miyaura),[12,13] organostannanes (Stille)[14] and organosilanes (Hiyama)[15] are the most commonly employed partners because of

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comparable excellent yields, high stereoselectivities and wide functional group tolerances. However, the toxicity of tin reagents in Stille couplings, and difficulties in the preparation and purification of organoboranes are disadvantages. On the other hand, organosilanes (Hiyama) are easily prepared, environmentally benign and stable agents under many reaction conditions.[15,16]

Experimental

General

All melting points were determined using a Büchi B-540 melting point apparatus. IR spectra were recorded with an ABB Bomem model FTLA 2000 spectrophotometer using KBr pellets. NMR spectra were recorded at 300 (^{1}H) and 75 (^{13}C) MHz with a commercial Bruker AQS-300 instrument using $CDCl_3$ as solvent. Solvents and all chemicals were purchased from Merck and Aldrich and were used as received. Aryltrialkoxysilanes were prepared from bromobenzene and tetraethoxysilanes/tetramethoxysilanes following a literature report.[17]

Catalyst Synthesis

Ligand and catalyst were synthesized following a procedure reported in our previous work,[18] which is briefly explained in the following paragraphs.

Synthesis of Schiff base ligand

A mixture of salicylaldehyde and 1,3-diamino-2-propanol in a 2:1 ratio and absolute ethanol were heated to reflux until the completion of the reaction. The yellow precipitate was separated, washed with diethyl ether and dried in vacuum to obtain the desired Schiff base. M.p. 100–102 °C. IR (KBr): $\nu_{C=N}$ 1632 cm^{-1}.

Palladium complex synthesis

A solution of the ligand in acetonitrile was magnetically stirred followed by addition of $PdCl_2$ salt (ligand-to-$PdCl_2$ ratio =1:1). The reaction mixture was refluxed for 1 h. The product (Pd(II)-Salen) was filtered off, washed with diethyl ether and dried in vacuum as a yellow solid. M.p. 250 °C (dec.). IR (KBr): $\nu_{C=N}$ 1615 cm^{-1}.

Preparation of Pd(II) salen complex anchored to multi-walled carbon nanotubes (Pd-Salen@MWCNTs)

Purchased MWCNTs–CO_2H (200 mg) were chlorinated using thionyl chloride (50 ml) in *N*,*N*-dimethylformamide (DMF; 2 ml) at 65 °C for 24 h. The solid was then separated by filtration and washed with anhydrous tetrahydrofuran (THF; 60 ml), and dried in vacuum to obtain MWCNTs–COCl. Then, MWCNTs–COCl (100 mg) were added to a solution of the previously prepared Pd(II)-Salen (200 mg) in degassed $CHCl_3$ (16 ml), and the suspension was refluxed for 20 h under nitrogen. The solid was then filtered and washed with THF (2 × 20 ml) and CH_2Cl_2 (2 × 20 ml) and dried in vacuum to afford the desired catalyst. The catalyst was characterized using attenuated total reflection infrared spectroscopy (ATR), Raman spectroscopy, inductively coupled plasma (ICP), X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy and thermogravimetric–differential thermal analysis data. The ATR spectrum of the catalyst showed a band at 1708 cm^{-1} associated with C=O stretching of the ester linkage between the CNT and the Schiff base complex. Moreover, the metal content of the complex was found to be 16.2 ppm using ICP, and the ratio of Pd/N in the catalyst was obtained to be 1.82%.

General Procedure for Mizoroki–Heck Coupling Reaction

A mixture of aryl halide (1.0 mmol), alkene (1.1 mmol), triethylamine (1.1 mmol), DMF (1 ml) and the catalyst (0.006 mmol, 0.6 mol% Pd) was stirred at 130 °C under atmospheric conditions. (For aryl bromides or chlorides, tetrabutylammonium bromide (TBAB; 1.0 mmol) was also added.) The progress of the reaction was monitored using TLC. After completion of the reaction, the mixture was cooled to room temperature, poured into water (10 ml) and extracted with $CHCl_3$ (3 × 10 ml). The combined organic extracts were washed with brine (2 × 10 ml), dried (Na_2SO_4) and concentrated in vacuum. The crude product was further purified by preparative TLC (silica gel) using *n*-hexane–EtOAc (9:1) to afford the desired product. The products were characterized using IR, ^{1}H NMR and ^{13}C NMR spectroscopies (see supporting information).

