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A Highly Active and General Catalyst for the Stille Coupling Reaction of Unreactive Aryl, Heteroaryl, and Vinyl Chlorides under Mild Conditions

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Abstract: A β-diketiminatophosphane-palladium complex was found to act as an efficient and general catalyst in the Stille coupling reaction of various aryl and heteroaryl chlorides with organostannanes. The results show that this catalytic system allows for the use of less reactive substrates such as deactivated or sterically hindered aryl chlorides. A catalyst loading of 0.5 mol% was sufficient to achieve excellent performance under relatively mild reaction conditions. Furthermore, the scope of catalyst was extended to the coupling of vinyl chlorides.

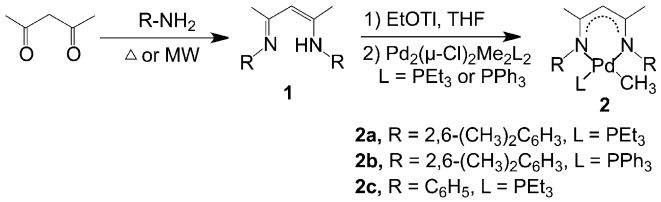
Keywords: aryl chlorides; C–C coupling; homogeneous catalysis; palladium; Stille reaction

The palladium-catalyzed Stille coupling reaction of organohalides with organostannane reagents has proven to be a valuable and powerful tool for the formation of carbon-carbon bonds.[1] This coupling has been employed in the synthesis of biaryl compounds that are important intermediates in natural products, polymers, and pharmaceuticals.[2] A number of effective palladium catalytic systems have been developed for the Stille coupling. Generally, phosphine ligands in combination with palladium precursors provide effective catalysts for the reaction.

A major limitation of the coupling is that it is necessary to use reactive aryl iodide or bromide substrates.[3] The use of aryl chlorides would be very desirable for industrial applications because they are cheaper and more widely available than their bromide or iodide counterparts.[4] However, the strong C–Cl bonds, which disfavour oxidative addition in the catalysis, make the coupling of aryl chlorides much more difficult.[5] Only few catalysts have been reported in this area.[6] Furthermore, most of the reactions always have some disadvantages including high catalyst loadings, long reaction times, and harsh reaction conditions. In particular, successful examples using deactivated aryl chlorides are quite rare. Therefore, there is growing interest in the development of catalysts that are able to work in the coupling of the unreactive substrates under mild conditions. We have recently reported β-diketiminatophosphane-palladium catalysts **2** for various cross-coupling reactions of aryl chlorides.[7] In a continuing effort to explore their catalytic potential, we herein describe the use of Pd catalyst **2a** in the Stille coupling reaction of less reactive aryl chlorides.

β-Diketiminatophosphane Pd complexes **2** were conveniently synthesized from acetylacetone by the following sequence: (i) condensation of acetylacetone and primary amines under microwave or conventional heating, (ii) deprotonation of **1** with EtOTl in THF at 0–20 °C, (iii) treatment with $Pd_2(\mu\text{-}Cl)_2Me_2L_2$ (L = PPh_3 or PEt_3)[8] (Scheme 1). It is noteworthy that the complexes have considerable air and moisture stability. They were characterized by elemental analysis, ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy.

Initial studies focused on the coupling of deactivated 2-chloroanisole with tributylphenylstannane because catalysts that can activate this aryl chloride would be expected to be effective with a wide range of aryl chlorides. At first, we performed this reaction in the presence of 0.5 mol% of **2a** and 2.0 equiv. of CsF in THF at 50 °C. The coupling proceeded very well to afford the desired product in 92% yield after 5 h (Table 1, entry 1). The activity obtained with **2a** is remarkably superior to any previously reported re-

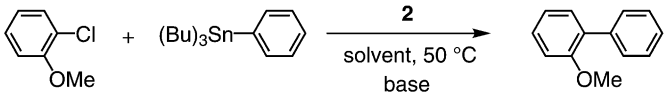


Scheme 1. Synthesis of β-diketiminatophosphane-Pd catalysts **2**.

sults on the Stille coupling. A catalyst loading as low as 0.1 mol% was shown to be effective (Table 1, entry 2). It was possible to achieve this coupling even at room temperature, though a prolonged reaction time was required (Table 1, entry 3). The solvent effect on the activity was examined with different solvents because the selection of the solvent is sometimes crucial in the coupling reactions. When the reaction was conducted in toluene, acetonitrile, NMP, DME and 1,4-dioxane instead of THF, the catalytic activity was reduced under the same conditions (Table 1, entries 4–8). By screening different bases including KF, K_3PO_4, Na_2CO_3, and Cs_2CO_3 (Table 1, entries 9–12), CsF was found to be the best one.

