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Monodispersed and Stable Nano Copper(0) from Copper-Aluminium Hydrotalcite: Importance in C–C Couplings of Deactivated Aryl Chlorides

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Abstract: A simple one-step approach for the preparation of highly monodispersed nano copper(0) stabilized on alumina [$Cu(0)/Al_2O_3$] by thermal reduction of copper-aluminium hydrotalcite (Cu-Al HT) under a hydrogen atmosphere is described. The transformation of Cu-Al HT to $Cu(0)/Al_2O_3$ occurrs *via* dehydroxylation of divalent and trivalent metal hydroxides and decarboxylation of carbonate anions present in the interlayers of hydrotalcite, as confirmed by XPS, XANES, XRD and TEM analysis. $Cu(0)/Al_2O_3$ nano composites were used as an efficient catalyst in the C–C coupling of deactivated aryl chlorides. The high efficiency and reusability exhibited by $Cu(0)/Al_2O_3$ outline its potential as an alternative over traditional noble metal-based catalysts in C–C coupling reactions.

Keywords: alkenes; alkynes; aryl chlorides; boronic acids; C–C couplings; nano copper

Introduction

Heterogeneous catalysis at the nanoparticle surface is currently a subject of investigation in the catalysis community because of the attractive physical and chemical properties as compared with the bulk materials.[1,2] The synthesis of metal nanoparticulates with controllable size, shape and surface properties is vital in exploring the catalytic activity in various organic transformations.[3,4] In this context, copper nanocolloids[5] and nanoclusters[6] have recently been tested in the C–C coupling and other cross-coupling reactions,[7] fundamental processes of paramount importance in organic synthesis, that are currently dominated by the use of gold, silver, platinum and palladium.[8] However, the propensity of surface oxidation of metallic Cu is a key issue in synthesizing the stable Cu nanoparticles.[9] To date, only limited success has been achieved in synthesizing stable Cu nanoparticles.[10] In general, the synthesized Cu nanoparticles (less than 10 nm) exhibit limited size monodispersity and/or are susceptible to oxidation. Consequently, attempts for developing stable and monodispersed copper nanoparticles using inexpensive precursors still remains a challenge and focus area of intense research.

For the past few years, our group has been involved in the synthesis and exploration of metal hydrotalcites in various organic transformations.[11] The general formula of metal hydrotalcites is as follows: $[M(II)_{1-x}M(III)_x(OH)_2]^{n-} A^{n-}{}_{x/n}\, y\, H_2O$, where M(II) and M(III) are divalent and trivalent cations such as Cu^{2+}, Mg^{2+} and Al^{3+}, respectively, and OH^-, Cl^-, NO_3^-, CO_3^{2-} etc.[12] can be the compensating anion. Cu-Al hydrotalcite (Cu-Al HT), in particular, is a subject of investigation in the cross-coupling reactions. With limitations in the synthesis of stable nanoparticulate Cu with controllable size, and high surface area, we envisaged Cu-Al HT as the appropriate precursor for the synthesis of Cu(0) nanoparticles.[13]

Results and Discussion

Preparation of Cu(0)/Al_2O_3 from Cu-Al HT

The precursor, Cu-Al HT, was prepared by the co-precipitation method reported in the literature.[11,12] In the synthesis of copper nanoparticles, Cu-Al HT (500 mg) was placed in a closed furnace equipped with an inlet and outlet for gas. The furnace was evacuated and refilled with nitrogen followed by introduction of molecular hydrogen (H_2) with a flow rate 1 mL per minute. The furnace was slowly heated to 190 °C in the presence of a hydrogen flow for 2 h. The resultant black-colored powder Cu(0)/Al_2O_3 was allowed to cool to room temperature under a nitrogen atmosphere. Cu(0)/Al_2O_3 was collected from the holder and stored in a dry desiccator.[14] Copper nanoparticles on alumina were characterized and confirmed by XPS, EXAFS-XANES, XRD, and TEM analyses.

