

## Retraction

---

### **Novel CuI/tributyl phosphine catalyst system for amination of aryl chlorides**

Nandkumar M. Patil, Ashutosh A. Kelkar, Zahid Nabi and Raghunath V. Chaudhari

*Chem. Commun.*, 2003, 2460 (DOI: 10.1039/b308034j). **Retraction published 27th September 2004**

---

We, the named authors, hereby wholly retract this Chemical Communication.

Signed: Nandkumar M. Patil, Ashutosh A. Kelkar, Zahid Nabi and Raghunath V. Chaudhar, Pune, India, September 2004.

Retraction endorsed by Sarah Thomas, Managing Editor

## Novel CuI/tributyl phosphine catalyst system for amination of aryl chlorides†

Nandkumar M. Patil, Ashutosh A. Kelkar, Zahid Nabi and Raghunath V. Chaudhari\*

Homogeneous Catalysis Division, National Chemical Laboratory, Pune-411008, India.

E-mail: rvc@ems.ncl.res.in; Tel: +91-20-5893260

Received (in Cambridge, UK) 15th July 2003, Accepted 18th August 2003

First published as an Advance Article on the web 26th August 2003

A simple and efficient methodology for the synthesis of triarylamines from aryl chlorides in a single step has been demonstrated using a novel CuI/tributyl phosphine catalyst system with high activity and selectivity (80–87% yield).

Arylamines are prevalent in compounds with end use in biological, pharmaceutical and novel materials.<sup>1–3</sup> Their widespread importance has led to the development of many synthetic methods for the formation of aryl–nitrogen bonds.<sup>4</sup> Amongst them, the classical copper-mediated Ullmann coupling and the recently developed palladium(0) catalyzed aryl couplings are the more commonly used methods.<sup>5a–d</sup> Although, the Pd-catalyzed C–N coupling has recently become the most important method for laboratory scale synthesis of substituted aryl amines, the copper mediated coupling is still the reaction of choice for large and industrial-scale production of these compounds<sup>6,7</sup> as shown in Scheme 1.

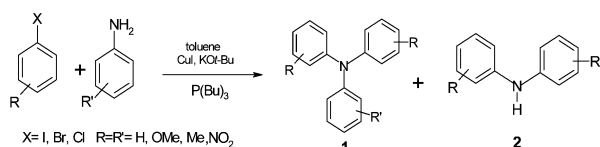
One of the earliest applications of triaryl amines was in the production of brightly colored synthetic dyes, introduced in the late nineteenth century.<sup>8</sup> High purity triarylamines find applications in xerographic photoreceptors,<sup>6</sup> as constituents of non-linear optical chromophores useful in the design of integrated electro-optic switches and modulators. Arylamines have a large number of other applications and are thus attractive targets for

chemical synthesis. Arylamines have also been employed as ligands for transition metals, and in the design of conducting polymers and other electronically interesting materials.<sup>6</sup>

Recently, milder Ullmann type methodologies for the N-arylation of anilines,<sup>9</sup> imidazoles,<sup>10a,b</sup> amides<sup>11</sup> and nitrogen heterocycles<sup>12</sup> have been developed. However, most of the work has been carried out using aryl iodides as reactants. Aryl chlorides are the most attractive aryl halides for synthetic applications on an industrial scale, because they are inexpensive and readily available in bulk quantities. However, there is only one report on the amination of aryl chlorides using copper catalyst with poor results (49% yield of triarylamine in 36 h).<sup>9</sup> Thus, there is a need to develop an improved catalyst system for copper catalyzed amination of aryl chlorides.

Our efforts have been directed towards the development of an improved and single step catalytic system for copper catalyzed amination of aryl chlorides. We wish to report here for the first time, the use of monodentate phosphine ligands in the activation of aryl chlorides with high activity and selectivity. Aryl chlorides are usually inert and the order of reactivity, ArI > ArBr > ArCl is consistent with the Ar–X bond strength.<sup>2</sup> Experimentally found bond dissociation energies for phenyl halide at 298 K for Cl, Br and I are 96, 81 and 65 Kcal mol<sup>–1</sup> respectively.<sup>13</sup> Also it is known that a metal center coordinated by electron-rich phosphine ligands can effectively activate C–Cl bonds of aryl chlorides.<sup>13,14</sup>