As expected, catalysts **2b** and **2c** exhibited inferior catalytic activities compared with **2a** (Table 1, entries 13 and 14). This indicates that the strong electron-donating triethylphosphane ligand increases the electron density on the palladium center,[9] facilitating the rate-limiting oxidative addition of the active Pd species to the less reactive aryl chlorides. In addition, *ortho*-methyl groups in the diketimine ligand exert beneficial electronic and steric effects in enhancing the reactivity and therefore giving a more active catalyst. It is supposed that the bulky diketimine and electron-rich triethylphosphane of **2a** cooperatively promote the oxidative addition and reductive elimination. With the optimized conditions in hand, we explored the coupling of various aryl chlorides with aryl- and vinylstannanes. The reactions of activated 4-chloro-acetophenone, 1-chloro-2-nitrobenzene, and chlorobenzene with tributylphenylstannane provided biaryls in excellent yields (Table 2, entries 1–3). Gratifyingly, comparable catalytic activities were observed in the couplings of deactivated aryl chlorides possessing electron-donating substituents (Table 2, entries 4–6). 1-Chloronaphthalene also reacted very well (Table 2, entry 7). Couplings of aryl chlorides containing a free amino or hydroxy group are typically difficult to accomplish.[6] It is therefore noteworthy that catalyst **2a** is effective for unprotected 2-chloroaniline and 4-chlorophenol (Table 2, entries 8 and 9). Moreover, satisfactory levels of activity were observed for the couplings with electron-rich arylstannanes (Table 2, entries 10–14). It should be noted that the sterically hindered 2-chloro-1,3-dimethylbenzene could be coupled well in 81% yield, although somewhat elevated temperatures were required (Table 2, entry 15). The Stille reaction is especially useful for the preparation of arylalkenes. Satisfactory results were obtained in the reactions of 4-chloroanisole and 2-chloro-1,3-dimethylbenzene with tributylvinylstanne (Table 2, entries 16 and 17). Regardless of the sub-

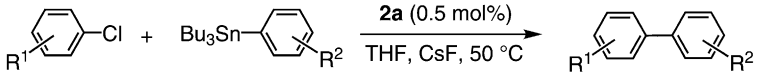
Table 1. Stille coupling of 2-chloroanisole with tributylphenylstannane.[a]

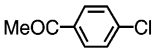
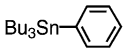
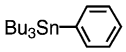
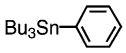
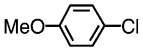
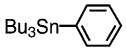
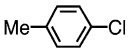
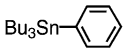
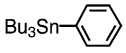
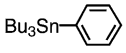
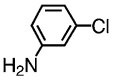
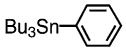
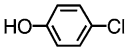
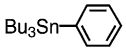
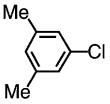
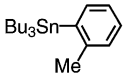
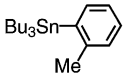
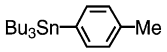
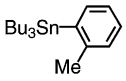
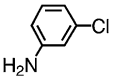
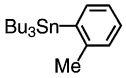
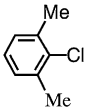
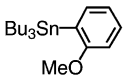
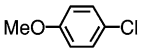
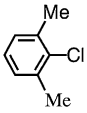


Entry	**2** [mol%]	Solvent	Base	Time [h]	Yield [%][b]
1	**2a** (0.5)	THF	CsF	5	92 (91)
2	**2a** (0.1)	THF	CsF	12	84
3[c]	**2a** (1.0)	THF	CsF	18	81
4	**2a** (0.5)	toluene	CsF	5	67
5	**2a** (0.5)	acetonitrile	CsF	5	72
6	**2a** (0.5)	NMP	CsF	5	86
7	**2a** (0.5)	DME	CsF	5	89 (86)
8	**2a** (0.5)	1,4-dioxane	CsF	5	75 (71)
9	**2a** (0.5)	THF	KF	5	69
10	**2a** (0.5)	THF	K_3PO_4	5	54
11	**2a** (0.5)	THF	Na_2CO_3	5	45
12	**2a** (0.5)	THF	Cs_2CO_3	5	51
13	**2b** (0.5)	THF	CsF	5	62
14	**2c** (0.5)	THF	CsF	5	79

