JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

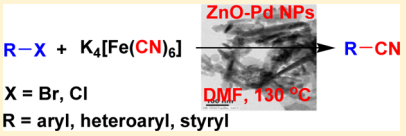
ZnO-Supported Pd Nanoparticle-Catalyzed Ligand- and Additive-Free Cyanation of Unactivated Aryl Halides Using $K_4[Fe(CN)_6]$

Tanmay Chatterjee, Raju Dey, and Brindaban C. Ranu*

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India

Supporting Information

ABSTRACT: The use of a new ZnO-supported palladium(0) nanoparticle catalyst for the cyanation of aryl halides using a relatively benign cyanide source, $K_4[Fe(CN)_6]$, is described. This catalyst has been applied for the efficient cyanation of a variety of functionalized aryl bromides and activated aryl chlorides. This process circumvents the need for an additive and a ligand for the reaction and offers the advantages of high product yields, low catalyst loading (0.2 mol % Pd), and recyclability of the catalyst.

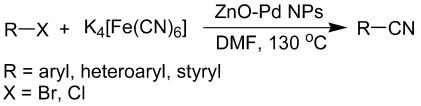


Aromatic nitriles are of much importance, as they are present in many natural products, pharmaceuticals, agrochemicals, and dyes.[1−3] Moreover, nitriles are useful building blocks in the synthesis of heterocycles, as they are easily converted into a variety of functional groups such as carboxylic acid, ketone, oxime, amine, amidine, etc.[4] Thus, the development of an efficient procedure for the synthesis of these compounds is of much interest.

The classical synthesis of aromatic nitriles by the Sandmeyer[5] and Rosenmund−von Braun[6] reactions are associated with serious drawbacks, including the use of high temperatures (150−250 °C) and stoichiometric amounts of copper(I) cyanide as the cyanating agent, which leads to equimolar amounts of heavy metal waste. The transition-metal-catalyzed cyanation of aryl halides has received wide attention in recent times.[7] Several transition metals, including Pd,[8] Ni,[9] and Cu,[10] have been involved in cyanation reactions using a variety of metal cyanide sources that are primarily toxic, such as alkali-metal cyanides,[8e,f,10a,11] $Zn(CN)_2$,[12] CuCN,[13] TMSCN,[14] KCN,[15] and NaCN,[8e,16] as well as relatively less toxic non-metallic agents[17a] such as acetone cyanohydrins,[17b] alkyl nitriles,[17c] phenyl cyanate,[17d] benzyl thiocyanate,[17e] and *N*-cyanobenzimidazole,[17f] usually in the presence of several nitrogen- and phosphorus-containing ligands, which are often hazardous and expensive. Although Pd catalysts are highly efficient for cyanation, their use is also associated with the formation of inactive palladium cyanide species due to the exposure of Pd to high concentration of cyanide ions, which significantly inhibits the catalytic cycle.[18] This problem is partially controlled with certain special measures related to the solvent and cyanide source.[4b] Significant improvement in the cyanation reaction was achieved with introduction of a relatively nontoxic and inexpensive $K_4[Fe(CN)_6]$ as a cyanide source by Beller and co-workers.[8i] Since then, a number of procedures using this reagent in the presence of several metal catalysts have been developed. They include $Pd(OAc)_2$ in dimethylacetamide (DMAC) in the presence of Na_2CO_3,[8o] $Pd(OAc)_2$ in combination with a phosphorus ligand in DMF in the presence of K_3PO_4,[8i] $Pd(OAc)_2$ in the presence of NaF and TBAB in H_2O under microwave irradiation in a sealed tube,[19] a palladacycle in DMF in the presence of K_2CO_3 under microwave heating,[20] $Pd(PPh_3)_4$/DBU in *t*-BuOH/H_2O,[4b] a palladium complex in NMP in the presence of Na_2CO_3,[8x] under homogeneous conditions with Pd/C in Bu_3N/Na_2CO_3,[21] and Pd/C in poly(ethylene glycol) (PEG)-4000/H_2O in the presence of NaF[22] under heterogeneous conditions. Although these methods are quite satisfactory, many of them use expensive ligands and additives, produce metal waste, and do not offer recyclability of the catalyst. Thus, a more efficient and convenient protocol for this important transformation would be appreciated.

