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Newly-generated Al(OH)₃-supported Pd nanoparticles-catalyzed Stille and Kumada coupling reactions of diazonium salts, (Het)aryl chlorides

Xing Li, Tingting Zhu, Zhongqi Shao, Yingjun Li, Honghong Chang, Wenchao Gao, Yongli Zhang, Wenlong Wei

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Newly-generated Al(OH)₃-supported Pd nanoparticles-catalyzed Stille and Kumada coupling reactions of diazonium salts, (Het)aryl chlorides

Xing Li,* Tingting Zhu, Zhongqi Shao, Yingjun Li, Honghong Chang, Wenchao Gao, Yongli Zhang and Wenlong Wei*

Department of Chemistry and Chemical Engineering, Taiyuan University of Technology, 79 West Yingze Street, Taiyuan 030024, People's Republic of China.

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ABSTRACT

A ligand-free $Pd/Al(OH)_3$ nano-catalyst which is prepared by one-pot three-component method using $Pd(PPh_3)_4$, tetra (ethylene glycol) and aluminum tri-sec-butoxide exhibits excellent catalytic activity in Stille cross-couplings of (Het)aryl chlorides, arenediazonium tetrafluoroborate salts with phenyltributylstannane, respectively, and Kumada couplings of (Het)aryl chlorides with various Grignard reagents. More importantly, these two processes show excellent functional group compatibility with moderate to good yields and they are also versatile with respect to not only (Het)aryl chlorides, but also diazonium salts, and heteroaryl Grignard reagents. The nano-catalyst could also be recycled and reused **5** times without loss of activity and decrease of yield.

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1. Introduction

The palladium-catalyzed Stille^{1,2} and Kumada^{3,4} crosscoupling reactions represent two of the most versatile tools in modern reliable methods for C-C bond formation. In the past few years, numerous kinds of palladium catalysts have been extensively investigated and some new catalysts are gradually developed which have enabled these two transformations to be applied with better catalytic results. Among these palladium catalysts, although the combination of palladium salts with various ligands provides excellent yields and high turnover numbers,⁵⁷ ligand-free catalysts,^{8,9} especially nano-catalysts are more practical, efficient and promising due to their advantages. Recently, some progresses have been made about them. In terms of the Stille cross-coupling reaction, tremendous attention and efforts have been devoted to developing various nano-catalysts which show enhanced reactivity with low catalyst loadings under mild conditions.¹⁰ Despite the significant progresses and creative efforts, the design and synthesis of versatile palladium nanocatalysts would represent important advances and the development of novel and green methods with wider substrate scope still remain highly desirable. In contrast, few reports on the use of nano-Pd catalysts in Kumada coupling reactions exist.

Although the cross couplings of inert aryl chlorides, which are the most practical aryl halides, can be smoothly accomplished with good results, their application as electrophilic coupling partners still represent a big challenge in nanoparticles palladium-catalyzed cross-couplings. At the same time, the couplings involving heteroaryl chlorides are still limited because the presence of heteroatoms capable of coordinating to the metal center can lead to catalyst inhibition and deactivation which renders the couplings of these heterocycles relatively difficult. Given the practicability of aryl chlorides and the importance of heteroaryl compounds in medicinal chemistry, biological, and material sciences, the development of general, environmentally friendly, and practical protocols for the couplings of aryl and heteroaryl chlorides is still highly demanded.¹¹ In addition, diazonium salts are frequently used as the electrophiles in Pd-catalyzed cross-coupling reactions due to their relatively high reactivity. However, there is no report about nano-palladium-catalyzed Stille coupling reactions of arenediazonium tetrafluoroborate salts to date.



Scheme 1. Preparation of Pd nano-catalyst 1.

Recently, we have reported effective cross couplings of arenediazonium salts using aluminum hydroxide-supported nanopalladium catalyst¹² which was prepared by a simple one-pot three-component method (See Scheme 1). Herein, we will report our efforts in catalyst development for the Stille and Kumada coupling reactions and want to present the efficiency and recovery of the palladium nanoparticles. With the catalyst, a wide range of aromatic substrates, especially including diazonium salts, heteroaryl chlorides and Grignard reagents can afford moderate

63 64 65 Tetrahedron

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to good results under non-anhydrous and C non-degassed M conditions.