Characterization of Cu(0)/Al_2O_3

The X-ray photoelectron spectrum (XPS) showed that the Cu 2*p* core level binding energies of Cu-Al HT were at 934.71 and 954.38 eV for the +2 oxidation state while peaks observed in the H_2 reduced sample were at 932.45 and 952.21 eV, corresponding to elemental Cu(0) (Figure 1). The absence of two satellite peaks at 962.63 eV and 942.98 eV strongly suggests the selective formation of Cu(0) metal as further confirmed with auger spectral analysis (see the Supporting Information).[15] The XPS results of Cu and Al clearly show that, under the reaction conditions, copper is selectively reduced to elemental copper whereas the oxidation state of aluminum remains the same (aluminum hydroxide transformed into its simple oxide through a dehydration process). Thus at elevated temperature and in the presence of hydrogen, the Cu-Al HT undergoes dehydroxylation and decarboxylation *via* H_2O and CO_2 evolution producing Cu(0)/Al_2O_3.

The XRD patterns of Cu(0)/Al_2O_3 showed that all the peak positions for the copper nanoparticles are consistent and comparable with metallic copper and signify the polycrystalline nature of Cu(0)/Al_2O_3 (Figure 2). The X-ray reflections are indexed on the basis of the fcc structure of copper with a space group of *Fm3m* (ASTM card no. 4-0836, X-ray diffraction files for inorganic materials). The calculated lattice constant, $a = 3.6147$ Å, is in good agreement with the literature value (3.6150 Å). The diffraction peaks at $2\theta = 43.5$, 50.6, and 74.3 can be indexed as the [111], [200], and [220] planes of copper with cubic symmetry.[16]

Transmission electron microscopic (TEM) images confirmed the monodispersity of Cu(0) nanoparticles reduced from Cu-Al HT precursor consisting of spherical nanoparticles with a narrow size disrtibu-

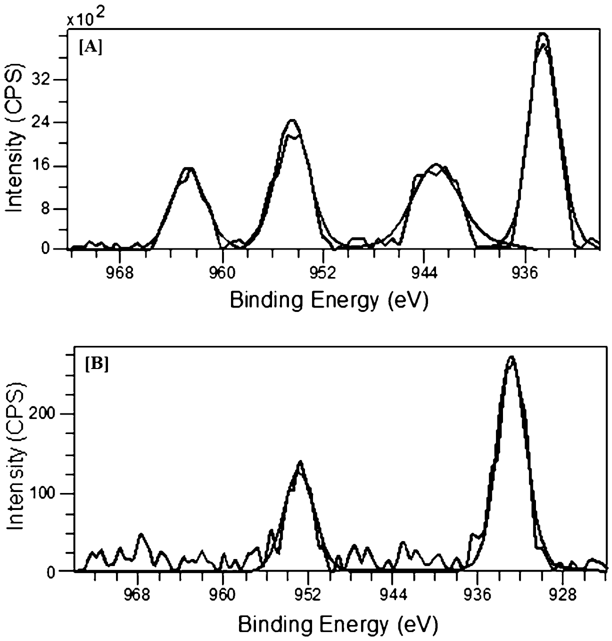


Figure 1. [A] XPS spectra of Cu-Al HT and [B] Cu(0)/Al_2O_3.

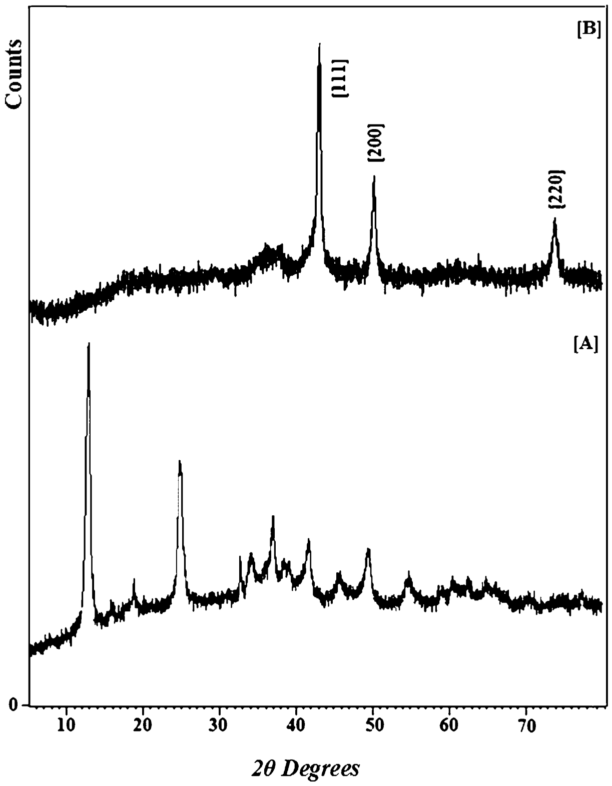


Figure 2. [A] XRD patterns of Cu-Al HT and [B] Cu(0)/Al_2O_3.

