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An efficient Stille cross-coupling reaction catalyzed by *ortho*-palladated complex of tribenzylamine under microwave irradiation

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The catalytic activity of $[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)\}(\mu\text{-}Br)]_2$ complex as an efficient, stable and catalyst that is non-sensitive to air and moisture was investigated in the Stille cross-coupling reaction of various aryl halides with phenyltributyltins under microwave irradiation. The substituted biaryls were produced in excellent yield in short reaction times using a catalytic amount of this complex in DMF at 100 C. The combination of dimeric complex as homogeneous catalyst and microwave irradiation and also DMF as microwave-active polar solvent gave higher yields in shorter reaction times. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: cyclopalladated catalyst; tribenzylamine; Stille reaction; biaryls

Introduction

The palladium-catalyzed cross-coupling of nucleophilic organostannanes with electrophilic organic halides and triflates, known as the Stille reaction,[1–3] has emerged as a powerful and versatile tool for the formation of C=C coupling reactions in the construction of new materials, natural product synthesis,[4] carbohydrate chemistry,[5] and biological research.[6] This cross-coupling reaction has gained importance due to the growing availability of the organostannanes, their stability to moisture and air, which leads to convenience in purification and storage of these reagents, and excellent compatibility with a large variety of functional groups, thereby eliminating the protection and then deprotection strategies that are a necessity with most organometallic reactions. The mild reaction conditions employed during couplings are reflected in the frequent use of Stille couplings among the final steps of complex natural-product syntheses.[7–9] The organostannane partner typically contains a single transferable group, most often aryl, heteroaryl, benzyl, allyl, alkenyl, or alkynyl. The remaining groups directly bound to tin transfer at a rate that essentially renders them non-transferable. These non-transferable groups are typically alkyl groups such as methyl or butyl. Trimethyltin derivatives as byproducts are easy to remove but toxic, while tributyltin by-products are less toxic but difficult to remove.[10,11] The Stille coupling is a powerful route to the formation of biaryls. Biaryls are applied as the building block of a wide range of herbicides,[12] pharmaceuticals,[13] natural and bioactive products,[14,15] microelectrode array,[16] conducting polymers, and liquid crystal materials.[17] In view of the importance of biaryls, a number of effective palladium catalytic systems have been developed for the Stille cross-coupling reaction. Generally, the combination of palladium catalysts with various phosphine ligands and also *N*-heterocyclic carbenes (NHC) results in excellent yields and high efficiency. However, most of the phosphine ligands are air-sensitive, expensive, and require an inert environment and large amounts of palladium source for carrying out the reaction, which places significant limits on their synthetic applications. Although carbene-type ligands are more stable than phosphines, they must be synthesized through multi-step processes.[18,19] Thus the development of new and efficient phosphine-free palladium catalytic systems remains a potentially promising field for organic synthesis.[20] Among the new methods the palladacycle catalysts are the most important classes used very efficiently in catalysis at very low concentration in organic synthesis,[21–24] material science,[25] biologically active compounds[26] and macromolecular chemistry.[27–29] The high productivity of the palladacycle catalysts is due to the slow generation of low ligated Pd(0) complexes from a stable palladium(II) pre-catalyst.[30]

Transition-metal-catalyzed cross-coupling reactions typically need long reaction times and an inert atmosphere to reach complete conversion with traditional heating. Microwave-assisted heating under controlled conditions is an alternative method to traditional heating. The real advantage of microwave irradiation is that it is generally quicker and cleaner than conventional heating, reducing reaction time, yielding products in high yield with fewer side products and increasing selectivity. The use of homogeneous metal catalysts in conjunction with microwaves leads to an increased lifetime of the catalyst. The high-speed Stille coupling reaction has been carried out successfully under controlled microwave conditions.[31,32]

In continuation of our recent investigations on the synthesis of the palladacycle catalysts,[33,34] and application of these complexes in microwave-assisted cross-coupling reactions,[35–40] we now wish to report the extension of $[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)(\mu\text{-}Br)\}]_2$ homogeneous complex as a thermally stable and oxygen-insensitive catalyst for the cross-coupling reaction of various aryl halides with phenyltributyltins under microwave irradiation.