We recently reported cyanation of aryl iodides by $K_4[Fe(CN)_6]$ catalyzed by hydroxyapatite-supported Cu(I)[23a] and CuO-supported palladium nanoparticles (NPs).[23b] However, although aryl iodides underwent reactions successfully, aryl bromides remained inert under these reaction conditions. With our continued interest in heterogeneous supported transition-metal-catalyzed cyanation reactions, we report here cyanation of aryl bromides and chlorides catalyzed by ZnO-supported Pd NPs (ZnO-Pd NPs) without using any ligand, base, or additive (Scheme 1).

Scheme 1. ZnO-Pd NP-Catalyzed Cyanation of Aryl Bromides and Chlorides Using $K_4[Fe(CN)_6]$



The catalyst, palladium-doped ZnO, was prepared by microwave irradiation of a solution of zinc nitrate hexahydrate, palladium acetate, and PEG-6000 in aqueous ethanol. Filtration of the solid material followed by washing with water and ethanol and drying provided the ZnO-Pd catalyst. The Pd content was determined to be 0.1109 mmol g^{-1} by atomic absorption spectroscopy (AAS). The catalyst was characterized

Received: April 12, 2014
Published: May 24, 2014

dx.doi.org/10.1021/jo500820q | J. Org. Chem. 2014, 79, 5875−5879

by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and powder X-ray diffraction (PXRD). The TEM image of the catalyst (Figure 1) shows rod-shaped Pd

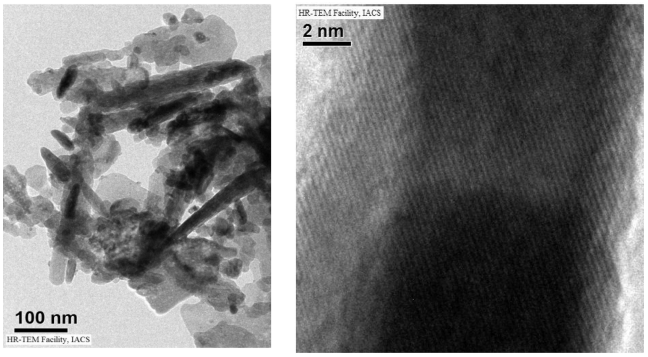


Figure 1. (a) TEM and (b) HR-TEM images of the ZnO-Pd catalyst.

NPs supported on ZnO. The average diameter and length of the palladium nanorods were found to be 15 and 96 nm, respectively. The SEM image (Figure 2) shows a rough morphology of the catalyst. The PXRD pattern of the catalyst (Figure 3) reveals a hexagonal lattice for ZnO and a face-centered cubic (fcc) lattice for Pd.

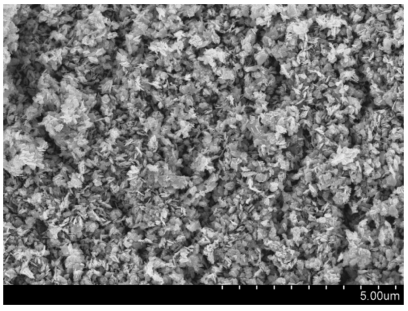


Figure 2. SEM image of the ZnO-Pd catalyst.

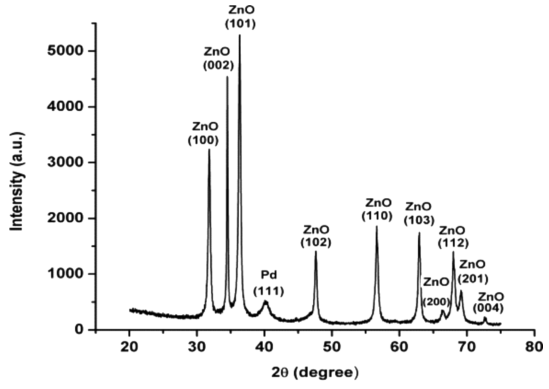
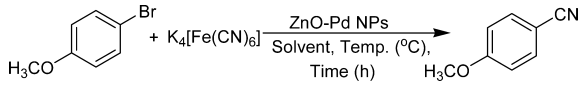


Figure 3. PXRD pattern of the ZnO-Pd catalyst.

