# Visible-Light-Induced Ni-Catalyzed Radical Borylation of Chloroarenes

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that employs  $[Ni(IMes)_2]$  (IMes = 1,3-dimesitylimidazoline-2-ylidene) for the radical borylation of chloroarenes is reported. This photoinduced system operates with visible light (400 nm) and achieves borylation of a wide range of chloroarenes with  $B_2pin_2$  at room temperature in excellent yields and with high selectivity, thereby demonstrating its broad utility and functional group tolerance. Mechanistic investigations suggest that the borylation reactions proceed via a radical process. EPR studies demonstrate that  $[Ni(IMes)_2]$  undergoes very fast chlorine atom abstraction from aryl chlorides to give  $[Ni^I(IMes)_2Cl]$  and aryl radicals. Control experiments indicate that light promotes the reaction of  $[Ni^I(IMes)_2Cl]$  with aryl chlorides generating additional aryl radicals and  $[Ni^{II}(IMes)_2Cl_2]$ . The aryl radicals react with an anionic  $sp^2-sp^3$  diborane  $[B_2pin_2(OMe)]^-$  formed from  $B_2pin_2$  and KOMe to yield the corresponding



borylation product and the  $[Bpin(OMe)]^{\bullet-}$  radical anion, which reduces  $[Ni^{II}(IMes)_2Cl_2]$  under irradiation to regenerate  $[Ni^{I}(IMes)_2Cl]$  and  $[Ni(IMes)_2]$  for the next catalytic cycle.

### INTRODUCTION

Arylboronic esters have been recognized as key building blocks in organic synthesis, materials science, and drug discovery.<sup>1</sup> Recently, highly selective transition-metal-catalyzed borylations of aryl halides, based on Pd,<sup>2</sup> Ni,<sup>3</sup> Fe,<sup>4</sup> Cu,<sup>5</sup> Co,<sup>6</sup> Zn,<sup>7</sup> have been developed as an efficient method to synthesize arylboronic esters. Aryl iodides and bromides are frequently employed as precursors to aryl boronate esters. However, although widely available and inexpensive, chloroarene borylation is more challenging due to the relatively high C-Cl bond energy. Ishiyama et al. first achieved the borylation of C–Cl bonds by using a Pd(0)-tricyclohexylphosphine complex as a catalyst in 2001.<sup>2d</sup> The groups of Yamakawa<sup>3h</sup> and Nakamura<sup>4e</sup> showed that  $[NiCl_2(PMe_3)_2]$  and  $[Fe(acac)_3]$  as catalyst efficiently borylate chloroarenes in the presence of cesium 2,2,2-trifluoroethoxide and KO<sup>t</sup>Bu at 100 and 130 °C, respectively. Our groups recently reported an efficient catalytic procedure for the C-Cl borylation of chloroarenes using NHC-Ni (NHC = N-heterocyclic carbene) complexes as catalysts and bis(pinacolato)diboron (B2pin2) as the boron source at 100  $^{\circ}$ C.<sup>3k</sup> In 2016, we showed that the selective C–F borylation of polyfluoroaromatic compounds can be catalyzed by [Ni(IMes)<sub>2</sub>] (IMes = 1,3-dimesitylimidazoline-2-ylidene) in the presence of [NMe4]F or CsF at 80 °C.8 Geetharani et al. also reported an efficient catalytic system based on a Co(II)-NHC precursor for the borylation of chloroarenes at 50 °C, affording the aryl boronates in good to excellent yields.<sup>6f</sup> Recently, our groups developed an efficient Cu-catalyzed

borylation of aryl chlorides at 90 °C.<sup>5i</sup> Jiao et al. reported a pyridine-catalyzed transition-metal-free radical borylation of aryl halides at 85 °C, but only two chloroarenes were described in this report.<sup>9</sup>

Photocatalysis, as an alternative to the thermally induced borylation of aryl halides by transition metals, has recently emerged as a powerful tool for the synthesis of aryl boronate esters due to the great enhancement of catalytic efficiency.<sup>10</sup> For example, Li et al.<sup>11</sup> and Larionov et al.<sup>12</sup> showed that aryl halides, mesitylates, and ammonium salts can be photochemically borylated (Scheme 1). Aryl radicals, produced by photoinduced homolytic or heterolytic cleavage of the C(arene)-X bond, react with a boron source to form the target aryl boronates. However, the necessary high-intensity UV irradiation poses potential limitations to the applicability of this method. Visible light photoredox catalysts can also be employed to generate aryl boronates from aryl halides. Fu et al. developed visible-light photoredox borylation of aryl halides with  $B_2 pin_2$  using fac-Ir(ppy)<sub>3</sub> as the photocatalyst (Scheme 1).<sup>13</sup> The method displays high tolerance for various functional groups; however, it is limited to aryl iodides and bromides.