[a] *Reaction conditions:* 2-chloroanisole (1.0 mmol), tributylphenylstannane (1.1 mmol), base (2.0 mmol), solvent (2.0 mL) and a catalytic amount of **2**, NMP = *N*-methylpyrrolidine, DME = dimethoxyethane.
[b] GC yield was determined using *n*-dodecane as an internal standard. Isolated yield is given in parenthesis.
[c] Reaction was performed at room temperature.

Table 2. Stille coupling of aryl chlorides with organostannanes.[a]



Entry	Aryl chloride	Organostannane	Time [h]	Yield [%][b]
1			3	91
2			3	93
3			4	90
4			4	89
5			4	86
6			6	91
7			4	87
8			6	85
9			5	89
10			8	87
11			8	83
12			6	91
13			8	83 (80)
14			8	87
15[c]			12	81
16			6	85
17[c]			12	78

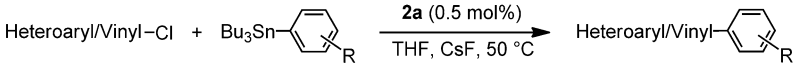
[a] *Reaction conditions:* aryl chloride (1.0 mmol), organostannane (1.1 mmol), CsF (2.0 mmol), 50 °C, and **2a** (0.5 mol%).
[b] Isolated yield.
[c] Reaction was performed at 80 °C.

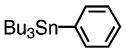
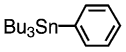
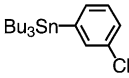
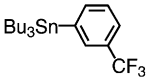
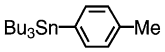
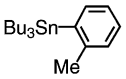
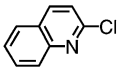
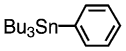
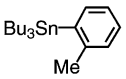
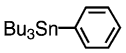
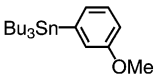
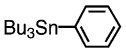
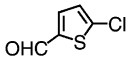
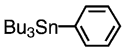
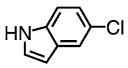
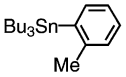
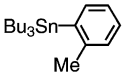
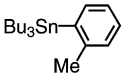
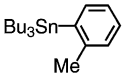
stituents, most of the couplings were very clean and efficient under mild heating.

The Stille coupling of heteroaryl halides is remarkably useful in the pharmaceutical industry since biologically active molecules are accessed through this methodology.[10] However, the reactions of heteroaryl chlorides give low conversions and remain challenging. Therefore, development of effective catalysts for this useful reaction is an important mission in the field.

We attempted the coupling of different heteroaryl chlorides with arylstannanes in the presence of

Table 3. Stille coupling of heteroaryl and vinyl chlorides with organostannanes.[a]

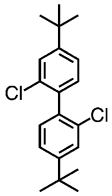
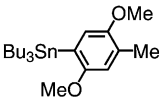
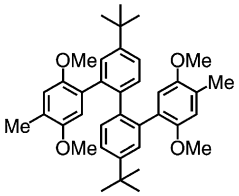
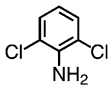
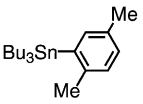
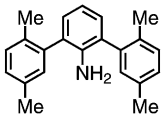
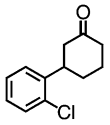
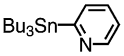
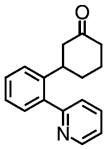
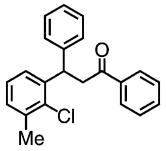
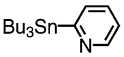
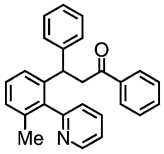
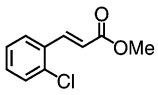
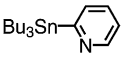
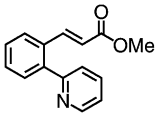
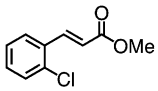
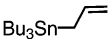
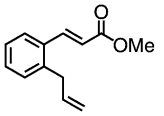
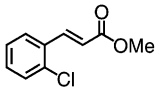
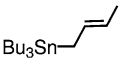
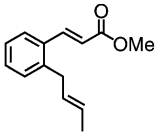
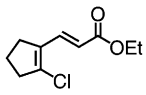
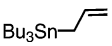
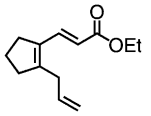
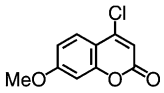
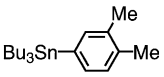
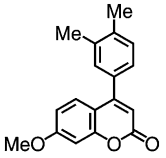
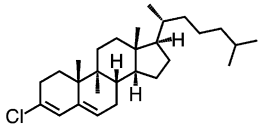
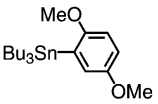
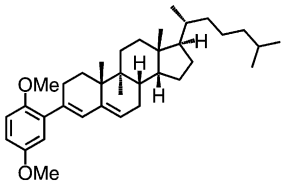