To optimize the reaction conditions, a series of experiments were performed for a representative reaction of 4-bromoanisole and potassium ferrocyanide with variation of solvent, catalyst loading, temperature, and time. The best result was obtained using 0.2 mol % ZnO-Pd NPs, 0.17 mmol of $K_4[Fe(CN)_6]$, and DMF as the solvent at 130 °C for 14 h (Table 1, entry 15). Use of 0.34 mmol of $K_4[Fe(CN)_6]$ decreased the yield to a

Table 1. Standardization of the Reaction Conditions for the Cyanation of 4-Bromoanisole[a]



entry	ZnO-Pd NPs (mol % Pd)	solvent	temp. (°C)	time (h)	yield (%)[b]
1	5	DMSO	140	15	65
2	5	NMP	140	15	71
3	5	DMF	140	15	76
4	5	PEG-600	140	15	62
5	5	H_2O	100	15	–
6	5	toluene	110	15	–
7	5	THF	65	15	–
8	1	DMF	140	15	76
9	0.5	DMF	140	15	76
10	0.2	DMF	140	15	76
11	0.1	DMF	140	15	65
13	0.2	DMF	130	15	76
14	0.2	DMF	120	15	70
15	**0.2**	**DMF**	**130**	**14**	**76**
16	0.2	DMF	130	12	69
17[c]	0.2	DMF	130	12	49

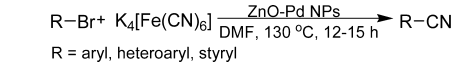
[a]Reactions were carried out using 0.17 mmol of $K_4[Fe(CN)_6]$, unless otherwise noted. [b]Yields of isolated pure products. [c]0.34 mmol of $K_4[Fe(CN)_6]$ was used

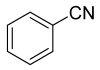
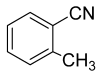
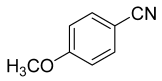
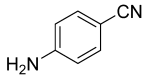
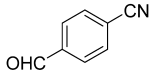
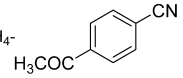
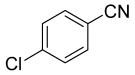
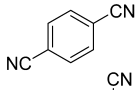
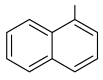
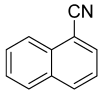
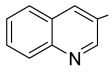
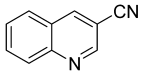
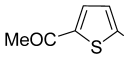
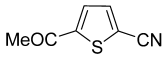
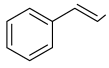
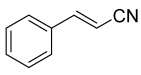
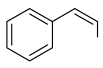
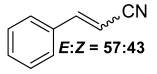
considerable extent (Table 1, entry 17), which implies that the excess concentration of cyanide ion deactivates the catalyst. Thus, in a typical reaction procedure, a mixture of aryl halide (1 mmol) and $K_4[Fe(CN)_6]$ (0.167 mmol) was heated in DMF at 130 °C in the presence of ZnO-Pd NPs (0.2 mol %) under argon for the required period of time (TLC). Standard workup of the reaction mixture followed by column chromatography provided the pure product.

A wide variety of diversely substituted aryl bromides underwent cyanation by this procedure to produce the corresponding nitriles. The results are summarized in Table 2. Both electron-donating (CH_3, OCH_3, NH_2) (Table 2, entries 2–4) and electron-withdrawing (CHO, $COCH_3$, Cl) (Table 2, entries 5–7) group-substituted aryl bromides smoothly participated in this reaction. However, the yields of products obtained from the electron-withdrawing-group-substituted aryl bromides were slightly higher than those of the electron-donating-group-substituted aryl bromides. Sterically hindered 2-bromotoluene also underwent the reaction without any difficulty (Table 2, entry 2). Significantly, 4-bromochlorobenzene reacted with $K_4[Fe(CN)_6]$ (0.34 mmol) under these reaction conditions to provide 4-chlorobenzonitrile selectively, leaving the chloro functionality unaffected (Table 2, entry 7). However, the yield of this product was comparatively low, which may be due to catalyst poisoning to some extent by the higher concentration of cyanide ions in the reaction mixture. 1,4-Dibromobenzene produced the corresponding dicyano product without any difficulty (Table 2, entry 8). 1-Bromonaphthalene was also cleanly converted to 1-cyanonaphthalene (Table 2, entry 9). Significantly, heteroaryl bromides such as 3-bromoquinoline (Table 2, entry 10) and 5-acetyl-2-bromothiophene (Table 2, entry 11) successfully participated in the cyanation reaction to furnish the corresponding nitriles. *trans*-Styrenyl bromide produced (*E*)-styrenylnitrile selectively,

