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Efficient and High Turnover Homocoupling Reaction of Aryl Iodide by the Use of Palladacycle Catalyst. A Convenient Way to Prepare Poly-*p*-phenylene.

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Abstract: Monoiodoarenes undergo reductive coupling to produce biaryls in high yields in the presence of less than 0.1 mol % of palladacyle and *N,N*-diisopropylethylamine in DMF at 100°C. Under similar reaction conditions, *p*-diiodobenzene produces poly-*p*-phenylene in greater than 85% isolated yields.

Keywords: Coupling reactions; Palladium and compounds; Aryl halides; Polymerisation.

The uses of copper,[1] magnesium,[2] or nickel[3] as the promoter to run the reductive homocoupling of aryl halides for preparing symmetrical biaryls under drastic or mild reaction conditions are important methods in synthetic organic chemistry. The use of catalytic amount of palladium complexes to produce biaryls has also been reported in the literature.[4] However, the long reaction time (≥ 48 hrs) and in low yields severely limits its practical applications in organic synthesis. Another drawback with the use of reported catalyst, palladium acetate, in the polymerization of diiodobenzene is that the contamination of black metallic palladium deposited in the polymer during the reaction are often observed.[4] Thus, a suitable catalyst to avoid contamination as well as to achieve good yield in a shorter reaction time would therefore be highly desirable. We reported here that the use of palladacycle catalyst, as reported to be the effective and stable catalyst for Heck reaction,[5] in conjunction with *N,N*-diisopropylethylamine as a base could solve the above problems.

The choice of tertiary amine is interesting in this reaction. As it was reported by Norman,[4] reaction took a long time and often did not go to the completion when triethylamine was used as a base.[6] When tri-*n*-butylamine was used as a base, a major side reaction to produce butyrophenone was observed. Similar results were obtained when we carried out reactions with either of these two bases and palladacycle catalyst in DMF. However, when *N,N*-diisopropylethylamine was used as a base, the results were greatly improved. We did not observe any side reaction products except protiodeiodination product was obtained in less than 5 % yield as judged by GC/MS and ^{1}H-NMR spectral analysis. The reactions can be over within 12 hrs at 100°C. Thus, both reaction rate and yield are higher by the use of palladacycle catalyst and *N,N*-diisopropylethylamine than the use of palladium acetate and triethylamine or tri-*n*-butylamine. The use of tetrakis(triphenylphosphine)palladium(0) or running the reaction in the absence of base for iodobenzene will give lower yield (~50%) and no reaction at all, respectively. However, we did not get any success when bromo or chloro arenes were used in the reaction as reported in the literature.[4] Actually, bromo- or

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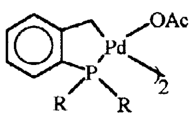
chlorobenzene was found to remain intact, under this reaction condition. Raising the temperature to 140°C and prolonging the reaction time to 24 hrs also did not bring about any positive improvements. Degassing of DMF and running the reaction under anhydrous condition are important to obtain good yield and avoid the formation of arenes via protiodeiodination of aryl iodides. We did not observe much difference in yields (see **Table 1**) with variation of the substituents. However, the rate is faster in the case of electron withdrawing group attached to the benzene ring than that with electron donating group. For example, the reaction of *p*-iodonitrobenzene to form biaryl could be completed in 7 hrs while it took 12 hrs for 1-iodo-4-methoxybenzene to complete the reaction. To check the efficiency of the catalyst, complete disappearance of the 4-iodotoluene was observed after 12 hrs when the catalyst quantity was reduced to 0.1 mol %. The use of tertiary amine is critically important in the homocoupling reaction. The use of other kinds of amine may lead to either lower yields or only trace amount of the homocoupling products (**Table 2**).

As a typical procedure, aryl iodide(0.21 g, 1 mmole) is stirred under nitrogen atmosphere for 8 to 12 hrs in the presence of palladacycle (5 mg, 0.005 mmole) and *N,N*-diisopropylethylamine(0.16 g, 1.2 mmole) in DMF (0.75 mL) at 100°C. Usual work up with water (5 mL) and extraction with ethyl acetate (2 mL x 3) gives a dark red colored solution, which on drying over $MgSO_4$ and passing through a column (silica gel) gives colorless or pale yellow solution. A semisolid mass was obtained after evaporation of the solvent. Recrystallization from ethanol afforded almost pure biaryls.

Table 1. Palladacycle-Catalyzed Homocoupling of Aryl Iodide

$$\text{ArI} \xrightarrow[\text{base, } 110^{\circ}\text{C, 12 h}]{\text{Pd cat./DMF}} \text{Ar-Ar}$$

Pd cat. =



R = *o*-tolyl

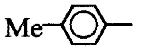
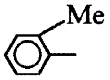
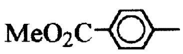
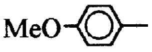
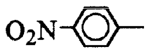
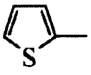
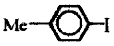
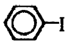
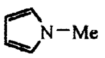
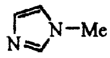
Entry	Ar =	Iso. Yield (%)
1	Ph-	85
2		87
3		74
4		76
5		70
6		80
7		87

Table 2. Base Effect for the Pd-Catalyzed Homocouplings.

