



Ligand-free CuI-catalyzed cyanation of aryl halides using $K_4[Fe(CN)_6]$ as cyanide source and water as solvent

Catherine DeBlase, Nicholas E. Leadbeater*

Department of Chemistry, University of Connecticut, 55 North Eagleville Road, Storrs, CT 06269-3060, USA

ARTICLE INFO

Article history:

Received 26 August 2009

Accepted 22 September 2009

Available online 6 November 2009

ABSTRACT

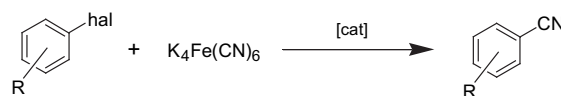
A methodology for the cyanation of aryl iodides is reported using copper iodide as the catalyst, $K_4[Fe(CN)_6]$ as the cyanide source, and small quantities of water and tetraethylene glycol as the solvent. Reactions are complete within 30 min of microwave heating at 175 °C. A simple work-up procedure has also been devised.

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1. Introduction

Cyanation of aryl halides to form nitriles represents an important synthetic transformation since the nitrile motif is found in a range of pharmaceuticals, dyes, agrochemicals, and natural products.^{1,2} Nitriles are also valuable intermediates in organic synthesis and can be easily transformed to a range of heterocycles. A number of synthetic methods for the preparation of aryl nitriles have been developed. The majority require the use of toxic inorganic or organic cyanide sources, such as alkali-metal cyanides, trimethylsilyl cyanide,³ or acetone cyanohydrin.^{4,5} In 2004, Beller and co-workers reported the use of potassium hexacyanoferrate (II), $K_4Fe(CN)_6$, as a cyanide source.^{6,7} This has greatly reduced toxicity as compared to alkali-metal cyanides such as KCN. It is used industrially for metal extractions and making a range of advanced materials. It is also used in low doses in some food preparation, serving as an anti-caking agent and removing copper from red wine. It therefore offers a much greener alternative to other cyanide sources for use in synthetic chemistry. In addition, all six of the CN moieties of $K_4Fe(CN)_6$ can be used for cyanation of aryl halides, harnessing the full potential of the reagent. Given these benefits, it is not surprising that a review of the recent literature shows that the application of $K_4Fe(CN)_6$ as a cyanide source is growing (Scheme 1). Most procedures involve the use of palladium complexes as catalysts for the reaction.⁸ An issue often encountered with palladium catalysis for this transformation is that over time the catalysts are deactivated due to the presence of excess cyanide in solution.⁹ As a result, higher catalyst loadings can be required and, when using palladium salts ligated with phosphine ligands it is costly. As a result, there has been growing interest in developing

cheaper alternatives. Historically, copper complexes have been used with success for cyanation reactions. The classical route to aryl nitriles is the Rosenmund–von Braun reaction involving use of stoichiometric quantities of copper(I) cyanide.¹⁰ However, this procedure can require harsh conditions, making it incompatible with sensitive substrates.¹¹ More recently, copper complexes have been used as catalysts for the reaction in conjunction with organic or inorganic cyanide sources,^{12,13} including a few recent reports using $K_4Fe(CN)_6$.¹⁴ These procedures tend to require the use of ligands or additives and also require prolonged reaction times.



Scheme 1. Cyanation of aryl halides using $K_4[Fe(CN)_6]$ as a cyanide source.

Research in our laboratory has been focused around the application of microwave heating as a tool for preparative chemistry, particularly in conjunction with the use of water as a solvent.^{15,16} Microwave heating often reduces reaction times dramatically, and in the case of metal-catalyzed processes, reduces catalyst loadings. A number of recent reports describe the cyanation of aryl halides facilitated using microwave heating.^{17,18} Furthermore, we have had previous interest in this transformation,^{19,20} and recently turned our attention to developing a palladium-catalyzed methodology based around the use of water as a solvent in conjunction with microwave heating and $K_4[Fe(CN)_6]$ as a cyanide source. Reactions are complete within 20 min microwave heating at 150 °C and use 5 mol % $Pd(OAc)_2$ as catalyst. Building on this work, we have become interested in developing a copper-catalyzed variant with the objective of developing a clean, cheap, and efficient methodology. We report the results from our first phase of work here.

* Corresponding author. Tel.: +1 860 486 5076; fax: +1 860 486 2981.

