Copper iodide nanoparticles-catalysed cyanation of aryl halides using non-toxic $K_4[Fe(CN)_6]$ in the presence of 1,2-bis(5-tetrazolyl)benzene as an efficient ligand

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Cyanation of aryl bromides were carried out with $K_4[Fe(CN)_6]$ in the presence of catalytic amounts of a copper salt and 1,2-bis(5-tetrazolyl)benzene as a ligand under thermal conditions. This method has the advantages of high yields, simple methodology and easy work up.

Keywords: 1,2-bis(5-tetrazolyl)benzene, aryl bromide, cyanation, CuI nanoparticles, $K_4Fe(CN)_6$, aryl nitriles

Nitriles are valuable intermediates in the construction of various pharmaceutical compounds, agrochemicals and dyes[1] and are also useful reagents in synthetic organic chemistry, since they can be easily transformed into other functional groups such as nitrogen-containing heterocycles, aldehydes, acids and acid derivatives.[2–13]

The earliest published methods for the preparation of nitriles were reactions including the following: (1) reaction of aryl halides with stoichiometric amounts of CuCN;[14] (2) the diazotisation of anilines and subsequent Sandmeyer reaction;[15,16] (3) the transition metal-catalysed cyanation of aryl halides using KCN, NaCN, Me_3SiCN and $Zn(CN)_2$ as cyanating agents.[17–21]

However, there are several factors in some of these methods which limit their applications. In many cases, the reagents are toxic, hazardous, sensitive to moisture, expensive or inaccessible and cannot be stored. Among cyanation agents in the synthesis of nitriles, CuCN and $Zn(CN)_2$ lead to heavy metal waste. Most of the other methods for the synthesis of nitriles have disadvantages such as long reaction times, formation of side products, use of expensive catalyst involve several steps and give low yields. Thus, the development of an efficient and versatile method for the synthesis of nitriles is an active ongoing research area.

Due to safety considerations, we must avoid methods which use toxic, hazardous, moisture sensitive and expensive reagents. Among the reagents for the synthesis of nitriles, $K_4Fe(CN)_6$ has received attention because it is not explosive or flammable and it is inexpensive. It can be easily stored and is neither moisture sensitive and nor very volatile. It is used in the food industry for metal precipitation and it is cheaper than KCN and NaCN. Beller and co-workers reported the synthesis of aryl nitriles using potassium hexacyanoferrate (II).[22]

Several syntheses of aryl nitriles have been reported using $K_4Fe(CN)_6$ in the presence of palladium catalysts,[23–25] while the less expensive copper catalysts have received less attention. The high cost of palladium salts restricts their applications, especially in large-scale process. For this reason, copper catalysts have been developed.

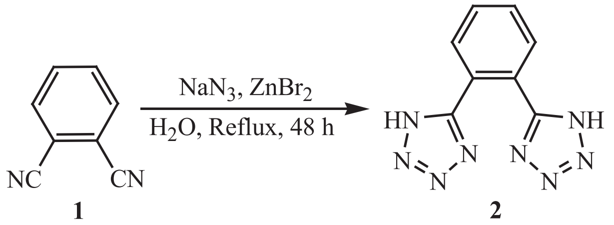
Among various ligands for the transition copper-catalysed cyanation of aryl halides with $K_4[Fe(CN)_6]$, diamines have been widely investigated,[26–29] while less expensive nitrogen-containing heterocycles such as tetrazoles have received scant attention. Recently, new types of nonphosphine ligands, such as heterocyclic carbenes, imines, imidazoles, and 1,2,4-triazoles, have emerged as alternatives for the carbon–carbon bond forming reactions.[28] Although heterocyclic carbenes show good to excellent catalytic activities with palladium, they easily undergo decomposition at higher temperature.[29] Nitrogen-based ligands are sensitive towards acidic conditions. There is a continuing need for simple and versatile synthetic ligands and catalysts for this type of reaction. Thus, the development of a new system for the synthesis of aryl nitriles still remains an active research area.

The growth of tetrazole chemistry over the last 30 years has been significant,[30–32] mainly as a result of the roles played by tetrazoles in coordination chemistry as ligands and in organic synthesis as an effective substrate.[33,34] We now describe a simple method of synthesis of aryl nitriles in high yields by the reaction of aryl bromides and $K_4Fe(CN)_6$ in the presence of copper salt and 2-bis(5-tetrazolyl)benzene as a ligand (**2**) (Scheme 1).

