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The Pd(0) nanoparticles stabilized by collagen fibres as a recyclable heterogeneous catalyst for the Stille reaction under aerobic condition

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Abstract. The stabilized palladium(0) nanoparticles by collagen fibres was a highly active, air-stable and recyclable heterogeneous catalyst that could be used for the Stille coupling reactions between aryl iodides and organostannanes under aerobic conditions. This method offered the several advantages: high yield under facile reaction condition and easy work-up procedure. The catalyst was easily recovered from the reaction mixture by filtration and reused multiple times without significant reduction or decrease in the activity.

Keywords. Stille coupling; Pd(0) nanoparticle catalyst; organostannanes; aryl iodide; heterogeneous catalyst; collagen fibres.

1. Introduction

The Stille cross-coupling reactions of organohalides with organotin compounds have been proven to be a useful synthetic method for the C–C bond formation in organic synthesis. Many homogeneous palladium catalysts such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$ and $PdCl_2(MeCN)_2$ for the Stille cross-coupling reaction are known.[1–5] Unfortunately, all of these known methods generally required dry, oxygen-free and drastic reaction conditions and tedious work-up procedures due to use of homogeneous catalyst. Therefore, it is desirable to develop a more efficient and convenient method employing the heterogeneous catalytic conditions.[6]

In recent years, heterogeneous catalysts have played a crucial role in organic syntheses because of economic and environmental considerations. These catalysts are generally less expensive, eco-friendly, highly reactive, easy to handle and recoverable.[7]

A number of effective methods have been reported in recent years for the Stille coupling reactions in the presence of heterogeneous catalysts.[6a] These catalysts possessing high activity have attracted significant interest because they can be easily recovered and reused, leading to a reduction in waste. The development of a catalytic synthetic method for still reaction remains an active research area.

Collagen is a class of renewable biopolymers originated from the skin of domestic animals, which are widely used as a potential biomaterial for the preparation of catalyst supporter. Collagen fibre-supported Pd catalysts having high activity and selectivity are currently attracting a great interest due to their easy separation and recovery.[8]

However, to the best of our knowledge, Stille reactions catalysed by CF-supported Pd catalysts have received less attention. This encouraged us to investigate the Pd(0) nanoparticle catalyst stabilized by EGCG-grafted CF (Pd(0)-EGCG-CF)[8e] for the Stille reaction (scheme 1). Our approach was guided by three imperatives: (i) the biopolymer reagent should be easily accessible; (ii) starting from readily available and cheap reagents; and (iii) the biopolymer reagent should be air stable, which should allow its storage in normal bottles with extended shelf life.

We report here a new protocol for the Stille coupling of aryl iodides with organostannanes under aerobic conditions using Pd(0) nanoparticle catalyst stabilized by EGCG-grafted CF (Pd(0)-EGCG-CF) as an efficient heterogeneous catalyst (scheme 1). This catalyst is safe, easy to handle, air stable, environmentally benign with fewer disposals problems. The catalyst was characterized by using powder XRD, XPS, SEM, TEM and FT-IR spectroscopy.[8e]

2. Experimental

2.1 *General*

All reagents were purchased from Merck and Aldrich and used without further purification. Products were

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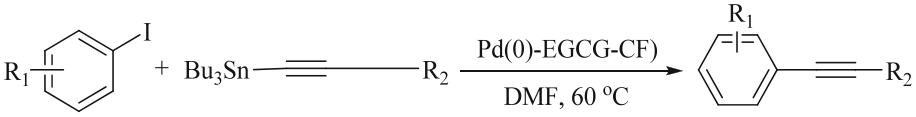


Scheme 1. Stille coupling of aryl iodides with alkynylstannanes in the presence of Pd(0)-EGCG-CF.

characterized by spectroscopy data (NMR spectra), and melting points. The NMR spectra were recorded in DMSO and $CDCl_3$. ^1H NMR spectra were recorded on a Bruker Avance DRX 300 and 400 MHz instruments.