dx.doi.org/10.1021/jo500820q | J. Org. Chem. 2014, 79, 5875–5879

Table 2. ZnO-Pd NP-Catalyzed Cyanation of Aryl Bromides Using $K_4[Fe(CN)_6]$[a]



entry	R	product	time (h)	Yield[b] (%)
1.	C_6H_5-		13	81
2.	2-CH_3-C_6H_4-		15	68
3.	4-OCH_3-C_6H_4-		14	76
4.	4-NH_2-C_6H_4-		15	69
5.	4-CHO-C_6H_4-		13	84
6.	4-$COCH_3$-C_6H_4-		13	85
7.[c]	4-Cl-C_6H_4-		12	62
8.[c]	4-Br-C_6H_4-		15	67
9.			15	77
10.			15	80
11.			15	73
12.			12	81
13.		 E:Z = 57:43	14	72

[a]Reaction conditions: Aryl halide (1 mmol), $K_4[Fe(CN)_6]$ (0.167 mmol), ZnO-Pd NPs (15 mg, 0.2 mol % Pd), DMF (3 mL), unless otherwise noted. [b]Yields of isolated pure products. [c]0.34 mmol of $K_4[Fe(CN)_6]$ was used.

whereas *cis*-styrenyl bromide provided a mixture of the *E* and *Z* isomers (Table 2, entries 12 and 13).

It is likely that the cyanation reaction follows a general catalytic cycle via oxidative addition and reductive elimination at the metal center (Scheme 2), in accordance with the related reactions reported earlier.[17b,24] *trans*-Styryl bromide leads to thermodynamically more stable (*E*)-styrenylnitrile in a straightforward way. However, in the case of *cis*-styryl bromide, the corresponding intermediate **I** (NC−Pd−styryl complex) may undergo *β*-elimination to form alkyne−Pd−CN intermediate **II**, which is rather free to lead to the mixture of *cis* and *trans* isomeric products. The probable reaction pathway is outlined in Scheme 2. This is a usual trend in related reactions as observed and reported earlier by us[25a] and other groups.[25b,c]

Aryl chlorides also participated in the cyanation reaction. Although chlorobenzene was converted to benzonitrile in moderate yield (Scheme 3, compound **A**), chlorobenzenes substituted with electron-withdrawing groups (F, CHO, CN, NO_2) provided better yields (Scheme 3, compounds **B**−**E**), while electron-donating substituents (OCH_3, NH_2) completely arrested the cyanation reaction.

In general, the cyanation reaction is clean. The pure products are obtained by a simple workup and column chromatography. Several useful functionalities and sensitive heterocyclic moieties are compatible with this procedure. Although the reaction was performed on a 1 mmol scale, reactions on a 10 mmol scale also provided uniform results.

The reusability of the ZnO-Pd catalyst in subsequent cyanation reactions was investigated. The performance of the recovered catalyst for the representative reaction was tested in up to five successive runs, and the corresponding yields are shown as a histogram in Figure 4. Although the catalytic activity of the recovered catalyst decreased gradually, the yield was still 70% even after the fourth run. The palladium loading of the catalyst after the fourth cycle was found to be 0.0963 mmol/g, compared with 0.1109 mmol/g in the fresh catalyst (as detected by AAS).

In conclusion, we have developed an improved methodology for ligand-, base-, and additive-free cyanation of unactivated aryl halides catalyzed by palladium nanoparticles supported on ZnO. The notable advantages offered by this methodology are cyanation of aryl bromides and chlorides using a very low catalyst loading (0.2 mol % Pd), operational simplicity, general applicability to the synthesis of a wide range of nitriles (including heterocyclic ones), recyclability of the catalyst, and considerably good product yields. Certainly, this would make an important addition to the existing methods for cyanation.