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#### Scheme 1. Examples of Photoinduced C-X Borylation of Aryl Halides



Table 1. Photoinduced Borylation of 1a



<sup>a</sup>The yields were determined by GC-MS analysis vs a calibrated internal standard and are averages of two runs.

The photocatalytic conversion of widely available aryl pseudohalides, carboxylic acids, aryldiazonium salts, and aromatic amines into versatile boronic esters has been reported by Li, Glorius, Aggarwal, Yan and Ranu et al.<sup>14</sup> Very recently, Jiao et al. reported a visible-light-induced organocatalytic method for the borylation of unactivated chloroarenes, and even fluorides, by photoactivation of the super electron donor (SED) complex generated in situ in a diboron/methoxide/ pyridine reaction system (Scheme 1).<sup>15</sup> Our groups recently reported a photocatalytic C-F borylation protocol that employs a Rh biphenyl complex ([Rh]) as a triplet sensitizer and the nickel catalyst  $[Ni(IMes)_2]$  for the borylation of C-F bonds in aryl fluorides (Scheme 1).<sup>16</sup> Further mechanistic studies showed that the exceptionally long-lived triplet excited state of the Rh biphenyl complex allows for efficient triplet energy transfer to the oxidative addition product trans- $[Ni^{II}F(Ar^{F})(IMes)_{2}]$  to greatly enhance the rate constant for the transmetalation step with  $B_2pin_2$  at room temperature.<sup>16,17</sup>

Cavell et al. found that small NHC ligands with less steric hindrance, such as 1,3,4,5-tetramethylimidazol-2-ylidene (tmiy), permit oxidative addition to form Ni<sup>II</sup> complexes,<sup>18</sup> while Matsubara et al. found that larger NHC ligands, such as 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr), favor

halide abstraction to form Ni<sup>1</sup> complexes plus aryl radicals.<sup>19</sup> Louie et al. and Nelson et al. further confirmed that the products of the reactions of  $[Ni(NHC)_2]$  with aryl halides are mainly dominated by the steric impact of the NHC ligand, based on experimental and computational investigations, respectively.<sup>20</sup> With this information, and the fact that aryl radicals are well-known intermediates in some catalytic borylation processes, we hoped to achieve the activation of chloroarenes to form corresponding arylboronic esters utilizing  $[Ni(IMes)_2]$  as the catalyst (Scheme 1).

#### RESULTS AND DISCUSSION

We first investigated the efficiency of the borylation reaction of 4-chloroanisole (1a) with  $B_2pin_2$  in the presence of KOMe using 10 mol % [Ni(IMes)<sub>2</sub>] as the catalyst at 25 °C, which gave a 12% yield of 1-Bpin-4-methoxybenzene (1b) after 2 h (Table 1, entry 1). When the reaction time was extended to 6 h, the yield of 1b was almost the same, suggesting that the protocol is inefficient.

Our previous work showed that the 5 mol % [**Rh**]/10 mol % [Ni(IMes)<sub>2</sub>] dual photocatalytic system exhibited excellent activity for selective C–F borylation of aryl fluorides (Scheme 1).<sup>16</sup> Therefore, the same system was examined for the