Several years ago Sharpless and his co-workers reported the synthesis of 1,2-bis(5-tetrazolyl)benzene (**2**) from the reaction between 1,2-phenylene-dinitrile (**1**) and sodium azide in the presence of zinc chloride as a homogeneous catalyst in water (Scheme 2).[35] We believe that ligand **2** can plays an important role in this reaction for the synthesis of aryl nitriles.

$$\mathrm{ArBr} \xrightarrow[\mathrm{K_4Fe(CN)_6,\ Cs_2CO_3,\ DMF,\ 130\ ^oC,\ 10\ h}]{\mathrm{CuI,\ ligand}\ \mathbf{2}} \mathrm{ArCN}$$

Scheme 1



Scheme 2

Results and discussion

The reaction conditions were optimised for the cyanation reaction using 4-methoxybromobenzene as a substrate, $K_4[Fe(CN)_6]$ as the cyanating agent, CuI nanoparticles as the catalyst and 1,2-bis(5-tetrazolyl)benzene as a ligand in the

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Table 1 The cyanation reaction 4-methoxybromobenzene with $K_4[Fe(CN)_6]$ under different reaction conditions[a]

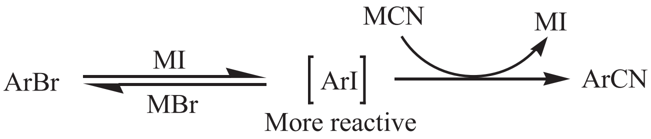
Entry	Base	KI	Solvent	Temperature/°C	Yield/%[b]
1	Cs_2CO_3	0	DMF	130	<6
2	Cs_2CO_3	50	DMF	130	93
3	Cs_2CO_3	50	CH_3CN	Reflux	76
4	Cs_2CO_3	50	MeOH	Reflux	77
5	Cs_2CO_3	50	Toluene	Reflux	80
6	Cs_2CO_3	50	NMP	130	90
7	KOAc	50	DMF	130	40
8	K_2CO_3	50	DMF	130	79
9	Na_2CO_3	50	DMF	130	85
10	Et_3N	50	DMF	130	29
11	NaF	50	DMF	130	35
12	–	50	DMF	130	0
13	Cs_2CO_3	50	DMF	130	40[c]

[a] Reaction conditions: 4-methoxybromobenzene (1.0 mmol), $K_4[Fe(CN)_6]$ (0.22 mmol), KI (0.5 mmol), base (1.0 mmol), ligand **2** (0.8 mmol), CuI nanoparticles (0.3 mmol), 130 °C, 15 h, pressure tube, N_2 atm.

[b] Isolated yield.

[c] The reaction was carried out in the absence of ligand at 130 °C, 25 h.

presence of various solvents and bases under various temperature conditions (Table 1). In our study, the optimal stoichiometry of $K_4[Fe(CN)_6]$ was found to be 0.22 mmol. Control experiments showed that there was no effective reaction in the absence of KI. However, addition of the KI to the mixture has rapidly increased the cyanation of aryl bromides in high yields. This result can be rationalised assuming *in situ* copper-catalysed conversion of the aryl bromide into the more reactive aryl iodide followed by the cyanation of the resulting aryl iodide (Scheme 3).[26] Interestingly, when the reaction was carried out in DMF, good conversion was achieved (Table 1, entry 2). Encouraged by this result, we decided to carry out the reaction in DMF using different bases. The results indicated that base had a remarkable effect on the yield of product (Table 1, entry 12). In the absence of base, the reactions did not proceed even after a long reaction time (15 h). Among the various bases tested, Cs_2CO_3 was an effective base (Table 1, entry 2). The best result was obtained with aryl bromide (1.0 mmol), **2** (0.8 mmol), CuI nanoparticles (0.3 mmol), KI (50 mol%), and Na_2CO_3 (1.0 mmol), which gave the product in a good yield (93%).



Scheme 3

The scope of this catalyst was then investigated for the cyanation reaction under the above optimised reaction conditions using a variety of aryl bromides (Table 2). In all cases, the reactions were carried out at 130 °C with DMF as solvent. Different aryl halides bearing either electron-donating or electron-withdrawing substituents were converted to the corresponding aryl nitriles.

2-Bromotoluene which is sterically hindered around the reaction site gave a high yield (Table 2, entry 2). The reactions appeared to be insensitive to steric hindrance. Apart from aryl bromides we also tested three heteroaromatic nitriles (Table 2, entries 11–13). As indicated in Table 2, it is evident that our method is reasonably general and can be applied to several types of aryl bromides. In all cases the reaction gave the corresponding aryl nitriles in good to excellent yields under the reaction conditions.

Several similar mechanisms have been reported for the palladium or copper-catalysed cyanation of aryl halides using various ligands. We believe that the tetrazole ligand **2** can coordinate with copper through the nitrogen atoms of the ring as in the case of 1,2,3-triazole pincer ligand (NCN).[36,37] Although we have not yet fully characterised the tetrazole pincer complexes, the ligand, in combination with CuI, has been shown to catalyse the coupling reactions of aryl halides with $K_4[Fe(CN)_6]$ efficiently. A characteristic feature of our system is the thermal stability, which makes it possible to perform the reactions even at a temperature above 100 °C, which is necessary for less reactive substrates such as aryl chlorides and aryl bromides.