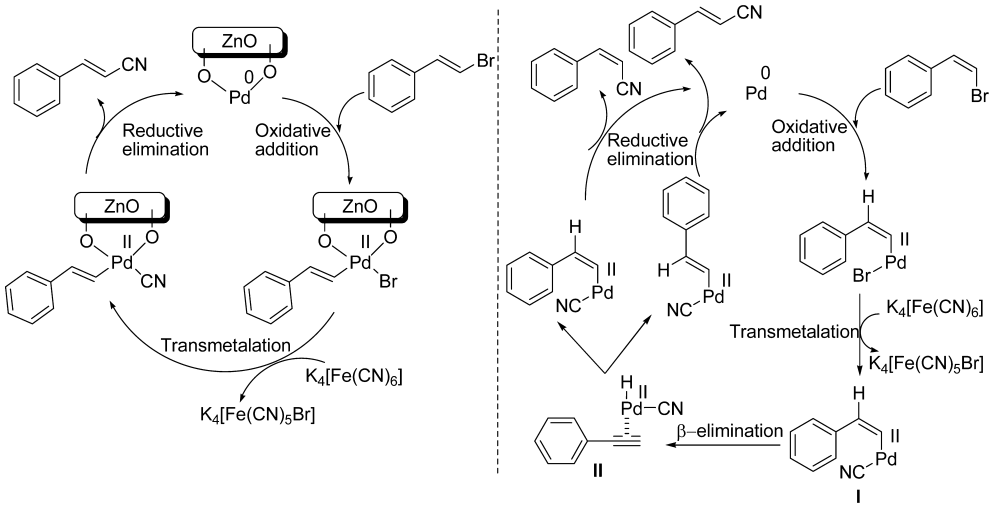
EXPERIMENTAL SECTION

Preparation of Palladium-Doped Zinc Oxide (ZnO-Pd) Catalyst. To a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (2.6 g, 8.7 mmol) and PEG-6000 (12 g) in rectified spirit (125 mL) and water (60 mL) was added $Pd(OAc)_2$ (112 mg, 0.5 mmol) with constant stirring, and 10 (N) NaOH was added dropwise with stirring until the pH of the resulting solution became 10. The solution was then irradiated in a domestic microwave oven (LG, Korea) at 360 W (30% of 1200 W; the maximum temperature recorded was 90 °C as measured by a thermometer inside the reaction vessel) for 20 min (4 × 5 min). The reaction mixture was filtered, and the solid mass was washed with water and ethanol successively and then dried in the oven at 70 °C to provide the catalyst ready for use.

General Experimental Procedure for Cyanation of Haloarenes: Representative Procedure for the Cyanation of 4-Bromoanisole with $K_4[Fe(CN)_6]$ (Table 2, entry 3). A mixture of 4-bromoanisole (187 mg, 1 mmol), $K_4[Fe(CN)_6]$ (123 mg, 0.34 mmol), and ZnO-Pd catalyst (15 mg, 0.2 mol % Pd) in DMF (4 mL) was heated with stirring at 130 °C under argon for 14 h (TLC). The reaction mixture was filtered to separate the solid catalyst, which was recycled. The filtrate was extracted with EtOAc (4 × 15 mL). The extract was washed with water and brine and then dried (Na_2SO_4). Evaporation of the solvent left the crude product, which was purified by column chromatography over silica gel (60−120 mesh), eluting with hexane/ethyl acetate (90:10), to afford pure 4-methoxybenzonitrile (101 mg, 76%) as a white solid. Mp 60−62 °C; IR (KBr) 3087, 2854, 2221, 1612, 1543, 1467, 1234, 1142, 1024 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.88 (s, 3H), 6.95 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.6, 103.9, 114.8 (2C), 119.2, 134.0 (2C), 162.9. The spectroscopic data (^1H and ^{13}C NMR) are in good agreement with those reported for an authentic sample. This procedure was followed for all of the reactions listed in Table 2. All of the products listed in Table 2 are known compounds, and they

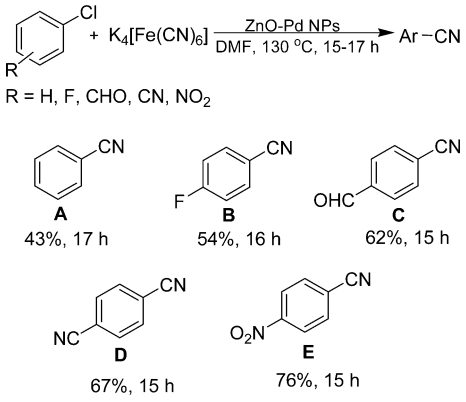
dx.doi.org/10.1021/jo500820q | J. Org. Chem. 2014, 79, 5875−5879

Scheme 2. Proposed Mechanistic Pathways for the Cyanation of Styryl Bromides[a]



[a]Reactions with aryl bromides also follow the same pathway.

