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# Roadmap to the Synthesis of Nickel Bisoxazoline Aryl Halide Complexes

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**ABSTRACT:** This manuscript discloses a synthetic route to a range of bisoxazoline-ligated Ni(II) aryl bromide and chloride complexes, which are widely proposed as key intermediates in Ni-catalyzed reactions. Structural characterization by NMR and X-ray crystallography confirms a distorted square planar geometry, while UV-Vis analysis reveals spectral variations influenced by the BOX ligand, aryl group, and halide identity. Given the challenges associated with synthesizing these complexes, our approach provides a practical and generalizable route to access them, facilitating their use in mechanistic studies. This work is expected to aid in distinguishing on-cycle and off-cycle species and in determining whether Ni(0) or Ni(I) pathways are operative in catalytic processes.

## INTRODUCTION

The discovery of Ni-catalyzed enantioconvergent strategies, cross electrophile coupling, and Ni-photoredox strategies has attracted a lot of attention from the synthetic community and highlighted the potential of reactivity accessible via open shell Ni chemistries.<sup>1</sup> Reports detailing the development of these strategies are numerous and include both racemic and enantioselective protocols. Commonly, these reactions start with an oxidative addition step into an aryl, alkenyl, or alkyl halide which may take place from either Ni(0) and render a Ni(II) intermediate or from a Ni(I) intermediate and generate a Ni(III) complex. The differentiation between these two pathways is not trivial and thus, the mechanism of the oxidative addition and subsequent steps is often unclear.

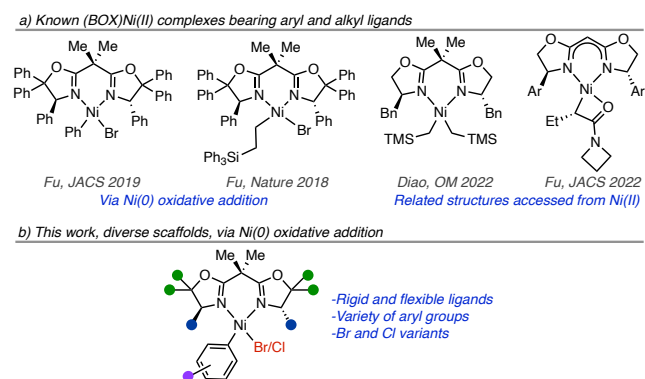
One possible approach to identifying the operative pathway is the isolation and reactivity study of the oxidative addition adducts. In this context, the isolation and characterization of the Ni(III) complexes is challenging due to their high reactivity and has only been possible when using specialized ligands.<sup>2</sup> In contrast, oxidative addition from Ni(0) leads to the formation of more thermodynamically and kinetically stable Ni(II) intermediates. Indeed, formation of Ni(II) intermediates has also been proposed to be accessible through the oxidative addition of C(sp<sup>2</sup>)-halides into Ni(I) complexes followed by rapid comproportionation of the transiently generated Ni(III) and a Ni(I).<sup>11,3</sup> Resultingly, reports describing the synthesis of Ni(II) oxidative addition intermediates are more common. However, most examples describe the use of strong phosphine or pyridine-based ligands which allow the formation of stable and easy to handle Ni(0) and Ni(II) complexes.<sup>1n-p, 3a, 3d, 4</sup>

In contrast, and despite the widespread use of oxazoline-based ligands such as bisoxazoline (BOX), reports on the synthesis of oxidative addition intermediates bearing these ligands remain scarce (Figure 1).<sup>1n-p, 3d, 4a, 4c-e</sup> The significance of synthesizing these intermediates extends beyond kinetic studies and reaction intermediate identification. Accessing these chiral complexes also enables valuable stoichiometric investigations to probe a system's enantioselectivity-

determining step. This approach was recently showcased by our lab when four (BOX)Ni(II) oxidative addition complexes were synthesized to study the mechanism of a Ni/Ir dual photoredox-catalyzed THF  $\alpha$ -arylation reaction.<sup>3d</sup>

In this paper we provide a roadmap to the synthesis of a variety of (BOX)Ni(II) aryl bromide and aryl chloride complexes.<sup>5</sup> The synthetic approaches detailed in this paper overcome the current lack of diversity of complexes that can be accessed. Specifically, previously known routes require the use of rigid ligands to allow for the oxidative addition complex to precipitate upon formation and thus prevent side reactions.<sup>1n, 1o</sup> As a result, only a small fraction of the highly tunable BOX scaffolds are amenable to those approaches.

