Rates and Mechanism of Organozinc Electrosynthesis Catalyzed by Co^{2+} in Pure Acetonitrile.

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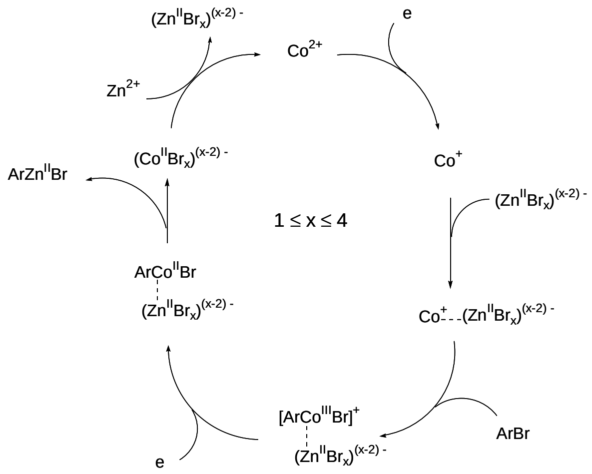
The preparation of arylzinc compounds which are key intermediates in the selective synthesis of carbon-carbon bonds from highly functionalized substrates [1] can be carried out by means of chemical or electrochemical methods.

The chemical procedure was formerly achieved by the preliminary formation of aryl-lithium reagents followed by transmetallation with zinc halides. Nevertheless, this method is not easily achieved with aryl compounds bearing reactive functional groups such as ketone, nitrile or ester, since very low reaction temperatures are required.[2] Alternatively, the Rieke method, which uses activated zinc obtained by reduction of zinc halide with alkali metal naphtalenide, is convenient with aromatic bromides, even those bearing an electron-withdrawing group.[3,4] Very recently, we discovered a new chemical synthesis of functionalized arylzinc compounds from aromatic or thienyl bromides under mild conditions and in pure acetonitrile using a simple cobalt catalyst (CoX_2, X = Cl, Br) and zinc dust.[5]

The preparation of arylzinc compounds via an electrochemical process has been developed in our group according to two procedures. In the former one, a nickel complex was used as the catalyst.[6] However, this method presents some disadvantages : (i) the low-valent nickel catalyst has to be stabilized by excess bipyridyl ligand, (ii) dimethylfomamide is the only solvent convenient for these electro-synthesis, and (iii) the use of nickel is now discouraged for environmental reasons. In this context, we have developed a simpler electro-catalytic system using cobalt salts (CoX_2, X = Br, Cl) as catalysts.[7] Indeed, reactions can be conducted in acetonitrile (ACN) or in dimethylformamide (DMF), and pyridine is used in the place of bipyridine both as ligand and co-solvent. Yet, the coupling reactions of organozinc reagents with electrophiles such as acyl chlorides could not be achieved in the presence of pyridine owing to a reaction between the two latter giving rise to the formation of pyridinium salts. In this context, we have recently developed a pyridine-free process for the electrochemical preparation of arylzinc compounds in pure acetonitrile.[8]

Surprisingly, the last two methods (chemical and electrochemical) discovered in our group for the preparation of organozinc compounds have been carried out in the absence of pyridine which was required in our former processes to stabilize the cobalt(I) catalyst. This prompted us to investigate the electrochemical behavior of $CoBr_2$ both in the absence and the presence of aryl halides and zinc bromide in pure acetonitrile. We especially showed by cyclic voltametry that $CoBr_2$ leads to an equilibrium mixture of various cobalt(II) species where Co^{2+} is the most easily reducible one. More importantly, we demonstrated that the presence of $ZnBr_2$ is crucial to stabilize the Co^{+} species coming from the reduction of Co^{2+} and to avoid the catalyst loss via a disproportionation reaction. This key-step is required to initiate the catalytic chain leading to arylzinc compounds and depicted in Scheme 1. Each step of this catalytic process has been evidenced. These results will be presented and compared in kinetic terms with those obtained in the presence of pyridine.[9-11]



Scheme 1. Proposed mechanism for the electrochemical conversion of aryl halides to arylzinc compounds by cobalt catalysis in pure acetonitrile and using the sacrificial zinc anode process.

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