The physical data (m.p., IR, NMR) of the products were found to be identical with those reported in the literature.[22,26,27] The formation of aryl nitriles was confirmed by IR spectra, which showed one characteristic peak for the CN stretching

Table 2 Copper-catalysed cyanation of various aryl bromides[a]

Entry	Substrate	Product	Time/h	Yield/%[b]	M.p. (lit. m.p.)[Ref.]
1	C_6H_5Br	C_6H_5CN	15	91	Oil[16]
2	*o*-MeC_6H_4Br	*o*-MeC_6H_4CN	15	91	Oil[39]
3	$3,5\text{-}(Me)_2C_6H_3Br$	$3,5\text{-}(Me)_2C_6H_3CN$	15	94	42–43 (42–43)[40]
4	*p*-$MeOC_6H_4Br$	*p*-$MeOC_6H_4CN$	15	93	59–60 (58–60)[16]
5	*p*-$COMeC_6H_4Br$	*p*-$COMeC_6H_4CN$	10	92	56–59 (56–59)[39]
6	*p*-$COOMeC_6H_4Br$	*p*-$COOMeC_6H_4CN$	10	89	65–67 (65–67)[39]
7	*p*-CNC_6H_4Br	*p*-CNC_6H_4CN	10	87	221–225 (221–225)[16]
8	$1\text{-}C_{10}H_7Br$	$1\text{-}C_{10}H_7CN$	10	89	36–38 (35–36)[40]
9	$3,5\text{-}(t\text{-}Bu)_2C_6H_3Br$	$3,5\text{-}(t\text{-}Bu)_2C_6H_3CN$	13	88	85–87 (85–87)[39]
10	*p*-$CHOC_6H_4Br$	*p*-$CHOC_6H_4CN$	10	86	100–102 (100–102)[39]
11	$3\text{-}BrC_5H_4N$	$3\text{-}CNC_5H_4N$	10	90	48–52 (48–52)[39]
12	$2\text{-}NH_2,5\text{-}C_5H_3NBr$	$2\text{-}NH_2,5\text{-}C_5H_3NCN$	20	82	160–162 (160–162)[40]
13	$3\text{-}C_9H_6NBr$	$3\text{-}C_9H_6NCN$	20	86	106–107 (105–107)[40]
14	$2,4,6\text{-}(Me)_3C_6H_2Br$	$2,4,6\text{-}(Me)_3C_6H_2CN$	35	80	52–53 (52–53)[16]
15	$3,5\text{-}(CF_3)_2C_6H_3Br$	$3,5\text{-}(CF_3)_2C_6H_3CN$	10	89	Oil[39]
16	C_6H_5Cl	C_6H_5CN	50	0	–

[a] Reaction conditions: aryl bromide (1 mmol), CuI (0.3 mmol), $K_4[Fe(CN)_6]$ (0.22 mmol), ligand **2** (0.8 mmol), Cs_2CO_3 (1.0 mmol), KI (0.5 mmol), DMF (5 mL), 130 °C, pressure tube, N_2 atm.

[b] Yield refers to pure isolated product.

band between 2225 and 2360 cm^{-1}. The ^{13}C NMR spectra of the products showed signals for the nitrile carbon at $\delta = 113–119$ ppm.

In summary, we have described an efficient protocol for the synthesis of aryl nitriles using a copper salt/1,2-bis(5-tetrazolyl) benzene combination as a catalytic system. The significant advantages of this methodology are high yields, elimination of dangerous and toxic reagents and a simple work-up procedure.

Experimental

All the solvents and reagents were purchased at the highest commercial quality and used without further purification. $K_4[Fe(CN)_6]$ was prepared by grinding $K_4[Fe(CN)_6].3H_2O$ to a fine powder and drying in vacuum. All reaction mixtures were stirred magnetically and were monitored by TLC using 0.25 mm E-Merck silica gel 60 F254 pre-coated glass plates, which were visualised with UV light and then developed by using iodine mixed with silica gel 60–120 mesh. Melting points were recorded on a Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a PerkinElmer FT-IR 240-C spectrometer using KBr optics. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 MHz spectrometers in $CDCl_3$ and DMSO using TMS as internal standard, with chemical shifts being given in ppm with respect to internal TMS and J values quoted in Hz.

