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Modified Ullmann coupling of 2-chloro-3-trifluoromethylpyridine

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Abstract

The application of the modified Ullmann reaction to 2-chloro-3-trifluoromethylpyridine furnishes 5,5′-bis(trifluoromethyl)-2,2′-bipyridine as the primary product, accompanied by small amounts of the expected 3,3′-bis(trifluoromethyl)-2,2′-bipyridine, 2-benzyl-3-(trifluoromethyl)pyridine, bibenzyl, 3-trifluoromethylpyridine, 3-methylpyridine, 2-hydroxyethyl-(3-trifluoromethylpyridyl) ether and 2-hydroxyethyl-(3-methylpyridyl) ether. For comparison purposes, a sample of 3,3′-bis-(trifluoromethyl)-2,2′-bipyridyl was prepared by the treatment of 2,2′-bipyridyl-3,3′-dicarboxylic acid with sulfur tetrafluoride. The formation of all but two compounds mentioned above can be rationalized on the basis of the single-electron-transfer process.

Keywords: Ullmann coupling; Chlorotrifluoromethylpyridine; Bis(trifluoromethyl)bipyridine; Synthesis; NMR spectroscopy; Mass spectrometry

1. Introduction

In view of their novel biological, chemical, electrochemical, photochemical, spectral and surfactant properties, the 2,2′-bipyridines have attracted considerable attention [1–4]. Since they exhibit high Stokes shifts after electronic excitation, 2,2′-bipyridines have found use as laser dyes [5]. Even their metal complexes have found clinical application [6a], and in particular their nickel and palladium complexes have been reported to possess carcinostatic and anti-cancer properties [6b,c]. Recently, a 2,2′-bipyridyl-based bidentate oxo-ruthenium dimer complex has been shown to be an excellent precursor of an efficient molecular water oxidation catalyst [7]. The 2,2′-bipyridyls have also found use as insecticides [8].

Although the 4,4′-, 5,5′- and 6,6′-disubstituted analogs can be convenienntly synthesized [3], only a limited number of 3,3′-disubstituted-2,2′-bipyridyls are presently available. Thus, the oxidation of *o*-phenanthroline yields 2,2′-bipyridine-3,3′-dicarboxylic acid (**1**) [9a]. The Ullmann reaction of 2-bromo-3-methylpyridine gave low yields of the 3,3′-dimethyl-2,2′-bipyridyl [9b]. Recently, the synthesis of 3,3′-dihydroxy-2,2′-bipyridyl via the modified Ullmann reaction in the presence of Zn/Ni^0 has been described [9c]. In continuation of our interest in the chemistry of the 2,2′-bipyridyls [7,9e,f], we have investigated the use of the modified Ullmann coupling reaction in the synthesis of 3,3′-bis(trifluoromethyl)-2,2′-bipyridines (**4**). Thus, the phase-catalyzed homocoupling of 2-chloro-3-trifluoromethylpyridine (**2**) in the presence of 10% Pd/C furnished 5,5′-bis(trifluoromethyl)-2,2′-bipyridyl (**3**) as the primary product. The expected isomeric 3,3′-bis(trifluoromethyl)-2,2′-bipyridine (**4**) was obtained in extremely trace amounts. In addition, 2-benzyl-3-trifluoromethylpyridine (**5**) (a viscous oil), bibenzyl (**6**), 3-trifluoromethylpyridine (**7**), 3-methylpyridine (**8**), 2-hydroxyethyl-(3-trifluoromethylpyridyl) ether (**9**) and 2-hydroxyethyl-(3-methylpyridyl) ether (**10**) have been characterized as the byproducts of the aforementioned coupling reaction (see Fig. 1). This communication describes their isolation and identification along with the possible mechanism of their formation.