2. Results and Discussion

2 Because of the importance of surface area for the catalytic 3 activity, the N₂ sorption analysis of samples prepared by the two 4 methods was done to demonstrate that the preparation methods of 5 the catalyst exerted an important impact on its surface area. As б seen from Figure 1, the BET surface area of the Pd nanoparticles Cat. 1 prepared by one-pot three-component method displayed 7 the large specific surface area of 612 m^2 g⁻¹, a pore volume of 8 1.16 cm^3/g , and an average pore size of 5.89 nm calculated from 9 the adsorption branch using the Barrett-Joyner-Halenda (BJH) 10 model. However, the BET surface area of the catalyst Cat. 2 11 prepared by co-precipitation were smaller than 70 m² g⁻¹ with a 12 pore volume of $0.16 \text{ cm}^3/\text{g}$ and an average pore size of 7.95 nm. 13 Owing to the larger BET surface area and pore volume of the 14 catalyst Cat. 1, it should possess higher catalytic activity. 15 Catalytic activity of the two catalysts was next examined through 16 the Stille coupling of iodobenzene and phenyltributylstannane. 17 The results demonstrated that the Cat. 1 exhibited higher catalytic 18 activity and produced diphenyl in 87% yield, and the Cat. 2 only 19 provided 62% yield under the same reaction conditions. 20



Figure 1. N₂ adsorption/desorption isotherm and the pore size distribution
curve of the catalyst Cat.1 and Cat 2.

Subsequently, we initiated the research by testing a series of 50 solvents for the Stille coupling reaction between chlorobenzene 51 and phenyltributylstannane in the presence of 0.7 mol% 52 Pd(PPh₃)₄-derived catalyst **1** and 1.0 equiv. of K₂CO₃ at 120 °C, 53 and the results are outlined in Table 1. Out of these solvents, 54 DMF showed good catalytic activity and provided the product in 55 80% yield. Unfortunately, DMSO, H₂O, Toluene and CH₃CN led 56 to a significant decrease in the yield (Table 1, entry 5 vs. 1-4). 57 The type of bases had a significant effect on the yield, too. 58 Among the tested bases, K_2CO_3 proved to be the most efficient 59 affording the product in the 80% yield (Table 1, entry 5). Et_3N 60 and NaHCO₃ showed moderate yields (Table 1, entries 8 and 9). 61

However, KOH and K_3PO_4 were totally ineffective (Table 1, entries 6-7). After the effects of solvent dosage, the amount of base, catalyst loading, the amount of chlorobenzene and reaction temperature on the coupling reaction were examined (See Table 8 in Supporting Information), the optimized reaction conditions obtained were 0.2 mmol phenyltributylstannane, 1.5 equiv. of chlorobenzene, 0.7 mol% Pd catalyst **1** and 1.0 equiv. of K₂CO₃ in 1.0 mL DMF under air atmosphere at 120 °C for 48 h (Table 1, entry 5).

Table 1

Screening of solvents and bases on the Stille coupling reaction of phenyltributylstannane with chlorobenzene ^a

$\bigcirc -\text{Cl} + \text{Bu}_3\text{SnPh} \frac{\text{Cat. I, 120 °C}}{\text{Base, Solvent}} \qquad \bigcirc \qquad$						
	1a 2		3a			
Entry	Solvent	Base	Yield (%) ^b			
1	DMSO	K ₂ CO ₃	3			
2	H ₂ O	K ₂ CO ₃	29			
3	Toluene	K_2CO_3	38			
4	CH ₃ CN	K ₂ CO ₃	51			
5 ^[c]	DMF	K_2CO_3	80			
6	DMF	КОН	Trace			
7	DMF	K_3PO_4	Trace			
8	DMF	Et ₃ N	41			
9	DMF	NaHCO ₃	57			

^a *Reaction conditions*: phenyltributylstannane (0.2 mmol), chlorobenzene (1.5 equiv.), Pd catalyst **1** (0.7 mol% Pd), base (1.0 equiv.), solvent (1.0 mL), temperature (120 °C), time (48 h).

^b Isolated yield.

^c Reaction conditions: DMF (1.0 mL), base (K_2CO_3 , 1.0 equiv.), Pd catalyst **1** (0.7 mol% Pd), chlorobenzene (1.5 equiv.), temperature (120 °C), time (48 h).

To demonstrate the efficiency of this protocol, we investigated the generality of this methodology for the cross-coupling reactions of a variety of substituted chlorobenzene under the optimal conditions. As shown in Table 2, it was noteworthy that all reactions gave good results for substrates with electron-poor or electron-rich functional groups (Table 2, entries 1-8). In addition, heteroaryl chlorides could also provide moderate to good yields (Table 2, entries 9-13).