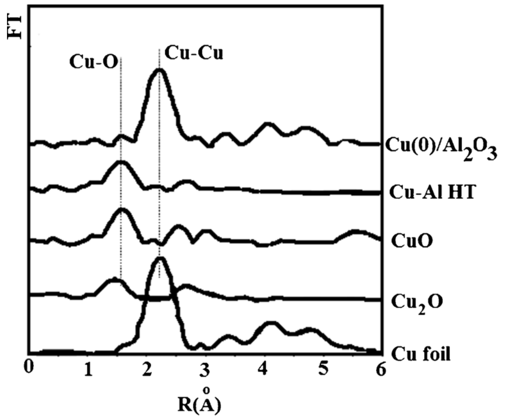


Figure 3. Fourier transform (FT) Cu K-edge spectra of the reduced Cu-Al HT ($Cu(0)/Al_2O_3$) and as synthesized Cu-Al HT.

Table 1. Structural parameters for the $Cu(0)/Al_2O_3$ and reference samples.

Sample	Scattering atom	CN	R [Å]	dF/DW
$Cu(0)/Al_2O_3$	Cu–Cu	8.9	2.450	−1.127/0.065
Cu_2O	Cu–O (1st)	2	1.859	
	Cu–Cu	12	3.104	
	Cu–O (2nd)	6	3.599	
CuO	Cu–O	1.901		
Cu foil	Cu–Cu	12	2.860	

tion. The histogram showed an average particle diameter of 7.6 nm with a standard deviation of 1.0 nm and relative standard deviation of 0.294 nm (see the Supporting Information for TEM images). The particle size, 7.6 nm calculated using Scherrer's equation was in agreement with the TEM analysis.

The formation of $Cu(0)/Al_2O_3$ was further investigated by EXAFS-XANES analysis (Figure 3). The atomic scale analysis of Cu(0) nanoparticles using Cu K-edge EXAFS showed that the position of the FT peak derived from the Cu–Cu shell for Cu(0) appears at 2.45 Å and is identical with the peak derived from Cu metal foil (Table 1).

Although there is no change observed in the oxidation state of Al in the XPS study before and after thermal reaction, the chemical shift of Al changes in ^{13}Al NMR and suggests the deformity in the HT frame-work[17] (see ^{13}Al NMR in the Supporting Information and its tranformation into Al_2O_3).

Catalytic Activity of $Cu(0)/Al_2O_3$ in C–C Coupling Reactions

The catalytic activity of Cu(0) nanoparticles was investigated in a number of industrially important C–C coupling reactions. Initially, the catalytic activity was examined in the Heck reaction of 4-chlorotoluene with styrene using $Cu(0)/Al_2O_3$ (25 mg, 0.97 mol% relative to aryl chloride) which yielded 1-methyl-4-styrylbenzene in 88% yield. In order to examine the efficiency of $Cu(0)/Al_2O_3$, several other copper-based catalysts were reduced and used in combination with different bases and solvents (see the Supporting Information for screening of various Cu catalysts, bases and solvents) for their catalytical activity.

Among the different bases screened, K_2CO_3 had a pronounced effect on product yield and an 88% yield of coupled product was obtained when *N,N*-dimethylformamide (DMF) solvent was used at 110 °C (Table 2). It was seen that the coupling of less reactive aryl chlorides such as 4-chlorotoluene and 4-chloroanisole with styrene and 4-methylstyrene, proceed smoothly and good to excellent yields were obtained under the optimized experimental conditions. Similarly, we have also examined the catalytic activity of $Cu(0)/Al_2O_3$ in the couplings of various aryl chlorides with phenylboronic acids (Suzuki); tributyl(phenyl)tin (Stille-type coupling); acetylenes (Sonogashira).

In the Suzuki coupling reactions, both electron-rich and electron-deficient aryl chlorides were allowed to couple with phenylboronic acid, excellent yields of biphenyls were obtained except in the case of coupling between phenylboronic acid and chlorobenzene.