2. Experimental details

Mass spectra were obtained on a Finnigan model 5100 GC/MS equipped with a silica 25 m×0.31 mm

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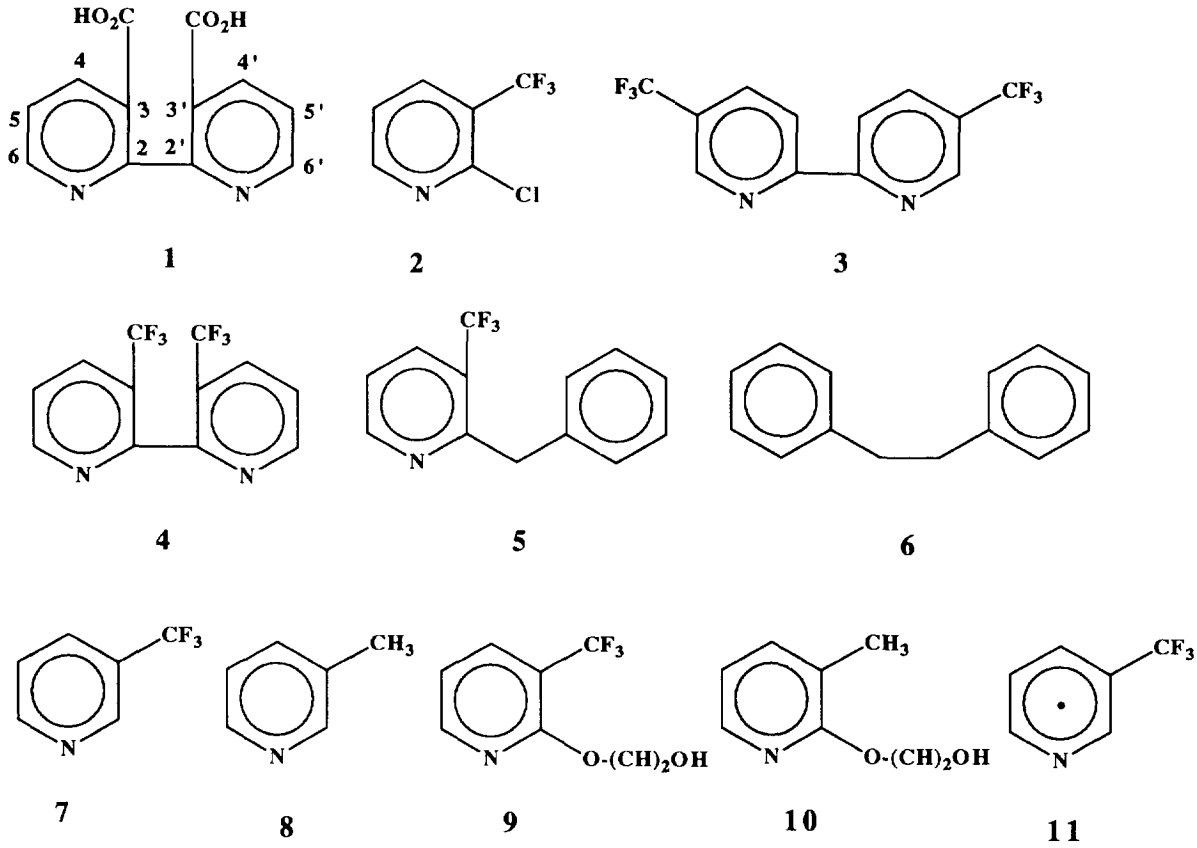


Fig. 1. Structures of compounds cited in the text.

i.d. SE-54 capillary column (J&W Scientific, Rancho Cordova, CA). Routine GC analyses were accomplished with a Hewlett Packard 5890A gas chromatograph equipped with a 30 m×0.51 mm i.d. DB-5 (J & W Scientific, Folsom, CA). NMR spectra (^{1}H, ^{13}C and ^{19}F) were recorded in $CDCl_3$ on a Varian VXR-400S spectrometer at 100 MHz and 376 MHz, respectively. The reference for ^{1}H and ^{13}C NMR was tetramethylsilane and $CFCl_3$ served as the external reference for ^{19}F NMR. The preparative thin layer chromatography (TLC) was carried out using Analtech 20×20 cm Uniplate Taperplate silica gel GF plates (catalog #A1013).

2.1. Synthesis of 5,5'-bis(trifluoromethyl)-2,2'-bipyridyl (3)

With a view to synthesizing 3,3'-bis(trifluoromethyl)-2,2'-bipyridyl (**4**), 2-chloro-3-trifluoromethylpyridine (**2**) (2.25 g, 12.5 mmol) was subjected to the modified Ullmann reaction in the presence of sodium formate (0.85 g, 12.5 mmol), triethylbenzylammonium chloride (0.5 g, 7.5 mmol), 10% Pd/C (0.25 g), sodium hydroxide (1.75 g, 26 mmol), ethylene glycol (3 ml), water and toluene (5 ml each). The reaction mixture was refluxed for 4 h with stirring. An additional amount (0.85 g) of sodium formate was added and the reaction mixture refluxed overnight. After cooling, the reaction mixture was filtered, the precipitate washed with chloroform and the filtrates extracted with 3×25 ml portions of chloroform. The combined extracts and washings were successively washed with water and saturated sodium chloride solution and dried over sodium sulfate. The solution was concentrated under reduced pressure on a roto-evaporator to yield 0.67 g of crude product.