Table 2

The couplings of aryl chlorides and phenyltributylstannane ^a



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^a Reaction conditions: phenyltributylstannane (0.2 mmol), aryl chloride (1.5 equiv.), Pd catalyst 1 (0.7 mol% Pd), K₂CO₃ (1.0 equiv.), DMF (1.0 mL), temperature (120 °C).

^b Isolated yield.

^c 0.5 mol% Pd was used.

Generally, the aryl electrophilic reagents are limited to the use of aryl halides¹³ or triflates¹⁴ in the Stille coupling reactions. Only few examples which diazonium salts were used as electrophilic partners have been reported.¹⁵ To the best of our knowledge, the nano-catalyst has never been utilized to date for the Stille reactions of diazonium salts. Subsequently, we will report the application of the Pd catalyst 1 in the Stille coupling of arenediazonium tetrafluoroborate salts with tributylphenyltin.

With the optimal conditions established,¹⁶ the scope of the 37 Stille reactions with respect to various diazonium salts was 38 examined (Table 3). To our delight, this catalyst exhibited the 39 remarkably broad substrate scope and the corresponding coupling 40 products were obtained in moderate to good yields (66-93%). The electronic nature of substituents on the diazonium salts had little effect on the yield. For example, the diazonium salts having 42 an electron-withdrawing or electron-donating group on the same 43 position of the phenyl ring were well tolerated and showed 44 similar catalytic reactivity (Table 3, entries 5-11 vs. 3-4). 45 Surprisingly, diazonium salts with methoxyl supplied better 46 results than those with methyl group (Table 3, entries 1 and 2 vs. 47 3 and 4). It was noteworthy that steric hindrance played an 48 important role on the yield. The para-substituted diazonium salts 49 afforded the better results than ortho- and meta-substituted ones 50 (Table 3, entries 7 and 10 vs. 5-6 and 8-9, entry 2 vs. 1 and entry 51 4 vs. 3). 52

53 Table 3

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¹ Unless otherwise noted, the reaction was carried out with Pd catalyst 1 (0.3 mol% Pd), diazonium salt (0.2 mmol), and tributylphenyltin (1.2 equiv) in CH₃CN (1.2 mL) at 35 °C for 18-35 h.

^b Isolated yield.

^c 0.2 mol% Pd catalyst 1, 1 mL of CH₃CN and room temperature was utilized.

^d 55 °C was used.

To demonstrate the generality of this nanoparticles pd catalyst 1, an examination of Kumada cross-coupling reactions of a series of (hetero)aryl chlorides with Grignard reagents was performed. Under the optimal experimental conditions obtained through the screening and optimization selecting the reaction of chlorobenzene with phenylmagnesium bromide as the model reaction,¹⁷ various aryl chlorides were firstly examined. As summarized in Table 4, this method was applicable for various functionalized aryl chlorides. For substrates bearing an electrondonating or electron-withdrawing group, the reactions smoothly were carried out and afforded the desired products in high yields (Table 4, entries 1-8). It was noted that 94% yield could be obtain with 1-chloronaphthalene (Table 4, entry 9).

Table 4

The couplings of aryl chlorides and phenylmagnesium bromide^a





^a Reaction conditions: aryl chloride (0.2 mmol), phenylmagnesium bromide (1.5 equiv.), Pd catalyst 1 (0.4 mol% Pd), toluene (2 mL), temperature (140 °C), N₂.

3w

^b Isolated yield.

In addition, the Kumada reactions of heteroaryl chlorides with phenylmagnesium bromide could be carried out using 0.45 mol% Pd catalyst 1 and 140 °C. Moderate yields might be attained about various Cl-substituted heteroaryl compounds. It was found that 3-chloro-pyridine exhibited better yield than 4-chloropyridine, which revealed the steric hindrance have little influence on the reaction yields (Table 5, entry 1 vs. 2). 31% and 61% yields were obtained with 2-chlorothiophene and 2chloroquinoline, respectively (Table 5, entries 3 and 4). Nitrosubstituted chloropyridine could offer higher yields than methylsubstituted chloropyridine (Table 5, entries 7-8 vs. 5-6).

Table 5







^a Reaction conditions: heteroaryl chloride (0.2 mmol), phenylmagnesium bromide (1.5 equiv.), Pd catalyst 1 (0.45 mol% Pd), toluene (2 mL), temperature (140 °C), N₂.

^b Isolated yield.

Furthermore, we explored the Kumada couplings of various Grignard reagents with chlorobenzene in the presence of the palladium catalyst 1. As shown in Table 6, various Grignard reagents substituted with an electron-donating or electronwithdrawing group could be employed in the coupling to produce desired products in good yields (Table 6, entries 1-6). Excitedly, heteroaryl Grignard reagents afforded the products in moderate to good yields (Table 6, entries 7-8). Good yields were also obtained about aryl magnesium chlorides (Table 6, entries 9-11).