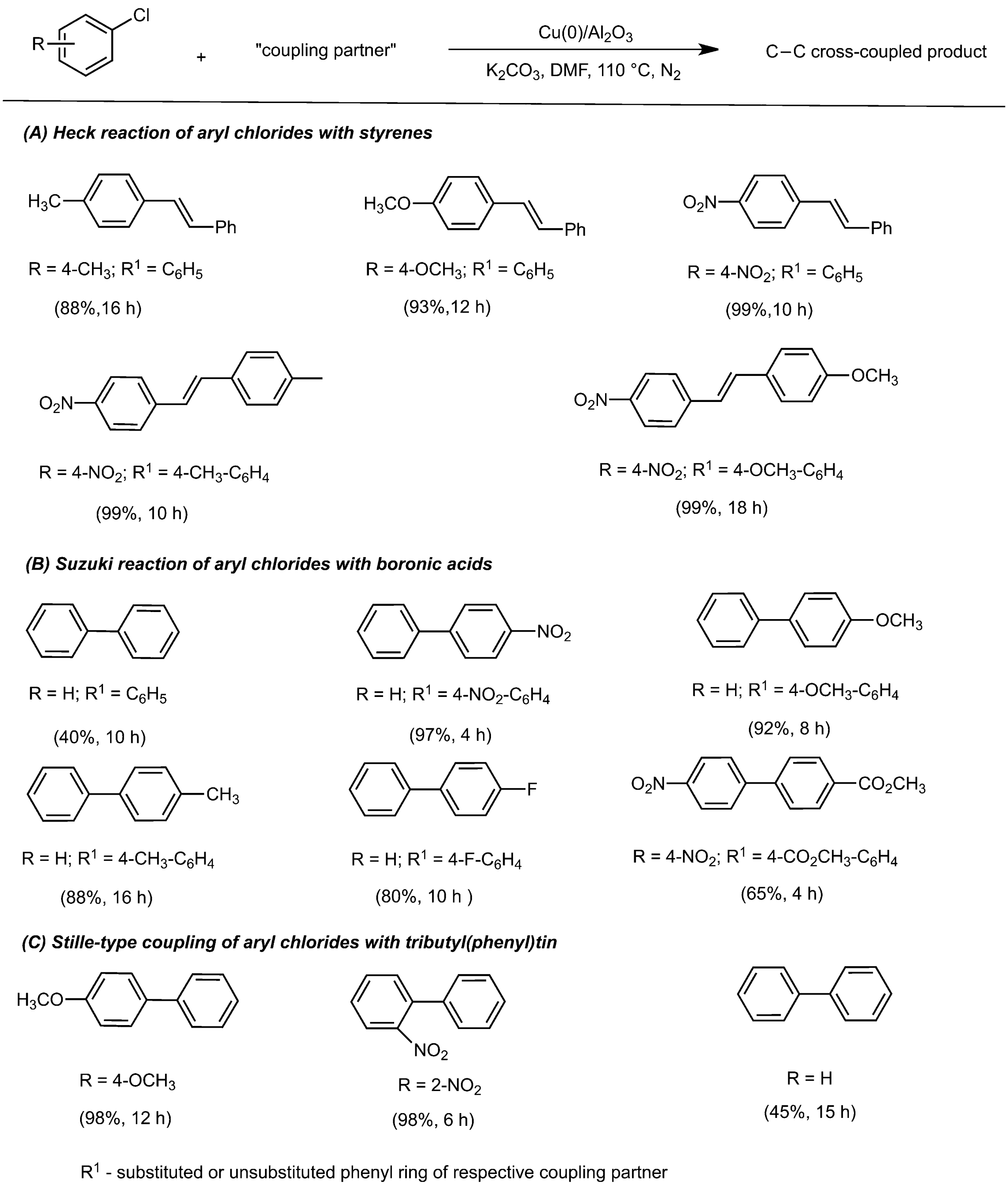
Various aryl chlorides were used with 1.5 equivalents of tributyl(phenyl)tin for the Stille-type coupling in the presence of catalytic amount of $Cu(0)/Al_2O_3$ and selectively gave the C–C coupled biaryls in excellent yields. The reaction of chlorobenezene with tributyl(phenyl)tin was sluggish and afforded a low yield of biphenyl after 15 h.

In the Sonogashira coupling reactions,[18] aromatic and aliphatic alkynes afforded excellent yields of the coupled products at room temperature, irrespective of the electronic nature of the substituent (generally deactivating group) present on the aromatic ring of chlorobenzene (Table 3). The catalytic activity of $Cu(0)/Al_2O_3$ was also investigated in the Sonogashira coupling of 4-methoxychlorobenzene with an unsaturated alcohol (propargyl alcohol) and excellent yields of the coupled product was observed.