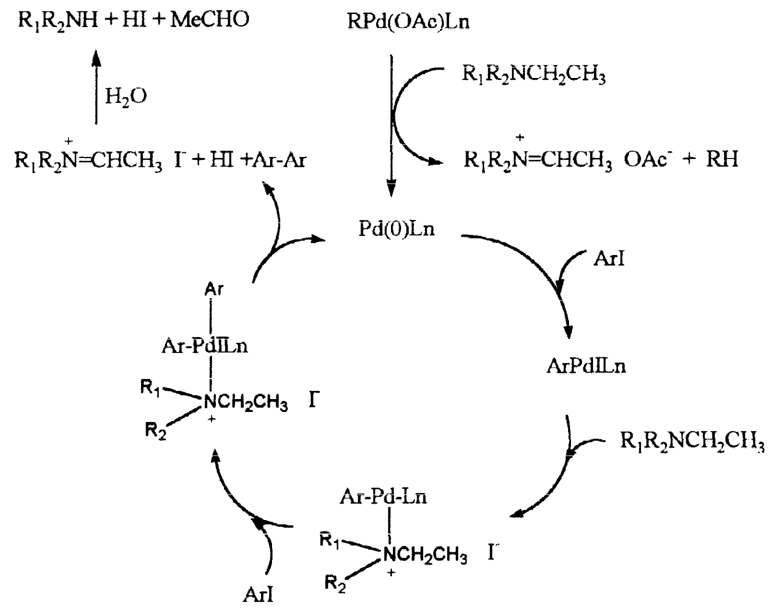
Entry	Base	ArI	Temp (℃)	Time(h)	Yield (%) of Biaryl
1	i-Pr$_2$NEt		110	12	87
2	n-Bu$_3$N	"	120	14	39
3	Et$_3$N	"	120	16	58
4			110	24	trace[a]
5		"	120	16	69
6		"	110	24	trace[a]
7		"	120	16	trace[a]
8		"	110	24	trace[a]
9	PhCHMeNH$_2$	"	110	16	trace[a]
10	PhNHEt		110	12	trace[a]

[a] Biaryl products were found in GC/MS spectral analysis.

In a similar way, 1,4-diiodobenzene (0.66 g, 2 mmole) was treated with palladacycle (1.4 mg, 0.0015 mmole) and *N,N*-diisopropylethylamine (0.62 g, 4.8 mmol) at 100°C for 8 hrs. Some solid was precipitated when the reaction mixture was diluted with cold water. After washing it thoroughly with water, acetone, and ethyl acetate, a pale yellow solid (210 mg) in ca 70 % yield was obtained. IR spectrum of this solid matches satisfactorily with that reported for poly-*p*-phenylene.[7]

Along with the synthetic utility, the pathway of the homocoupling reaction of using palladium catalyst draws attention since it has to be very different from Heck or cross-coupling reaction, because the substrates do not provide any hydrogen to form hydrogen iodide which would be used for forming quarternary ammonium salt with amines. The possibility of a radical pathway in the reaction might be eliminated because hardly any change in the reaction yield or the rate of the reaction was observed when it was carried out in the presence of 5 mol % of galvinoxyl. Moreover, neither aqueous nor organic layer during work up process undergoes any observable color changes on treatment with sodium thiosulfate, indicating the absence of iodine, which is likely to be generated in radical pathway. On the contrary, the aqueous layer produces iodine on treatment with hydrogen peroxide, indicating the presence of hydrogen iodide as salt of amine. The plausible pathway for the above reaction was shown in **Scheme I**. Thus, oxidation of tertiary amine by palladacycle may form iminium salt and palladium(0) complexes. The replacement of iodo with amido group followed by another oxidative addition of aryl iodide to form Pd(IV) complexes. The following reductive elimination will form biaryl, hydrogen iodide and iminium salt. The presentation of hydrogen iodide ammonium salt leads us to accept the suggested mechanism as the most likely pathway for this apparently simple but mechanistically complicated reaction.

Scheme I. The Plausible Reaction Pathway for the Homocoupling Reaction of Aryl Iodide in the Presence of Palladacycle Catalyst.



Result of this work provides an efficient method for homocoupling reaction of aryl iodide. While its applicability in polymerization will be further established, the success of using palladacycle in homocoupling reaction and Heck reaction[5] reconfirms its superiority as a catalyst over conventional ordinary palladium acetate.

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References:

1. P. E. Fanta, *Synthesis*, **1974**, 9.
2. S. Stokes, *J. Chem. Soc.*, **1908**, *93*, 70.
3. S.I. Inaba, H. Matsumoto, R.D. Rieke, *Tetrahedron Lett.*, **1982**, *23*, 4215.
4. F.R.S. Clark, R.O.C. Norman, C.B. Thomas, *J. Chem. Soc., Perkin I*, **1975**, 121.
5. (a) W.A. Herrmann, C. Brossmer, K. Öfele, C.P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem. Int. Edu.Engl.* **1995**, *34*, 1844. (b) M. Beller, T.H. Riermeier, *Tetrahedron Lett.*, **1996**, *37*, 6535.
6. The lower b.p. of triethylamine (b.p. 89°C) than that of *N,N*-diisopropylethylamine (b.p. 127°C) may be responsible for this different result.
7. T. Yamamoto, Y. Hayashi, A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **1978**, *51*, 2091.