We investigated amination of iodobenzene using CuI as a catalyst and *o*-tolyl phosphine and tributyl phosphine as ligands (Table 1; entries 4 and 9). High activity and selectivity for amination of iodobenzene was observed even at a CuI : ligand ratio of 1 : 1 for both the ligands. This is in sharp contrast to no activity with PPh<sub>3</sub> as a ligand at CuI : PPh<sub>3</sub> ratio of 1 : 1<sup>10a</sup> and poor activity at higher ratios (Table 1 entries 1–3),<sup>15</sup> clearly showing the influence of the nature of ligand on catalytic activity. Best results were obtained at a CuI : ligand ratio of 1 : 2 (Table 1; entries 5 and 10). Both the ligands were tested for catalytic activity using bromobenzene and chlorobenzene as



Scheme 1

† Electronic supplementary information (ESI) available: experimental and analytical details (G.C. and NMR analysis). See <http://www.rsc.org/suppdata/cc/b3/b308034j/>

Table 1 Copper catalyzed amination reaction using different monodentate phosphine ligands

Entry	Ligand	CuI : Ligand Ratio	Reaction time/h	X	Conv. of aniline (%)	Product yield (%)	
						1	2
1 <sup>a</sup>	PPh <sub>3</sub>	1 : 1	3.5	I	12	0	0
2 <sup>a</sup>	PPh <sub>3</sub>	1 : 2	3.5	I	62	15	17
3 <sup>a</sup>	PPh <sub>3</sub>	1 : 3	3.5	I	73	19	25
4	( <i>o</i> -tol) <sub>3</sub> P	1 : 1	3.5	I	89	80	5
5	( <i>o</i> -tol) <sub>3</sub> P	1 : 2	3.5	I	95	87	5
6	( <i>o</i> -tol) <sub>3</sub> P	1 : 3	3.5	I	94	83	6
7 <sup>b</sup>	( <i>o</i> -tol) <sub>3</sub> P	1 : 2	10.5	Br	81	58	12
8 <sup>b</sup>	( <i>o</i> -tol) <sub>3</sub> P	1 : 2	10.5	Cl	58	41	8
9	P(Bu) <sub>3</sub>	1 : 1	3.5	I	91	80	6
10	P(Bu) <sub>3</sub>	1 : 2	3.5	I	100	93	2
11	P(Bu) <sub>3</sub>	1 : 3	3.5	I	95	88	2
12 <sup>b</sup>	P(Bu) <sub>3</sub>	1 : 2	10.5	Br	100	92	1
13 <sup>b</sup>	P(Bu) <sub>3</sub>	1 : 2	10.5	Cl	99	87	1

Reaction conditions: aryl halide: 16.48 mmol; aniline: 7.85 mmol; CuI: 0.28 mmol; toluene: 23 ml; temperature: 110 °C; <sup>a</sup> = literature reports see ref. 15; <sup>b</sup> = 135 °C.

reactants. Interestingly in both the cases good activity was observed (Table 1; entries 7,8 and 12,13). It may be noted that the results obtained with tributyl phosphine as a ligand are better than the previous reports (bromobenzene: 92% yield in 10.5 h at 135 °C as compared to 73% by Gujadhur *et al.*<sup>9</sup> and chlorobenzene: 87% yield in 10.5 h at 135 °C compared to 49% in 36 h at 110 °C by Gujadhur *et al.*<sup>9</sup>). Better results obtained with tributyl phosphine as a ligand may be due to electron rich nature of PBu<sub>3</sub> (Compare entries 7 and 8 with 12 and 13 of Table 1). This is the first report on the amination of aryl chlorides using CuI as a catalyst and a monodentate phosphine as ligand.

A number of bases were screened with CuI as a catalyst, aniline, chlorobenzene as reactants and tributylphosphine as a ligand. Of all the bases, KO<sup>t</sup>Bu gave best results (87% yield of triphenylamine, Table 1; entry 13). Very poor results were obtained with NaO<sup>t</sup>Bu and reaction did not proceed with other bases.

Thus, CuI/PBu<sub>3</sub> catalyst system with KO<sup>t</sup>Bu as a base was found to be the best system for amination of aryl chlorides. In order to check the tolerance of substituents a few substituted chlorobenzenes, bromobenzenes and aniline derivatives were screened using the CuI/PBu<sub>3</sub> catalyst system and KO<sup>t</sup>Bu as a base (See Table 2). A marginal increase in yield was observed with electron donating –OCH<sub>3</sub> groups at *para* positions

**Table 2** Copper catalysed amination reactions involving substituted aryl chlorides and bromides using tributylphosphine as a ligand

