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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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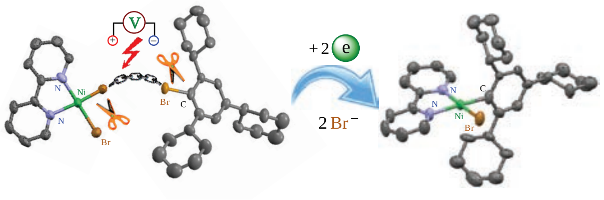
The electrochemical reduction of [NiBr$_2$(bpy)] (bpy is 2,2′-bipyridine) complex in the presence of 2,4,6-tricyclohexylphenyl bromide (TchpBr) in undivided electrochemical cell supplied with a sacrificial nickel anode results in the one-pot formation of an organonickel complex [NiBr(Tchp)(bpy)] bearing 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 ligands[10] 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 phenylpyridine[12] and pincer-type[13] ligands. Some other derivatives involve only mono- and disubstituted aromatic fragments, including binuclear[14] and sterically hindered[15] 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 [NiBr(Tchp)(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 [NiX(aryl)(L)] are represented by a 2,4,6-trimethylphenyl group with a variety of diimine[10] and halogen[19] 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 [NiBr$_2$(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

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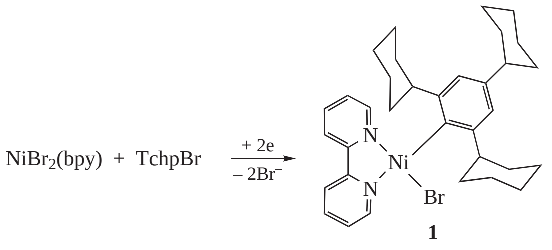
† For synthesis and characteristics of complex **1**, see Online Supplementary Materials.



Scheme 1

by a chelating bpy ligand [*via* N(1) and N(2)], a σ-bonded Tchp group and a bromo ligand in a *cis* arrangement (Figure 1). The Tchp aromatic ring is perpendicular to the N–N–Ni–Br plane, apparently due to the steric interaction of cyclohexyl groups with the bromo ligand and the *o*-hydrogen atom (H^6) of the bpy ligand. Bond lengths and angles of **1** are very similar to those reported for related complexes formed by 2,2′-bipyridine and other diimine ligands.[10,21]

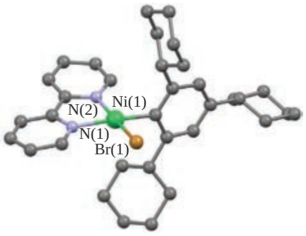


Figure 1 Molecular structure of complex **1**. Hydrogen atoms have been omitted for clarity.

The characterization of complex **1** in solution was performed by ESI-MS and ^{1}H-^{13}C HSQC NMR analysis (see Online Supplementary Materials for the latter case). The ESI-MS spectrum of [NiBr(Tchp)(bpy)] in DMF was recorded in the positive ion mode in order to confirm the identity of the complex in solution. As depicted in Figure 2, the ESI-MS spectrum shows a series of peaks. The highest intensity signal appears at *m*/*z* 610.5, which is unambiguously attributed to the cation $[Ni(Tchp)(bpy)(DMF)]^+$ formed in the reaction medium by ligand exchange reaction with DMF molecule and lower peak, appearing at 537.4, is assigned to $[Ni(Tchp)(bpy)]^+$ cation. The isotopic patterns for all peaks are in good agreement with the predicted isotopic distribution patterns. The assignments of these peaks indicate that the cationic species remain their structural integrity in solution that is in accordance with X-ray crystal structure analysis.

Thus, the new organonickel complex [NiBr(Tchp)(bpy)] bearing three cyclic substituents in σ-bonded aromatic group has been synthesized from nickel dibromide, bpy and TchpBr using one-pot electrochemical technique in a good yield and fully characterized by physico-chemical methods including ^{1}H-^{13}C HSQC NMR spectroscopy, ESI-MS spectrometry and single crystal X-ray analysis.

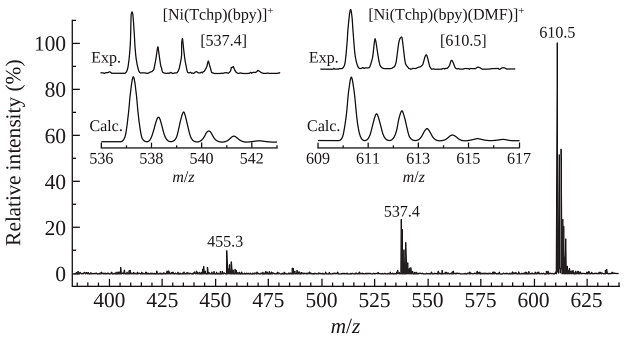


Figure 2 ESI-MS of complex [NiBr(Tchp)(bpy)] **1** in DMF. Inserts: the experimental and calculated isotopic patterns for the cations $[Ni(Tchp)(bpy)]^+$ ($[M-Br]^+$ = 537.4) and $[NiBr(Tchp)(bpy)(DMF)]^+$ ($[M-Br+C_3H_7NO]^+$ = = 610.5).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.03.016.

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[‡] *Crystal data for* **1**: dark red crystal, $C_{34}H_{43}BrN_2Ni$ (M = 618.29), triclinic, space group $P\bar{1}$, at 296(2) K: a = 10.825(4), b = 14.705(6) and c = 20.915(8) Å, α = 80.608(8)°, β = 86.773(11)°, γ = 89.694(8)°, V = = 3279(2) Å^3, Z = 4, d_{calc} = 1.252 g cm^{-3}, μ = 1.833 mm^{-1}, R_{int} = 0.00, θ_{max} = 27.0. The analysis was performed on a Bruker Smart Apex II CCD diffractometer. 14209 reflections collected, 6026 observed reflections with $I > 2\sigma(I)$, final R = 0.1020, wR_2 = 0.2901, 14209 independent reflections with $F^2 \geqslant 2\sigma(I)$, S = 0.93. The contribution of the solvent was removed from overall scattering by using the PLATON/SQUEEZE program.[20] The total number of the electrons removed is 5 per cell. Final structure contains voids of 319.2 Å^3.

CCDC 1437864 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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