**Figure 1:** (BOX)Ni(II) oxidative addition complexes and related structures



a) Previously reported (BOX)Ni(II) oxidative addition complexes. b) (BOX)Ni(II) oxidative addition complexes reported in this paper.

To address the limitations of current synthetic routes to these catalytically ubiquitous intermediates, this paper presents a general strategy accounting for the diversity of BOX ligands, aryl bromides, and chlorides to access a variety of (BOX)Ni(II) aryl halide complexes. A comprehensive characterization of these complexes through

improved NMR, UV-vis, and X-ray crystallographic analysis is also provided.

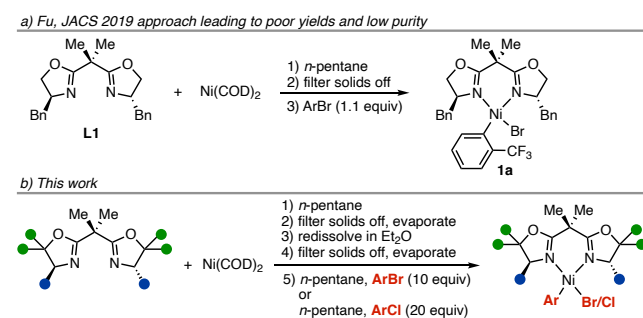
## RESULTS AND DISCUSSION

### OXIDATIVE ADDITION COMPLEX SYNTHESIS

We initiated this project with the goal of synthesizing complex **1a**, featuring ligand **L1** with benzyl group substituents—providing some conformational flexibility without excessive steric bulk—and an *ortho*-trifluoromethylated aryl bromide. The fluorine substituent not only offers a useful handle for monitoring the reaction via  $^{19}\text{F}$  NMR but also helps mitigate potential bimolecular side reactions that will hamper the complex isolation (Scheme 1a).

Our initial synthetic approach was a direct adaptation of the procedure reported by the Fu group, which had been successfully applied in the isolation of a (BOX)Ni(II) phenyl bromide complex bearing a tetraphenyl BOX ligand (Figure 1a).<sup>10</sup> A mixture of **L1** and Ni(COD)<sub>2</sub> was stirred in pentane, then remaining solids were filtered off before the addition of the aryl bromide. After several hours of stirring, when using the tetraphenyl derivative, the (BOX)Ni(II) oxidative addition complex was reported to precipitate from solution. This allows for straightforward isolation via filtration through a fine frit. Final purification was achieved through a series of pentane washes.

**Scheme 1:** Evolution of the strategies to synthesize (BOX)Ni(II) aryl bromide complexes



Unfortunately, our efforts to synthesize complex **1a**, by attempting to directly apply the procedure described by the Fu lab for related reactions, led to low purity and poor yields.<sup>10</sup>  $^1\text{H}$  NMR analysis of the reaction mixture revealed residual unreacted **L1** and Ni(COD)<sub>2</sub>. Additionally, significant peak broadening was observed, making it difficult to determine whether the oxidative addition complex **1a** had indeed formed and was paramagnetic or if the broadening was caused by paramagnetic impurities.

To further assess the reaction outcome, the  $^{19}\text{F}$  NMR spectrum was analyzed. A peak corresponding to unreacted 2-bromobenzotrifluoride was detected, along with a minor signal tentatively assigned to complex **1a**. This assignment was based on comparison to a previously reported  $^{19}\text{F}$  NMR shift for a 4,4'-di-*tert*-butyl-2,2'-dipyridyl (dtbbpy) Ni oxidative addition complex with 2-bromobenzotrifluoride.<sup>6</sup> The observed shift for **1a** at -57.3 ppm closely matched the dtbbpy analogue at -58.2 ppm. Using the  $^{19}\text{F}$  NMR data, we estimated the product yield to be approximately 10%. Further pentane washes were unsuccessful at increasing the sample purity.