#### Table 2. Optimization of the Reaction Conditions for the Photoinduced Borylation of 4-Chloroanisole

	OMe		OMe O	Me OMe	
	+ B <sub>2</sub> pin <sub>2</sub> -	[Ni(IMes)₂] (10 mol%) base (1.5 equiv), solvent (2 mL) 400 nm LED, RT, 6 h	Bpin B	Bpin +	
	<b>1a</b> , 0.2 mmol 0.3 mmol		1b 1c	: 1d	
				Yield (%) <sup>a</sup>	
Entry	Base (1.5 equiv)	Solvent (2 mL)	1b	1c	1d
1	KOMe	hexane	86	11	2
2	KOMe	methylcyclohexane	79	9	7
3	KOMe	toluene	71	5	15
4	KOMe	THF	67	4	23
5	KOMe	$THF-d_8$	61	3	20 <sup>b</sup>
6	KOMe	MTBE	45	13	5
7	KOMe	Et <sub>2</sub> O	16	trace	12
8	NaOMe	hexane	21	5	5
9	KO <sup>t</sup> Bu	hexane	72	13	9
10	Li <sub>2</sub> CO <sub>3</sub>	hexane	13	7	3
11	$Cs_2CO_3$	hexane	18	8	4
12	KOAc	hexane	54	4	3
13	NaOAc	hexane	53	4	3
14	KF	hexane	9	6	4
15	CsF	hexane	12	8	5
16	_	hexane	4	3	trace

<sup>*a*</sup>The yields were determined by GC-MS analysis vs a calibrated internal standard and are averages of two runs. <sup>*b*</sup>The ratio of anisole-4- $d_1$  to anisole was ca. 1:1.

borylation of 1a. First, a reaction carried out in the dark for 2 h yielded ca. 13% of 1b (Table 1, entry 3), indicating that the [Rh] complex has no effect on the thermal borylation reaction. The yield of 1b reached 72% after only 2 h of irradiation of the reaction mixture with a 400 nm LED (Table 1, entry 4), suggesting that the dual photocatalytic system works efficiently for the borylation of aryl chlorides. However, the photocatalytic process yielded more dechlorohydrogenated byproduct anisole (1d, 15%) compared with that obtained when the reaction was performed in the dark. Interestingly, highly efficient and selective borylation of 1a under visible light (400 nm) irradiation at 25 °C was observed using only [Ni(IMes)<sub>2</sub>] as the photocatalyst without [Rh] complex, giving 1b in 86% yield after 6 h (Table 1, entry 2). Our group developed a Zn-catalyzed 1,2-selective dual C-H/C-X borylation of aryl iodides and bromides in 2015.<sup>7c</sup> Then, Larionov et al. reported an additive- and metal-free photoinduced regioselective 1,2- and 1,3-C-H/C-X diborylation of aryl halides, including three examples of chloroarenes, under batch and continuous flow conditions.<sup>12b</sup> In this work, we also observed both C-Cl and C-H borylation of chloroarenes, and the yield of  $1,2-(Bpin)_2$ -4-methoxybenzene (1c) in the photoinduced reaction, is slightly higher compared to that from the reaction without irradiation (Table 1, entries 1-4). It is worth pointing out that this is the first report of Ni-catalyzed C-X/C-H diborylation of arenes. The reaction did not occur under light irradiation in the absence of [Ni(IMes)<sub>2</sub>] (Table 1, entries 5 and 6).

We screened a range of solvents and bases, with hexane and KOMe proving to be optimal (Table 2). Importantly, THF gave more of the hydrodehalogenation product ArH (Table 2, entry 4) than other solvents and there was significant deuterium incorporation when THF- $d_8$  was used (Table 2,

entry 5), suggesting a radical process. The yield is significantly influenced by the amount of both  $B_2pin_2$  and KOMe, with 1.5 equiv of each providing an excellent yield (Table S1).

We further examined the scope of chloroarene substrates for the photoinduced borylation under the optimized conditions, and the results are summarized in Table 3. Chloroarenes with either electron-donating (1a-13a) or electron-withdrawing (14a-18a) groups including esters, ketones, and nitriles reacted smoothly to afford the corresponding arylboronic esters in good to excellent yields, highlighting the excellent functional group tolerance of this method. Ortho-substitution with MeO (2a) or Me (4a, 7a, 9a) groups did not significantly lower the yield of the product, while substitution with two ortho-methyl groups (10a, 11a) somewhat reduced the yield. Importantly, both strong  $\pi$ -donor (NMe<sub>2</sub>, **13a**) and  $\pi$ -acceptor (CO<sub>2</sub>CH<sub>3</sub>, 14a; COCH<sub>3</sub>, 15a) substituents, as well as the inductively withdrawing  $CF_3$  group (16a) at the para-position, resulted in excellent yields of the product. 4-Chlorobiphenyl (20a), naphthyl chlorides (21a, 22a), and several chloroheteroarenes (23a-27a) are also compatible substrates. Notably, the protocol worked well with 5-chloroindole bearing an NH group (28a), enabling convenient borylation of such substrates without the need for a protecting group. High yields of diborylation products were also achieved with dichlorobenzenes as substrates (29a and 30a). Not only does the reaction show wide scope with respect to B<sub>2</sub>pin<sub>2</sub>, but bis(neopentyl glycolato)diboron  $(B_2 neop_2)^{21}$  can be substituted for  $B_2 pin_2$  as the diboron reagent to give the corresponding aryl neopentylglycolato boronate ester products (31b-34b) in similar yields to those observed with B<sub>2</sub>pin<sub>2</sub>.

