Form 2

Dissertation Abstract

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Dissertation title	Copper-Catalyzed Cross-Coupling of Aryl Halides and Phenols by N_2/N_3 Ligands		

Abstract

The purpose of this study is to explore more efficient and economical copper-based catalyst systems for the synthesis of diaryl ethers. To promote *O*-arylation reaction, relatively expensive reagents, such as $Cu(CH_3CN)_4BF_4$, Cu/C and $CuI/KF/Al_2O_3$ and moisture sensitive Cs_2CO_3 are used for the typical *N*,*N*-bidentate ligands, such as 2,2'-bipyridine, 1,10-phenanthroline and it reduces the applicability and should be preferably avoided.

Several Cu(I) complexes of 2,2'-bipyridines (**L1**-**L6**) were studied for the catalytic coupling of aryl iodides and phenols and 4,4'-dimethoxy-2,2'-bipyridine (**L6**) was shown to be an effective ligand of CuI in 1:2 (CuI:ligand) ratio for the synthesis of a wide range of diaryl ethers (up to 97% yield) using K_3PO_4 as base in DMF at 100 °C. The catalysis was highly dependent on the reaction temperature and was successfully applied in the coupling with more attractive and challenging substrates, aryl bromides, at 140 °C in good-to-excellent yields (78–95%). Significantly, a structurally related *N*,*N*-bidentate ligand, 4,7-dimethoxy-1,10-phenanthroline (**L7**), exhibited better performance for less-reactive combinations of aryl halides and phenols.

In order to lower the catalyst loading and keep the high efficiency of the catalyst system, the exploration of new ligands is still necessary. As a result, three pyrazol-containing N_2- and N_3-ligands (**L8**–**L10**) and four N_3-tripyridine ligands (**L11**–**L14**) were developed and tested in the copper-catalyzed arylation of *p*-cresol with 4-iodotoluene. The catalyst loading was reduced to 10/10% (CuI/**L**) and only 2-(1-pyrazolyl)pyridine (**L8**) achieved the assumed result of 90% yield. However, **L9**-**L14** also performed well and kept the yields above 60% in spite of the reduction of the catalyst loading to 10/10% (CuI/**L**) from 20/40 % (CuI/**L**). In addition, three plausible catalytic cycles are proposed in the presence of **L8**.

Finally, instead of CuI, $Cu(OAc)_2•H_2O$ as an economical and stable copper source was applied into the synthesis of diaryl ethers and exhibited higher efficiency which might due to its higher stability.

In conclusion, it was shown that pyridine type ligands, **L6** and **L7** combined with a simple CuI can promote the synthesis of diaryl ether efficiently, even though 20/40% (CuI/**L**) of the catalyst loading is necessary. In addition, pyrazol-pyridine type ligand, **L8** reduced the catalyst loading to 10/10% (CuI/L) from 20/40% and hold the yield to 90%. More economical and stable $Cu(OAc)_2•H_2O$ was applied into the coupling reaction and exhibited excellent performance, even better than CuI.