General Procedure for Hiyama Coupling Reaction

The catalyst (5.3 mg, 0.8 mol% Pd) was added to a solution of aryl halide (1 mmol), phenyltrialkoxysilane (1.5 mmol) and tetrabutylammonium fluoride (TBAF·3H_2O; 631 mg, 2 mmol) in toluene (2 ml). The reaction mixture was heated to 90 °C under atmospheric conditions. The progress of the reaction was monitored using TLC. After completion, the reaction mixture was cooled to room temperature, and the solvent was evaporated. Then EtOAc (10 ml) was added to the reaction mixture, and the catalyst was recovered with centrifugation. The organic layer was washed with water (2 × 5 ml), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuum. The crude product was further purified by preparative TLC (silica gel) using *n*-hexane as eluent to afford the desired product. The products were characterized using IR, ^{1}H NMR and ^{13}C NMR spectroscopies (see supporting information).

General Procedure for Recycling of Catalyst

The reaction mixture of either Mizoroki–Heck or Hiyama reaction was cooled to room temperature and the catalyst was separated from the reaction mixture by centrifugation, washed with water and $CHCl_3$ and dried in vacuum at 70 °C for 24 h before being used in subsequent reactions.

Results and Discussion

Recently, stabilization of Pd(II) complexes on high-surface-area materials and their use in Mizoroki–Heck and Hiyama cross-coupling reactions have been reported.[19] We previously developed air-/moisture-stable and reusable Pd-Salen@MWCNTs (Fig. 1) as an efficient heterogeneous catalyst in the Suzuki–Miyaura and Sonogashira–Hagihara reactions,[18] and in the solvent-free synthesis of ynones.[18] In this paper, we extend the scope of this catalytic system to coupling of aryl halides (iodides, bromides and chlorides) with various olefins (Mizoroki–Heck reaction) and aryl iodides or

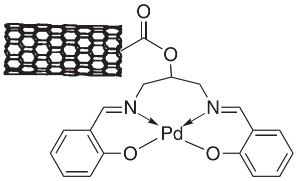
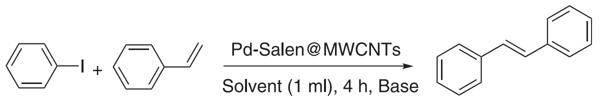


Figure 1. Heterogeneous Pd-Salen@MWCNTs catalyst.

Table 1. Optimization of reaction conditions[a]



Entry	Base	Solvent	Temperature (°C)	Amount of catalyst (mol% Pd)	Yield (%)[b]	TON
1	Et_3N	DMF	25	0.6	17	28
2	Et_3N	DMF	60	0.6	25	42
3	Et_3N	DMF	90	0.6	47	78
4	Et_3N	DMF	115	0.6	87	145
5	**Et_3N**	**DMF**	**130**	**0.6**	**95**	158
6	Et_3N	DMF	140	0.6	91	152
7	Et_3N	DMAc	130	0.6	84	140
8	Et_3N	NMP	130	0.6	78	130
9	Et_3N	DMSO	130	0.6	73	122
10	Et_3N	H_2O	80	0.6	No reaction	—
11	Et_3N	Neat	130	0.6	82	137
12	DIPEA	DMF	130	0.6	76	127
13	KO^tBu	DMF	130	0.6	40	67
14	K_2CO_3	DMF	130	0.6	46	77
15	Et_3N	DMF	130	0.4	58	145
16	Et_3N	DMF	130	0.6	85	142
17	Et_3N	DMF	130	0.8	85	106
18	Et_3N	DMF	130	1.0	81	81

[a] Reaction conditions: iodobenzene (1 mmol), styrene (1.1 mmol), base (1.1 mmol), solvent (1 ml) at various temperatures under air.

[b] Isolated yields.