Scheme 3. ZnO-Pd NP-Catalyzed Cyanation of Aryl Chlorides using $K_4[Fe(CN)_6]$



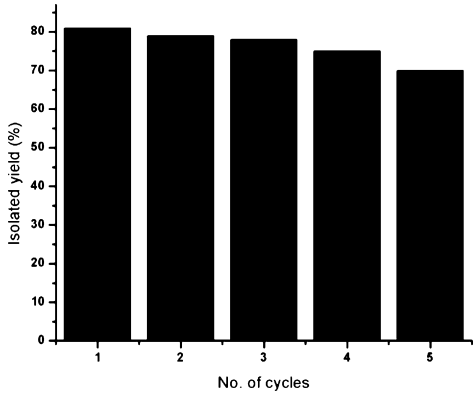


Figure 4. Recyclability of the ZnO-Pd catalyst.

were identified by comparison of their spectroscopic data with those reported.

Procedure for Recovery and Reactivation of the Catalyst. After the first cycle of reaction was over, the catalyst was filtered through a sintered-glass bed (G-4) and washed with ethanol followed by acetone. The catalyst was then dried in an oven at 100 °C for 8 h and was ready for subsequent reactions.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra of all products listed in Table 2 and Scheme 3. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ocbcr@iacs.res.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are pleased to acknowledge the financial support from DST, New Delhi, for the award of the J. C. Bose Fellowship to B.C.R. (Grant SR/S2/JCB-11/2008). T.C. and R.D. thank CSIR for their fellowships.

■ REFERENCES

(1) (a) Grundmann, C. In *Houben-Weyl: Methoden der Organischen Chemie*, 4th ed.; Thieme: Stuttgart, Germany, 1985; Vol. *E5*. (b) Larock, R. C. *Comprehensive Organic Transformations*; VCH: Weinheim, Germany, 1989.

(2) Kleemann, A.; Engel, J.; Kutscher, B.; Reichert, D. In *Pharmaceutical Substances: Syntheses, Patents, Applications*, 4th ed.; Thieme: Stuttgart, Germany, 2001; pp 241–242, 488–489, 553, 825–826, 1154, 1598–1599.

(3) (a) Kleemann, A.; Engel, J.; Kutscher, B.; Reichert, D. *Pharmaceutical Substances: Syntheses, Patents, Applications*, 5th ed.; Thieme: Stuttgart, Germany, 2009. (b) Cantrell, A. S.; Engelhardt, P.; Högberg, M.; Jaskunas, S. R.; Johansson, N. G.; Jordan, C. L.; Kangasmetsa, J.; Kinnick, M. D.; Lind, P.; Morin, J. M., Jr.; Muesing, M. A.; Noreén, R.; Öberg, B.; Pranc, P.; Sahlberg, C.; Ternansky, R. J.; Vasileff, R. T.; Vrang, L.; West, S. J.; Zhang, H. *J. Med. Chem.* **1996**, *39*, 4261. (c) Sanderson, P. E. J.; Lyle, T. A.; Cutrona, K. J.; Dyer, D. L.; Dorsey, B. D.; McDonough, C. M.; Naylor-Olsen, A. M.; Chen, I. W.; Chen, Z.; Cook, J. J.; Cooper, C. M.; Gardell, S. J.; Hare, T. R.; Krueger, J. A.; Lewis, S. D.; Lin, B.; Lucas, J.; Lyle, E. A.; Lynch, J. J.; Stranieri, M. T.; Vastag, K.; Yan, Y.; Shafer, J. A.; Vacca, J. P. *J. Med. Chem.* **1998**, *41*, 4466. (d) Sanderson, P. E. J.; Stanton, M. G.; Dorsey, B. D.; Lyle, T. A.; McDonough, C.; Sanders, W. M.; Savage, K. L.; Naylor-Olsen, A. M.; Krueger, J. A.; Lewis, S. D.; Lucas, B. J.; Lynch, J. J.; Yan, Y. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 795.