Entry	X	R	R'	Conv. of aryl amines (%)	Product yield (%) <sup>*</sup>	
					1	2
1	Cl	H	H	100	82	2
2	Cl	<i>p</i> -OMe	H	94	84	5
3	Cl	<i>o</i> -CH <sub>3</sub>	H	96	80	4
4	Cl	<i>p</i> -OMe	<i>p</i> -OMe	100	87	3
5	Cl	H	<i>p</i> -OMe	98	85	3
6	Cl	H	<i>o</i> -CH <sub>3</sub>	94	80	3
7	Br	H	<i>p</i> -OMe	100	86	2
8	Br	H	<i>o</i> -CH <sub>3</sub>	97	82	2
9	Br	<i>p</i> -OMe	H	100	85	5
10	Br	<i>p</i> -OMe	<i>p</i> -OMe	100	87	2
11	Br	H	<i>p</i> -NO <sub>2</sub>	62	35	11
12	Cl	H	<i>p</i> -NO <sub>2</sub>	55	31	9
13	Cl	<i>p</i> -NO <sub>2</sub>	H	59	41	10
14	Cl	<i>p</i> -NO <sub>2</sub>	<i>p</i> -NO <sub>2</sub>	52	29	8

Reaction conditions: aryl halide: 16.48 mmol; aryl amine: 7.85 mmol; CuI: 0.28 mmol; tributylphosphine: 0.56 mmol; toluene: 23 ml; time 10.5 h; temperature: 135 °C; \* = isolated yields

(85–87%) while lower yield (~80%) was obtained with a CH<sub>3</sub> group at *ortho* positions. However, with electron deficient –NO<sub>2</sub> groups in *para* positions very poor results were obtained (Table 2, entries 11–14). Results obtained with the CuI/PBu<sub>3</sub> catalyst system for chlorobenzene and aniline as reactants (80–87% yield) in 10.5 h, show significant improvement over literature reports (49% yield in 36 h).<sup>9</sup> Improved results obtained are mainly due to combination of electronic as well as steric effects of tributylphosphine. Further work is necessary to understand the exact role of ligands.

In summary we have demonstrated for the first time a high yield of triaryl amines (80–87%) using the CuI/PBu<sub>3</sub> catalyst system. Further work on understanding the role of ligands is in progress in our laboratory.

N.M.P. thanks the Council of Scientific and Industrial Research, New Delhi, India for financial assistance for this work.

## Notes and references

- J. P. Wolfe, S. Wagaw, J. F. Marcoux and S. L. Buchwald, *Acc. Chem. Res.*, 1998, **31**, 805–818.
- J. F. Hartwig, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 2046–2067.
- M. Beller, C. Breindl, T. H. Riermeier and A. Tillack, *J. Org. Chem.*, 2001, **66**, 1403–1412.
- M. S. Driver and J. F. Hartwig, *J. Am. Chem. Soc.*, 1997, **119**, 8232–8245.
- (a) J. Lindley, *Tetrahedron*, 1984, **40**, 1433–1456; (b) Y. Hong, C. H. Senanayake, T. Xiang, C. P. Vandenbossche, G. J. Tanoury, R. P. Bakale and S. A. Wald, *Tetrahedron Lett.*, 1998, **39**, 3121–3124; (c) J. P. Wolfe, H. Tomori, J. P. Sadighi, J. J. Yin and S. L. Buchwald, *J. Org. Chem.*, 2000, **65**, 1158–1174; (d) A. H. Lewin, M. J. Zovko, M. J. Rosewater and T. Cohen, *J. Chem. Soc., Chem. Commun.*, 1967, **80**.
- H. B. Goodbrand and N-X. Hu, *J. Org. Chem.*, 1999, **64**, 670–674.
- P. J. Fagan, E. Hauptman, R. Shapiro and A. J. Casalnuovo, *J. Am. Chem. Soc.*, 2000, **122**, 5043–5051.
- B. H. Yang and S. L. Buchwald, *J. Organomet. Chem.*, 1999, **576**, 125–146.
- R. K. Gujadhur, C. G. Bates and D. Venkataraman, *Org. Lett.*, 2001, **3**, 4315–4317.
- (a) R. K. Gujadhur, D. Venkataraman and T. J. Kintigh, *Tetrahedron Lett.*, 2001, **42**, 4791–4793; (b) R. Gujadhur and D. Venkataraman, *Synth. Commun.*, 2001, **31**, 139–153.
- A. Kiyomori, J. F. Marcoux and S. L. Buchwald, *Tetrahedron Lett.*, 1999, **40**, 2657–2660.
- M. Wolter, A. Klapars and S. L. Buchwald, *Org. Lett.*, 2001, **3**, 3803–3805.
- V. V. Grushin and H. Alper, *Chem. Rev.*, 1994, **94**, 1047–1062.
- A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed. Engl.*, 2002, **41**, 4176–4211.
- A. A. Kelkar, N. M. Patil and R. V. Chaudhari, *Tetrahedron Lett.*, 2002, **43**, 7143–7146.