Reaction conditions: chlorobenzene (0.2 mmol), Grignard reagent (1.5 equiv.), Pd catalyst **1** (0.4 mol% Pd), toluene (2 mL), temperature (140 °C), t (48 h).

^b Isolated yield.

We further explored the recovery and reuse of the catalyst 1 through the Stille coupling reaction of chlorobenzene with phenyltributylstannane and the results are listed in Table 7. The catalyst could be recovered through membrane filtration and reused in the next reaction with freshly added chlorobenzene, phenyltributylstannane and K_2CO_3 . The experimental results showed that the catalytic activity of the catalyst did not obviously decrease after the sixth consecutive cycles, and it could be reused five times without a significant reduction in the yield (Table 7, runs 2-6).

³ Table 7

9 Recycling and reuse of the Pd catalyst **1.**

0 1		$\square Cl + Bu_3 SnPh \frac{Cat 1 (0.7 \text{ mol% Pd})}{K_2 CO_3, DMF, 120 \degree C}$		
2		1a 2		3a
3	Run		<i>t</i> (h)	Yield (%) ^a
4	1		48	97
5 6	2		48	97
7	3		50	96
8	4	7	50	95
9 0	5		52	93
1	6		52	92

^a Isolated yield.

3. Conclusion

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In summary, we have reported the Stille cross-coupling reactions of (hetero)aryl chlorides, and arenediazonium tetrafluoroborate salts with phenyltributylstannane, respectively, and Kumada cross-coupling reactions of (hetero)aryl chlorides with various Grignard reagents catalyzed by a highly active, airstable, and readily-synthesized Pd nano-catalyst supported on aluminum hydroxide, and developed two novel and efficient strategies for the synthesis of various biaryls. In terms of a range of aryl chlorides, it could show remarkable catalytic reactivity and good to high yields. More importantly, this catalyst has also proved to be highly efficient for various diazonium salts, heteroaryl chlorides and Grignard reagents.

4. Experimental Section

4.1. General

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. Deuterated solvents were purchased from Aldrich. Column chromatography was performed on silica gel (200-300 mesh) with petroleum ether /ethyl acetate gradients, unless otherwise specified. All yields were referred to isolated yields (average of two runs) of compounds. The known compounds were partly characterized by melting points (for solid samples), ¹H NMR, and compared to authentic samples or the literature data. Melting points were measured with a RD-II digital melting point apparatus and are uncorrected. ¹H NMR data were acquired at 300 K on a Bruker Advance 600 MHz spectrometer or Avarian Inova 500 MHz spectrometer using CDCl₃ as solvent. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3 = 7.26$). Spectra are reported as follows: chemical shift (δ = ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment.

4.2. General reaction procedures

4.2.1. General procedure for Stille couplings of aryl chlorides

To a tube equipped with a magnetic stir bar were added the Pd catalyst 1 (19.6 mg, 0.7 mol% Pd), 1.0 equiv. of K₂CO₃ (27.6 mg, 0.2 mmol) and 1.5 equiv. of aryl chloride (0.3 mmol) in turn. Subsequently, the solvent (DMF, 1.0 mL) and phenyltributylstannane (0.2 mmol) were added under air atmosphere, respectively. The reaction was then heated to 120 °C and stirred until aryl chloride was completely consumed as determined by TLC. At last, the reaction mixture was purified by silica gel column chromatography to afford the desired pure coupling product.

4.2.2. General procedure for Stille couplings of diazonium salts with phenyltributylstannane

Phenyltributylstannane (81 μ L, 1.2 equiv) was added to the mixture of the Pd catalyst **1** (8.4 mg, 0.3 mol% Pd) and diazonium salt (0.2 mmol, 44.4 mg) in acetonitrile (1.2 mL) at room temperature. The reaction mixture was stirred in a test tube under air atmosphere at 35 °C until the diazonium salt was consumed fully as determined by TLC. The reaction mixture was concentrated and then purified by column chromatography on silica gel.

4.2.3. General procedure for Kumada-Corriu couplings of aryl chlorides

To a tube equipped with a magnetic stir bar were added the Pd catalyst 1 (11.2 mg, 0.4 mol% Pd) and 1.0 equiv. of aryl chloride (0.2 mmol) in turn. Subsequently, the solvent (toluene, 2.0 mL) and Grignard reagent (0.3 mmol, 1.5 equiv) were added under N_2 atmosphere, respectively. The reaction was then heated to 140 °C and stirred until aryl chloride was completely consumed as determined by TLC. At last, the reaction mixture was purified by silica gel column chromatography to afford the desired pure coupling product.