We then explored an alternative approach by subjecting the corresponding Ni(II) dihalides with aryl Grignard reagents, a method successfully demonstrated by the Diao group for synthesizing

(BiOX)Ni(II) complexes.<sup>4c, 4d</sup> The higher solubility of Ni(II) precatalysts compared to Ni(COD)<sub>2</sub> allowed for the use of a broader range of solvents. However, the subsequent transmetalation step proved challenging. We struggled to prevent double transmetalation of the Grignard reagent onto the Ni center, leading again to low yields of the desired product alongside significant formation of homocoupled biaryl side products, further complicating the isolation of the target complex. These byproducts were likely generated from reductive elimination from the putative Ni(II) biaryl intermediates

Given these challenges, we decided to revisit the Ni(0)-initiated approach. Our focus shifted toward optimizing the COD displacement step to promote removal of excess ligand and unreacted Ni(COD)<sub>2</sub> before proceeding with oxidative addition. We hypothesized that once complex **1a** was formed, any remaining aryl halide could be effectively removed through subsequent pentane washes, improving the overall yield and purity of the desired oxidative addition complex.

Multiple solvents were screened for the initial ligand displacement step between Ni(COD)<sub>2</sub> and **L1**. Toluene, benzene, acetonitrile, and tetrahydrofuran quickly led to the formation of a black precipitate, which was hypothesized to be Ni black, rendering the ligand exchange unsuccessful. Diethyl ether was found to be a suitable solvent, but  $^1\text{H}$  NMR of the resulting Ni(0) complex showed remaining free COD that could not be completely removed via pentane washes.

At this stage, we considered whether we could exploit the differing solubilities of the starting materials and reaction intermediates in pentane and diethyl ether to obtain a cleaner product. Depending on the ligand used (see SI for details), pentane or pentane-ether mixtures were employed to facilitate the initial COD displacement reaction. This step led to the formation of an oily residue, which was subsequently filtered off, effectively removing any unreacted COD and excess BOX ligand that was not coordinated to Ni.

Following filtration, the solvent was evaporated, and the residue was redissolved in diethyl ether to eliminate any remaining unreacted Ni(COD)<sub>2</sub>. This purification step was critical, it allow us to separate Ni(COD)<sub>2</sub> from the BOX ligated Ni(0). Residual Ni(COD)<sub>2</sub>, which is commonly observed floating in solution, was efficiently removed by filtration at this stage. This process ultimately yielded a high-purity BOX ligated Ni(0) complex, which was then suitable to be used in the oxidative addition step (Scheme 1b).

The next step in the synthesis is the Ni(0) oxidative addition into the aryl bromide to form the (BOX)Ni(II) complexes. Pentane was identified as the optimal solvent for this transformation, necessitating a final solvent exchange. To achieve this, the ethereal solution was evaporated, and the residue was redissolved in pentane before the addition of the aryl bromide. The use of 10 equivalents of the electrophile was found to be optimal for ensuring high yields.

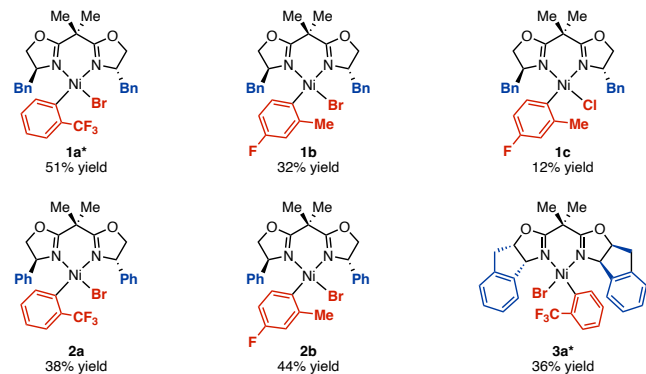
The resulting (BOX)Ni(II) aryl bromide complexes highlighted in this paper are insoluble in pentane, leading to their precipitation directly from the reaction mixture, which facilitates isolation. The precipitate is collected by filtration over a frit and washed with pentane, requiring no additional purification steps. While this strategy is generally applicable, exceptions arise when working with highly rigid BOX ligands like those containing a dihydro-indene moiety (to eventually afford **3a**), as the (BOX)Ni(0) adduct exhibits poor solubility in pentane. In such cases, the oxidative addition step can be carried out in diethyl ether, followed either by direct precipitation in ether or precipitation facilitated by pentane addition, to afford the final product as a solid.