E-mail address: nicholas.leadbeater@uconn.edu (N.E. Leadbeater).

2. Results and discussion

Our objective was to develop a procedure for cyanation of aryl halides that used a simple copper salt as catalyst (no added ligands), $K_4[Fe(CN)_6]$ as the cyanide source, and water as the solvent. Our starting point was to use similar reaction conditions to those from our previously reported palladium-catalyzed procedure but using copper salts in the place of palladium acetate and without base. With 4-iodoanisole as a test substrate and copper(II) acetate (10 mol%) as a catalyst candidate, we performed the reaction using 2 mL water as solvent and 0.3 equiv $K_4[Fe(CN)_6]$ and tetrabutylammonium bromide (TBAB) as a phase-transfer agent. After heating the reaction to 150 °C and holding at this temperature for 20 min, no product was observed (Table 1, entry 1). Increasing the temperature to 175 °C had no effect (Table 1, entry 2). We have found in our other protocols that reactions performed using water as solvent can be highly concentration dependent. Therefore, we re-screened the same reaction conditions but using just 0.25 mL water. This small modification led to a 71% conversion to the desired nitrile product (Table 1, entry 3). We next wanted to determine if the use of TBAB was essential and found that indeed it was, performing the reaction in its absence not resulting in product formation (Table 1, entry 4). Given the recent upsurge in procedures published using iron catalysts,^{21,22} we wanted to determine whether $K_4[Fe(CN)_6]$ could serve as both cyanide source and also catalyst, although unlikely. No product was observed in the absence of the copper salt (Table 1, entry 5). We next screened a range of other copper salts as well as copper metal. We found copper(I) iodide to be the most catalytically active, giving a 74% conversion in the cyanation of 4-iodoanisole (Table 1, entry 6). Choosing this as our catalyst candidate for further study, we next sought to optimize the catalyst loading. When using less than 10 mol% CuI, we found conversion dropped significantly. When using greater than 10 mol% CuI, we observed a plateau at 15 mol% (79% conversion; Table 1, entry 7), above which the conversion did not increase. Interested in determining if ligation of the copper salt would increase the effectiveness of the catalyst system, we screened two diamine-based candidates, both of which had shown applicability in other procedures.¹³ However use of *trans*-cyclohexane-1,2-diamine or *N,N'*-dimethylenediamine had a deleterious effect (Table 1, entries 8 and 9).

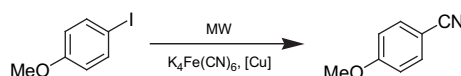
At this point, we wanted to assess our procedure from a green chemistry standpoint. We were using $K_4[Fe(CN)_6]$ as our cyanide source, a small volume of water as solvent, and a non-toxic, readily available copper salt as catalyst. These were all positive factors, as was the short reaction time. However, one major disadvantage of

the procedure was the amount of waste the post-reaction work-up generated. In order to purify the product and ensure complete removal of the TBAB it was necessary to perform numerous aqueous-organic extractions, this involving the use of significant quantities of water and organic solvent. Knowing that the use of water as solvent in the absence of TBAB was not successful, we screened a number of co-solvents. Use of tetraethylene glycol (TEG) proved to be optimal; polyethylene glycol (PEG) or water-PEG mixtures also finding application in other copper-catalyzed reactions.²³ In the cyanation of 4-iodoanisole we obtained an 81% conversion and the work-up was greatly simplified (Table 1, entry 10). It now required addition of small volumes of organic solvent (4×3 mL) followed by water (2×3 mL) to the reaction vessel, emptying the contents into a separatory funnel and performing one single wash with brine. In an attempt to drive the reaction to completion, we extended the time from 20 min to 30 min and this resulted in a 96% conversion to the desired nitrile product (Table 1, entry 11). Thus our optimal conditions for the reaction were: aryl halide, $K_4[Fe(CN)_6]$ (0.3 equiv), CuI (15 mol%), water (0.25 mL), tetraethylene glycol (0.25 mL); heat to 175 °C and hold at this temperature for 30 min.