Preliminary mechanistic studies were conducted to provide insight into the photoinduced borylation process. First, using allyl *o*-chlorophenyl ether (1aa) as the substrate gave the

# Table 3. Scope of the Photoinduced Borylation of Chloroarenes $^{a}$



#### Table 3. continued



<sup>*a*</sup>Reaction conditions:  $B_2pin_2$  (0.3 mmol), chloroarene (0.2 mmol), KOMe (0.3 mmol),  $[Ni(IMes)_2]$  (10 mol %), hexane (2 mL), at room temperature under irradiation with a 400 nm-LED for 6 h unless otherwise stated. <sup>*b*</sup>The yields are based on aryl chlorides and were determined by GC-MS analysis vs a calibrated internal standard and are averages of two runs. <sup>*c*</sup>Isolated yields based on 1 mmol of aryl chloride are given in parentheses. <sup>*d*</sup>The reaction time was 24 h. <sup>*e*</sup>B<sub>2</sub>pin<sub>2</sub> (0.6 mmol) and KOMe (0.6 mmol) were used. <sup>*f*</sup>B<sub>2</sub>pin<sub>2</sub> (3 mmol) and KOMe (3 mmol) were used. <sup>*g*</sup>B<sub>2</sub>neop<sub>2</sub> (0.3 mmol) was used. <sup>*h*</sup>B<sub>2</sub>neop<sub>2</sub> (1.5 mmol) was used.

#### Scheme 2. Preliminary Mechanistic Studies: (a) Aryl Radical Trapping; (b) Hydrogen Atom Transfer from THF-d<sub>8</sub>

a) Aryl radical trapping:



monoborylated product **1ab**, but the cyclized (borylmethyl) indane (**1ac**) was the main product, indicating an intramolecular trapping of the aryl radical by the olefin moiety, followed by coupling with the boryl species (Scheme 2a). Second, when the reaction of **1a** with  $B_2pin_2$  was conducted in THF- $d_8$  instead of hexane, the borylation product **1b** was observed in a lower yield (61%), together with a significant amount of dehalogenation product anisole (**1d**, 10%) and anisole-4- $d_1$  (**1e**, 10%), due to hydrogen atom transfer from THF to *p*-MeO-C<sub>6</sub>H<sub>4</sub>• (Table 2, entry 5, Scheme 2b, and Figure S1). Thus, the hydrogen atom donor THF competes with the boryl species to react with the aryl radical. When the reaction of **1a** was performed in the presence of 2 equiv of the hydrogen atom donor 9,10-dihydroanthracene as a radical trap, both borylation products were obtained in lower yields (**1b**: 73%; **1c**: 7%) with an increased yield of **1d** (17%). Increasing the amount of the dihydroanthracene radical trap to 10 equiv significantly reduced the yield of **1b** to 49% and **1c** to 1%, and increased the yield of **1d** to 42%. The presence of 0.4 equiv of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as a radical trap shut down the reaction almost completely. The above intra- and intermolecular trapping reactions clearly indicate the generation of aryl radicals from the aryl chlorides.

*In situ* EPR spectra at 70 K in frozen hexane after 1, 2, 3, and 5 min were recorded to confirm the formation of radical species. From Figure 1A, it can be seen that the signals increase



Figure 1. (A) Changes in the low-temperature CW EPR spectra of the reaction of  $[Ni(IMes)_2]$  and 1a in hexane with the reaction time at 70 K and (B) the simulated spectrum shown in red; (C) simulated (red) and experimental (black) CW EPR spectra of isolated  $[Ni^I(IMes)_2Cl]$  in frozen hexane (see SI for details).