Both TLC and GC/MS analysis showed the crude material to be a complex mixture of several compounds. Flash chromatography on silica gel, followed by preparative TLC of the various fractions, facilitated the identification of the various compounds as follows: (a) 2-chloro-3-trifluoromethylpyridine (**2**, 60%), (b) 3-trifluoromethylpyridine (**7**, 5.1%), (c) 5,5'-bis(trifluoromethyl)-2,2'-bipyridyl (**3**, 0.4%), (d) bibenzyl (**6**, 0.25%), (e) 2-benzyl-3-trifluoromethylpyridine (**5**, 0.2%) and (f) 3,3'-bis(trifluoromethyl)-2,2'-bipyridyl (**4**, trace amounts). In addition, small amounts of two more compounds having molecular weights of 207 and 153 were isolated and identified as 2-hydroxyethyl-(3-trifluoromethylpyridyl) ether (**9**) and 2-hydroxyethyl-(3-methylpyridyl) ether (**10**) by their NMR and mass spectral fragmentation data.

The structure of compounds **3**, **4**, **5**, **6**, **7**, **9** and **10** have been confirmed by ^{1}H, ^{13}C and ^{19}F NMR (Table 1) and by GC/MS data (Table 2). The ^{1}H and ^{13}C NMR assignments of compound **9** have been further

Table 1
^1H, ^{13}C and ^{19}F NMR data on new compounds

Compound **5**	^1H NMR δ	7.91 (J=8.0, 1.8, 0.6 Hz, F-H, γ-H); 7.18 (m, β-H); 8.71 (d, J=4.1, 1.5±0.5 Hz, α-H); 4.31 (J=0.7 Hz, benzylic Hs); 7.22–7.28 (all Hs on the phenyl ring) ppm
	^{13}C NMR δ	158.8 (C_2); 124.8 (J=32 Hz, C_3); 134.1 (C_4); 120.9 (C_5); 152.3 (C_6); 123.9 (J=273 Hz, $\underline{C}F_3$); 41.2 (benzylic carbon); 138.5 (C'_1); 128.3 (C'_2); 128.3 (C'_3); 126.4 (C'_4); 129.0 (C'_5); 128.3 (C'_6) ppm [(C' refers to carbon atoms on the phenyl ring]
	^{19}F NMR δ	−59.39 (rel. to $CFCl_3$) ppm
Compound **9** [a]	^1H NMR δ	8.27 (d, α-H); 6.98 (dd, β-H); 7.87 (d, γ-H); 4.54 (m, 2H, –O–CH_2–C–); 3.94 (m, 2H, –CH_2–OH and 2.60 –O$\underline{H}$) ppm
	^{13}C NMR δ	160.5 (C_2); 122.8 (J=272 Hz, –$\underline{C}F_3$); 113.6 (J=33 Hz, C_3); 136.8 (J=4.6 Hz, C_4); 116.5 (C_5); 150.2 (C_6); 69.1 (O–$\underline{C}H_2$–C); 61.8 (–$\underline{C}H_2$OH) ppm
Compound **10**	^1H NMR δ	8.02 (d, α-H); 6.99 (dd, β-H); 7.65 (d, γ-H); 2.27 (s, CH_3); 4.77 (m, –O–CH_2–C); 4.00 (m, –CH_2–O); 1.0–2.6 (broad signal, –OH) ppm
	^{13}C NMR δ	15.9 (CH_3); 117.3 (C_5); 71.4 (O–$\underline{C}H_2$–C); 62.2 (–$\underline{C}H_2$OH) ppm
Compound **3**	^1H NMR δ	8.96 (6,6' Hs); 8.10 (dd, J=1.6, 8.4 Hz, 4,4' Hs); 8.67 (d, J=8 Hz, 3,3' Hs) ppm
	^{13}C NMR δ	157.7 (C_2); 121.2 (C_3); 134.3 (C_4); 127.1 (J_{C-F}=32.8 Hz C_5); 123.5 (J_{C-F}=272 Hz, $\underline{C}F_3$); 146.3 (J_{C-F}=4.0 Hz, C_6) ppm

[a] The ^1H and ^{13}C (HETCOR) 2D NMR analysis of compound **9** gave the following results and confirmed assignments made above: ^1H NMR δ: 3.94; 4.54; 6.98; 7.87; 8.27 ppm. ^{13}C NMR δ: 61.8; 69.1; 116.5; 136.8; 150.2 ppm.

confirmed by Heteronuclear Correlated Proton–Carbon (HETCOR) 2D NMR spectroscopy (Table 1).