Before proceeding, we wanted to determine if the reaction was indeed copper catalyzed. Previous work in our laboratory, as well as examples from other groups, has shown that the outcome of reactions may in some cases be significantly affected by trace levels of metal contaminants. In one example, Suzuki-type couplings, initially thought to be catalyst-free,²⁴ were found to be affected by ppb levels of palladium contaminants found in sodium carbonate base.²⁵ In a very recent case, cross-couplings performed using $FeCl_3$ as the catalyst were re-investigated, the results suggesting that copper contaminants played an important role in the reactions.^{26,27} Knowing the reaction was not iron catalyzed (Table 1, entry 5), we decided to probe whether trace palladium impurities could be catalytically active. To achieve this we first attempted to perform the cyanation chemistry using palladium catalysis. Using our optimal conditions (Table 1, entry 11) we performed the reaction using a number of palladium salts in place of copper iodide. In each case no product was observed. We next decided to screen our copper iodide source as a potential catalyst for Suzuki couplings using our previously reported conditions for this reaction.^{24,25} When using 4-bromoanisole as a substrate we knew this protocol was sensitive to levels of palladium down to 5 ppm. Using previously certified palladium-free sodium carbonate as base, no product was observed in the Suzuki coupling with phenylboronic acid when using our copper iodide source as the catalyst candidate. These two tests supported the assertion that the cyanation reaction was indeed copper catalyzed.

Table 1

Optimization of reaction conditions for the copper-catalyzed cyanation of 4-iodoanisole using $K_4[Fe(CN)_6]$ as a cyanide source^a

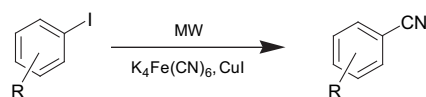


Entry	Conditions	Conversion (%)
1	Cu(OAc) ₂ (10 mol %), water (2 mL), TBAB as additive, 150 °C for 20 min	0
2	Cu(OAc) ₂ (10 mol %), water (2 mL), TBAB as additive, 175 °C for 20 min	0
3	Cu(OAc) ₂ (10 mol %), water (0.25 mL), TBAB as additive, 175 °C for 20 min	71
4	Cu(OAc) ₂ (10 mol %), water (0.25 mL), TBAB as additive, 175 °C for 20 min	0
5	No copper catalyst, water (0.25 mL), TBAB as additive, 175 °C for 20 min	0
6	CuI (10 mol %), water (0.25 mL), TBAB as additive, 175 °C for 20 min	74
7	CuI (15 mol %), water (0.25 mL), TBAB as additive, 175 °C for 20 min	79
8	CuI (15 mol %), <i>trans</i> -cyclohexane-1,2-diamine (15 mol %), water (0.25 mL), TBAB as additive, 175 °C for 20 min	56
9	CuI (15 mol %), <i>N,N'</i> -dimethylenediamine (15 mol %), water (0.25 mL), TBAB as additive, 175 °C for 20 min	46
10	CuI (15 mol %), water (0.25 mL), TEG (0.25 mL), 175 °C for 20 min	81
11	CuI (15 mol %), water (0.25 mL), TEG (0.25 mL), 175 °C for 30 min	95

^a Reactions were performed in a sealed tube, using 1 mmol 4-iodoanisole and 0.3 mmol $K_4[Fe(CN)_6]$.

Table 2

Substrate screening for the CuI-catalyzed cyanation of aryl halides using $K_4[Fe(CN)_6]$ as a cyanide source^a



Entry	Aryl halide	Conversion (%)	Yield (%)
1		94	72
2		87	70
3		79	66
4		89	79
5		85	63
6		93	73
7		79	66
8		93	40
9		0	0
10		12	9

^a Sealed tube, using 1.0 mmol aryl halide, 0.3 mmol $K_4[Fe(CN)_6]$, 15 mol % CuI, 0.25 mL water, 0.25 mL tetraethylene glycol. Initial microwave irradiation of 150 W, temperature ramped from rt to 175 °C, held for 30 min.

We moved to undertake a substrate screen using our optimal reaction conditions, the results being shown in Table 2. A number of aryl iodides could be converted to the corresponding nitriles in good yields (Table 2, entries 1–7). In the case of 2-iodopyridine, although a high conversion to the desired nitrile was observed, product purification was difficult and so the isolated yield was modest (Table 1, entry 8).