dx.doi.org/10.1021/jo500820q | *J. Org. Chem.* 2014, 79, 5875–5879

(4) (a) Larock, R. C. *Comprehensive Organic Transformations*; VCH: Weinheim, Germany, 1989; p 819. (b) Zhang, D.; Sun, H.; Zhang, L.; Zhou, Y.; Li, C.; Jiang, H.; Chen, K.; Liu, H. *Chem. Commun.* **2012**, *48*, 2909. (c) Rappoport, Z. *Chemistry of the Cyano Group*; John Wiley & Sons: London, 1970.
(5) (a) Sandmeyer, T. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 1633. (b) Hodgson, H. H. *Chem. Rev.* **1947**, *40*, 251. (c) Galli, C. *Chem. Rev.* **1988**, *88*, 765.
(6) Mowry, D. T. *Chem. Rev.* **1948**, *42*, 189.
(7) (a) Sundermeier, M.; Zapf, A.; Beller, M. *Eur. J. Inorg. Chem.* **2003**, 3513. (b) Ellis, G. P.; Romney-Alexander, T. M. *Chem. Rev.* **1987**, *87*, 779. (c) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.
(8) (a) Tschaen, D. M.; Desmond, R.; King, A. O.; Fortin, M. C.; Pipik, B.; King, S.; Verhoeven, T. R. *Synth. Commun.* **1994**, *24*, 887. (b) Anderson, B. A.; Bell, E. C.; Ginah, F. O.; Harn, N. K.; Pagh, L. M.; Wepsiec, J. P. *J. Org. Chem.* **1998**, *63*, 8224. (c) Maligres, P. E. *Tetrahedron Lett.* **1999**, *40*, 8193. (d) Jin, F.; Confalone, P. N. *Tetrahedron Lett.* **2000**, *41*, 3271. (e) Zanon, J.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 2890. (f) Sundermeier, M.; Zapf, A.; Mutyala, S.; Baumann, W.; Sans, J.; Weiss, S.; Beller, M. *Chem.—Eur. J.* **2003**, *9*, 1828. (g) Chidambaram, R. *Tetrahedron Lett.* **2004**, *45*, 1441. (h) Yang, C.; Williams, J. M. *Org. Lett.* **2004**, *6*, 2837. (i) Schareina, T.; Zapf, A.; Beller, M. *Chem. Commun.* **2004**, 1388. (j) Schareina, T.; Zapf, A.; Beller, M. *J. Organomet. Chem.* **2004**, *689*, 4576. (k) Stazi, F.; Palmisano, G.; Turconi, M.; Santagostino, M. *Tetrahedron Lett.* **2005**, *46*, 1815. (l) Schareina, T.; Zapf, A.; Beller, M. *Tetrahedron Lett.* **2005**, *46*, 2585. (m) Jensen, R. S.; Gajare, A. S.; Toyota, K.; Yoshifuji, M.; Ozawa, F. *Tetrahedron Lett.* **2005**, *46*, 8645. (n) Hatsuda, M.; Seki, M. *Tetrahedron* **2005**, *61*, 9908. (o) Weissman, S. A.; Zewge, D.; Chen, C. *J. Org. Chem.* **2005**, *70*, 1508. (p) Grossman, O.; Gelman, D. *Org. Lett.* **2006**, *8*, 1189. (q) Pitts, M. R.; McCormack, P.; Whittall, J. *Tetrahedron* **2006**, *62*, 4705. (r) Littke, A.; Soumeillant, M.; Kaltenback, R. F., III; Cherney, R. J.; Tarby, C. M.; Kiau, S. *Org. Lett.* **2007**, *9*, 1711. (s) Schareina, T.; Zapf, A.; Magerlein, W.; Muller, N.; Beller, M. *Tetrahedron Lett.* **2007**, *48*, 1087. (t) Zhu, Y.; Cai, C. *Synth. Commun.* **2007**, *37*, 3359. (u) Ryberg, P. *Org. Process Res. Dev.* **2008**, *12*, 540. (v) Ren, Y.; Liu, Z.; He, S.; Zhao, S.; Wang, J.; Niu, R.; Yin, W. *Org. Process Res. Dev.* **2009**, *13*, 764. (w) Shevlin, M. *Tetrahedron Lett.* **2010**, *51*, 4833. (x) Gerber, R.; Oberholzer, M.; Frech, C. M. *Chem.—Eur. J.* **2012**, *18*, 2978. (y) Ushkov, A. V.; Grushin, V. V. *J. Am. Chem. Soc.* **2011**, *133*, 10999.