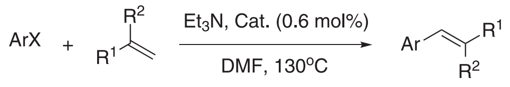
bromides with phenylsiloxanes (Hiyama reaction) under aerobic conditions and examine its reusability.

Optimized conditions for the Mizoroki–Heck coupling reaction were obtained using the reaction of iodobenzene (1 mmol) and styrene (1.1 mmol) in the presence of the catalyst under various atmospheric conditions (Table 1). The reaction rates are markedly dependent on the solvent, base and temperature, as well as the concentration of the palladium complex. Various organic and inorganic bases were screened, and the yield of the products is reduced when inorganic bases such as KO^tBu or K_2CO_3 are employed (Table 1, entries 13 and 14). A considerable increase in product formation is observed in the presence of organic bases, such as triethylamine, in DMF at a high temperature. Several other solvents, including dimethylacetamide (DMAc), *N*-methylpyrrolidin-2-one (NMP), dimethylsulfoxide (DMSO) and water, as well as neat condition were also surveyed under similar conditions, but compared with DMF all give inferior results (Table 1, entries 7–11). Then, various amounts of catalyst between 0.4 and 1.0 mol% were investigated for the reaction (Table 1, entries 5, 15–18). Among the various amounts, 0.6 mol% of the catalyst is found to be the best (Table 1, entry 5). Therefore, it was decided to use Et_3N as the base and DMF as solvent at 130 °C in the presence of 0.6 mol% of the catalyst as the optimal conditions in further studies.

The resulting optimized conditions were then applied to the coupling reactions of activated, nonactivated or deactivated aryl halides **1** with various vinylic substrates **2** in DMF/Et_3N at 130 °C in the presence of 0.6 mol% of the catalyst (Table 2). The results show that the catalyst is remarkably active and tolerates a range of functional groups. As expected, the reaction of aryl iodides proceeds smoothly within 0.25 to 2 h to give the desired products in 82–95% isolated yield (Table 2, entries 1–5, 7–9). However, the reaction of sterically hindered 2-iodoanisole with styrene gives a lower yield (Table 2, entry 6). Under these same conditions, coupling of bromobenzene with styrene gives a poor yield (26%) after 24 h (Table 2, entry 10); therefore, TBAB (1 equiv.) was added to the reaction mixture for the cross-coupling of aryl bromides or chlorides with alkenes. A variety of aryl bromides bearing electron-donating and electron-withdrawing groups were examined. Activated aryl bromides, such as 4-bromobenzonitrile, 1-bromo-4-nitrobenzene and 4-bromobenzaldehyde, coupled rapidly in high to excellent yields (Table 2, entries 16–18). The Mizoroki–Heck cross-coupling of chlorobenzene with styrene and 4-methoxystyrene was also investigated under similar reaction conditions (Table 2, entries 21 and 22). Compared with the corresponding bromo analogues, the reaction of the chloro derivatives gives poor yields and requires longer times.

In continuation of this study, we also applied the catalyst to the Hiyama cross-coupling reaction of aryl halides with phenyltrialkoxysilanes. Initially, the coupling of iodobenzene (1 mmol) and phenyltriethoxysilane (1.5 mmol) in the presence of TBAF·$3H_2O$ (2 mmol) and the catalyst in air was chosen as a model reaction to determine the optimum reaction conditions (Table 3). The effect of

Table 2. Reaction of various aryl halides with olefins in the presence of the catalyst in DMF[a]