Reusability of the Catalyst

The extent of Cu leaching and the change in the chemical or electronic state of Cu from the spent $Cu(0)/Al_2O_3$ catalyst after the Heck and Sonogashira coupling reactions were studied by AAS and XPS analysis. The true heterogeneity of the catalyst was examined with the experimental evidence that when the reaction was discontinued during the first half of its reaction time (progress of reaction was monitored

Table 2. Cross-coupling reactions of aryl chlorides.[a]



(A) Heck reaction of aryl chlorides with styrenes

R = 4-CH_3; R^1 = C_6H_5 (88%,16 h)

R = 4-OCH_3; R^1 = C_6H_5 (93%,12 h)

R = 4-NO_2; R^1 = C_6H_5 (99%,10 h)

R = 4-NO_2; R^1 = 4-CH_3-C_6H_4 (99%, 10 h)

R = 4-NO_2; R^1 = 4-OCH_3-C_6H_4 (99%, 18 h)

(B) Suzuki reaction of aryl chlorides with boronic acids

R = H; R^1 = C_6H_5 (40%, 10 h)

R = H; R^1 = 4-NO_2-C_6H_4 (97%, 4 h)

R = H; R^1 = 4-OCH_3-C_6H_4 (92%, 8 h)

R = H; R^1 = 4-CH_3-C_6H_4 (88%, 16 h)

R = H; R^1 = 4-F-C_6H_4 (80%, 10 h)

R = 4-NO_2; R^1 = 4-CO_2CH_3-C_6H_4 (65%, 4 h)

(C) Stille-type coupling of aryl chlorides with tributyl(phenyl)tin

R = 4-OCH_3 (98%, 12 h)

R = 2-NO_2 (98%, 6 h)

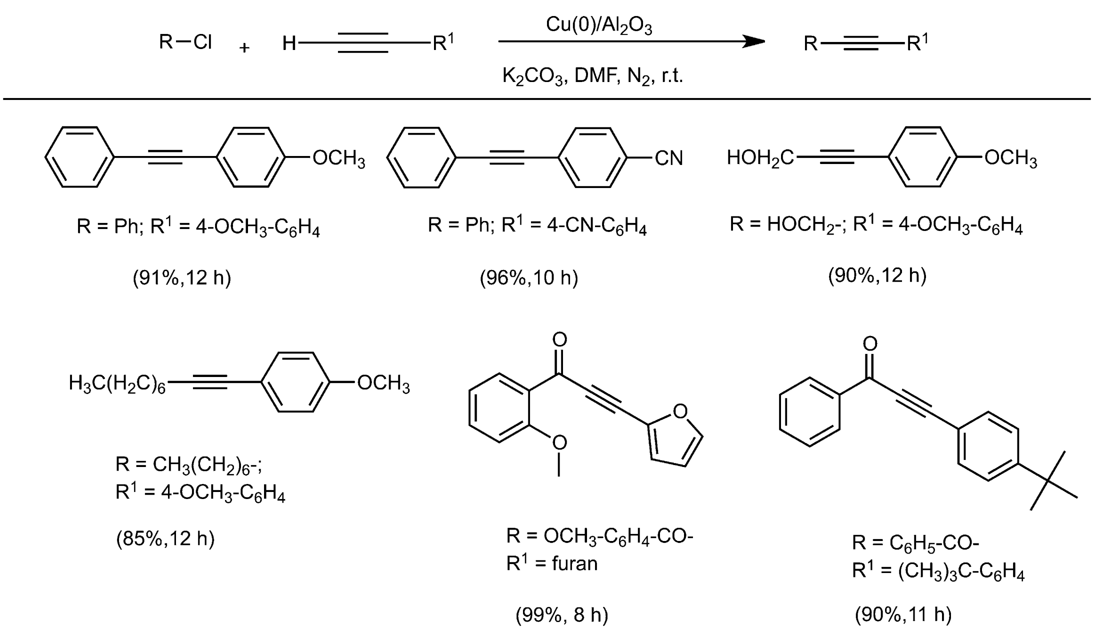
R = H (45%, 15 h)

