COPPER (I) COMPLEX CATALYZED CROSS-COUPLING REACTION OF ARYL ZINC HALIDE WITH ARYL BROMIDE

[1]R. B. Gawade, [2]A. S. Pise, [3]A. S. Burungale
[1]Assistant Professor, [2]Assistant Professor, [3]Associate Professor,
Department of Chemistry S. M. Joshi College Hadapsar Dist Pune 411028 (M. S.) India.

Abstract : The development of an efficient copper (I) complex catalytic system for carbon-carbon bond formation by cross-coupling reaction. The functional arylzinc halide was generated from the direct oxidative addition of rieke zinc to functional aryl halide in presence of lithium chloride. These organozinc reagents were undergone copper (I) complex catalyzed coupling reaction with aryl bromide produce biphenyl compound in good yield under mild condition. A practical coupling of arylzinc halide with aryl bromide catalyzed by tetrakisacetonitrile copper(I)tetrafluroborte is described.

Keywords: Copper (I) complex, Cross-coupling, Aryl zinc halide, Biaryl.

INTRODUCTION

Organozinc compounds have been known for more than 150 years.[1] Organozinc reagents are most useful intermediate in organic transformation especially Negeshi cross-coupling reaction.[2] Today they are contribute a major role in organometallic chemistry and occupied unique position in synthetic organometallic chemistry due to large number of functional group tolerance, low toxicity, moderate price, easy formation and transmetalation.[3] The organozinc halide reagents play key role in synthesis of polyfunctional molecules without protection and deprotection.[4] The organozinc reagents are prepared by various synthetic methods such as direct zinc insertion, base directed metalation, boron-zinc exchange, transmetalations, halide zinc exchange perform with dialkyl organozinc reagent, Zinc-copper coupled, zinc-silver coupled, Eletrochemical, cobalt mediated have been used. The insertion of zinc in organic halide remarkably chemoselectivity and high tolerance to a broad range of functional group such as Ester, Ether, Acetate, Ketone, Cyano, Halide, Amino, Amide & Pthalimide, Sulfoxide, Sulfide, Sulfone, Thioester, Boronic ester, Enone, and Phosphate[4-5]. In the organometallic chemistry organozinc reagent valuable due to high functional group compatibility because of less polar C-Zn covalent bond[6] and facile transmetallation with transition metal salt or complex[7] A very large range of functional organic halides are convert to organozinc compounds include aliphatic, allylic Propargylic, benzylic, aryl, heterocyclic aliphatic and aryl are simply undergo zinc insertion reaction as well as transmetallation. organozinc compounds are undergoes broad range of transition metal mediated transmetallation because of presence of empty low lying p orbitals that eagerly interact with the d-orbitals of many transition metal ions leading to highly reactive intermediates which open new number of reaction pathways.[7-9] The Lewis acid lithium chloride play key role in organozinc compound preparation and reaction.[10]

The highly active zinc metal known as reike zinc often by reduction of zinc chloride in lithium naphthalenide is prove excellent for oxidative addition of zinc in various aryl halide and heteroaryl halide.[11] Second advantage of organozinc reagent is non pyrophoric and stable over diorganozinc reagent. Recently, organozinc compounds have emerged as key reagent for transition metal catalyzed cross coupling, nucleophilic addition reaction and nuclephilic displacement of halides, sulphonates, allylic acetates.[12-13] Transition metal palladium, nickel, copper, cobalt, titanium and zirconium catalyzed coupling of organozinc halide with alkyl or aryl halide are valuable tools for carbon-carbon bond forming reaction.[14] The coupling reaction of organozinc reagents are dominantly catalyzed by palladium metal salt and complexes[15-16] Nickel is second prominent catalyst for cross-coupling reaction of organozinc,[17] then cobalt and copper catalysis observed.[18] Few reactions are catalyzed by titanium and zirconium.[19]