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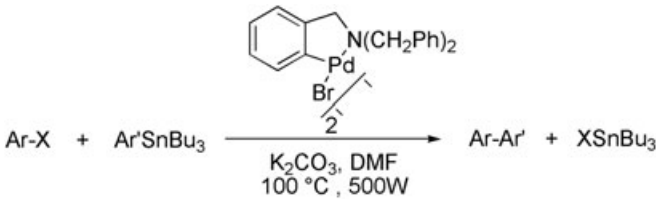
Results and Discussion

We have recently employed dimeric *ortho*-palladate complex $[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)\}(\mu\text{-}Br)]_2$ in the Heck coupling reaction.[41] A suitable chemical production process via palladium catalysis requires high catalyst productivity and activity. Also the availability and cost of catalysts and the price of the organic starting materials are of great importance for industrial processes. Tribenzylamine as an *N*-donor ligand is an available and inexpensive amine. The *ortho*-palladation reaction of this substrate is simple and leads to an efficient catalyst for coupling reactions even with unreactive aryl chlorides, which are available and cheap substrates. Herein, the efficiency of this catalytic system is evaluated in the Stille cross-coupling reaction under microwave irradiation (Scheme 1).

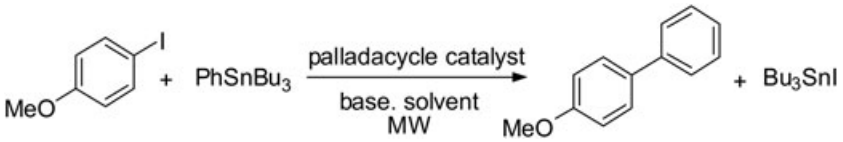
Initially, to determine the optimum conditions, Stille cross-coupling reaction was examined between 4-iodoanisole and phenyltributyltin using dimeric *ortho*-palladate complex of tribenzylamine in different solvents and bases under microwave irradiation. The results are summarized in Table 1. The monitoring system for reaction times, temperature, pressure, and power in a microwave reactor allows for excellent control of reaction parameters, which generally leads to rapid optimization and more reproducible reaction conditions. The direct control of reaction mixture temperature is carried out with infrared sensors.

Among the selected bases, K_2CO_3 was found to be the most effective. Potassium carbonate as a co-catalyst facilitates the reduction of palladium(II) species and has a positive effect on the reaction.[42] Other bases such as Cs_2CO_3, Na_2CO_3, K_3PO_4, NaOAc, and NEt_3 were less effective (Table 1, entries 9–11). We also investigated the efficacy of fluoride salts such as KF, NaF, CsF and tetrabutylammonium fluoride (TBAF) as a base in this reaction (Table 1, entries 10–17). The results using TBAF as base were close to K_2CO_3. A low yield was obtained in the case of no addition of the base (Table 1, entry 18). Several different solvents such as toluene, *p*-xylene, acetonitrile, DMF, *N*-methyl-2-pyrrolidone (NMP), dioxane, THF, methanol and ethanol were examined. Among the tested solvents DMF, as a



Scheme 1. The Stille cross-coupling reaction by a cyclopalladated complex of tribenzylamine.

Table 1. Optimization of base and solvent for Stille cross coupling reaction[a]



Entry	Base	Solvent	Temperature (°C)	4-methoxybiphenyl (%)[b]
1	K_2CO_3	NMP	120	80
2	K_2CO_3	DMF	100	97
3	K_2CO_3	CH_3CN	80	Trace
4	K_2CO_3	Methanol	55	42
5	K_2CO_3	Ethanol	65	54
6	K_2CO_3	Toluene	100	48
7	K_2CO_3	p-Xylene	110	52
8	K_2CO_3	THF	60	36
9	Cs_2CO_3	DMF	100	52
10	Na_2CO_3	DMF	100	65
11	NaOAc	DMF	100	70
12	K_3PO_4	DMF	100	25
13	Et_3N	DMF	100	Trace
14	KF	DMF	100	60
15	NaF	DMF	100	53
16	CsF	DMF	100	70
17	TBAF	DMF	100	90
18	-	DMF	100	30

[a]Reaction conditions: 4-iodoanisole (1 mmol), phenyltributyltin (1.2 mmol), base (1 mmol), solvent (2 ml), palladacycle catalyst (0.3 mol%), 500 W, 3 min.
[b]GC yield.

microwave-absorbing polar aprotic solvent having an ability to additionally stabilize palladium species by weak coordination, gave the best result. Under these conditions 4-methoxybiphenyl was obtained as the desired product in 97% yield and 4,4′-dimethoxybiphenyl was formed due to homocoupling of 4-iodoanisole (2.2%) and biphenyl due to homocoupling of phenyltributyltin (0.8%) as by-products. We also examined homocoupling of $PhSnBu_3$ in the absence of 4-iodoanisole, when biphenyl product was formed in 25% yield.