Finally, to our delight aryl chlorides were also amenable to this synthetic route. Due to their lower reactivity 20 equivalents and longer reaction times are required for the oxidative addition step.

Following this procedure, we were able to access a range of complexes (Figure 2). Complexes bearing the same **L1** ligand with different aryl and halogen substitution were targeted to explore the effects of changes on the aryl and halogen groups on the synthesis and complex properties (**1a-1c**). For comparison with **1a** and **1b**, **2a** and **2b** analogs bearing a more rigid phenyl-substituted ligand were also synthesized. Finally, given the ubiquity of dihydro-indene moiety **3a** was also accessed.

The complexes reported in this manuscript all bear *ortho* substituents to slow down transmetalation between two aryl halide Ni species. For less sterically encumbered complexes, this is a fast side reaction that hampers the complex isolation and quickly leads to the formation of biaryl species. It should be noted we have previously reported the synthesis of a (BOX)Ni(II) aryl halide complex without *ortho*-substituents.<sup>3d</sup> To afford these reactive species, the oxidative addition step must be run in pentane. This allows for the desired Ni(II) complex to precipitate upon formation and prevents side reactions. However, subsequent characterization of these complexes by NMR proved challenging, as fast decomposition via transmetalation and biaryl formation readily occurs when these complexes are in solution. While the *ortho*-substituted Ni complexes reported here do present greater stability, we have observed significant decay in the first hour for Ni(II) aryl bromide and chloride complexes in both C<sub>6</sub>D<sub>6</sub> solution (under N<sub>2</sub>) and in the solid-state under ambient conditions (section 5 in the SI).

**Figure 2:** (BOX)Ni(II) aryl halide complexes accessed through this synthetic pathway



All reported values are yields of the isolated products. \*Complexes characterized by X-ray single crystal analysis.

It was found that a limitation of this approach is accessing complexes with BOX ligands bearing alkyl chains, like the ubiquitous valine-derived ligands. Following this procedure both ligand exchange with Ni(COD)<sub>2</sub> and the oxidative addition are favorable. However, the high solubility of alkyl-substituted (BOX)Ni(II) complexes in pentane hampers their isolation and purification from residual unbound ligand and unreactive aryl halide. The overall solubility of the Ni(II) complexes in pentane, which is key to identify a synthetic route was found to depend on aryl group, the halide nature, and BOX ligand used (see SI for more details).

## Characterization

The structure of **1a** and **3a** was unambiguously established by X-ray single crystal diffraction.<sup>7</sup> In line with the other Ni aryl halide complexes,<sup>1n-p, 3a, 3d, 4, 8</sup> the X-ray analysis revealed a distorted square planar geometry. To quantify the distortion of these complexes, the geometry indexes ( $\tau_4$  and  $\tau'_4$ ) were calculated (Table 1). The geometry indexes revealed a slight distortion from the square planar geometry ( $\tau_4 = 0$  and  $\tau'_4 = 0$ ). The geometry around the Ni center of complex was found to be in agreement with the indexes calculated from a previously reported bipyridine analogue bearing the same arene as **1b**<sup>8</sup> (entry 4). Finally, for comparison, the parameters calculated from a crystal structure of distorted tetrahedral (**L1**)NiBr<sub>2</sub> complex are also depicted in Table 1, entry 5.<sup>9</sup>

**Table 1:** Geometry indexes calculated for complexes that afforded a crystal structure.

Entry	Complex	$\tau_4$	$\tau'_4$
1	<b>1a</b>	0.098	0.085
2	<b>3a</b>	0.110	0.099
3	bpy analogue of <b>1b</b>	0.046	0.041
4	( <b>L1</b> )NiBr <sub>2</sub>	0.869	0.849