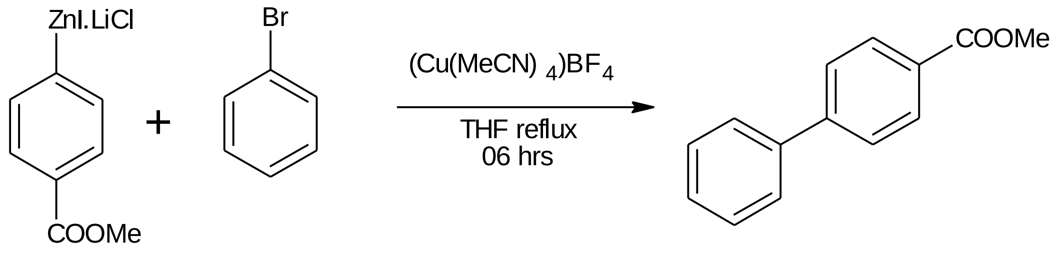
Herein we report the synthesis of biphenyl compound using copper (I) complex catalyzed coupling of aryl zinc halide with aryl halide. The biphenyl compounds are valuable synthetic intermediate, many synthetic method involve key step transition metal catalyzed coupling of organomeallic reagent with aryl halide.[20] palladium catalyzed coupling of aryl zinc halide with aryl iodide lead to biphenyl derivatives.[21] But this method has several drawbacks such as high price of metal, toxicology and need of sophisticated ligands to achieve broad reaction scope. Therefore we have developed copper catalyzed powerful tool for biaryl compound synthesis via coupling reaction of organozinc compound and aryl bromide. copper has an indisputable advantage over the other catalytic system due to low cost and use of readily accessible stable ligand. The zinc insertion reaction in aryl halide is difficult than alkyl halide, therefore need highly active rieke zinc We have prepared functionalized aryl zinc halide using Rieke zinc in presence of lithium chloride. Lithium chloride is not only promotes zinc insertion in mild condition but also solubilize organozinc compound and catalyst in THF. Aryl zinc halide from p-iodomethylbenzoate and p-bromobenzonitril were prepared using rieke zinc in presence of LiCl. We have screen different Copper (I) complexes for coupling of organozinc halide with aryl halide. We found that tetrakisacetonitrile copper(I)tetrafluroborte is best for coupling reaction, therefore various bromo or Iodo aryl halide coupled with organozinc reagent.

EXPERIMENITAL

Precaution 1) strictly anhydrous condition was maintained.
2) All glassware dried overnight 150^0C before use.

All analytical grade chemicals were purchased and used without further purification. All solvents were dried as per Vogel's practical book procedure. The ^{1}HNMR and ^{13}CNMR spectra were obtained on Bruker DRX – 400 advance instrument using $CDCl_3$ as solvent and TMS as internal standard at 400 MHz and 100 MHz respectively.

Scheme: Copper (I) catalysed Negeshi cross-coupling reaction.



Typical procedure for preparation of copper (I) catalyst

4g (0.028 mole) cuprous oxide mixed with 80 ml acetonitrile in RBF suspension was observed. 113 mmole acid was added slowly with constant stirring at room temp. exotherm observed. The reaction mixture was keep at 50^0C for 30 min then filtered removing any unreacted copper (I) oxide. The colorless clear solution was then cooled at -10^0C in a freezer and left overnight. A white colored crystal settle at the bottom of RBF which was separated by filtration washed with diethyl ether under nitrogen atmosphere. Then the copper salt was recrystallised and store in acetonitrile. All the copper salts were confirmed by melting point.[22-28]

Typical procedure for preparation of rieke zinc metal

One 50 ml two neck RBF was equipped with rubber septa, stopper and magnetic bar flush by nitrogen. A small amount freshly cut of lithium 0.05g (7.204 mmole), naphthalene 0.1 g (0.7813 mmole) and 5 ml dry THF was charged by syringe clear solution was observed. The mixture was stirred at room temp. Colorless solution changes to dark green. Second 50 ml two neck RBF was equipped with rubber septa, stopper and magnetic bar flush by nitrogen. Anhydrous Zinc chloride 0.5g (3.724mmole) was charged and 5ml dry THF added by syringe clear solution obtained. The zinc chloride solution was added to above dark green solution by syringe through septum. The mixture was stirred for 1 hr black-grey colored zinc metal observed in RBF. The weight of zinc metal generated after reduction was 0.210 gram i.e.0.003211 mole.

Typical procedure for preparation of methyl 4-iodozinc benzoate and methyl 2-iodozinc benzoate.

Anhydrous LiCl (2 equivalent) was dissolved in 3 ml dry THF and charged to zinc metal (2.5 equivalent) solution by syringe. Iodo methyl benzoate (1 equivalent) was dissolved in 2ml dry THF add to heterogeneous zinc metal solution at room temperature after 24 hrs stirring complete zinc insertion takes place. organozinc reagent formation confirm by TLC i.e. consumption of Iodomethylbenzote.

Typical procedure for preparation of 4-zincbromo bezonitrile coupling to aryl halide.

Anhydrous LiCl (2 equivalent) was dissolved in 3 ml dry THF and charged to zinc metal (2.5 equivalent) solution by syringe. aryl halide (1 equivalent) was dissolved in 2ml dry THF add to heterogeneous zinc metal solution at room temperature after 3 hrs reflux complete zinc insertion takes place. organozinc reagent formation confirm by TLC i.e. consumption of aryl halide.

