



Synthesis, structure and electrochemical properties of the organonickel complex [NiBr(Mes)(phen)] (Mes = 2,4,6-trimethylphenyl, phen = 1,10-phenanthroline)



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ABSTRACT

The organonickel complex [NiBr(Mes)(phen)] (**1**) (Mes = 2,4,6-trimethylphenyl, phen = 1,10-phenanthroline) was synthesized by oxidative addition of MesBr to nickel(0) complexes, obtained from [Ni(COD)₂] (COD = 1,5-cyclooctadiene) and phen, or electrochemically generated from [NiBr₂(-phen)], and by ligand exchange reaction from [NiBr(Mes)(PPh₃)₂]. The electrochemical properties of [NiBr(Mes)(phen)] were investigated by cyclic voltammetry and *in situ* EPR spectroelectrochemistry. The cathodic reduction of **1** resulted in formation of the neutral radical complex [Ni(Mes)(phen^{•-})] with a 1,10-phenanthroline radical anion bound to a nickel(II) centre. The electrochemical generation of the free 1,10-phenanthroline radical anion from 1,10-phenanthroline is also described.

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1. Introduction

Organonickel complexes with a sigma-C–Ni-bond (sigma-complexes) are important intermediates in several catalytic processes involving nickel catalysts [1,2]. These species are very reactive and only a limited number has been isolated and characterized. The first organonickel sigma-complexes were reported in the early 1960s [3], and derivatives containing the bpy ligand were described about twenty years later [4,5]. Chatt and Shaw [3] had shown in the 1960s that *ortho*-substituents in a σ -bonded aryl substituent can stabilize the complex by preventing free rotation about the nickel-carbon σ bond. Since then, the synthesis and

reactivity of σ -aryl nickel complexes bearing diimine ligands have been the focus of several reports [6–11].

The major route to organonickel sigma-complexes is the reaction of nickel halide complexes with organomagnesium or organolithium reagents followed by a ligand exchange reaction [1,2]. Alternatively, organonickel sigma-complexes can be obtained by oxidative addition of organic halides to nickel(0) complexes [1,2].

Recently, we have shown that diimine organonickel σ -aryl complexes [NiBr(aryl)(bpy)] (bpy = 2,2'-bipyridine) bearing *ortho*-substituents in the σ -bonded aromatic ring can be efficiently synthesized using electrochemical techniques, either in a single electrochemical cell with a sacrificial nickel anode [12], or in an electrochemical cell supplied with a diaphragm for separation of the anodic and cathodic compartments [13]. The first approach, use of a sacrificial anode, proved to be the most efficient procedure. The mechanism of the overall process involves cathodic *in situ* electrochemical generation of the highly reactive nickel(0) complex [Ni⁰(bpy)] followed by oxidative addition of *ortho*-substituted aryl

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