Figure 2. (A) UV-visible absorption of  $[Ni(IMes)_2]$ ,  $[Ni^{I}(IMes)_2Cl]$ ,  $[Ni^{II}(IMes)_2Cl_2]$ ,  $K[B_2pin_2(OMe)]$ , and IMes in degassed hexane solution at room temperature; (B) emission (excited at 400 nm) and excitation spectra of solid  $[Ni^{II}(IMes)_2Cl_2]$  under air at room temperature.

with time. Comparison of the *in situ* EPR spectrum at 70 K (Figure 1B) with the EPR spectrum of isolated  $[Ni^{1}(IMes)_{2}Cl]$  (for synthesis and molecular structure, see Supporting Information (SI)) in frozen hexane (Figure 1C) revealed that they are essentially identical. The similarity of *in situ* EPR spectra of the reaction of  $[Ni(IMes)_{2}]$  with chlorobenzene also confirmed the formation of the complex  $[Ni^{1}(IMes)_{2}Cl]$  during the reaction (Figure S2). While the main contribution to the observed EPR spectrum is from  $[Ni^{1}(IMes)_{2}Cl]$ , a second small signal which is attributed to  $[Ni^{1}(IMes)_{2}Ph]$  was observed. The result is consistent with literature reports, <sup>19,20</sup> that steric impact of the IMes ligands prevents coordination of  $[Ni(IMes)_{2}]$  to the chloroarene and leads to chlorine atom abstraction to form an aryl radical Ar<sup>•</sup> and the complex

 $[Ni^{I}(IMes)_{2}CI]$ . No signal for Ar<sup>•</sup> was detected in the *in situ* EPR spectra, and neither benzene nor biphenyl compounds were detected by GC-MS. However, from our *in situ* NMR spectra and HRMS measurements of the reaction of chlorobenzene with  $[Ni(IMes)_{2}]$ , the aryl complex  $[Ni^{I}(IMes)_{2}Ph]$  was detected in addition to  $[Ni^{I}(IMes)_{2}CI]$  (Figure S140). Therefore, we speculated that the Ar<sup>•</sup> species likely reacts very quickly with  $[Ni(IMes)_{2}]$  to form  $[Ni^{I}(IMes)_{2}Ar]$ , whereas, in the catalytic reaction system, Ar<sup>•</sup> is more likely to react with  $B_{2}pin_{2}$  or with the more nucleophilic  $[B_{2}pin_{2}(OMe)]^{-}$  to form the borylation product.

To clarify the role of light, we investigated the photophysical properties of the different compounds in the reaction mixture. From the UV-vis spectra (Figure 2A), both IMes and

F

 $K[B_2pin_2(OMe)]$  (the product of the direct reaction of KOMe with  $B_2pin_2$ )<sup>9h,i</sup> have almost no absorption at wavelengths >300 nm in hexane. [Ni(IMes)<sub>2</sub>] has a very broad absorption spectrum with two absorption maxima at 508 and 616 nm, while [Ni<sup>1</sup>(IMes)<sub>2</sub>Cl] has an absorption band between 300– 450 nm with a maximum at 340 nm. However, [Ni<sup>1</sup>(IMes)<sub>2</sub>Cl] and [Ni(IMes)<sub>2</sub>] do not show any detectable emission, preventing us from obtaining the energies of their lowest singlet or triplet states via emission spectroscopy. We know that the chlorine atom abstraction of chloroarenes by [Ni(IMes)<sub>2</sub>] to give [Ni<sup>1</sup>(IMes)<sub>2</sub>Cl] is very fast at room temperature, and therefore we focused on the role of [Ni<sup>1</sup>(IMes)<sub>2</sub>Cl] in subsequent photochemical processes.