Typical procedure for cross-coupling of organozinc halide with aryl halide.

The substituted aryl bromide (0.9 eq.) was dissolved in 2 ml dry THF added by syringe to above organozinc halide solution and solid catalyst 15 mol %. The temperature of reaction mixture was allow to rise slowly reflux 06 hr. Add 30 ml saturated ammonium chloride solution stir reaction mixture for 1 hr at rt and heat the reaction mixture to evaporate THF completely. The product was extracted in ethyl acetate wash by aq. $NaHCO_3$ and water dried organic layer over sodium sulphate. The product was purified using column chromatography by mobile phase hexane: ethyl acetate. The yield was reported after column purification.

Spectral Analysis

1a. Methyl biphenyl-4-carboxylate Colorless solid M. P.118^0C **^{1}HNMR** $CDCl_3$ 400 MHz 8.039-8.008 δ (m, 2H) 7.590-7.521 δ(m 4H) 7.400 -7.355 δ(m 2H) 7.328-7.288 δ(m 1 H) 3.855 δ(s 3 H) **^{13}CNMR** ($CDCl_3$ 100 MHz) δ: 166.91, 145.67, 139.91, 130.09, 128.80, 128.14, 127.27. 127.07, 52.00

1b. Methyl 4-(5-methylpyridin-2-yl)benzoate Yellow Solid M.P. 113^0C **^{1}HNMR** $CDCl_3$ 400 MHz 8.552 -8.542 δ(m 1 H), 8.130- 8.104 δ(m 2 H), 8.082-8.051 δ(m 2 H) 7.762-7.736 δ(m 1 H) 7.301-7.260 δ(m 1 H) 3.891 δ(m 3 H), 2.351 δ(s 3 H) **^{13}CNMR** ($CDCl_3$ 100 MHz) δ: 167.02, 154,02, 150.89, 143.58, 137.49, 132.67, 130.12, 130.00, 126.59, 120.54, 52.43, 18.37.

1c. Methyl 4-(6-methoxypyridin-2-yl)benzoate Colorless Solid M.P. 94 ^{0}C **^{1}HNMR** $CDCl_3$ 400 MHz 8.099-8.012 δ(m 4 H), 7.681-7.642 δ(m 1 H), 7.411-7.382 δ(m 1 H) 6.751-6.709 δ(m 1 H) 3.991 δ(s 3 H), 3.900 δ(s 3 H) **^{13}CNMR** ($CDCl_3$ 100 MHz) δ:168.10, 164.12, 152.94, 143.22,138.84, 130.78,129.81, 126.38, 113.55, 110.45, 53.78, 52.98.

1d Methyl 4-(naphthalen-2-yl)benzoate Colorless Liquid **^{1}HNMR** $CDCl_3$ 400 MHz 8.152-8.24 δ (m, 2H) 8.061-8.068 δ (d, J=2.8Hz 1H) 7.928-7.832 δ (m, 3H) 7.785-7.725 δ (m, 3H) 7.536 – 7.476 δ (m, 2H) 3.95 (s 3H) **^{13}CNMR** ($CDCl_3$ 100 MHz) δ: 166.79, 146.00, 137.32, 133.25, 132.50, 130.31, 129.00, 128.26, 128.03, 127.46, 127.42, 126.84, 126.80, 126.03, 125.81, 52.01.

2a. Methyl biphenyl-2-carboxylate Colorless Liquid **^{1}HNMR** $CDCl_3$ 400 MHz 7.828-7.806 (dd J= 2.0Hz, J=7.88Hz 1H) 7.531-7.593 δ (m, 1H) 7.419-7.235 δ (m, 7H) 3.652 δ (m, 3H) **^{13}CNMR** ($CDCl_3$ 100 MHz) δ:169.00, 142.18, 141.11, 131.21, 130.99, 129.77, 128.26, 127.84, 127.44, 127.28 51.00.

3a. Biphenyl-4-carbonitrile Colorless Solid M.P. 85-87^{0}C ^{1}HNMR CDCl$_3$ 400 MHz 7.306-7.396 δ (m 1 H) 7.400-7.483 δ (m 2H) 7.512-7.596 δ (m 2H) 7.618-7.692 δ (m 4H) ^{13}CNMR (CDCl$_3$ 100 MHz) δ: 110.19, 118.19, 127.12, 127.17, 128.46, 129.90, 132.15, 139.11, 145.00.