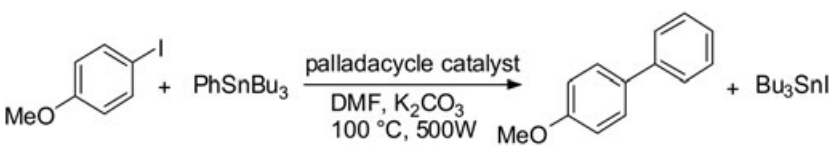
We optimized the concentration of catalyst, employing various amounts of catalyst for this cross-coupling using K_2CO_3 as base and DMF as solvent. The results are summarized in Table 2. The low palladium concentration usually led to a long period of reaction, as increasing the amount of palladium catalyst shortened the reaction time but did not increase the yield of 4-methoxybiphenyl. The best result was obtained when the cross-coupling reaction was carried out with 0.3 mol% of dimeric complex in DMF at 100 °C (Table 2, entry 7).

These optimized reaction conditions were applied in the Stille cross-coupling reaction of various aryl halides under microwave irradiation (Table 3). As this catalytic system is not sensitive to oxygen, the reactions were carried out under air atmosphere.

We examined the electronic and steric effects of various aryl halides bearing electron-donating and electron-wit drawing groups on the resulting yields and conversion times of the reactions. The substituent effects in the aryl iodides emerged to be less significant than in the aryl bromides, and the reactivity of aryl bromides with electron-withdrawing substituent was higher than that of aryl bromides with electron-donating substituent. I- and Br-substituted aryl halides are most reactive; however, Cl analogues are cheaper and more readily available. As expected, the reactivity of aryl chlorides was lower than that of aryl iodides and bromides as the Stille coupling reactions of aryl chlorides required longer times (Table 3, entries 24–28) and lower yields were obtained. The cross-coupling reactions of the less reactive aryl chlorides were examined using a higher load of catalyst (1 mol%); only trace amounts of the cross-coupled products were obtained and biphenyl byproduct was resulted as the main product (Table 3, entries 29 and 30). In some of these cross-coupling reactions, symmetrical biphenyls were produced in low yield (0–5%) due to homocoupling reactions of aryl halides and of phenyltributyltins (0–3%) as byproducts. The steric hindrance of the procedure was examined using 2-, 3- and 4-bromoacetophenone as hindered substituted aryls. Increased hindrance in the vicinity of the leaving group can cause a decrease in the reaction conversion (Table 3, entries 14–16). 2-Bromoacetophenone showed slower reaction times and therefore only a reasonable yield was obtained. The chemoselectivity of the procedure was examined using chlorobromobenzene derivatives (Table 3, entries 17–19). In these reactions Br acted as a better leaving group. This catalytic complex was compatible with a wide range of functional groups such as nitro, cyano, methoxy, halogen, and carbonyl on aryl halides. In comparison with other catalytic systems, a smaller amount of this dimeric *ortho*-palladate complex showed much shorter reaction times, with excellent yields. For example, $Pd_2(dba)_3$ (1.5 mol%)–triaminophosphine ligands (3–6 mol%),[9] $Pd_2(dba)_3$ (0.5–1.5 mol%)–P(t-Bu)$_3$ (1.1–6 mol%) or Pd–P(t-Bu)$_3$ (3 mol%) as an air-stable alternative to $Pd_2(dba)_3$–P(t-Bu)$_3$,[43] $Pd_2(dba)_3$ (1 mol%)–pyrazolyl-based phosphine ligands (2 mol%),[44] $Pd(OAc)_2$ (3 mol%)–Dabco (6 mol%),[45] and $Pd(dba)_2$ (3 mol%)–DAB-Cy (6 mol%)[45b] have been reported in Stille cross-coupling reactions. Higher loads of palladium sources and expensive ligands have been used in these catalytic systems. Among the systems mentioned Pd–P(t-Bu)$_3$ and $Pd_2(dba)_3$–triaminophosphine ligands are active for the cross-coupling reactions of sterically hindered (di-, tri-, and tetra-*ortho*-substituted), deactivated and electron-rich aryl chlorides with organotin compounds. Although the *ortho*-palladated complex of tribenzylamine is a suitable and effective catalyst for the Stille coupling reactions of aryl iodides, bromides and also electronically poor aryl chlorides, it is not effective for deactivated and hindered aryl chlorides. Oxime[46] (3 mol%, at 110 °C, 5–8 h) and phosphite[47] (0.2 mol%, at 120 °C, 15 h) palladacycle complexes have catalyzed the Stille coupling reaction of phenyltributyltin with 4-bromoacetophenone. Stille reaction using the dimeric *ortho*-palladate complex of tribenzylamine is carried out at a lower temperature and shorter reaction time.