The extinction coefficient of  $[Ni^{I}(IMes)_{2}CI]$  at 400 nm is ca. 1320 cm<sup>-1</sup> M<sup>-1</sup> (Figure 2A). Independently prepared  $[Ni^{I}(IMes)_{2}CI]$  was employed as catalyst instead of  $[Ni-(IMes)_{2}]$  for the photoinduced reaction of chlorobenzene (19a) with B<sub>2</sub>pin<sub>2</sub> under otherwise identical conditions, giving 68% and 17% yields of 19b and 19c, respectively (Table 4,

# Table 4. Photoinduced Borylation of 19a with $[Ni^{\rm I}(IMes)_2Cl]$ and $[Ni^{\rm II}(IMes)_2Cl_2]$ as Catalysts or Catalyst Precursors

↓ +	cataly B <sub>2</sub> pin <sub>2</sub> KOM hexa I	st (10 mol%) e (1.5 equiv) ane (2 mL) RT, 6 h	+ Bpin +	Bpin	pin +
19a, 0.2 mmol	0.3 mmol		19b	19c	19d
Entres	Castalaast	yst Blue LED	Yield (%) <sup>a</sup>		
Entry	Catalyst		19b	19c	19d
1	[Ni <sup>I</sup> (IMes)2Cl]	$\checkmark$	68	17	13
2	[Ni <sup>I</sup> (IMes)2Cl]	×	15	-	trace
3	[Ni <sup>II</sup> (IMes)2Cl2]	$\checkmark$	75	11	11
4	[Ni <sup>II</sup> (IMes) <sub>2</sub> Cl <sub>2</sub> ]	×	-	-	-

"The yields were determined by GC-MS analysis vs a calibrated internal standard and are averages of two runs.

entry 1). When the reaction was carried out in the dark, the yield of **19b** was only 15% (Table 4, entry 2), indicating that light is necessary for an efficient reaction. Further control experiments showed that  $[Ni^{I}(IMes)_{2}CI]$  had good stability under continuous irradiation (Figures S145 and S146) for 2 h with 400 nm LEDs, and it did not react with B<sub>2</sub>pin<sub>2</sub> in either the presence or absence of KOMe or light (Scheme 3 and

Scheme 3. Control Reactions of  $[Ni^{I}(IMes)_{2}Cl]$  with  $B_{2}pin_{2}$ , KOMe, and Chlorobenzene, Respectively, without (left) and with (right) Irradiation



Figures S147–S154). The reaction of  $[Ni^{I}(IMes)_{2}Cl]$  with 19a yielded 5% of  $[Ni^{II}(IMes)_{2}Cl_{2}]$  in the dark after 2 h (Scheme 3 and Figures S155 and S156). However, almost complete conversion of  $[Ni^{II}(IMes)_{2}Cl]$  to  $[Ni^{II}(IMes)_{2}Cl_{2}]$  in the presence of 19a was observed under 400 nm LED irradiation for the same time (Scheme 3 and Figures S157 and S158), and biphenyl was detected by GC-MS from the photoinduced reaction, indicating that a rapid photochemical reaction of  $[Ni^{I}(IMes)_{2}Cl_{2}]$  with 19a generates  $[Ni^{II}(IMes)_{2}Cl_{2}]$  and a phenyl radical.

Furthermore, the redox potentials of the participating and isolated metal complexes were investigated. The onset oxidation of  $[Ni^{I}(IMes)_{2}CI]$  was found to occur at  $E_{pa} = -0.94$  V (Figure 3 and Figure S5A), which is not sufficient to



**Figure 3.** Comparison of redox potentials of the Ni species,  $K[B_2pin_2(OMe)]$ , MeO-Bpin, and chlorobenzene<sup>22</sup> potentially involved in the photocatalytic C–Cl borylation reaction. Potentials are referenced to the ferrocene/ferrocenium couple. Solvent effects on the redox potentials have not been considered.

reduce chlorobenzene to its corresponding radical anion  $[E_{red}(PhCl/PhCl^{\bullet-}) = -2.78 \text{ V}]$ .<sup>22</sup> Therefore,  $[Ni^{l}(IMes)_{2}Cl]$  is expected to react with chlorobenzene via chlorine atom abstraction to generate a phenyl radical and the  $[Ni^{II}(IMes)_{2}Cl_{2}]$  complex. Light irradiation greatly enhances the efficiency of this reaction achieving almost 100% yield of  $[Ni^{II}(IMes)_{2}Cl_{2}]$ .

