

The role of Ni(0) complexes in electrochemical phosphorylation of organic halides

Part 1. Factors determining catalytic activity¹

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Abstract

The catalytic efficiency of Ni(0) complexes in coupling reactions of organic and organoelemental halides is shown to be determined by the degree of charge transfer, the value of the electrochemical gap, and the availability or absence of competitive redox reactions. © 1997 Elsevier Science S.A.

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1. Introduction

The elaboration of highly selective reactions leading to formation of carbon–carbon and carbon–element bonds is amongst the most important problems in the rapidly expanding area of metallocatalysis. Organic halide functionalization can be achieved by the use of some organometallic compounds; however, traditional chemical methods of catalyst regeneration are inconvenient because they demand stoichiometric amounts of reductants like zinc dust or Grignard reagents. Electrochemical methods for generation and regeneration of catalysts may work very productive in this respect, and in some instances one can obtain cross-coupling products from various halogen-containing compounds or mercaptans and to carboxylate aryl-halides [1–6], and the like.

Presently, one of the most important problems is to elucidate the factors determining catalyst reactivity and their quantitative evaluation. However, the mechanism of these reactions is not absolutely clear, causing trouble in the choices of optimal conditions and catalyst.

We present here a brief overview of our recent work on electrochemical metallocatalysis. We have

succeeded in recent years in expanding the application area of familiar reactions of organic halide coupling on the basis of oxidative addition reactions. Thus, preliminary data show that one can perform phosphorylation of some organic halides under the action of electrochemically generated Ni complexes(0) with π -acceptor ligands using phosphorus chlorides [7,8] or white phosphorus as phosphorylating agents. Nickel complexes are very attractive catalysts because of their availability and ability to yield stable forms in low oxidation states (0, +1).

The main objective of this paper is to find factors determining the reactivity of Ni(0) complexes in oxidative addition reactions and to use the information obtained to make an informed choice of the catalyst when performing the synthesis on a large scale.

Among the other metals of the platinum group, nickel is noted for the least atomic size and d-orbital filling, resulting in a more effective display of electronic interactions between metal and ligand determining in many respects the catalytic ability of the complex. However, an analysis of the reduction process having regard to competitive homogeneous redox equilibria, limiting stages, calculation of rate and equilibrium constants is, in general, insufficient. Undoubtedly, a more comprehensive concept of the complex reduction mechanism, its redox properties and electron interactions between

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¹ To the memory of Professor Yu.T. Struchkov.