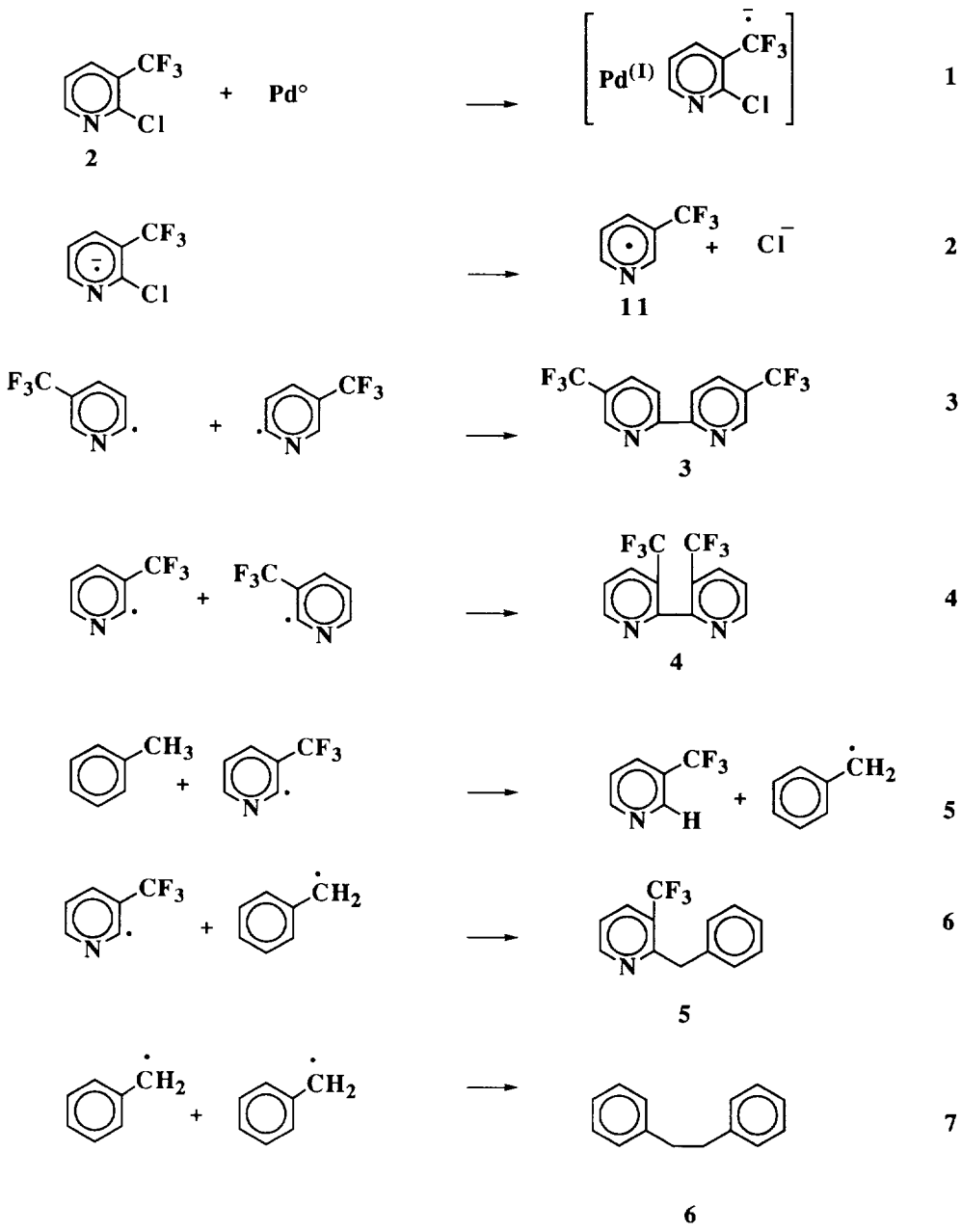
3. Results and discussion

The classical Ullmann reaction has inherent problems and its mechanism "is not known with certainty" as yet [10]. Some of the problems associated with it, however, have been overcome by the use of Zn/Ni^0 [9b,c,10c]. A number of modifications of the classical Ullmann reaction, such as the use of copper(I) t-butoxide in the presence of pyridine [11a], the phase-catalyzed coupling of aryl and pyridyl halides with 50% Pd/C paste, sodium formate, ammonium formate and triethylbenzylammonium chloride [11b], and photo-induced and electrochemical reductive homocoupling [11c], have been introduced. Another novel modification of the Ullmann reaction uses intramolecularly coordinated organocopper catalyst and permits the preparation of cross-coupled unsymmetric biphenyls at room temperature [11d]. Munavalli and coworkers have successfully

Table 2
Mass spectral fragmentation of compounds [a]

Compound	Mol. formula	Fragmentation pattern
3-Trifluoromethylpyridine (**7**)	$C_6H_4F_3N$	M^+=147 (EI, 100%); 127 (M−F); 120 (M−HCN); 97 (M−CF_2); 78 (M−CF_3); 51 (C_4H_3)
Bibenzyl (**6**)	$C_{14}H_{14}$	M^+=183 (CI, M+1, 100%); 105 (M−C_6H_5, 100%); 91 ($C_6H_5CH_2$)
2-Benzyl-3-trifluoromethylpyridine (**5**)	$C_{13}H_{10}F_3N$	M^+=238 (CI, M+1, 100%); 218 (M−F); 198 (218−HF); 168 (M− CF_3); 91 ($C_6H_5CH_2$); 69 (CF_3)
5,5'-Bis(trifluoromethyl)-2,2'-bipyridyl (**3**)	$C_{12}H_6F_6N_2$	M^+=293 (CI, M+1, 100%); 273 (M−F); 223 (M−CF_3); 196 (223− HCN); 146 ($C_5H_3NCF_3$); 126 (146−HF); 69 (CF_3)
3,3'-Bis(trifluoromethyl)-2,2'-bipyridyl (**4**)	$C_{12}H_6F_6N_2$	M^+=293 (CI, M+1, 100%); 273 (M−F); 223 (M−CF_3); 203 (223−HF); 153 (203−CF_2); 69 (CF_3)
2-Hydroxyethyl-(3-trifluoromethylpyridyl) ether (**9**)	$C_8H_8F_3NO_2$	M^+=208 (M+1, CI); 190 (208−H_2O); 188 (208−HF); 177 (208−CH_2OH); 164 (208−C_2H_4O, 100%); 144 (164−HF or 188−C_2H_4O); 69 (CF_3)