4.2.4. General procedure for Kumada-Corriu couplings of heteroaryl chlorides

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To a tube equipped with a magnetic stir bar were added the MAN Pd catalyst 1 (12.6 mg, 0.45 mol% Pd) and 1.0 equiv. of heteroaryl chloride (0.2 mmol) in turn. Subsequently, the solvent (toluene, 2.0 mL) and phenylmagnesium bromide (0.3 mmol, 1.5 equiv) were added under N_2 atmosphere, respectively. The reaction was then heated to 140 °C and stirred until heteroaryl chloride was completely consumed as determined by TLC. At last, the reaction mixture was purified by silica gel column chromatography to afford the desired pure coupling product.

7 4.2.5. General procedure for recycled Stille

8 coupling of chlorobenzene and

9 phenyltributylstannane

10 To a tube equipped with a magnetic stir bar were added potassium carbonate (27.6 mg, 0.2 mmol, 1.0 equiv.) and the 11 palladium catalyst 1 (19.6 mg, 0.7 mol% Pd) in turn. 12 Subsequently, the solvent (DMF, 1.0 mL), chlorobenzene (1.5 13 equiv.) and phenyltributylstannane (0.2 mmol) were added under 14 air atmosphere, respectively. The reaction mixture was then 15 stirred at 120 °C for the specified time. The corresponding 16 recycling reactions were carried out with the recovered Pd 17 catalyst 1 that determined the amount of the substrate and reagent 18 as reference at 120 °C. Reaction times were 48, 50, 50, 52 and 52 19 h for cycles 1, 2, 3, 4 and 5, respectively. After the reactions were 20 fully carried out as determined by TLC, 3 mL H₂O and 5 mL 21 CH₂Cl₂ were added and the reaction system was shaken well. 22 Subsequently, the catalyst 1 was recovered through membrane 23 filtration and reused in the next reaction. After the organic phase 24 was separated from the reaction system, the water phase was 25 extracted with CH_2Cl_2 (2 × 5 mL). The organic layer was then 26 combined and dried over anhydrous Na₂SO₄. At last, the solvent 27 was removed in vacuum and the residue was purified by silica 28 gel column chromatography to afford the pure product. 29

Acknowledgements

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References and notes

- For recent reviews of Stille cross-coupling reaction, see: (a) Littke, A. F.; Fu, G. C. Angew. Chem. 2002, 114, 4350–4386; Angew. Chem. Int. Ed. 2002, 41, 4176–4211; (b) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. Chem. Rev. 2002, 102, 1359–1469; (c) Espinet, P.; Echavarren, A. M. Angew. Chem. 2004, 116, 4808–4839. Angew. Chem., Int. Ed. 2004, 43, 4704–4734; (d) Schnürch, M.; Flasik, R.; Khan, A. F.; Spina, M.; Mihovilovic, M. D.; Stanetty, P. Eur. J. Org. Chem. 2006, 3283– 3307; (e) Polshettiwar, V.; Len, C.; Fihri, A. Coord. Chem. Rev. 2009, 253, 2599–2626; (f) Molnár, A. Chem. Rev. 2011, 111, 2251–2320; (g) See Ref [3b], [3d] and [3e].
- For recent selected examples of Stille cross-coupling reaction, see:

 (a) Jensen, M. S.; Yang, C. H.; Hsiao, Y.; Rivera, N.; Wells, K. M.; Chung, J. Y. L.; Yasuda, N.; Hughes, D. L.; Reider, P. J. Org. Lett. 2000, 2, 1081–1084;
 (b) Wolf, C.; Lerebours, R. J. Org. Chem. 2003, 68, 7551–7554;
 (c) Chiappe, C.; Pieraccini, D.; Zhao, D.; Fei, Z.; Dyson, P. J. Adv. Synth. Catal. 2006, 348, 68– 74;
 (d) Zhao, H.; Wang, Y.; Sha, J.; Sheng, S.; Cai, M. Tetrahedron 2008, 64, 7517–7523;
 (e) Susanto, W.; Chu, C. -Y.; Ang, W. J.; Chou, T. -C.; Lo, L. -C.; Lam, Y. J. Org. Chem. 2012, 77, 2729–2742;
 (f) Hajipour, A. R.; Najafi, N.; Rafiee, F. Appl. Organometal. Chem. 2013, 27, 228–231.
- For recent reviews of Kumada-Corriu cross-coupling reaction, see:

 (a) Banno, T.; Hayakawa, Y.; Umeno, M. J. Organomet. Chem.
 2002, 653, 288-291; (b) Schröter, S.; Stock, C.; Bach, T. Tetrahedron 2005, 61, 2245–2267; (c) Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Schneider, S. K. J. Organomet. Chem. 2003, 687, 229–248; (d) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. J. Organomet. Chem. 2002, 653, 69-82; (e) Frisch, A. C.; Beller, M.; Angew. Chem. Int. Ed. 2005, 44,

- S 674-688; (f) Slagt, V. F.; de Vries, A. H. M.; de Vries, J. G.; Kellogg, R. M. *Org. Process Res. Dev.* **2010**, *14*, 30–47; (g) See Ref [1a].
- 4. For recent selected examples of Kumada-Corriu cross-coupling reaction, see: (a) Hölzer, B.; Hoffmann, R. W. Chem. Commun. 2003, 732-733; (b) Yang, L. M.; Huang, L. F.; Luh, T. Y. Org. Lett. 2004, 6, 1461-1463; (c) Limmert, M. E.; Roy, A. H.; Hartwig, J. F. J. Org. Chem. 2005, 70, 9364-9370; (d) Martin, R.; Buchwald, S. L. J. Am. Chem. Soc. 2007, 129, 3844-3845; (e) Mehta, V. P.; Modha, S. G.; der Eycken, E. V. J. Org. Chem. 2009, 74, 6870-6873; (f) Zacuto, M. J.; Shultz, C. S.; Journet, M. Org. Process Res. Dev. 2011, 15, 158-161; (g) Krasovskiy, A. L.; Haley, S.; Voigtritter, K.; Lipshutz, B. H. Org. Lett. 2014, 16, 4066-4069; (h) Dai, W. P.; Xiao, J.; Jin, G. Y.; Wu, J. J.; Cao, S. J. Org. Chem. 2014, 79, 10537-10546; (i) Sémeril, D.; Lejeune, M.; Jeunesse, C.; Matt, D. J. Mol. Catal. A: Chem. 2005, 239, 257-262; (j) Manolikakes, G.; Knochel, P. Angew. Chem. Int. Ed. 2009, 48, 205-209; (k) Werner, V.; Klatt, T.; Fujii, M.; Markiewicz, J.; Apeloig, Y.; Knochel, P. Chem. Eur. J. 2014, 20, 8338–8342; (1) Klatt, T.; Werner, V.; Maximova, M. G.; Didier, D.; Apeloig, Y.; Knochel, P. Chem. Eur. J. 2015, 21, 1-6; (m) Adrio, J.; Carretero, J. C. ChemCatChem 2010, 2, 1384-1386; (n) Gu, X. X.; Luhman, W. A.; Yagodkin, E.; Holmes, R. J.; Douglas, C. J. Org. Lett. 2012, 14, 1390-1393; (o) Terao, J.; Naitoh, Y.; Kuniyasu, H.; Kambe, N. Chem. Lett. 2003, 32, 890-891; (p) Ren, G. R.; Cui, X. L.; Wu, Y. J. Eur. J. Org. Chem. 2010, 2372-2378; (q) Reeves, J. T.; Fandrick, D. R.; Tan, Z. L.; Song, J. J.; Lee, H.; Yee, N. K.; Senanayake, C. H. Org. Lett. 2010, 12, 4388-4391; (r) See Ref [2e].
- 5. For recent examples in Stille cross-coupling reaction catalyzed by different complexes, see: (a) Netherton, M. R.; Fu, G. C. Org. Lett. 2001, 3, 4295-4298; (b) Littke, A. F.; Schwarz, L.; Fu, G. C. J. Am. Chem. Soc. 2002, 124, 6343-6348; (c) Bedford, R. B.; Cazin, C. S. J.; Hazelwood, S. L.; Chem. Commun. 2002, 2608-2609; (d) Tang, H.; Menzel, K.; Fu, G. C. Angew. Chem. 2003, 115, 5233-5236; Angew. Chem., Int. Ed. 2003, 42, 5079-5082; (e) Mee, S. P. H.; Lee, V.; Baldwin, J. E. Angew. Chem. 2004, 116, 1152-1156; Angew. Chem., Int. Ed. 2004, 43, 1132-1136; (f) Su, W.; Urgaonkar, S.; Verkade, J. G. Org. Lett. 2004, 6, 1421-1424; (g) Li, J. H.; Liang, Y.; Wang, D. P.; Liu, W. J.; Xie, Y. X.; Yin, D. L. J. Org. Chem. 2005, 70, 2832-2834; (h) Li, J. H.; Liang, Y.; Xie, Y. X. Tetrahedron 2005, 61, 7289-7293; (i) Kim, Y. M.; Yu, S. J. Am. Chem. Soc. 2003, 125, 1696-1697; (j) Menzel, K.; Fu, G. C. J. Am. Chem. Soc. 2003, 125, 3718-3719; (k) Kim, W. S.; Kim, H. J.; Cho, C. G. J. Am. Chem. Soc. 2003, 125, 14288-14289; (l) Dubbaka, S. R.; Vogel, P. J. Am. Chem. Soc. 2003, 125, 15292-15293; (m) Beccalli, E. M.; Borsini, E.; Brenna, S.; Galli, S.; Rigamonti, M.; Broggini, G. Chem. Eur. J. 2010, 16, 1670-1678; (n) Naber, J. R.; Buchwald, S. L. Adv. Synth. Catal. 2008, 350, 957-961; (o) Hajipour, A. R.; Karami, K.; Rafiee, F. Appl. Organometal. Chem. 2012, 26, 27-31; (p) Zhao, H.; Zheng, G.; Hao, W.; Cai, M. Appl. Organometal. Chem. 2010, 24, 92-98; (q) Schneider, S.; Bannwarth, W. Angew. Chem., Int. Ed. 2000, 39, 4142-4145; (r) Dell'Anna, M. M.; Lofù, A.; Mastrorilli, P.; Mucciante, V.; Nobile, C. F. J. Organomet. Chem. 2006, 691, 131-137; (s) Cai, M.; Zheng, G.; Ding, G. Green Chem. 2009, 11, 1687-1693; (t) Su, W.; Urgaonkar, S.; McLaughlin, P. A.; Verkade, J. G. J. Am. Chem. Soc. 2004, 126, 16433-16439; (u) Jin, M. J.; Lee, D. H. Angew. Chem. 2010, 122, 1137-1140; Angew. Chem., Int. Ed. 2010, 49, 1119-1122; (v) Bradley, D.; Williams, G.; Pretorius, M. J. Mol. Catal. A: Chem. 2008, 284, 77-84.
- For recent advances in Kumada-Corriu cross-coupling reaction catalyzed by different ligands, see: Heravi, M. M.; Hajiabbasi, P. *Monatsh Chem.* 2012, 143, 1575–1592.
- For recent examples in Kumada-Corriu cross-coupling reaction catalyzed by different complexes, see: (a) Wolf, C.; Xu, H. J. Org. Chem. 2008, 73, 162–167; (b) Organ, M. G.; Abdel-Hadi, M.; Avola, S.; Hadei, N.; Nasielski, J.; O'Brien, C. J.; Valente, C. Chem. Eur. J. 2007, 13, 150–157; (c) Huang, J. K.; Nolan, S. P. J. Am. Chem. Soc., 1999, 121, 9889–9890; (d) Bonnet, V.; Mongin, F.; Trécourt, F.; Quéguiner, G.; Knochel, P. Tetrahedron Lett. 2001, 42, 5717–5719; (e) Ackermann, L.; Kapdi, A. R.; Schulzke, C. Org. Lett. 2010, 12, 2298–2301; (f) Horibe, H.; Fukuda, Y.; Kondo, K.; Okuno, H.; Murakami, Y.; Aoyama, T. Tetrahedron, 2004, 60, 10701–10709; (g) Tsai, F. Y.; Lin, B. N.; Chen, M. J.; Mou, C. Y.; Liu, S. T. Tetrahedron, 2007, 63, 4304–4309; (h) Phan, N. T. S.; Brown, D. H.; Adams, H.; Spey, S. E.; Styring, P. Dalton Trans. 2004, 1348–1357; (i) Bonnet, V.; Mongin, F.;

