

Nickel-catalysed cross-coupling reactions of aryl halides with organostannanes

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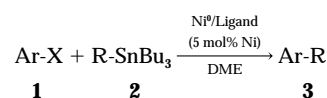
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A triphenylphosphine–nickel complex is found to be an active catalyst for the cross-coupling reactions of various types of aryl halides, including unactivated aryl chlorides, with alkynyl-, alkenyl- and allyl-stannanes to give the corresponding coupled products in high yields.

Transition metal-catalysed cross-coupling reactions are now powerful tools in organic synthesis.¹ Amongst these, the palladium-catalysed coupling of organostannanes with aryl halides has gained increasing popularity.² Much attention has been paid to the creation of an active catalyst with the aim of expanding the utility of this already useful reaction.³ There are, however, few examples that utilize transition metals other than palladium in the coupling of aryl halides (or pseudohalides) with organostannanes.⁴ Nickel catalysts have never been used for this reaction,⁵ except for the coupling of an aryl methanesulfonate (mesylate) with tributylphenyltin as reported by Percec *et al.*, who observed that the homo-coupling of aryl mesylates predominated (45–64%) and the yields of the cross-coupled product were low (23–24%).⁶ Here we report that a triphenylphosphine–nickel complex is a highly active catalyst for the coupling of aryl halides, including aryl chlorides, with organostannanes. This is the first demonstration that even unactivated aryl chlorides can be used as substrates of the coupling reaction.⁷ From an industrial point of view it is noteworthy that aryl chlorides are applicable to the coupling reaction⁸ because they are inexpensive and easily available in bulk quantities compared with aryl bromides or iodides.

We first examined the catalytic activity of various nickel complexes for the reaction of 2-chloronaphthalene **1a** with

tributylvinyltin **2a** (Scheme 1). A zero valent nickel species was



Scheme 1

generated *in situ* from Ni(acac)₂ and diisobutylaluminium hydride (1:2 ratio). We found that the nickel(0) species in the presence of four equivalents of triphenylphosphine catalysed the reaction highly efficiently. For example, the coupling of **1a** with **2a** in the presence of 5 mol% of the nickel(0) catalyst and 20 mol% of triphenylphosphine in 1,2-dimethoxyethane at 80 °C for 9 h gave an 86% yield of 2-vinylnaphthalene **3a** (entry 1 of Table 1). Under the same reaction conditions, the use of tri(*o*-tolyl)phosphine, tri(2-furyl)phosphine or tributylphosphine was less effective, giving lower yields of **3a** (entries 2–4). Among bidentate phosphine ligands, 1,1'-bis(triphenylphosphino)ferrocene⁹ gave a moderate yield of **3a** after a prolonged reaction time (entry 5), whereas 1,3-bis(triphenylphosphino)propane only gave very poor yields (entry 6).

The triphenylphosphine–nickel-catalysed coupling reaction was applied to various aryl halides with organostannanes (Table 1, entries 7–14). The coupling reaction of tributylvinyltin with chloro arenes having an electron-withdrawing group, such as a formyl or acetyl group, gave good yields of the corresponding vinyl arenes in yields over 80% (entries 7–9). It is noteworthy that a substituent at the *ortho* position neither retarded the reaction nor reduced the yields (entries 8 and 9). Phenylethynyl- and hex-1-ynyl-tributyltin also coupled with 2-

Table 1 Ni⁰-catalysed coupling of aryl halides with organostannanes^a

Entry	Ligand (ligand : Ni)	1		2 R	t/h	Yield (%) ^b of 3
		X	Ar			
1	Ph ₃ P (4)	Cl	2-naphthyl	vinyl	9	86
2	(<i>o</i> -tolyl) ₃ P (4)	Cl	2-naphthyl	vinyl	18	<5 ^c
3	(2-furyl) ₃ P (4)	Cl	2-naphthyl	vinyl	41	64
4	Bu ₃ P (4)	Cl	2-naphthyl	vinyl	17	<5 ^c
5	dppf ^d (2)	Cl	2-naphthyl	vinyl	31	65
6	dppp ^e (2)	Cl	2-naphthyl	vinyl	20	<5 ^c
7	Ph ₃ P (4)	Cl	4-CHO-C ₆ H ₄	vinyl	9	86
8	Ph ₃ P (4)	Cl	4-MeCO-C ₆ H ₄	vinyl	24	88
9	Ph ₃ P (4)	Cl	2-MeCO-C ₆ H ₄	vinyl	16	81
10	Ph ₃ P (4)	Cl	2-naphthyl	PhC≡C	70	79
11	Ph ₃ P (4)	Cl	2-naphthyl	BuC≡C	38	81
12	Ph ₃ P (4)	Br	2-naphthyl	PhC≡C	17	89
13	Ph ₃ P (4)	Br	2-naphthyl	vinyl	6	86
14 ^f	Ph ₃ P (4)	Br	2-naphthyl	allyl	24	69