1 **2** **3**

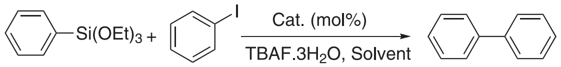
Entry	ArX	R^1	R^2	Product	Time (h)	Yield (%)[b]	TON
1	PhI	Ph	H	**3a**	0.25	95	158
2	PhI	$4\text{-}MeOC_6H_4$	H	**3b**	1.5	83	138
3	PhI	$4\text{-}ClC_6H_4$	H	**3c**	1.5	82	137
4	PhI	CN	H	**3d**	2	87	145
5	$4\text{-}MeOC_6H_4I$	Ph	H	**3b**	2	91	152
6	$2\text{-}MeOC_6H_4I$	Ph	H	**3e**	2	70	117
7	1-I-naphthalene	Ph	H	**3f**	2	83	138
8	$4\text{-}MeC_6H_4I$	CO_2Me	H	**3 g**	2	90	150
9	2-I-thiophene	CO_2Bu	H	**3 h**	0.5	92	153
10	PhBr	Ph	H	**3a**	24	26	43
11	PhBr	Ph	H	**3a**[c]	5	85	142
12	PhBr	$4\text{-}MeOC_6H_4$	H	**3b**[c]	6	76	127
13	PhBr	CO_2Et	H	**3i**[c]	4	87	145
14	PhBr	CN	H	**3d**[c]	4.5	80	133
15	$4\text{-}MeC_6H_4Br$	Ph	Me	**3j**[c]	6	79	132
16	$4\text{-}NCC_6H_4Br$	Ph	H	**3k**[c]	3	89	148
17	$4\text{-}O_2NC_6H_4Br$	Ph	H	**3l**[c]	3	93	155
18	$4\text{-}OHCC_6H_4Br$	Ph	H	**3m**[c]	5	88	147
19	1-Br-naphthalene	Ph	H	**3f**[c]	7	81	135
20	1-Br-naphthalene	CO_2Et	H	**3n**[c]	5	84	140
21	PhCl	Ph	H	**3a**[c]	24	23	38
22	$4\text{-}MeCOC_6H_4Cl$	Ph	H	**3o**[c]	24	15	25
23	$4\text{-}O_2NC_6H_4Cl$	Ph	H	**3l**[c]	24	37	62
24	$4\text{-}NCC_6H_4Cl$	Ph	H	**3k**[c]	24	29	48

[a] Reaction conditions: aryl halide (1 mmol), olefin (1.1 mmol), Et_3N (1.1 mmol), Pd-Salen@MWCNTs (0.6 mol%) in DMF (1 ml), 130 °C, under air.

[b] Isolated yields.

[c] TBAB (1 mmol) was added.

Table 3. Optimization of reaction of phenyltriethoxysilane with iodobenzene in the presence of the catalyst[a]



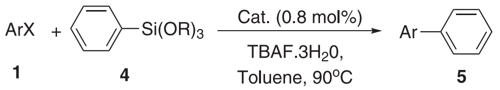
Entry	Solvent	Temperature (°C)	Amount of catalyst (mol% Pd)	Yield (%)[b]	TON
1	THF	50	0.8	47	59
2	—	90	0.8	32	40
3	DMF	100	0.8	64	80
4	DMF	90	0.8	67	84
5	Toluene	25	0.8	26	33
6	Toluene	60	0.8	57	71
7	**Toluene**	**90**	**0.8**	**93**	116
8	Toluene	90	1.0	93	93
9	Toluene	90	0.7	81	115
10	Toluene	90	0.6	77	128
11	Toluene	90	0.4	44	110

[a] Reaction conditions: phenyltriethoxysilane (1.5 mmol), iodobenzene (1 mmol), TBAF.3H$_2$O (2 mmol), Pd-Salen@MWCNTs in solvent (2 ml) at various temperatures.

[b] Isolated yields.

various reaction parameters such as solvent, temperature and catalyst concentration was evaluated. As the results in Table 3 show, toluene is the most suitable solvent for the reaction. Next, various temperatures and amounts of catalyst were screened. Increasing the temperature from 25 °C to higher (60 and 90 °C) leads to a substantial rate acceleration of the reaction (Table 3, entries 5–7). Among the various catalyst amounts, 0.8 mol% of the catalyst is found to be the best (Table 3, entry 7). Therefore, it was decided to use toluene as solvent, 90 °C as temperature and 0.8 mol% of the catalyst as the optimal conditions in further studies.