2-Hydroxyethyl-(3-methylpyridyl)ether (**10**)	$C_8H_{11}NO_2$	M^+=154 (M+1, CI, 100%); 138 (154−16); 136 (154−H_2O); 134 (M^+−CH_4); 123 (154−CH_2OH); 110 (154−C_2H_4O); 80 (C_5H_6N); 65 (C_4H_3N)
3-Methylpyridine (**8**)	C_6H_7N	M^+=94 (M+1, CI, 100%); 92 (C_6H_6N); 66 (C_5H_6); 65 (C_5H_5)

[a] The number in parentheses next to the name of the compound refers to the compound in the text.



Scheme 1.

used 10% Pd/C to homo-couple non-halogenated pyridines [2f,3,7,9e,f]. Also, the metal-catalyzed dehydrodimerization has been described [12]. In the present study, the phase-catalyzed homo-coupling of **2** in the presence of 10% Pd/C, sodium formate, ammonium formate, triethylbenzylammonium chloride, aqueous sodium hydroxide, toluene and ethylene glycol has been shown to furnish compounds **3–10**.

The unusual formation of compounds **3–8** can be ascribed to both the steric hindrance and the participation of the single-electron-transfer (SET) process. Analogous to the transfer of one electron from Mg to organic halide [13a], the SET process is initiated with the transfer of an electron from the catalyst to **2** (step 1, Scheme 1). This proposal derives additional support from the observation that the transformations brought about by the zerovalent metal during the coupling reaction occur chemically with one-electron acceptors like aryl halides [13b,c]. Also, the coupling process involved in these reactions is said to begin with the transfer of an electron from zerovalent metal catalysts to electron-deficient aryl halides to give the ion pair [M^{I} $ArX^{\cdot -}$] intermediate (M = metal, ArX = aryl halide) [14]. The ion-pair intermediate has been suggested to initially fragment into the [$ArX^{\cdot -}$] moiety and subsequently to undergo metathesis to aryl radical and halide ion [14a].