At this stage we focused on analyzing if the geometry of the complex in solution, analyzed by NMR, matched the distorted square planar geometry observed in the solid state. A significant broadening was observed for the <sup>1</sup>H NMR signals of these complexes which may be related to an equilibrium between a diamagnetic and paramagnetic species or the presence of paramagnetic impurities. The possible presence of Ni(I) impurities was assessed by EPR spectroscopy, which showed no detectable signals for frozen benzene solutions at 77 K, suggesting that Ni(I) species, if present, are not formed in appreciable concentrations. Another potential impurity that would lead to broadening is tetrahedral complex (**L1**)NiBr<sub>2</sub>, which could also be formed during the synthesis of the complexes. To discard that the broadening was due to the presence of (**L1**)NiBr<sub>2</sub>, this complex was synthesized following a reported procedure.<sup>9</sup> This Ni(II)Br<sub>2</sub> complex presents a characteristic peak ~20 ppm which was not observed in the spectra of the isolated complexes (see broad <sup>1</sup>H NMR spectra for the complexes in the SI) suggesting that the peak broadening is intrinsic of the aryl halide complexes. Additionally, the <sup>1</sup>H NMR of (**L1**)NiBr<sub>2</sub> displays significant shifts in some signals. These shifts are characteristic of paramagnetic species and are not observed for the <sup>1</sup>H NMR of aryl halide complexes described in this paper.

A magnetic susceptibility of  $2.78 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$  was calculated using Evans method for complex **1b**, which equates to an effective magnetic moment ( $\mu_{\text{eff}}$ ) of  $0.72 \mu_{\text{B}}$  and less than 1 unpaired spins.<sup>10</sup> This non-zero small magnetic moment is consistent with a ground state square planar diamagnetic complex which is in equilibrium with a high-spin tetrahedral complex.<sup>11</sup> This observation is also in line with the slightly distorted square planar geometry observed in the crystal structures.

Finally, the absorption spectra of complexes **1a**, **1b**, **1c**, and **2a** was collected to investigate the effect of aryl group, halide, and BOX ligand on the spectral properties (Figure S5). The X-type ligands were observed to have the largest effect on the absorption spectra. Switching the halogen from Br to Cl led to a red shift the  $\lambda_{\text{max}}$  with **1c**  $\lambda_{\text{max}} = 460 \text{ nm}$  (see purple spectrum) compared to the bromide analogue **1b**  $\lambda_{\text{max}} = 420 \text{ nm}$  (see green spectrum). A smaller but significant shift was also observed when changing the aryl moiety with  $\lambda_{\text{max}} =$

420 nm vs  $\lambda_{\text{max}} = 430$  nm from **1b** and **1a** (see green and blue spectra, respectively). Finally changing the ligand from benzyl- to phenyl-substituted had little effect on the absorption spectra (see green and orange spectra for **1b** and **2b**, respectively).

## CONCLUSIONS

The development of a synthetic route to a series of (BOX)Ni(II) aryl halide complexes is described. The structures of three of these complexes were determined by X-ray single-crystal analysis, revealing a distorted square planar geometry. NMR analysis suggests that this geometry is also predominant in solution. Additionally, the UV-Vis absorption spectra exhibited a dependence on the nature of the halogen and aryl moiety, while the effect of the BOX ligand was comparatively milder.

These Ni(II) aryl halide complexes are frequently proposed as key intermediates in Ni-catalyzed reactions.<sup>1</sup> Therefore, establishing a straightforward synthetic route to access them is expected to facilitate their study. This work provides a valuable tool for the mechanistic elucidation of Ni-catalyzed reactions enabling stoichiometric experiments that are expected to simplify the identification of on-cycle and off-cycle species and aid in the distinction between Ni(0)- and Ni(I)-mediated processes.

## ASSOCIATED CONTENT

### Supporting Information

The supporting information containing all synthetic procedures, characterization of the Ni complexes, and summary for the X-ray diffraction study of **1a** and **3a** is available free of charge on...

CCDC deposition numbers for **1a** and **3a** 2430045 and 2430046, respectively.

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### Author Contributions

The manuscript was written through contributions of all authors. The authors declare no competing financial interests.

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