Table 4. Pd-Salen@MWCNTs-catalysed Hiyama cross-coupling of aryl halides with phenylsiloxanes[a]



Entry	ArX	R	Time (h)	Product	Yield (%)[b]	TON
1	PhI	Et	4	**5a**	93	116
2	2-I-thiophene	Et	4	**5b**	91	114
3	4-MeOC$_6$H$_4$I	Et	7	**5c**	73	91
4	2-MeOC$_6$H$_4$I	Et	8.5	**5d**	66	83
5	2-MeC$_6$H$_4$I	Et	7	**5e**	70	88
6	4-MeCOC$_6$H$_4$I	Et	4.5	**5f**	93	116
7	4-MeC$_6$H$_4$I	Me	5.5	**5g**	82	103
8	1-I-naphthalene	Me	5	**5h**	80	100
9	PhBr	Et	8	**5a**	81	101
10	1,4-Br$_2$C$_6$H$_4$	Et	10	**5j**	74	93
11	4-O$_2$NC$_6$H$_4$Br	Et	8	**5k**	90	113
12	4-NCC$_6$H$_4$Br	Et	9	**5l**	86	108
13	PhCl	Et	24	**5a**	Trace	—
14	4-MeCOC$_6$H$_4$Cl	Et	24	**5f**	Trace	—
15	4-NCC$_6$H$_4$Cl	Et	24	**5l**	Trace	—
16	4-O$_2$NC$_6$H$_4$Cl	Et	24	**5k**	Trace	—

[a] Reaction conditions: aryl halide (1 mmol), phenylsiloxane (1.5 mmol), TBAF.3H$_2$O (2 mmol), and 0.8 mol% of the catalyst in toluene (2 ml) at 90 °C.

[b] Isolated yields.

Table 5. Recycling of catalyst for the reaction of iodobenzene with styrene and phenyltriethoxysilane[a]

Entry	Cycle	Mizoroki–Heck yield (%)[b]	Hiyama yield (%)[b]
1	1	95	93
2	2	93	92
3	3	89	85
4	4	81	78

[a] Reaction conditions were the same as that of Table 2, entry 1 (**3a**) for the Mizoroki–Heck reaction, and Table 4, entry 1 (**5a**) for the Hiyama reaction.

[b] Isolated yields.

To survey the generality of the catalytic protocol, we investigated the reaction using various aryl halides coupled with phenylsiloxanes under the optimized conditions. The results are summarized in Table 4. We examined the electronic and steric effects of various aryl halides bearing electron-releasing and electron-withdrawing groups on the resulting yields and reaction times. As is evident from Table 4, the cross-coupling reactions of aryl iodides and bromides with phenylsiloxanes all proceed smoothly to give the desired products in good to excellent yields. Under the same reaction conditions, aryl chlorides give trace amounts of the corresponding products even after 24 h (Table 4, entries 13 and 14). Generally, compared with the corresponding bromo analogues, the reaction of aryl iodides requires shorter times. The reactions of sterically hindered 2-iodoanisole and 2-iodotoluene with phenyltriethoxysilane give lower yields (Table 4, entries 4 and 5). This catalytic complex was compatible with a wide range of functional groups, such as carbonyl, nitro, cyano and methoxy, on aryl halides.

Finally, the recovery and reusability of the catalyst were investigated using the reaction of iodobenzene with styrene (Heck reaction) and iodobenzene with phenyltriethoxysilane (Hiyama reaction) as representative reactants, in the presence of 0.6 and 0.8 mol%, respectively, of Pd-Salen@MWCNTs in order to study the recyclability of this heterogeneous catalyst. The recycling process was repeated for four cycles with some decrease in the catalytic activity of the catalyst (Table 5).

Another point of great concern for most anchored catalysts is the possibility that some active metal migrates from the solid support to the liquid phase and that this leached metal would become responsible for a significant part of the catalytic activity.[20] In order to determine if leaching was a problem, an experiment was performed with the Mizoroki–Heck coupling reaction of iodobenzene and styrene at 130 °C under air. After 15 min, the catalyst was separated from the reaction mixture, and the amount of the Pd species dissolved into solution caused by leaching was determined using ICP after evaporation of the solution to dryness. The ICP result shows that about 0.8% of the total amount of the original Pd species is lost into solution during the course of the reaction.