 $[Ni^{II}(IMes)_2Cl_2]$  dissolved in degassed hexane has an absorption band at 305 nm and a very weak and broad absorption band between 350 to 600 nm, and its extinction coefficient at 400 nm is only 66 cm<sup>-1</sup> M<sup>-1</sup> (Figure 2A). Although there was no emission detected spectroscopically from  $[Ni^{II}(IMes)_2Cl_2]$  in hexane, we observed that the "solution" appeared to be cloudy under UV irradiation and an orange-red luminescence was observed by eye. This indicates the presence of very fine [Ni<sup>II</sup>(IMes)<sub>2</sub>Cl<sub>2</sub>] particles which did not dissolve in hexane. We therefore recorded the spectroscopic properties of [Ni<sup>II</sup>(IMes)<sub>2</sub>Cl<sub>2</sub>] in the solid state under air<sup>23</sup> at room temperature (Figures 2B and S4). Interestingly, in contrast to the absorption spectra in dilute solution, a broad excitation between 320 and 500 nm is visible with a maximum at 365 nm. A broad solid-state emission with  $\lambda_{\text{max}} = 625 \text{ nm}$  was observed for [Ni<sup>II</sup>(IMes)<sub>2</sub>Cl<sub>2</sub>], which is

absent in solution, probably due to rapid nonradiative decay processes.

We then employed  $[Ni^{II}(IMes)_2Cl_2]$  as a catalyst for the photocatalytic reaction of **19a** with B<sub>2</sub>pin<sub>2</sub>, which resulted in a 75% yield of **19b** and an 11% yield of **19c**, respectively, after 6 h. No reaction was detected without irradiation. *In situ* NMR experiments showed that  $[Ni^{II}(IMes)_2Cl_2]$  is stable under irradiation with 400 nm LEDs for 2 h (Figures S159 and S160) and did not react with **19a**, B<sub>2</sub>pin<sub>2</sub>, or KOMe alone either in the dark or under irradiation at 400 nm (Scheme 4 and Figures

Scheme 4. Control Reactions of  $[Ni^{II}(IMes)_2Cl_2]$  with  $B_2pin_2$ , KOMe, Chlorobenzene, and  $B_2pin_2$ /KOMe, Respectively, without (left) and with (right) Irradiation



S161–S172). Very recently, Doyle et al. reported that a metalto-ligand charge transfer (MLCT) state of  $[Ni(^Rbpy)(Ar)X]$ ( $^Rbpy$  = substituted 2,2'-bipyridine) complexes, generated initially upon excitation, rapidly decays into a long-lived  $^3d-d$ state, which features a weak Ni-aryl bond.<sup>24</sup> This results in excited Ni<sup>II</sup> complexes undergoing Ni–C bond homolysis to generate aryl radicals and Ni<sup>1</sup>. In our case, when  $[Ni^{II}(IMes)_2Cl_2]$  was employed together with  $B_2pin_2$  and KOMe under irradiation for 2 h, the formation of  $[Ni^{I}(IMes)_2Cl]$  and  $[Ni(IMes)_2]$  in 23% and 5% yield, respectively, was observed accompanied by the formation of MeO-Bpin (Scheme 4 and Figures S175 and S176); both reduced Ni compounds were not detected when the reaction was performed in the dark (Scheme 4 and Figures S173 and S174).

Aryl radicals, as key intermediates, should react in our process with the nucleophilic sp<sup>2</sup>-sp<sup>3</sup> diborane anion  $[B_2pin_2(OMe)]^-$  formed from  $B_2pin_2^-$  and  $KOMe^{9h,i}$  to generate the corresponding borylated product and the [Bpin(OMe)]<sup>•-</sup> radical anion.<sup>9a,11a</sup> We collected the <sup>11</sup>B NMR spectra of MeO-Bpin using C<sub>6</sub>D<sub>6</sub>, CD<sub>3</sub>CN, and THF-d<sub>8</sub> as solvent, respectively (Figures S181–S183). No obvious shift was found from the NMR spectra, indicating that MeO-Bpin is stable in these solvents and no adducts are formed. The redox behavior of MeO-Bpin was also investigated. No reduction peak was observed within the electrochemical window of the THF solvent (Figure 3 and Figure S5B), indicating that MeO-Bpin has a very negative reduction potential  $[E_{pc}(MeO-Bpin)]$ < -3.4 V], making [Bpin(OMe)]<sup>•-</sup> a particularly strong reducing agent. [Ni<sup>II</sup>(IMes)<sub>2</sub>Cl<sub>2</sub>] undergoes a reversible oneelectron oxidation and an irreversible one-electron reduction at  $E_{\rm pa}$  = 0.78 V and  $E_{\rm pc}$  = -2.82 V in CH<sub>3</sub>CN and THF solution, respectively (Figure 3 and Figures S5C and S5D). In the solid state,  $[Ni^{II}(IMes)_2Cl_2]$  exhibits a broad emission with  $\lambda_{max} =$ 625 nm; therefore, the oxidation and reduction potentials of excited  $[Ni^{II}(IMes)_2Cl_2]^*$  were calculated to be -1.20 V and  $-0.84 \text{ V} \left[ E(\text{Ni}^{\text{III}}/\text{Ni}^{\text{*II}}) = E(\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}) - E_0 = 0.78 \text{ V} - 1.98 \right]$ 