3b. 4'-Methoxybiphenyl-4-carbonitrile light brown solid M.P. 100-102^{0}C ^{1}HNMR CDCl$_3$ 400 MHz 7.682-7.622 δ (m 2H) 7.547-7.511 δ (m 2H) 7.011-6.978 δ (m 2H) 3.845 δ (s 3 H)^{13}CNMR (CDCl$_3$ 100 MHz) δ: 160.44, 145.31, 132.86,131.56,128.11, 126.91, 118.85, 114.45, 110.26, 55.78.

3c. 3'-Methoxybiphenyl-4-carbonitrile Colorless liquid ^{1}HNMR CDCl$_3$ 400 MHz 7.732-7.551 δ (m 4 H) 7.412-7.350 δ (m 1 H) 7.181-7.135 δ (m 1 H) 7.121-7.095 δ (m 1 H) 6.971-6.931 δ (m 1 H) 3.785 δ (s 3 H) ^{13}CNMR (CDCl$_3$ 100 MHz) δ: 160.21, 146.00, 141.11, 131.98, 129.91, 127.57, 120.00, 118.41,113.84, 113.12, 109.86, 55.76.

3d. 4-(4-*tert*-Butylphenyl)benzonitrile Colorless liquid ^{1}HNMR CDCl$_3$ 400 MHz 7.691-7.629 δ (m 4 H) 7.571-7.501 δ (m 4 H) 1.411 δ (m 9 H) ^{13}CNMR (CDCl$_3$ 100 MHz) δ: 152.00, 145.39, 137.98, 132.44, 126.41, 127.00, 125.85, 118.76, 110.11, 35.01, 30.96.

3e. Methyl 4'-cyanobiphenyl-4-carboxylate Colorless solid M. P.135 - 145^{0}C ^{1}HNMR CDCl$_3$ 400 MHz 8.171-8.110 δ (m 2 H) 7.811-7.699 δ (m 6 H) 3.894 δ (m 3 H) ^{13}CNMR (CDCl$_3$ 100 MHz) δ: 165.91, 144.81, 142.89, 133.01, 130.52, 130.00, 128.02, 127.4, 119.21, 112.15, 61.00, 14.19.

3f. 4-(pyridin-3-yl)benzonitrile White Solid M. P. 102-103^{0}C ^{1}HNMR CDCl$_3$ 400 MHz 8.838-8.811(m 1H) 8.657-8.639(m 1H) 7.921-7.839(m 1H) 7.802-718(m 2 H)7.714-7.633 (m 2H) 7.456-7.344(m 1H) ^{13}CNMR (CDCl$_3$ 100 MHz): 150.01, 147.98, 142.45, 135.11, 134.94, 133.00, 127.15, 124.05, 118.58, 111.96.

4a.4-Methoxy-biphenyl Cream solid M.P. 87-90^{0}C ^{1}HNMR CDCl$_3$ 400 MHz 7.559-7.506 δ (m 4 H) 7.427-7.384 δ (m 2 H) 7.316-7.233 δ (m 1 H) 6.991-6.952 δ (m 2 H) 3.881 δ (s 3 H) ^{13}CNMR (CDCl$_3$ 100 MHz) δ: 159.63, 140.75, 133.80, 128.32, 128.00, 126.68,126.11, 114.31, 55.17

4b. 4-Methoxy-4'-methylbiphenyl solid M.P. ^{1}HNMR CDCl$_3$ 400 MHz 7.535-7.471 δ (m 2 H) 7.465-7.441 δ (m 2 H) 7.260-7.223 δ (m 2 H) 6.999-6.961 δ (m 2 H) 3.873 δ (s 3 H) 2.400 δ (s 3 H) ^{13}CNMR (CDCl$_3$ 100 MHz) δ: 159.12, 138.00, 136.72,133.87, 139.54, 128.11, 126.78, 114.27, 55.77, 21.12.

4c. 4'-Methoxy-3-methylbiphenyl solid M.P. ^{1}HNMR CDCl$_3$ 400 MHz 7.560-7.508 δ (m 2 H) 7.390-7.271 δ (m 3 H) 7.139-7.001 δ (m 1 H) 6.990-6.959 δ (m 2 H) 3.861 δ (s 3 H) 2.401 δ (s 3 H) ^{13}CNMR (CDCl$_3$ 100 MHz) δ: 159.12, 141.00, 138.30, 134.11, 128.92, 128.09, 127.74, 127.14, 124.34, 113.85, 55.44, 21.68.