^a The reaction was carried out at 80 °C in 1,2-dimethoxyethane (2 ml) using an aryl halide (0.756 mmol) and an organostannane (0.911 mmol) in the presence of 5 mol% of a Ni⁰ complex. The Ni⁰ complex was prepared *in situ* from Ni(acac)₂ (0.038 mmol) and a 0.95 M hexane solution of diisobutylaluminium hydride (0.076 mmol) in the presence of a ligand. ^b Isolated yield based on aryl halide. ^c Determined by ¹H NMR spectroscopy. ^d 1,1'-Bis(diphenylphosphino)ferrocene. ^e 1,3-Bis(diphenylphosphino)propane. ^f Large excess of allyltributyltin (1.52 mmol) was used.

chloronaphthalene in high yields (entries 10 and 11). The nickel complex was also effective for the coupling reaction of 2-bromonaphthalene with phenylethynyl-, vinyl- and allyl-tributyltin in good yields (entries 12–14).

Experimental

Preparation of 2-(hex-1-ynyl)naphthalene

Under an argon atmosphere, a 0.95 M solution of diisobutylaluminium hydride in hexane (0.08 ml) was added to a mixture of Ni(acac)₂ (9.8 mg, 0.038 mmol), triphenylphosphine (39.8 mg, 0.152 mmol), 2-chloronaphthalene (123 mg, 0.756 mmol) and tributyl(hex-1-ynyl)tin (338 mg, 0.911 mmol) in 1,2-dimethoxyethane (DME) (2 ml) at room temp. After stirring for 38 h at 80 °C, the solution was treated with aqueous 1 M KF (2 ml) for 30 min. Filtration through a Celite plug was followed by addition of ethyl acetate (30 ml). After separation of the aqueous layer, the organic layer was washed successively with water and brine, dried over MgSO₄ and concentrated. Gel permeation chromatography gave 2-(hex-1-ynyl)naphthalene (0.128 g, 81%) as a colorless oil; δ_{H} (CDCl₃) \dagger 0.97 (t, *J* 7.0, 3 H), 1.41–1.72 (m, 4 H), 2.46 (t, *J* 6.8, 2 H), 7.39–7.52 (m, 4 H), 7.69–7.96 (m, 3 H) (Calc. for C₁₆H₁₆: C, 92.26; H, 7.74. Found: C, 92.48; H, 7.70%).

Other products, which have already been reported in the literature, were obtained in a similar manner. \ddagger

\dagger *J* Values are given in Hz.

\ddagger ¹H NMR data for the products: 2-Vinylnaphthalene δ_{H} (270 MHz, CDCl₃) 5.34 (dd, *J* 10.9, 0.7, 1 H), 5.88 (dd, *J* 17.7, 0.7, 1 H), 6.89 (dd, *J* 17.7, 10.9, 1 H), 7.40–7.50 (m, 2 H), 7.61–7.67 (m, 1 H), 7.72–7.86 (m, 4 H). 4-Vinylbenzaldehyde¹⁰ δ_{H} (270 MHz, CDCl₃) 5.44 (d, *J* 10.9, 1 H), 5.91 (d, *J* 17.7, 1 H), 6.77 (dd, *J* 17.7, 10.9, 1 H), 7.52–7.58 (m, 2 H), 7.82–7.87 (m, 2 H), 9.99 (s, 1 H). 4-Vinylacetophenone¹¹ δ_{H} (200 MHz, CDCl₃) 2.59 (s, 3 H), 5.39 (dd, *J* 11.0, 0.7, 1 H), 5.87 (dd, *J* 17.6, 0.7, 1 H), 6.75 (dd, *J* 17.6, 11.0, 1 H), 7.41–7.56 (m, 2 H), 7.84–8.00 (m, 2 H). 2-Vinylacetophenone¹² δ_{H} (200 MHz, CDCl₃) 2.58 (s, 3 H), 5.34 (dd, *J* 10.9, 1.3, 1 H), 5.64 (dd, *J* 17.4, 1.3, 1 H), 7.20 (dd, *J* 17.4, 10.9, 1 H), 7.28–7.68 (m, 4 H). 2-(Phenylethynyl)naphthalene¹³ δ_{H} (270 MHz, CDCl₃) 7.20–7.71 (m, 8 H), 7.73–7.96 (m, 3 H), 8.06 (s, 1 H). 2-Allylnaphthalene¹⁴ δ_{H} (270 MHz, CDCl₃) 3.47–3.64 (m, 2 H), 5.02–5.25 (m, 2 H), 5.95–6.16 (m, 1 H), 7.29–7.50 (m, 3 H), 7.63 (s, 1 H), 7.73–7.85 (m, 3 H).

Acknowledgements

We thank Professor Tamio Hayashi (Kyoto University) for helpful discussions.

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Paper 7/05078J

Received 15th July 1997

Accepted 15th July 1997