(9) (a) Sakakibara, Y.; Okuda, F.; Shimobayashi, A.; Kirino, K.; Sakai, M.; Uchino, N.; Takagi, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1985. (b) Arvela, R. K.; Leadbeater, N. E. *J. Org. Chem.* **2003**, *68*, 9122.
(10) (a) Cristau, H. J.; Ouali, A.; Spindler, J. F.; Taillefer, M. *Chem.—Eur. J.* **2005**, *11*, 2483. (b) Schareina, T.; Zapf, A.; Magerlein, W.; Muller, N.; Beller, M. *Chem.—Eur. J.* **2007**, *13*, 6249. (c) Ren, Y.; Wang, W.; Zhao, S.; Tian, X.; Wang, J.; Yin, W.; Cheng, L. *Tetrahedron Lett.* **2009**, *50*, 4595.
(11) Zheng, S.; Yu, C.; Shen, Z. *Org. Lett.* **2012**, *14*, 3644.
(12) (a) Mariampillai, B.; Alberico, D.; Bidau, V.; Lautens, M. *J. Am. Chem. Soc.* **2006**, *128*, 14436. (b) Martin, M. T.; Liu, B.; Cooley, B. E., Jr.; Eaddy, J. F. *Tetrahedron Lett.* **2007**, *48*, 2555. (c) Chobanian, H. R.; Fors, B. P.; Lin, L. S. *Tetrahedron Lett.* **2006**, *47*, 3303.
(13) (a) Cai, L.; Liu, X.; Tao, X.; Shen, D. *Synth. Commun.* **2004**, *34*, 1215. (b) Lindley, J. *Tetrahedron* **1984**, *40*, 1433.
(14) Sundermeier, M.; Mutyala, S.; Zapf, A.; Spannenberg, A.; Beller, M. *J. Organomet. Chem.* **2003**, *684*, 50.
(15) (a) Srivastava, R. R.; Collibee, S. E. *Tetrahedron Lett.* **2004**, *45*, 8895. (b) Ren, Y.; Liu, Z.; Zhao, S.; Tian, X.; Wang, J.; Yin, W.; He, S. *Catal. Commun.* **2009**, *10*, 768.
(16) Yu, H.; Richey, R. N.; Miller, W. D.; Xu, J.; May, S. A. *J. Org. Chem.* **2011**, *76*, 665.
(17) (a) Kim, J.; Kim, H. J.; Chang, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 11948. (b) Sundermeier, M.; Zapf, A.; Beller, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1661. (c) Luo, F.-H.; Chu, C.-I.; Cheng, C.-H. *Organometallics* **1998**, *17*, 1025. (d) Sato, N.; Yue, Q. *Tetrahedron* **2003**, *59*, 5831. (e) Zhang, Z.; Liebeskind, L. S. *Org. Lett.* **2006**, *8*, 4331. (f) Anbarasan, P.; Neumann, H.; Beller, M. *Chem.—Eur. J.* **2010**, *16*, 4725.
(18) Takagi, K.; Okamoto, T.; Sakakibara, Y.; Oka, S. *Chem. Lett.* **1973**, 471.
(19) Velmathi, S.; Leadbeater, N. E. *Tetrahedron Lett.* **2008**, *49*, 4693.
(20) Hajipour, A. R.; Karami, K.; Pirisedigh, A. *Appl. Organomet. Chem.* **2010**, *24*, 454.
(21) Zhu, Y.; Cai, C. *Eur. J. Org. Chem.* **2007**, 2401.
(22) Chen, G.; Weng, J.; Zheng, Z.; Zhu, X.; Cai, Y.; Cai, J.; Wan, Y. *Eur. J. Org. Chem.* **2008**, 3524.
(23) (a) Saha, D.; Adak, L.; Mukherjee, M.; Ranu, B. C. *Org. Biomol. Chem.* **2012**, *10*, 952. (b) Chattopadhyay, K.; Dey, R.; Ranu, B. C. *Tetrahedron Lett.* **2009**, *50*, 3164.
(24) Modak, A.; Mondal, J.; Bhaumik, A. *Green Chem.* **2012**, *14*, 2840.
(25) (a) Ranu, B. C.; Chattopadhyay, K.; Banerjee, S. *J. Org. Chem.* **2006**, *71*, 423. (b) Murahashi, S.-I.; Yamamura, M.; Yanagisawa, K.-i.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408. (c) Carpita, A.; Rossi, R.; Scamuzzi, B. *Tetrahedron Lett.* **1989**, *30*, 2699.