A study on palladacycle catalyst cross-couplings showed that the catalyst role in these reactions probably involves palladium nanoparticles, and palladacycles behave as a mere resource for

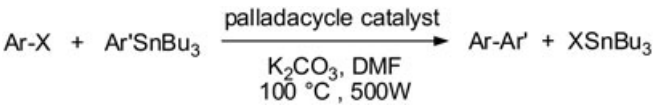
Table 2. Optimization of catalyst concentration in Stille reaction under microwave irradiation[a]



Entry	Catalyst (mol%)	Time (min)	Conversion (%)
1	None	8	0
2	0.005	8	10
3	0.01	8	25
4	0.05	8	50
5	0.1	8	95
6	0.2	6	100
7	0.3	3	100
8	0.4	3	100

[a]Reaction conditions: 4-iodoanisole (1 mmol), phenyltributyltin (1.2 mmol) K_2CO_3 (1 mmol), DMF (2 ml), palladacycle catalyst, 100°C, 500 W.

Table 3. Stille reaction of various aryl halides with phenyltributyltins under microwave irradiation[a]



Entry	Ar-X	$Ar'SnBu_3$	Biaryl product	Time (min)	Yield (%)[a]
1	Ph-I	$PhSnBu_3$	Ph-Ph	2	95
2	Ph-I	*p*-MeO-$PhSnBu_3$	*p*-MeO-Ph-Ph	2	96
3	*p*-MeO-Ph-I	$PhSnBu_3$	*p*-MeO-Ph-Ph	3	94
4	*p*-O_2N-Ph-I	$PhSnBu_3$	*p*-O_2N-Ph-Ph	3	90
5	*p*-HOOC-Ph-I	$PhSnBu_3$	*p*-HOOC-Ph-Ph	6	88
6	Ph-Br	*p*-MeO-$PhSnBu_3$	*p*-MeO-Ph-Ph	2	94
7	Ph-Br	$PhSnBu_3$	Ph-Ph	2	92
8	Ph-Br	*p*-MeOC-$PhSnBu_3$	*p*-MeOC-Ph-Ph	5	86
9	*p*-MeO-Ph-Br	$PhSnBu_3$	*p*-MeO-Ph-Ph	5	92
10	*p*-MeO-Ph-Br	*p*-MeO-$PhSnBu_3$	*p*-MeO-Ph-Ph-*p*-OMe	3	88
11	*p*-O_2N-Ph-Br	$PhSnBu_3$	*p*-O_2N-Ph-Ph	4	90
12	*p*-NC-Ph-Br	$PhSnBu_3$	*p*-NC-Ph-Ph	5	93
13	*p*-MeOC-Ph-Br	*p*-MeOC-$PhSnBu_3$	*p*-MeOC-Ph-Ph-*p*-COMe	7	83
14	*p*-MeOC-Ph-Br	$PhSnBu_3$	*p*-MeOC-Ph-Ph	5	88
15	*m*-MeOC-Ph-Br	$PhSnBu_3$	*m*-MeOC-Ph-Ph	9	76
16	*o*-MeOC-Ph-Br	$PhSnBu_3$	*o*-MeOC-Ph-Ph	12	68
17	*p*-Cl-Ph-Br	$PhSnBu_3$	*p*-Cl-Ph-Ph	3	87
18	*m*-Cl-Ph-Br	$PhSnBu_3$	*m*-Cl-Ph-Ph	4	90
19	*o*-Cl-Ph-Br	$PhSnBu_3$	*o*-Cl-Ph-Ph	10	81
20	*p*-OHC-Ph-Br	$PhSnBu_3$	*p*-OHC-Ph-Ph	6	89
21	*p*-HOOC-Ph-Br	$PhSnBu_3$	*p*-HOOC-Ph-Ph	7	84
22	1-Br-Naphtalene	$PhSnBu_3$	1-Ph-Naphtalene	7	87
23	9-Br-Phenanterene	$PhSnBu_3$	9-Ph-Phenanterene	8	88
24	Ph-Cl	$PhSnBu_3$	Ph-Ph	8	80
25	*p*-OHC-Ph-Cl	$PhSnBu_3$	*p*-OHC-Ph-Ph	10	75
26	*p*-MeOC-Ph-Cl	*p*-MeO-$PhSnBu_3$	*p*-MeOC-Ph-Ph-*p*-OMe	10	86
27	*p*-MeOC-Ph-Cl	$PhSnBu_3$	*p*-MeOC-Ph-Ph	10	80
28	*p*-O_2NPh-Cl	$PhSnBu_3$	*p*-O_2N-Ph-Ph	10	71
29[b]	*p*-H_2NPh-Cl	$PhSnBu_3$	*p*-H_2NPh-Ph	20	Trace
30[b]	*p*-HOPh-Cl	$PhSnBu_3$	*p*-HOPh-Ph	20	Trace