Entry	Heteroaryl/vinyl chloride	Organostannane	Time [h]	Yield [%][b]
1			4	87
2			4	94
3			4	83
4			4	86
5			5	82
6			6	81
7			8	89
8			8	86
9			8	87
10			8	78
11			5	84
12			4	92
13			6	76
14			6	82
15			6	87
16			6	79

[a] *Reaction conditions:* aryl chloride (1.0 mmol), organostannane (1.1 mmol), CsF (2.0 mmol), 50 °C, and **2a** (0.5 mol%).
[b] Isolated yield.

0.5 mol% of **2a** at 50 °C (Table 3). Chloropyridines were coupled to tributylphenylstannane in high yields (Table 3, entries 1 and 2). The electronic property of the substituents in the arylstannanes had a small influence to the formation of biaryls (Table 3, entries 3–6). 2-Chloroquinoline and 1-chloroisoquinoline could be successfully transformed to the desired products (Table 3, entries 7 and 8). 2-Chloro-3-methylpyridine was also found to be a suitable coupling partner (Table 3, entries 9 and 10). Chlorothiophenes are problematic substrates due to the strong affinity of the sulfur for Pd.[11] 3-Chlorothiophene coupled effectively with tributylphenylstannane in 84% yield (Table 3, entry 11). An aldehyde functional group was tolerated under the present conditions (Table 3, entry 12). This catalyst was also active for the reaction of unprotected 5-chloroindole with tributyl(*o*-tolyl)-stannane (Table 3, entry 13).

Table 4. Stille coupling of various aryl and vinyl chlorides with organostannanes.[a]

Entry	Aryl chloride	Organostannane	Product	Temperature [°C]	Time [h]	Yield [%][b]
1[c]				70	8	72
2[c]				70	8	81
3				50	5	86
4				70	8	76
5				70	6	79
6				70	6	73
7				70	8	68
8				70	8	82
9				70	8	75
10[d]				70	10	71

[a] *Reaction conditions:* aryl chloride (1.0 mmol), organostannane (1.3 mmol), CsF (2.0 mmol), and **2a** (0.5 mol%).
[b] Isolated yield.
[c] Organostannane (2.6 mmol) and **2a** (1.0 mol%).
[d] Organostannane (1.4 mmol) and **2a** (1.0 mol%).

Next, we tested catalyst **2a** in the very important Stille coupling of vinyl chlorides.[6b,12] Gratifyingly, 1-chlorocycloalkenes could be coupled to tributyl(*o*-tolyl)stannane in good yields (Table 3, entries 14–16). Previously, long reaction time, high temperature, and high catalyst loading (40 h, 100 °C, and 3.5 mol%) were required for this substrate.[6b]

Encouraged by the above success, we subsequently studied the scope and generality of this process and its applicability for synthetic problems. As illustrated in Table 4, an array of functionalized aryl and vinyl chlorides underwent effective coupling reactions with organostannanes to afforded potentially valuable products. Quite interestingly, the effectiveness of catalyst **2a** was observed in a one-pot double coupling of a sterically hindered aryl dichloride and an arylstannane (Table 4, entry 1). This method would be desirable for the preparation of arylated biphenyls.[13] Hindered and electron-rich 2,6-dichloroaniline having a free amino group was also combined with a hindered arylstannane to provide the dicoupled product in 81% yield (Table 4, entry 2).