2.2 *General procedure for the Stille coupling reaction*

Aryl iodide (1.0 mmol), Pd(0)-EGCG-CF (2.0 mol%), and DMF (3 mL) were added to a flask, and the resulting mixture was stirred at room temperature for 15 min under aerobic conditions. To this, suspension was added organostannane (1.2 mmol) and the reaction mixture was stirred at 60°C for an appropriate time (TLC). The mixture was dissolved in Et_2O (30 mL). The Pd(0)-EGCG-CF catalyst was separated from the reaction mixture by filtration after each experiment, washed with water and acetonitrile and dried carefully before use in subsequent runs. The ethereal solution was treated with 20% aqueous KF (10 mL) for 30 min before being dried and concentrated. The solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as eluent to give the desired product. The pure products were characterized by IR, ^1H NMR and melting point. All the products are known compounds and the spectral data and melting points were identical to those reported in the literature.[9]

2.3 *Spectroscopic data of selected products*

2.3a *Diphenylacetylene (table 2, entry 1)*: Mp 61–62°C (lit.[17] 60–62°C); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.55–7.50 (m, 4H), 7.34–7.30 (m, 6H).

2.3b *(4-Methoxyphenyl)phenylacetylene (table 2, entry 2)*: Mp 60–61°C (lit.[18] 57–61°C); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.57–7.51 (m, 2H), 7.50 (d, J = 8.9 Hz, 2H), 7.40–7.35 (m, 3H), 6.91 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H).

2.3c *Phenyl-p-tolyacetylene (table 2, entry 3)*: Mp 70–72°C (lit.[19] 72–73°C); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53–7.48 (m, 2H), 7.43 (d, J = 7.91 Hz, 2H), 7.30–7.25 (m, 3H), 7.10 (d, J = 7.91 Hz, 2H), 2.32 (s, 3H).

2.3d *(4-Acetylphenyl)phenylacetylene (table 2, entry 4)*: Mp 95–97°C (lit.[20] 94–96°C); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.94 (d, J = 8.52 Hz, 2H), 7.60 (d, J = 8.52 Hz, 2H), 7.55–7.51 (m, 2H), 7.39–7.35 (m, 3H), 2.61 (s, 3H).

2.3e *(4-Nitrophenyl)phenylacetylene (table 2, entry 5)*: Mp 121–122°C (lit.[21] 120–121°C); ^1H NMR ($CDCl_3$, 300 MHz) δ 8.21 (d, J = 8.83 Hz, 2H), 7.66 (d, J = 8.73 Hz, 2H), 7.57–7.53 (m, 2H), 7.40–7.37 (m, 3H).

2.3f *(3-Nitrophenyl)phenylacetylene (table 2, entry 6)*: Mp 68–70°C (lit.[22] 68–70°C); ^1H NMR ($CDCl_3$, 300 MHz) δ 8.32 (s, 1H), 8.12 (d, J = 8.10 Hz, 1H), 7.77 (d, J = 7.81 Hz, 1H), 7.52–7.48 (m, 3H), 7.36–7.31 (m, 3H).

2.3g *1-Phenylhex-1-yne (table 2, entry 7)*: Oil[23]; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, J = 7.4 Hz, 3H), 1.65–1.49 (m, 4H), 2.43 (t, J = 7.4 Hz, 2H), 7.30–7.25 (m, 3H), 7.44–7.41 (m, 2H).

2.3h *1-(1-Hexynyl)-4-methylbenzene (table 2, entry 8)*: Oil[24]; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.92 (t, J = 7.4 Hz, 3H), 1.61–1.42 (m, 4H), 2.30 (s, 3H), 2.37 (t, J = 7.0 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H).

2.3i *1-(1-Hexynyl)-4-nitrobenzene (table 2, entry 9)*: Oil[14]; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.17 (d, J = 8.9 Hz, 2H), 7.53 (d, J = 8.9 Hz, 2H), 2.50 (t, J = 7.1 Hz, 2H), 1.65–1.58 (m, 2H), 1.53–1.48 (m, 2H), 0.98 (t, J = 7.1 Hz, 3H).

2.3j *1-(1-Hexynyl)-4-methoxybenzene (table 2, entry 10)*: Oil[25]; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, J = 7.4 Hz, 3H), 1.64–1.45 (m, 4H), 2.91 (t, J = 7.1 Hz, 2H), 3.82 (s, 3H), 6.8 k (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H).

2.3k *Trimethyl(2-phenyl-1-ethynyl)silane (table 2, entry 11)*: Oil[26]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.47–7.43 (m, 2H), 7.31–7.28 (m, 3H), 0.24 (m, 9H).