V = -1.20 V,  $E(Ni^{*II}/Ni^{I}) = E(Ni^{II}/Ni^{I}) + E_0 = -2.82 V + 1.98 V = -0.84 V$ ,  $E_0$  is the emission energy]. Thus, electron transfer would be expected to occur from the reactive  $[Bpin(OMe)]^{\bullet-}$  species, formed by the *in situ* reaction of the aryl radical with  $[B_2pin_2(OMe)]^{-,9a,11a}$  to the excited  $[Ni^{II}(IMes)_2Cl_2]^* [E(Ni^{*II}/Ni^{I}) = -0.84 V]$  under irradiation, reducing it to  $[Ni^{I}(IMes)_2Cl]$  and then  $[Ni(IMes)_2]$ .

In light of these findings, a plausible mechanism for the borylation of chloroarenes under irradiation is shown in Scheme 5.  $[Ni(IMes)_2]$  undergoes very fast chlorine atom

Scheme 5. Plausible Mechanism for the Photoinduced Borylation of Aryl Chlorides by Transformations between Ni Species in the 0, I, and II Oxidation States



abstraction from aryl chlorides to give  $[Ni^{l}(IMes)_{2}Cl]$  and aryl radicals. Under further irradiation,  $[Ni^{l}(IMes)_{2}Cl]$  reacts with aryl chlorides to form  $[Ni^{II}(IMes)_{2}Cl_{2}]$  and another aryl radical. The reaction of the generated aryl radicals with nucleophilic  $[B_{2}pin_{2}(OMe)]^{-}$  yields the final borylated product and the  $[Bpin(OMe)]^{\bullet-}$  radical anion.  $[Bpin(OMe)]^{\bullet-}$  is a strong reducing agent, capable of converting  $[Ni^{II}(IMes)_{2}Cl_{2}]$  to  $[Ni^{II}(IMes)_{2}Cl]$  and  $[Ni(IMes)_{2}]$ .

## CONCLUSIONS

In conclusion, we have developed an efficient photocatalytic procedure for the C-Cl borylation of chloroarenes using  $[Ni(IMes)_2]$  as a catalyst operating with visible light. The reaction proceeds under mild conditions, displays broad scope and functional group tolerance, and furnishes arylboronates in good to excellent yields. Our investigations of the mechanism suggest that abstraction of a chlorine atom from an aryl chloride by  $[Ni(IMes)_2]$  is facile at room temperature, forming an aryl radical and [Ni<sup>I</sup>(IMes)<sub>2</sub>Cl]. Aided by light, a similar process is expected to occur for [Ni<sup>I</sup>(IMes)<sub>2</sub>Cl] producing additional aryl radicals and [Ni<sup>II</sup>(IMes)<sub>2</sub>Cl<sub>2</sub>]. The aryl radicals are believed to react with nucleophilic  $[B_2pin_2(OMe)]^-$  to form the final borylation product and the [Bpin(OMe)]. radical anion, which in turn reduces [Ni<sup>II</sup>(IMes)<sub>2</sub>Cl<sub>2</sub>] to regenerate [Ni<sup>I</sup>(IMes)<sub>2</sub>Cl] and [Ni(IMes)<sub>2</sub>] for the next catalytic cycle.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c08834.

Details of synthetic methods, characterization (GC-MS, NMR and HRMS data) of products, and investigations of the reaction mechanism (PDF)

Crystallographic data for [Ni<sup>I</sup>(IMes)<sub>2</sub>Cl] (CIF)

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#### Notes

The authors declare no competing financial interest.

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# DEDICATION

Dedicated to Prof. Pierre H. Dixneuf in recognition of his outstanding contributions to organometallic chemistry and catalysis.

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