We have now extended this process to aryl chlorides containing electrophilic functional groups such as ketones and α, β-unsaturated ester. For examples, 3-(2-chlorophenyl)cyclohexanone and 3-(2-chloro-3-methylphenyl)-1,3-diphenyl-1-propanone coupled with 2-(tributylstannyl)pyridine in good yields (Table 4, entries 3 and 4). Similarly, this method was effective for (2*E*)-3-(2-chlorophenyl)-2-propenoate (Table 4, entries 5–7). This compound can be used as a precursor for the facile construction of bicyclic skeletons.[14]

It was also possible to couple functionalized vinyl chloride derivatives under our standard protocol. Examples of this class of compounds, ethyl (*E*)-3-(2-chlorocyclopent-1-enyl)-2-propenoate and 4-chloro-7-methoxy-2*H*-1-benzopyran-2-one could all be transformed to the expected products (Table 4, entries 8 and 9). The later coupling was proven to be useful for the synthesis of 4-arylcoumarins.[15] In particular, we were pleased to observe that this catalytic system allows for a facile synthesis of biologically active molecules. 3-Chlorocholesta-3,5-diene[16] was reacted with tributyl(2,5-dimethoxyphenyl)stannane to give the target compound in 71% yield (Table 4, entry 10). The use of vinyl chlorides allows for structural diversity of the products as well as expanding the scope of Stille reactions.

We previously demonstrated that β-diketoiminatophosphane Pd complexes act as highly active catalysts in the Stille reaction of (hetero)aryl chlorides.[6e] However, the catalysts were not applied to the coupling of vinyl chlorides due to their unsatisfactory performance. Recently, the efficient reaction of aryl chlorides using Pd-PEPPSI catalysts was described by Organ and co-workers.[6f] Heteroaryl chlorides were primarily evaluated with 4–8 mol% of the catalysts at 30–80 °C. Very recently, Ma and co-workers used 1 mol% of palladacycle catalysts for the coupling of aryl chlorides with tributylstannylpyridine.[6g] The reactions require a high temperature of 110 °C to obtain the desired products in high yields. Lipshulz and co-workers also described mild Stille couplings in water.[6h] Although 2–4 mol% of their catalytic system was quite effective for the reaction of activated aryl chlorides at room temperature to 60 °C, the application to vinyl chlorides and deactivated aryl chlorides such as 2-chloroanisole seems to be difficult to accomplish. In contrast, our present catalyst **2a** showed both high activity and excellent functional group compatibility. Regardless of the substituent, most of the coupling reactions of (hetero)aryl chlorides and vinyl chlorides were very efficient in the presence of only 0.5 mol% catalyst at low temperature of 50 °C.

To the best of our knowledge, catalyst **2a** is one of the most general and active catalysts reported so far for the coupling of both (hetero)aryl chlorides and vinyl chlorides. These results represent a significant advancement in the Stille reaction. Pd complex **2a** has a unique structural feature containing both electron-rich triethylphosphane and bulky diketimine moieties on the palladium center. Although the mechanism of **2a**-catalyzed coupling is not obvious, the high catalytic activity is probably attributed to the enhanced nucleophilicity of the active palladium(0) species which undergo Ar–Cl bond cleavage in the rate-limiting oxidation step.

In summary, the present work has resulted in the development of an excellent catalyst **2a** for the Stille coupling reaction. We have demonstrated that β-diketiminatophosphane-palladium complex **2a** serves as an active catalyst for the Stille coupling reaction. Various aryl, heteroaryl, and vinyl chlorides coupled effectively with organostannanes under mild conditions. We envision that extensions of this catalyst will permit the development of superior catalytic systems.

Experimental Section

General Procedure for Stille Coupling Reactions

Aryl chloride (1.0 mmol), organostannane (1.1 mmol), CsF (2.0 mmol), and a catalytic amount of Pd complex **2** (0.5 mol%) were added in THF (2.0 mL). The reaction mixture was stirred at 50 °C and monitored by GC/GC-MS. After completion of the reaction, THF solvent was finally evaporated under reduced pressure. The residue was treated with diethyl ether (10 mL) and water (5 mL). The layers were separated and the aqueous phase was extracted with diethyl ether (2×10 mL). The combined organic phases were washed with brine (10 mL), dried with $MgSO_4$, and concentrated in vacuo. The crude product was purified by

short column chromatography on silica gel to afford the desired product.

Acknowledgements

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