Conclusions

Mizoroki–Heck and Hiyama couplings were performed in the presence of the air-/moisture-stable and recyclable Pd-Salen@MWCNTs catalyst. In the presence of this catalyst, aryl iodides and bromides could be coupled with a variety of vinylic substrates in high to excellent yields. This thermally stable catalyst was also used for the Hiyama cross-coupling reaction of aryl halides with phenylsiloxanes. The catalyst shows not only high catalytic activity, but also offers many practical advantages such as thermal stability, oxygen insensitivity and recyclability. The catalyst was reused for four consecutive runs in both reactions with consistent activity. Easy preparation and separation of the catalyst and excellent catalytic performance make it a good heterogeneous system and a useful alternative to other heterogeneous palladium catalysts.

Acknowledgements

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References

[1] a) P. A. Vigoto, V. Peruzzo, S. Tamburini, *Coord. Chem. Rev.* **2012**, *256*, 953; b) A. Garoufis, S. K. Hadjikakou, N. Hadjiliadis, *Coord. Chem. Rev.* **2009**, *253*, 1384; c) R. N. Prabhu, R. Ramesh, *J. Organometal. Chem.* **2012**, *718*, 43; d) A. Dewan, *Bull. Korean Chem. Soc.* **2014**, *35*, 1855; e) K. J. Miller, J. H. Baag, M. M. Abu-Omar, *Inorg. Chem.* **1999**, *38*, 4510; f) P. Liu, X.-J. Feng, R. He, *Tetrahedron* **2010**, *66*, 631; g) N. T. S. Phan, D. H. Brown, P. Styring, *Tetrahedron Lett.* **2004**, *45*, 7915; h) V. Ayala, A. Corma, M. Iglesias, J. A. Rinćon, F. Sánchez, *J. Catal.* **2004**, *224*, 170.

[2] a) J. Guerra, M. A. Herrero, *Nanoscale* **2010**, *2*, 1390; b) J. Jin, Z. Dong, J. He, R. Li, J. Ma, *Nanoscale Res. Lett.* **2009**, *4*, 578; c) H. X. Wu, R. Tong, X. Q. Qiu, H. F. Yang, Y. H. Lin, R. F. Cai, S. X. Qian, *Carbon* **2007**, *45*, 152.

[3] a) M. Salavati-Niasari, M. Bazarganipour, *Appl. Surf. Sci.* **2009**, *255*, 7610; b) M. Salavati-Niasari, M. Bazarganipour, *Transit. Met. Chem.* **2009**, *34*, 605.

[4] a) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009; b) C. E. Tucker, J. G. de Vries, *Top. Catal.* **2002**, *19*, 111; c) R. F. Heck, in *Comprehensive Organic Synthesis*, Vol. 4 (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, p. 833; d) M. Oestrich, *The Mizoroki-Heck Reaction*, 4th edn, Wiley, Chichester, **2009**.

[5] a) G. Ren, X. Cui, E. Yang, F. Yang, Y. Wu, *Tetrahedron* **2010**, *66*, 4022; b) L. F. Tietze, W. Ruhr, *Angew. Chem. Int. Ed.* **1995**, *34*, 1366; c) J. G. de Vries, *Can. J. Chem.* **2001**, *79*, 1086.

[6] a) A. C. Spivey, T. Fekner, S. E. Spey, *J. Org. Chem.* **2000**, *65*, 3154; b) M. E. Matheron, M. Porchas, *Plant Dis.* **2004**, *88*, 665; c) J. N. Moorthy, P. Venkatakrishnan, D.-F. Huang, T. J. Chow, *Chem. Commun.* **2008**, 2146; d) P. Lloyd-Williams, E. Giralt, *Chem. Soc. Rev.* **2001**, *30*, 145.

[7] a) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239; b) R. N. Prabhu, R. Ramesh, *Tetrahedron Lett.* **2012**, *53*, 5961; c) R. F. Heck, *Acc. Chem. Res.* **1979**, *12*, 146.

[8] a) L. L. Hill, J. M. Smith, W. S. Brown, L. R. Moore, P. Guevera, E. S. Pair, J. Porter, J. Chou, C. J. Wolterman, R. Craciun, D. A. Dixon, K. H. Shaughnessy, *Tetrahedron* **2008**, *64*, 6920; b) A. F. Littke, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 6989.