Preparation of the catalyst

CuI nanoparticles were prepared by the reaction of $Cu(dmg)_2$ and KI in the autoclave with ethanol as solvent, solvothermal method. Firstly, dimethylglyoxime (0.464 g, 4 mmol) (dmgH) and $Cu(OAc)_2{\bullet}H_2O$ (0.400 g, 2 mmol) were added into absolute ethanol 50 mL of (50 mL) in sequence. This was stirred at 0 °C for 30 min to give a brown precipitate of $Cu(dmg)_2$. Then the collected precipitate was dispersed in 50 mL of absolute ethanol again. Secondly, KI (0.664 g, 4 mmol) was added and stirred vigorously for 2 h. After that, the mixture was transferred into 60 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 180 °C for 6 h, the reactor bomb was then allowed to cool to room temperature. A black precipitate was obtained which was then centrifuged and washed with ethanol and deionised water three times to ensure the removal of impurities. The final product was then dried in a vacuum oven at room temperature for 12 h. The catalyst was characterised by XRD and TEM.[38]

*Synthesis of 1,2-bis(5-tetrazolyl)benzene (**2**)*

The nitrile (10 mmol), sodium azide (1.43 g, 22 mmol), zinc bromide (4.50 g, 20 mmol), and water (40 mL) was added to a 250 mL round-bottomed flask.[35] The reaction mixture was refluxed for 48 h; vigorous stirring is essential. HCl (3 N, 30 mL) and ethyl acetate (100 mL) were added, and vigorous stirring was continued until no solid was present and the aqueous layer had a pH of 1. If necessary, additional ethyl acetate was added. The organic layer was isolated and the aqueous layer extracted with 2 × 100 mL of ethyl acetate. The combined organic layers were evaporated, 200 mL of 0.25 N NaOH was added, and the mixture was stirred for 30 min, until the original precipitate was dissolved and a suspension of zinc hydroxide was formed. The suspension was filtered, and the solid washed with NaOH (1N, 20 mL). HCl (3N, 40 mL) was added to the filtrate with vigorous stirring causing the tetrazole to precipitate. The tetrazole was filtered and washed with HCl (3N, 2 × 20 mL) and dried in a drying oven to furnish the tetrazole as a white or slightly coloured powder, m.p. 228–230 °C (lit.[35] 228–230 °C) ^1H NMR: 7.87 (m, 2H), 7.80 (m, 2H).

Cyanation of aryl bromides with $K_4Fe(CN)_6$; general procedure

A mixture of copper salt (0.3 mmol) and **2** (0.8 mmol) in DMF (2 mL) was stirred at room temperature under a dry nitrogen atmosphere for 10 min to give a homogeneous solution. Next the aryl bromide (1 mmol), base (1.0 mmol), KI (0.5 mmol), $K_4Fe(CN)_6$ (0.22 mmol) and DMF (2 mL) were added and the mixture stirred at 130 °C for 10 h (Table 2). After completion (as monitored by TLC), H_2O (15 mL) was added and the organic layer was extracted with EtOAc (3 × 15 mL), washed with brine (15 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by column chromatography. All the products are known and were characterised by IR, NMR and melting points and their spectroscopic data identical to that reported in the literature.[22,26,27]

Benzonitrile (Table 2, entry 1): ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55–7.60 (m, 2H), 7.52–7.54 (m, 1H), 7.38–7.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 132.6, 132.0, 129.0, 118.6, 112.1.

2-Methylbenzonitrile (Table 2, entry 2): ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38–7.43 (m, 1H), 7.34–7.36 (m, 1H), 7.12–7.19 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.5, 132.5, 132.2, 130.0, 126.1, 117.8, 112.4, 20.1.

4-Methoxybenzonitrile (Table 2, entry 4): ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.55–7.60 (m, 2H), 6.93–6.96 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.6, 133.8, 119.0, 114.6, 103.7, 55.3.

4-Acetylbenzonitrile (Table 2, entry 5): ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03–8.06 (m, 2H), 7.76–7.79 (m, 2H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.3, 139.7, 132.3, 128.5, 117.6, 116.2, 26.6.

Methyl-4-cyanobenzoate (Table 2, entry 6): ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11–8.14 (m, 2H), 7.72–7.76 (m, 2H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.1, 133.7, 132.1, 130.0, 117.8, 116.2, 52.6.

2-Amino-5-cyanopyridine (Table 2, entry 12): ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.30 (d, J=2.1 Hz, 1H), 7.68 (d, J=8.7 Hz, 1H), 7.04 (s, 2H), 6.50 (d, J=8.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 161.6, 153.3, 139.5, 119.0, 107.8, 94.7.

Quinoline-6-carbonitrile (Table 2, entry 13): ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) 9.09 (dd, J=1.9, 4.3 Hz, 1H), 8.67 (d, J=1.3 Hz, 1H), 8.50 (d, J=8.5 Hz, 1H), 8.17 (d, J=8.5 Hz, 1H), 8.05 (dd, J=1.9, 8.6 Hz, 1H), 7.70 (dd, J=4.3, 8.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 153.7, 148.5, 136.8, 135.1, 130.5, 130.2, 127.3, 123.1, 118.6, 109.1.

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