63 64 65 Trécourt, F.; Quéguiner, G.; Knochel, P. *Tetrahedron* 2002, *58*, MANUS 4429–4438; (j) Nasielski, J.; Hadei, N.; Achonduh, G.; Kantchev, E. A. B.; O'Brien, C. J.; Lough, A.; Organ, M. G. *Chem. Eur. J.* 2010, *16*, 10844–10853; (k) Ackermann, L.; Kapdi, A. R.; Fenner, S.; Kornhaa, C.; Schulzke, C. *Chem. Eur. J.* 2011, *17*, 2965–2971; (l) Türkmen, H.; Kani, İ. *Appl. Organometal. Chem.* 2013, *27*, 489–493; (m) Kremzow, D.; Seidel, G.; Lehmann, C. W.; Fürstner, A. *Chem. Eur. J.* 2005, *11*, 1833–1853; (n) López-Pérez, A.; Adrio, J.; Carretero, J. C. *Org. Lett.* 2009, *11*, 5514–5517; (o) Larrosa, I.; Somoza, C.; Banquy, A.; Goldup, S. M. *Org. Lett.* 2011, *13*, 146-149; (p) Bastug, G.; Nolan, S. P. *Organometallics*, 2014, *33*, 1253–1258; (q) Li, G. Y. *J. Organomet. Chem.* 2002, 11. *653*, 63–68; (r) Chen, C.; Qiu, H. Y.; Chen, W. Z. J. *Organomet. Chem.* 2012, *696*, 4166–4172; (s) Ackermann, L.; Althammer, A. *Org. Lett.* 2006, *8*, 3457–3460.