[9] a) R. B. Bedford, S. L. Welch, *Chem. Commun.* **2001**, 192; b) D. Morales-Morales, R. Redón, C. Yung, C. M. Jensen, *Chem. Commun.* **2000**, 1619.

[10] a) A. L. Gottumukkala, J. F. Teichert, D. Heijnen, N. Eisink, S. V. Dijk, C. Ferrer, A. V. D. Hoogenband, A. J. Miannaard, *J. Org. Chem.* **2006**, *71*, 426; b) H. J. Li, L. Wang, *Eur. J. Org. Chem.* **2006**, 5099; c) G. A. Grasa, A. C. Hillier, S. P. Nolan, *Org. Lett.* **2001**, *3*, 1077; d) Z. Zhou, M. Liu, X. Wu, H. Yu, G. Xu, Y. Xie, *Appl. Organometal. Chem.* **2013**, *27*, 562; e) M. Gholinejad, V. Karimkhani, I. Kim, *Appl. Organometal. Chem.* **2014**, *28*, 221; f) S. Mohanty, D. Suresh, M. S. Balakrishna, J. T. Mague, *J. Organometal. Chem.* **2009**, *694*, 2114; g) M. Gholinejad, H. R. Shahsavari, *Inorg. Chim. Acta* **2014**, *421*, 433.

[11] X. Cui, Y. Zhou, N. Wang, L. Liu, Q. X. Guo, *Tetrahedron Lett.* **2007**, *48*, 163.

[12] J. Tsuji, *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*, Wiley, New York, **2004**.

[13] a) X. F. Wu, P. Anbarasan, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* **2010**, 49; b) J. Hassan, M. Sevigon, C. Gozzi, E. Schulz, M. Lemair, *Chem. Rev.* **2002**, *102*, 1359.

[14] a) J. K. Stille, *Angew. Chem. Int. Ed.* **1986**, *25*, 508; b) P. Espinet, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2004**, *43*, 4704.

[15] a) T. Hiyama, *J. Organometal. Chem.* **2002**, 653; b) Y. Hatanaka, T. Hiyama, *J. Org. Chem.* **1998**, *53*, 918.

[16] a) T. Hiyama, in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**, chap. 10; b) T. Nokami, Y. Tomida, T. Kamei, K. Itami, J.-I. Yoshida, *Org. Lett.* **2006**, *8*, 729; c) C. M. So, H. W. Lee, C. P. Lau, F. Y. Kwong, *Org. Lett.* **2009**, *11*, 317; d) K. Cheng, B. Zhao, S. Hu, X.-M. Zhang, C. Qi, *Tetrahedron Lett.* **2013**, *54*, 6211; e) S.-N. Chen, W.-Y. Wu, F.-Y. Tsai, *Tetrahedron* **2008**, *64*, 8164; f) C. Diebold, A. Derible, J.-M. Becht, C. L. Drian, *Tetrahedron* **2013**, *69*, 264; g) E. Alacid, C. Nájera, *Adv. Synth. Catal.* **2006**, *348*, 945.

[17] A. S. Manoso, C. Ahn, A. Soheili, C. J. Handy, R. Correia, W. M. Seganish, P. Deshong, *J. Org. Chem.* **2004**, *69*, 8305.

[18] a) M. Navidi, N. Rezaei, B. Movassagh, *J. Organometal. Chem.* **2013**, *743*, 63; b) M. Navidi, B. Movassagh, S. Rayati, *Appl. Catal. A* **2013**, *452*, 24.

[19] a) A. Modak, J. Mondal, A. Bhaumik, *Green Chem.* **2012**, *14*, 2840; b) A. Modak, J. Mondal, V. K. Aswal, A. Bhaumik, *J. Mater. Chem.* **2010**, *20*, 8099.

[20] a) S. Paul, J. H. Clark, *Green Chem.* **2003**, *5*, 635; b) E. B. Mubofu, J. H. Clark, D. J. Macquarrie, *Green Chem.* **2001**, *3*, 23.

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