2.3l *Trimethyl[(4-nitrophenyl)ethynyl]silane (table 2, entry 12)*: Oil[10]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.16 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 0.18 (s, 9H).

2.3m *(E) 1-(3-methoxyprop-1-enyl)benzene (table 3, entry 1)*: Oil[16]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.37 (s, 3H), 4.04 (d, J = 6.1 Hz, 2H), 6.27–6.30 (m, 1H), 6.62 (d, J = 15.9 Hz, 1H), 7.42–7.20 (m, 5H).

2.3n *(E) 1-methoxy-4-styrylbenzene (table 3, entry 2)*: Mp 135–136°C (lit.[16] 134–135°C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (d, J = 7.5 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.27–7.22 (m, 1H), 7.09 (d, J = 16.7 Hz, 1H), 7.00 (d, J = 16.7 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H).

2.3o *(Z) 1-methyl-4-styrylbenzene (table 3, entry 3)*: Oil[16]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30–7.20 (m, 5H), 7.17 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.60 (s, 2H), 2.34 (s, 3H).

2.3p *(E) 1-(hex-1-enyl)-4-methoxybenzene (table 3, entry 4)*: Oil[16]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.29 (d, J = 15.4 Hz, 1H), 5.93 (dt, J = 15.4, 7.0 Hz, 1H), 3.82 (s, 3H), 2.20–2.15 (m, 2H), 1.45–1.33 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H).

2.3q *(Z) 1-nitro-4-styrylbenzene (table 3, entry 5)*: Mp 60–62°C (lit.[16] 60.5–61.5°C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.25–7.18 (m, 5H), 6.80 (d, J = 12.5 Hz, 1H), 6.60 (d, J = 12.5 Hz, 1H).

2.3r *(Z) 1-(hex-1-enyl)-4-nitrobenzene (table 3, entry 6)*: Oil[16]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 6.44 (d, J = 11.5 Hz, 1H), 5.84 (dt, J = 11.5, 7.0 Hz, 1H), 2.35–2.30 (m, 2H), 1.49–1.43 (m, 2H), 1.39–1.33 (m, 2H), 0.89 (t, J = 7.0 Hz, 3H).

3. Results and discussion

In the first set of experiments, for optimization of the reaction conditions, the catalytic potential of Pd(0)-EGCG-CF, the effects of the solvents and temperature was investigated for the reaction between iodobenzene and 1-(tributylstannyl)-2-phenylethyne (table 1). As shown in table 1, the reaction was influenced significantly by the solvent employed. The reaction was successful when DMF and NMP were used as the solvent (entries 4 and 7, table 1), especially resulting in the best result in the case of DMF (entry 7, table 1). THF, PhH and CH_3CN were not suitable solvent for this reaction. The optimum amount of Pd(0)-EGCG-CF was found to be 2.0 mol% in the presence of iodobenzene (1 mmol) and 1-(tributylstannyl)-2-phenylethyne (1.2 mmol) in DMF (3 mL) at 60°C under the presented reaction condition. The increase in the amount of the palladium catalyst reduced the reaction time whereas it did not improve the yield of the product (entry 10). A low palladium concentration prolonged the reaction time and led to a reduction in the yield (entry 9).

We have examined the coupling reaction of alkynylstannanes with various aryl iodides containing electron-withdrawing or electron-donating groups (scheme 1). As shown in table 2, alkynylstannanes were converted into the corresponding products in high yields under mild conditions.

The optimized catalyst system was quite general and compatible with a wide range of functional groups such as nitro, methoxy, carbonyl and silyl on either partner. We attempted to carry out the coupling reactions of heteroaryl iodides such as 3-iodopyridine with alkynylstannanes under the same reaction conditions,

Table 1. Stille coupling of iodobenzene with 1-(tributylstannyl)-2-phenylethyne under various reaction conditions.[a]

Entry	Solvent	Pd(0)-EGCG-CF (mol %)	Temp (°C)	Time (h)	Yield[b] (%)
1	THF	2.0	60	24	20
2	PhH	2.0	60	24	21
3	MeCN	2.0	60	24	30
4	NMP	2.0	60	5	82
5	DMF	2.0	30	24	31
6	DMF	2.0	40	24	62
7	DMF	2.0	60	5	87
8	DMF	2.0	80	5	76
9	DMF	1.0	60	9	72
10	DMF	2.5	60	5	76