R^1 - substituted or unsubstituted phenyl ring of respective coupling partner

[a] *Reaction conditions:* aryl chloride (1 mmol), olefin (1.2 mmol, for Heck coupling), boronic acid (1.2 mmol, for Suzuki coupling), tributyl(phenyl)tin (1.2 mmol, for Stille-type coupling), Cu(0)/Al_2O_3 (25 mg, Cu: 0.97 mol%), K_2CO_3 (1.5 mmol), DMF (2 mL), 110 °C.

by GC), the hot filtrate (solid catalyst was removed by filtration under hot conditions) was stirred for the next half reaction time, and no further coupling product was observed, which clearly suggests that the reaction does not proceed when devoid of the active catalyst. Similarly, the filtrate from the above experimentation was tested by the AAS technique and no Cu leaching from Cu(0)/Al_2O_3 catalyst was found. The ICP/AES and XPS analyses of recovered catalyst also suggest that the Cu content is unchanged as well as there being no changes in the chemical or electronic state of elemental Cu which rule out the possible formation of $CuAl_2O_4$ species during coupling reactions (see the Supporting Information for AAS and XPS

Table 3. Sonogashira coupling reaction of aryl chlorides.[a]



[a] *Reaction conditions:* aryl chloride (1 mmol), alkyne (1.2 mmol) $Cu(0)/Al_2O_3$ (25 mg, Cu: 0.97 mol%), K_2CO_3 (1.5 mmol), DMF (2 mL) at room temperature.

study). Advantageously, $Cu(0)/Al_2O_3$ can be used for a number of important C−C coupling reactions, thereby eliminating the use of expensive conventional palladium-based catalysts, organic ligands, the need for very high temperatures and high catalyst loadings. Moreover, the catalyst can be recovered and reused in all reactions for several cycles (see the Supporting Information for recovery and reusability study for all C−C coupling reactions). The size and oxidation state of the Cu(0) nanoparticles of the reused $Cu(0)/Al_2O_3$ catalyst remained unchanged as shown in the TEM and XPS analyses (see the Supporting Information for TEM and XPS of reused $Cu(0)/Al_2O_3$, respectively).

Conclusions

We have developed a simple and efficient method for the preparation of monodispersed and highly stable Cu nanoparticles from Cu aluminium hydrotalcite precursor for industrially important catalytic C−C coupling reactions (Heck, Suzuki, Sonogashira and Stille-type coupling). The efficiency and stability of the $Cu(0)/Al_2O_3$ catalyst has been demonstrated by activating unreactive aryl chlorides and studying the recovery and reusability properties for coupling reactions. Thus, $Cu(0)/Al_2O_3$ constitutes a unique catalytic system and opens up an attractive alternative to noble metal-based catalysts for the formation of C−C bond.

Experimental Section

General Procedure for Heck, Suzuki and Stille Coupling Reactions

A 25-mL round-bottomed flask equipped with a magnetic stir bar was charged with aryl chloride (1.0 mmol), coupling partner (1.2 mmol), K_2CO_3 (1.5 mmol), $Cu(0)/Al_2O_3$ (25 mg, Cu:0.97 mol%) and DMF (2 mL) under an N_2 atmosphere. The reaction mixture was stirred at 110 °C for the required period of time. After completion of the reaction, as judged by TLC, the reaction mixture was diluted with ethyl acetate and centrifuged to separate the catalyst. The catalyst was washed several times with ethyl acetate to extract all organic compounds. The reaction mixture was concentrated to a small volume and purified by silica gel chromatography column to afford the corresponding C−C coupled product. All the products were characterized by ^1H and ^{13}C NMR and their mass spectral data were compared with those of the literature reports.

General Procedure for Sonogashira Coupling Reactions

In a Schlenck tube dried under vacuum and filled with N_2 were placed aryl chloride (1.0 mmol), phenylacetylene (1.2 mmol), K_2CO_3 (1.5 mmol), $Cu(0)/Al_2O_3$ (25 mg, Cu: 0.97 mol%) and DMF (2 mL). The reaction mixture was stirred at room temperature. After completion of the reaction, as judged by TLC, the reaction mixture was diluted with diethyl ether. The catalyst was removed by centrifuging the reaction mixture and the organic layer was washed with water and dried over anhydrous Na_2SO_4. The organic layer was concentrated under vacuum and subjected to flash column chromatography using silica gel 60–120 to afford the corresponding C−C coupled product.

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