4d. 4'-methoxy-2-methylbiphenyl solid M.P. ^{1}HNMR CDCl$_3$ 400 MHz 7.268-7.129 δ (m 6 H) 6.890-6.842 δ (m 2 H) 3.792 δ (s 3 H) 2.210 δ (s 3 H) ^{13}CNMR (CDCl$_3$ 100 MHz) δ: 158.84, 141.65, 135.78, 134.58, 130.92, 130.23, 129.49, 127.04, 126.18, 113.76, 55.17, 20.94,

RESULTS AND DISCUSSION

In general the nature of aryl halide is neural but readily undergoes rieke zinc insertion reaction in presence of lithium chloride. The rieke zinc was prepared in THF by reduction of anhydrous zinc chloride using lithium napthalenide. The mossy form of zinc was settled rapidly at the bottom of RBF. The supernant liquid was remove by decantation and wash metal with anhydrous fresh THF. Methyl 4-iodobenzoate and methyl 2-iodobenzoate readily undergo zinc insertion reaction at room temperature by 24 hrs stirring.[34] The zinc insertion do not occur in absence of lithium chloride. The organozinc iodide couple with various aryl bromide in presence of copper (I) salt catalyst to afford the corresponding product 1a-1d and 2a in good yield. 4-cyano arylzinc bromide was easily prepared by rieke zinc insertion from corresponding functional aryl halide at 3 hrs reflux condition.[35] The prepared functional aryl zinc halide was coupled in presence of catalyst with various aryl bromide generate biaryl derivatives 3a-3f in good yield. First we did general screening of various copper (I) Complex salt, catalyst for coupling reaction in THF. The result of catalyst screening in coupling reaction of iodozincbenzoate with aryl bromide using different catalyst as follows.

Table 1 screening of different copper complexes in cross-coupling reaction.

Sr. No.	Copper (I) Catalyst	% Yield
1	....	No reaction
2	Cu(MeCN)$_4$BF$_4$	82 %
3	Cu(MeCN)$_2$F$_3$CSO$_3$	74 %
4	Cu(MeCN)$_4$ClO$_4$	60 %
5	Cu(MeCN)$_4$NO$_3$	56 %
6	Cu(MeCN)$_4$ PF$_6$	68 %

We found that coupling reaction between aryl bromide and functional arylzinc halide is catalyzed by different copper (I) complexes to produce biphenyl compound. In the screening of catalyst, tetrakis acetonitrile copper (I) tetrafluroborate is best catalyst for coupling reaction. In summary the coupling reaction between functional aryl organozinc compounds and aryl bromide catalyzed by tetrakis acetonitrile copper (I) tetrafluroborate gives high yield of variety of coupled product under mild condition.

Table 2 Copper-Catalyzed Cross-Couplings between functionalized organo zinc reagents and aryl halides.

Entry	Organozinc Reagent	Aryl halide	Yield	M.P.	Ref.
1a	4-MeOOC-C$_6$H$_4$ZnI.LiCl	Br-C$_6$H$_5$	82 %	118 ^{0}C	29
1b	4-MeOOC-C$_6$H$_4$ZnI.LiCl	2-Br-5-CH$_3$C$_5$NH$_3$	76 %	113 ^{0}C	30
1c	4-MeOOC-C$_6$H$_4$ZnI.LiCl	2-Br-6-OMe C$_6$NH$_3$	68 %	94 ^{0}C	30
1d	4-MeOOC-C$_6$H$_4$ZnI.LiCl	2-Br C$_{10}$H$_7$	62 %	Liq.	29
2a	2-MeOOC-C$_6$H$_4$ZnI.LiCl	Br-C$_6$H$_5$	65 %	Liq.	29
3a	4-NC-C$_6$H$_4$ZnBr.LiCl	Br-C$_6$H$_5$	71 %	85-87 ^{0}C	29
3b	4-NC-C$_6$H$_4$ZnBr.LiCl	4-Br –OMe	74 %	100-	31

		C_6H_4		102 ^{0}C	
3c	4-NC-C_6H_4ZnBr.LiCl	3-Br –OMe C_6H_4	67 %	Liq.	32
3d	4-NC-C_6H_4ZnBr.LiCl	Br -4-^{t}Bu C_6H_4	62 %	Liq.	32
3e	4-NC-C_6H_4ZnBr.LiCl	4-MeOOC-C_6H_4I	78 %	137-142 ^{0}C	29
3f	4-NC-C_6H_4ZnBr.LiCl	3-Br-C_5NH_4	73%	102 – 103 ^{0}C	33

Functionalized aryl zinc halide compound bears functional group such as ester and cyano easily coupled with various aryl halides using catalyst tetrakis acetonitrile copper (I) tetrafluroborate.

CONCLUSION

We have developed process optimized efficient protocol for coupling reaction of functional aryl zinc halide with aryl bromide catalyzed by tetrakisacetonitrile copper(I)tetrafluroborte.

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