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Recent advances in the transition metal catalyzed etherification reactions



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1. Introduction

The C–O bond-forming reactions are important in organic synthesis due to the presence of these bonds in numerous natural products, biologically important compounds, pharmaceuticals, fragrances, cosmetics and polymers.¹ Traditionally, aryl ethers have been prepared by copper mediated Ullmann coupling reactions of aryl bromides or iodides with phenols. However, the traditional Ullmann coupling reactions often suffer from many drawbacks such as long reaction time, high reaction temperature and expensive metal catalysts.² To overcome these disadvantages, great efforts have been made in the past several years. The major advances focus on the cross-coupling reactions catalyzed by Cu³ and Pd.⁴ Very recently there is an upsurge of reports in this area highlighting the use of Fe,⁵ Co,⁶ Rh⁷ and a combination of Co–Cu,⁸ Ni–Cu,⁹ Cu–Fe¹⁰ and Pd–Zn–Fe¹¹ systems which efficiently catalyzed the C–O cross-coupling reactions. Clearly, each of these protocols has its own virtues; however, limitations still exist with respect to substrate scope, use of excess of alkoxides and undesirable solvents.

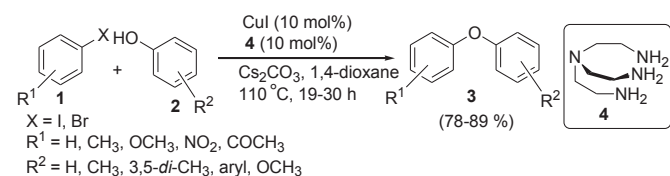
Although a few reviews describing the C–O bond formation using specific transition metal catalysts are reported.¹² To the best of our knowledge, no review is available discussing the etherification reaction using different transition metal catalysts or a combination of transition metals¹³ after 2007. Therefore, in the present review, we discuss the various transition metal catalysts used for C–O bond-forming reactions including the ligand free systems and covers the literature from 2008 to 2016. We have classified the reaction based on the central metal ion and further subdivided based on the type of ligand coordination.

2. Cu-catalyzed C–O bond formation

Metal mediated Ullmann reaction has been extensively used for the synthesis of ethers. Copper-catalyzed syntheses of diaryl ethers were discussed more than a century ago.¹⁴ Several catalytic methods have been developed to improve the efficiency of the copper salt used and the ligand associated with it. The ligands that have been found to promote Cu-catalyzed aryl-oxygen coupling reactions include copper salt and bulky phosphine ligands,¹⁵ β -keto ester,¹⁶ 1,10-phenanthroline,¹⁷ Cu(OTf)₂·PhH and ethyl acetate,¹⁸ silica-supported Cu(II),¹⁹ 2,2,6,6-tetramethylheptane-3,5-dione,²⁰ 8-hydroxy quinoline etc.²¹ These developments have significantly expanded the scope and utility of synthetic transformations. The latest review on Cu-catalyzed C–O bond formation has been reported by Panda et al. in 2015.²²

2.1. Ligand-based Cu-catalyzed C–O bond formation

2.1.1. Bidentate N–N ligand. A novel, efficient, commercially available and economically attractive N-donor tripod ligand, *tris*-(2-aminoethyl) amine **4** has been introduced for the copper-catalyzed Ullmann diaryl ether synthesis.³ This protocol was found to be efficient for both aryl iodides and aryl bromides. Various substituted diaryl ethers have been synthesized in good to excellent yields (Scheme 1).



Scheme 1. Coupling of aryl halides with phenols in the presence of a *tris*-(2-aminoethyl) amine–Cu catalyst.

A wide range of alkyl aryl ethers have been synthesized from the corresponding aryl iodides and aliphatic alcohols through intermolecular C–O coupling reactions in the presence of a catalytic amount of easily available BINAM–Cu complex (Scheme 2).²³ Less reactive aryl bromides have also been shown to react with aliphatic alcohols under identical reaction conditions to give good yields of the alkyl aryl ethers without increasing the reaction temperature and time.

An efficient O-arylation of phenols and aliphatic alcohols with aryl halides has been developed by the use of an air-stable copper(I) complex **12** as the catalyst (Scheme 3).²⁴ A variety of functional groups are compatible with these reaction conditions with low catalyst loading.

A new, efficient and environmentally friendly protocol for O-arylation has been developed using CuBr as a catalyst and 1,1'-azobis(cyclohexane carbonitrile) **16** (ACHN) as a ligand under microwave irradiation, which provided diaryl ethers in moderate to excellent yields (Scheme 4).²⁵ The single process is clean, simple and different phenols and substituted aryl halides were well tolerated in this cross-coupling reaction. Electron-withdrawing groups (e.g., –NO₂, –CN, –SO₂CH₃) in the aryl halides favored the coupling reaction, while phenols with electron-donating substituents (e.g., –CH₃, –OCH₃) gave the diaryl ethers in lower yields. The method offers advantages such as the use of low amounts of catalyst and ligand, low temperatures and reduced reaction times.

An efficient, stereospecific Cu-mediated catalytic system (CuI/**20**) has been developed for the synthesis of aryl vinyl ethers (Schemes 5 and 6).²⁶ Ligand **20** was shown to be very effective in

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