[a]Reaction conditions: iodobenzene (1 mmol), 1-(tributylstannyl)-2-phenylethyne (1.2 mmol), solvent (3 mL), aerobic conditions
[b]Isolated yield

Table 2. Stille coupling of aryl iodides with alkynylstannanes.[a]

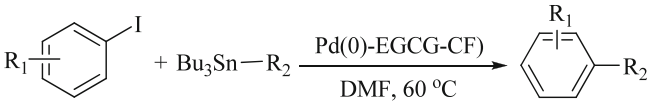
Entry	R_1	R_2	Time (h)	Yield[b] (%)
1	H	Ph	5	88, 85[b]
2	4-OMe	Ph	5	86
3	4-Me	Ph	5	84
4	4-COMe	Ph	5	85
5	4-NO_2	Ph	5	87
6	3-NO_2	Ph	5	86
7	H	n-C_4H_9	5	86
8	4-Me	n-C_4H_9	7	87
9	4-NO_2	n-C_4H_9	5	89
10	4-OMe	n-C_4H_9	7	87
11	H	Me_3Si	7	86
12	4-NO_2	Me_3Si	7	85

[a]Reaction conditions: iodobenzene (1 mmol), alkynylstannanes (1.2 mmol), Pd(0)-EGCG-CF (2.0 mol%), DMF (3 mL), aerobic conditions, 65°C
[b]Isolated yield
[c]Yield after the 5th cycle

but this was unsuccessful, no desired coupled product was detected after 30 h of reaction time.

The yields of coupled products are high and the organotin reagents can be readily synthesized, purified, and stored. The developed methodology was also applicable for the Stille coupling reactions of vinylstannanes with aryl iodides. The Stille coupling of aryl iodides with a variety of vinylstannanes was investigated (scheme 2), the experimental results are summarized in table 3. The Stille coupling reactions of a variety of aryl iodides with (*Z*)- or (*E*)-vinylstannanes proceeded smoothly in the presence of a catalytic amount of Pd(0)-EGCG-CF in DMF at 60°C to afford the corresponding coupled products in high yields with retention of the configuration (entries 1–6).

In a typical experiment, after the reaction was completed, Pd(0)-EGCG-CF as a catalyst was isolated from the reaction mixture by simple filtration in the work-up stage. The reusability of the catalyst was evaluated after washing the catalyst by water and acetonitrile and drying in an oven. Pd(0)-EGCG-CF was reused for five repeated times with consistent activity (table 2, entry 1). Moreover, even after five time uses of the Pd(0)-EGCG-CF, there was no decrease in the activity of the catalyst. This reusability demonstrates the high stability and



Scheme 2. Stille coupling of aryl iodides with vinylstannanes in the presence of Pd(0)-EGCG-CF.

Table 3. Stille coupling of aryl iodides with vinylstannanes.[a]

Entry	R_1	R_2	Time (h)	Yield[b] (%)
1	H	(*E*)-$MeOCH_2CH$=CH	5	90
2	4-OMe	(*E*)-PhCH=CH	7	90
3	4-Me	(*Z*)-PhCH=CH	7	87
4	4-OMe	(E)-BuCH=CH	5	88
5	4-NO_2	(*Z*)-PhCH=CH	5	89
6	4-NO_2	(*Z*)-BuCH=CH	5	86

[a]Reaction conditions: iodobenzene (1 mmol), vinylstannanes (1.2 mmol), Pd(0)-EGCG-CF (2.0 mol%), DMF (3 mL), aerobic conditions, 60°C
[b]Isolated yield

turnover of Pd(0)-EGCG-CF under operating condition. The reusability of the catalysts is one of the most important benefits and makes them useful for commercial applications.

4. Conclusion

In conclusion, we have developed a simple and highly efficient method for the heterogeneous Stille coupling reaction of alkynylstannane with aryl iodides under aerobic conditions using Pd(0)-EGCG-CF as a reusable catalyst. The significant advantages of this methodology are high yields, simple work-up procedure, excellent performance and reusability of the catalyst. The catalyst was separated from the reaction mixture and reused five times without significant loss of catalytic activity. This catalyst also has shown excellent activity on an industrial scale and in most cases it can be recovered from reaction mixture and reused. This methodology may be widely applied for the Stille reaction coupling in organic synthesis.

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