Reaction conditions: aryl halide (1 mmol), phenyltributyltin (1.2 mmol), K_2CO_3 (1 mmol), DMF (2 ml), palladacycle catalyst (0.3 mol%), 100°C, 500 W.
[a]Isolated yield.
[b]Palladacycle catalyst (1 mol%)

producing Pd(0) nanoparticles.[48] NC palladacycles decompose to liberate catalytic Pd(0) species and show a positive Hg(0) test which was assigned as probable evidence for catalysis by Pd nanoparticles.[49] To evaluate the proposed mechanism, the mercury drop test was applied. In the presence of a heterogeneous catalyst, mercury leads to the amalgamation of its surface. In contrast, Hg(0) cannot have a poisoning effect on homogeneous palladium complexes, where the Pd(II) metal center is tightly bound to the ligand. When a drop of Hg(0) was added to the reaction mixture of 4-iodoanisole and phenyltributyltin under the mentioned optimized conditions and the reaction mixture was heated, no catalytic activity was observed for the catalyst.

Conclusions

In this work, a general protocol was applied for the microwave-promoted Stille reaction of various aryl halides using the *ortho*-palladated complex of tribenzylamine. Catalytic amounts of this dimeric complex as an inherent air- and moisture-resistant catalyst converted various aryl halides to the corresponding biaryls in excellent yield. The combination of homogeneous complex as catalyst and microwave irradiation caused the lifetime of the catalyst to increase, improved the yield of the reactions and decreased reaction times.

Experimental

General

All melting points were taken on a Gallenkamp melting apparatus and are uncorrected. ^1H NMR spectra were recorded at 400 MHz in $CDCl_3$ solution at room temperature, with tetramethylsilane (TMS) as internal standard) on a Bruker Avance 500 instrument (Rheinstetten, Germany) and Varian 400 NMR. FT-IR spectra were recorded on a spectrophotometer (Jasco-680, Japan). Spectra of

solids were obtained using KBr pellets. Vibrational transition frequencies are reported as wave number (cm^{-1}). We used a Milestone microwave (Microwave Labstation- MLS GmbH- ATC-FO 300) for synthesis. We also used gas chromatography (GC) (BEIFIN 3420 gas chromatograph equipped a Varian CP SIL 5CB column: 30 m, 0.32 mm, 0.25 μm) for examination of reaction completion and yields. Palladium acetate, aryl halides and all chemicals were purchased from Merck and Aldrich and were used as received.

General Procedure for the Stille Reaction of Aryl Halides

A mixture of the aryl halide (1 mmol), phenyltributyltin (1.2 mmol), K_2CO_3 (1 mmol) and palladacycle catalyst A (0.3 mol%) was added to DMF (2 ml) in a round-bottom flask equipped with a condenser and placed in the Milestone microwave. Initially using a microwave power of 500 W, the temperature was ramped from room temperature to 100 °C, this taking approximately 1 min, and then held at this temperature until the reaction was completed. During this time, the power was modulated automatically to keep the reaction mixture at 100 °C. The mixture was stirred continuously using an appropriate magnet during the reaction. After the reaction was completed, the mixture was cooled to room temperature and diluted with water and *n*-hexane or diethyl ether. The organic phase was washed with saturated KF solution and dried over $MgSO_4$. The solution was then filtered and the solvent was evaporated using a rotary evaporator. The residue was purified by silica gel column chromatography (*n*-hexane or *n*-hexane–ethyl acetate (9:1)) (Table 3, entries 15–16, 19, 21, 25–30) or by recrystallization (Table 3, entries 8 and 12).

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