Cyanation of aryl bromides under the optimal reaction conditions was not successful (Table 1, entries 9 and 10). This represents a limitation of the methodology in its current form. Buchwald and co-workers reported a methodology for tandem halogen exchange/cyanation of aryl halides using CuI as the catalyst in the presence of nitrogen-based ligands.¹³ Using this, they could cyanate a range of aryl bromides, first converting them to the corresponding aryl iodide in an aromatic Finkelstein-type reaction using KI as a source of iodide.²⁸ We wanted to explore the possibility of incorporating such a halogen-exchange step into our procedure, thus opening avenues for our use of aryl bromides as substrates. However, we were unsuccessful. This could be attributed, at least in part, to the observation made by Klapars and Buchwald that a high concentration of halide salts in solution inhibits the desired halogen-exchange reaction via formation of poorly reactive halocuprate complexes. Since our

cyanation methodology requires a high concentration of reagents, this could be incompatible with a preceding halogen-exchange step.

During the time we were completing our studies, a report appeared in the literature presenting cyanation and tandem halogen-exchange/cyanation protocols catalyzed by copper(II) acetate.²⁹ This sparked our interest to compare with our methodology. The work was performed using a domestic microwave oven, the reaction vessel being sealed, and placed into a glycerol bath. There was no stirring or in-situ temperature measurement during the course of the reaction. Attempts to reproduce the procedure using our scientific microwave apparatus were unsuccessful, even after modification to take into account that the reaction mixture may be significantly hotter than reported in the procedure. We tried repeating the procedure using 4-iodoanisole, 4-iodotoluene, and 4-iodoacetophenone as aryl halide substrates.

3. Summary

We have developed a methodology for the cyanation of aryl iodides using copper iodide as the catalyst, $K_4[Fe(CN)_6]$ as the cyanide source, and small quantities of water and tetraethylene glycol as the solvent. Reactions are complete within 30 min microwave heating at 175 °C. A simple work-up procedure has also been devised. Work is now underway to expand the substrate scope of the protocol to include aryl bromides. In addition, similar approaches to C–C, C–N, and C–O bond-forming reactions are being developed.

4. Experimental

4.1. General experimental

All materials were obtained from commercial suppliers and used without further purification. All reactions were carried out in air. NMR spectra were recorded at 293 K on a 300 or 400 MHz spectrometer. All products are known and were characterized by comparison of NMR data with that in the literature. A commercially available monomode microwave unit (CEM Discover) was used. The machine consists of a continuous focused microwave power delivery system with operator selectable power output from 0 to 300 W. Reactions were performed in 10 mL capacity vessels sealed with a septum. The pressure was controlled by a load cell connected directly to the vessel and the temperature of the contents of the vessel was monitored using a calibrated IR sensor located outside the reaction vessel. The contents of the vessel were stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar in the vessel. Temperature, pressure, and power profiles were monitored using commercially available software provided by the microwave manufacturer.

4.2. Representative procedure for the cyanation of aryl iodides: cyanation of 4-iodoanisole

In a 10 mL glass tube were placed 4-iodoanisole (243 mg, 1.0 mmol), potassium hexacyanoferrate(II) (126 mg, 0.3 mmol), and CuI (28 mg, 15 mol %). After adding water (0.25 mL) and tetraethylene glycol (0.25 mL), the vessel was sealed with a septum and placed into the microwave cavity. Initial microwave irradiation of 150 W was used, the temperature being ramped from rt to the desired temperature of 175 °C where it was held for 30 min. During this time, the power was modulated automatically to hold the reaction mixture at 175 °C. The mixture was stirred continuously during the reaction. After allowing the mixture to cool to room temperature, the reaction vessel was opened and the contents transferred to a separatory funnel using 2×3 mL of acetonitrile,

2×3 mL of diethyl ether, and 2×3 mL of distilled water. Additional portions (3 mL each) of diethyl ether and distilled water were added to the separatory funnel and the organic material extracted and removed. The organic layer was rinsed one time with brine (10 mL), dried over MgSO₄, and the solvent removed in vacuo leaving the crude product. The product was then isolated and characterized by comparison of NMR spectra with those in the literature.³⁰ Yield and conversion data were obtained by integration of signals in the ¹H NMR and comparison with an internal standard.

Acknowledgements

This work was supported by the University of Connecticut Department of Chemistry NSF-REU program (CHE-0754580) and the University of Connecticut College of Liberal Arts and Sciences. Equipment support from CEM Corporation is acknowledged.

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