Advancing a similar argument to our case, this leads directly to the formation of trifluoromethylpyridyl radical (**11**, step 2), which has three options open to it: (i) to dimerize to bis-5,5′-(trifluoromethyl)-2,2′-bipyridine (**3**) and bis-3,3′-(trifluoromethyl)-2,2′-bipyridine (**4**); (ii) to abstract hydrogen from solvents (toluene) to give trifluoromethylpyridine (**7**) (step 5); and (iii) to combine with the benzyl radical generated according to option (ii) and to furnish 2-benzyl-3-trifluoromethylpyridine (**5**) (step 6). Indeed, the isolation and characterization of the above compounds by their GC/MS and NMR data clearly indicates that the three options cited above are operating in this homo-coupling process. Steric considerations suggest that **3** should predominate over its isomer **4**. This is what is actually observed. The identity of **3** and **4** was further confirmed by the preparation via the homo-coupling of 2-chloro-5-(trifluoromethyl)pyridine and the treatment of 2,2′-bipyridyl-3,3′-dicarboxylic acid with sulfur tetrafluoride respectively [15a]. There are several precedents for hydrogen abstraction from solvents by free radicals [15b–d]. The structure of compound **5** stands supported by its ^{1}H and ^{13}C NMR spectra. Bibenzyl (**6**) could have arisen only from the dimerization of the benzyl radical (step 7). The formation of the dimerized products is usually regarded as definite proof of the participation of radical species [16 and references cited therein]. Also, the homo-coupling of benzyl radicals to bibenzyl and its ^{1}H NMR spectrum have been described earlier [17a,b]. The GC/MS identification of 3-methylpyridine as one of the byproducts of the coupling process suggests that either **2** or **7** must have undergone hydrogenolysis. There is a precedent for the reductive formation of CH_3 from CF_3 [18]. The absence of both **7** and **8** in the starting material was ascertained by its GC/MS analysis. Finally, the formation of small amounts of 2-hydroxyethyl-(3-trifluoromethylpyridyl) ether (**9**) and 2-hydroxyethyl-(3-methylpyridyl) ether (**10**) can be conveniently attributed to base-catalyzed displacement of chlorine by ethylene glycol. The structures of **9** and **10** were established with the aid of their GC/MS and ^{1}H and ^{13}C NMR data. Additional support for the structure of **9** was obtained through its (HETCOR) 2D NMR spectrum.

In brief, the molecular ion peaks were observed for all compounds (Table 2). Except for compounds **6** and **9**, the molecular ion peaks represent the most prominent peak in the mass spectra of **3**, **4**, **5**, **7**, **8** and **10**. Compounds containing the trifluoromethyl group exhibit common characteristics such as the loss of CF_3, HF and F. The carbon–carbon bond joining the pyridyl rings to form the 2,2′-bipyridyl derivatives is easily cleaved to give the second most prominent peak. This is typical of the symmetrically disubstituted 2,2′-bipyridyls [19a]. As has been described earlier, the pyridine derivatives split off HCN [19b–d] and the benzyl derivatives lose the benzyl moiety [15d, 19c]. Both compounds **9** and **10** exhibit similar mass spectral fragmentation patterns in that they split off H_2O, CH_2OH, side-chain and fragmentation of the pyridyl moiety. It has been suggested that 3-(2-pyridyl)propanol (also 2-propylpyridine) and 2-butylpyridine undergo facile γ- and δ-cleavages owing to participation of the ring nitrogen to give spirocyclic and cyclic dihydro-indolizinium ions respectively [19b, pp. 184–185]. It is conceivable that *m/e* 177 and 190 ions indicate the formation of analogous ions from **9**. A similar fragmentation behavior is observed in the mass spectral fragmentation of **10**.

In summary, the formation of **3**, **4**, **5**, **6**, **7** and **8** (Fig. 1) has been rationalized on the basis of an earlier observation [12–14] involving the transfer of an electron from the catalyst to the aryl halide during the metal-catalyzed coupling reaction.

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