- For recent examples of ligandless Stille cross-coupling reaction, see: (a) Chiappe, C.; Imperato, G.; Napolitano, E.; Pieraccini, D. Green Chem. 2004, 6, 33–36; (b) Herve, A.; Rodriguez, A. L.; Fouquet, E. J. Org. Chem. 2005, 70, 1953–1956; (c) Handy, S. T.; Zhang, X. Org. Lett. 2001, 3, 233–236; (d) Jana, S.; Haldar, S.; Koner, S. Tetrahedron Lett. 2009, 50, 4820–4823; (e) Kerric, G.; Grognec, E. L.; Zammattio, F.; Paris, M.; Quintard, J. P. J. Organomet. Chem. 2010, 695, 103–110.
 - Gauthier, D.; Beckendorf, S.; Gøgsig, T. M.; Lindhardt, A. T.; Skrydstrup, T. J. Org. Chem. 2009, 74, 3536–3539.
 - For recent examples palladium nanoparticles catalyzed Stille cross-coupling reaction, see: (a) Calò, V.; Nacci, A.; Monopoli, A.; Montingelli, F. J. Org. Chem. 2005, 70, 6040–6044; (b) Garcia-Martinez, J. C.; Lezutekong, R.; Crooks, R. M. J. Am. Chem. Soc.

Supplementary Material

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic

- **US** (2005, 127, 5097–5103; (c) Kantam, M. L.; Roy, S.; Roy, M.; Sreedhar, B.; Choudary, B. M. Adv. Synth. Catal. 2005, 347, 2002–2008; (d) Choudary, B. M.; Madhi, S.; Chowdari, N. S.; Kantam, M. L.; Sreedhar, B. J. Am. Chem. Soc. 2002, 124, 14127–14136; (e) Kogan, V.; Aizenshtat, Z.; Popovitz-Biro, R.; Neumann, R. Org. Lett. 2002, 4, 3529–3532; (f) Wu, L.; Li, Z. W.; Zhang, F.; He, Y. M.; Fan, Q. H. Adv. Synth. Catal. 2008, 350, 846–862; (g) Yang, X.; Fei, Z.; Zhao, D.; Ang, W. H.; Li, Y.; Dyson, P. J. Inorg. Chem. 2008, 47, 3292–3297; (h) Bernechea, M.; de Jesús, E.; López-Mardomingo, C.; Terreros, P. Inorg. Chem. 2009, 48, 4491–4496.
- (a) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. Angew. Chem., Int. Ed. 2005, 44, 4442–4489; (b) Zeni, G.; Larock, R. C. Chem. Rev. 2006, 106, 4644–4680.
- (a) Li, X.; Yan, X. Y.; Chang, H. H.; Wang, L. C.; Zhang, Y.; Chen, W. W.; Li, Y. W.; Wei, W. L. Org. Biomol. Chem. 2012, 10, 495–497; (b) Li, X.; Wang, L. C.; Chang, H. H.; Zhang, C. X.; Wei, W. L. Appl. Catal. A: Gen. 2013, 462, 15–22.
- 13. See Ref [1], [2], [5], [8] and [10].
- 14. See Ref [5e] and [5t].
- 15. Dughera, S. Synthesis 2006, 1117-1122.
- Extensive screening showed that the optimized reaction conditions were 0.2 mmol diazonium salt, 1.2 equiv. of tributylphenyltin and 0.3 mol% Pd catalyst 1 in 1.2 mL CH₃CN at 35 °C.
- 17. The optimal reaction conditions screened were 0.2 mmol aryl chlorides, 1.5 equiv. of phenylmagnesiu bromide and 0.4 mol% Pd catalyst 1 under N_2 atmosphere in 2.0 mL toluene at 140 °C.

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