

First example of organonickel complex bearing three cyclic substituents in the σ -bonded aromatic ring: bromo[(2,2'-bipyridine)-2,4,6-tricyclohexylphenylnickel]

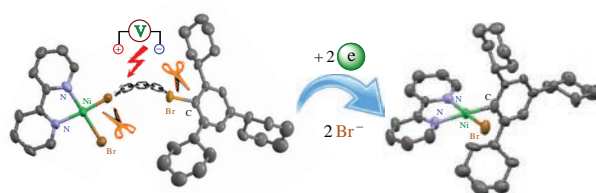
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The electrochemical reduction of $[\text{NiBr}_2(\text{bpy})]$ (bpy is 2,2'-bipyridine) complex in the presence of 2,4,6-tricyclohexylphenyl bromide (TchpBr) in undivided electrochemical cell supplied with a sacrificial nickel anode results in the one-pot formation of an organonickel complex $[\text{NiBr}(\text{Tchp})(\text{bpy})]$ bearing three cyclic substituents in the σ -bonded aromatic ring. The synthesized complex was characterized by various methods including single crystal X-ray analysis.



The organonickel complexes are intermediates in various coupling processes catalyzed by nickel compounds.^{1–4} Moreover, they have been successfully applied to the preparation of organophosphorus compounds directly from elemental (white) phosphorus,⁵ and they can be used for the activation and functionalization of small phosphorus molecules like phosphine PH_3 and phosphine oxide H_3PO ⁶ in the coordination sphere of a nickel atom bearing a σ -bonded organic group. In general, the stability of these intermediates is very low due to the presence of a highly reactive metal–carbon σ -bond. While the first stable organonickel complexes bearing Ni–C σ -bonds based on phosphine ligands were reported in the early 1960s,^{3,4} the derivatives containing nitrogen ligands were described one decade later.⁷ It was experimentally found that organonickel complexes can be isolated by the preliminary stabilization of highly reactive C–Ni σ -bond using *ortho*-substituted aryl fragments bound to nickel.⁷ At the same time, according to Yamamoto *et al.*,⁸ the protection of the axial positions of a nickel center in square planar organonickel σ -complexes is also important for the stabilization of organonickel species. The synthesis and reactivity of σ -aryl nickel complexes bearing *ortho* substituents in the aromatic ring have been reported.^{9,10} Special attention has been paid to organonickel derivatives bearing the substituents capable to shield axial positions of a nickel center. Recent examples include organonickel σ -complexes formed by pyridine ligands¹⁰ prepared by modified Seidel's procedure.¹¹ The proposed method involves the use of Grignard reagents whose preparation is limited by the reactivity of starting aryl bromide. However, to the best of our knowledge, there are no examples of organonickel complexes with σ -bonded to nickel center aryl group bearing three cyclic substituents, like cyclohexyl, which are able to shield the axial positions at nickel center stabilizing coordinatively unsaturated cationic forms. The known organonickel complexes with cyclic substituents in aromatic fragments are very rare, and they can be exemplified by phenylpyridine¹² and pincer-type¹³ ligands. Some other derivatives involve only mono- and disubstituted aromatic fragments, including

binuclear¹⁴ and sterically hindered¹⁵ organonickel complexes. Moreover, the presence of a σ -bonded organic group as a strong field ligand allows one to realize a low spin state of the nickel(II) center leading to additional possibility of the tuning of magnetic properties.¹⁶

Here, we describe the synthesis and X-ray crystal structure of the new organonickel σ -complex $[\text{NiBr}(\text{Tchp})(\text{bpy})]$ **1**, where Tchp is 2,4,6-tricyclohexylphenyl, and bpy is 2,2'-bipyridine, which represents the first example of organonickel σ -complex bearing three cyclic substituents in the σ -bonded aromatic fragment.

We have found that the preparation of organonickel σ -complexes can be effectively performed by a one-step procedure using electrochemical techniques,¹⁷ which have some advantages over the classical methods of organic synthesis.¹⁸ This procedure allows one to vary an aromatic group in organonickel complexes, whereas classical chemical methods are limited due to low reactivity of starting aromatic halides in a Grignard reagent preparation procedure. Thus, the main examples of synthesized organonickel complexes like $[\text{NiX}(\text{aryl})(\text{L})]$ are represented by a 2,4,6-trimethylphenyl group with a variety of diimine¹⁰ and halogen¹⁹ ligands, while electrochemical techniques provide easy access to organonickel species bearing various aromatic groups.^{4,17}

Complex **1** was prepared in 58% yield at room temperature directly from 2,4,6-tricyclohexylphenyl bromide (TchpBr) and $[\text{NiBr}_2(\text{bpy})]$ by one-pot electrosynthesis in DMF as a solvent (Scheme 1).[†] The synthesis was performed in an undivided electrochemical cell supplied with a sacrificial nickel anode.¹⁷

Complex **1** was isolated as dark red crystals suitable for X-ray crystal structure analysis[‡] after solvent evaporation and extraction of the product with acetone at room temperature. Compound **1** crystallizes from acetone in the triclinic space group $P\bar{1}$ with two independent molecules in the unit cell. The nickel atom in a molecule of **1** is coordinated in a distorted square-planar fashion

[†] For synthesis and characteristics of complex **1**, see Online Supplementary Materials.