# ORGANOMETALLICS

# N-Heterocyclic Carbene Bound Nickel(I) Complexes and Their Roles in Catalysis

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Supporting Information

**ABSTRACT:** The new paramagnetic complexes Ni<sup>I</sup>(IMes)<sub>2</sub>X (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) were prepared from the reaction of Ni(IMes)<sub>2</sub> with aryl halides. Products that would arise from oxidative addition were not observed. In contrast, Ni<sup>II</sup>(tmiy)<sub>2</sub>(X)(Ar) complexes were formed from the oxidative addition of aryl halides to Ni bound by a sterically less hindered NHC ligand, tmiy (tetra-methylimidazol-2-ylidene). The paramagnetic Ni<sup>I</sup>(IMes)<sub>2</sub>X complexes were compared to known Ni(0) and Ni(II) catalysts for Kumada and Suzuki coupling reactions. Stochometric



reactions between the  $Ni^{I}(IMes)_{2}X$  complexes with any halides and transmetalating agents were also evaluated.

#### INTRODUCTION

Cross-coupling chemistry is one of the premiere methods for constructing new carbon—carbon bonds.<sup>1</sup> Although Pd catalysts dominate this field,<sup>2</sup> a recent surge of interest has been devoted to the discovery of efficient Ni-based catalysts.<sup>3–10</sup> In both fields, NHC ligands have fostered significant advances.<sup>11</sup> In general, it is believed that Ni catalysts follow the same overall mechanism as Pd-based systems. That is, oxidative addition from Ni(0) to Ni(II) initiates cross-coupling chemistry. Although much research has been done elaborating the details of the mechanism of oxidative addition to Pd(0) complexes, far less is understood about oxidative addition to Ni(0) complexes. This is especially true for Ni(0) complexes that are bound by the newer, more effective N-heterocyclic carbene (NHC) ligands. The formation of a (NHC)<sub>n</sub>Ni<sup>II</sup>(Ar)X species has been presumed, yet only two examples of this reaction actually exist.<sup>12</sup> Herein we report our findings that the reaction of Ni(NHC)<sub>n</sub> with aryl halides predominately forms Ni<sup>I</sup>(NHC)<sub>n</sub>X complexes.<sup>13,14</sup>

#### RESULTS AND DISCUSSION

**Formation of Ni(I) Complexes.** The reaction of iodobenzene with Ni(IMes)<sub>2</sub> (1)<sup>15</sup> in THF proceeded smoothly at room temperature to give a yellow-brown solid in 77% yield. X-ray analysis revealed that the product was Ni(IMes)<sub>2</sub>I (2) rather than the expected (IMes)<sub>2</sub>Ni(Ph)I (Scheme 1). Given the propensity for radical chemistry of iodide-containing complexes,<sup>16</sup> we turned our focus toward the reaction of bromobenzene and chlorobenzene. Surprisingly, both reactions behaved analogously to that of iodobenzene. Namely, Ni(IMes)<sub>2</sub>Br (3) and Ni-(IMes)<sub>2</sub>Cl (4) were formed in 80% and 77% yields, respectively (Scheme 1).<sup>17</sup> Benzene was formed quantitatively in all three reactions, as determined by GC-MS analysis. Single crystals of

Scheme 1. Formation of Ni<sup>I</sup>(IMes)<sub>2</sub>X Complexes



**2**–4 were grown and evaluated by X-ray analysis (Figures 1–3). The bond lengths between Ni and the C(1) carbon of the NHC ligand are 1.924, 1.929, and 1.922 Å, respectively, in complexes **2**–**4**. These bond lengths are in the same range as found in other Ni/NHC complexes.<sup>18</sup> Each of the Ni(I) complexes possess a distorted T-shaped geometry. For example, the C(1)–Ni–C-(22) bond angles are 168.26, 166.46, and 166.47°, respectively, in complexes **2**–**4**.

In addition to X-ray analysis, <sup>1</sup>H NMR and EPR studies further supported the formation of paramagnetic Ni(I) species. Broad but distinct <sup>1</sup>H NMR signals with the appropriate integration were observed. In addition, EPR analysis of **2** gave a *g* value of 2.22,<sup>19</sup> which indicates the existence of an unpaired spin. Finally, further corroboration was obtained from synthesizing authentic samples of **3** and **4** through the comproportionation reaction between Ni-(IMes)<sub>2</sub> (**1**) and Ni(IMes)<sub>2</sub>X<sub>2</sub> (X = Br (**5**), Cl (**6**); Scheme 1).<sup>20</sup>

In an effort to determine whether  $(IMes)_2Ni^{II}(Ar)X$  complexes could be made in an alternative fashion, the reactions of

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Figure 1. ORTEP diagram of the molecular structure of  $Ni(IMes)_2(I)$ (2). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)-C(1) = 1.924(3), Ni(1)-C(22) = 1.923(3), Ni(1)-I(1) = 2.6084(4); C(1)-Ni(1)-I(1) = 96.74(8), C(22)-Ni(1)-I(1) = 94.97(8), C(1)-Ni(1)-C(22) = 168.26(12).



Figure 2. ORTEP diagram of the molecular structure of Ni(IMes)<sub>2</sub>-(Br) (3). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)-C(1) = 1.913(4), Ni(1)-C(22) = 1.929(4), Ni(1)-Br(1) = 2.4428(6); C(1)-Ni(1)-Br(1) = 95.94(12), C(22)-Ni(1)-Br(1) = 97.58(11), C(1)-Ni(1)-C(22) = 166.46(16).

Ni(PPh<sub>3</sub>)<sub>2</sub>(Ar)(X)<sup>21</sup> with IMes were evaluated (Scheme 2). Nickel phosphine complexes possessing a variety of aryl groups (C<sub>6</sub>H<sub>4</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>, and *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) were prepared and subjected to IMes at room temperature in C<sub>6</sub>D<sub>6</sub>. Again, Ni(II) complexes, such as (IMes)<sub>2</sub>Ni(Ar)(Br), were not observed. Instead, Ni(IMes)<sub>2</sub>X (**3**, **4**) was formed immediately after the addition of IMes regardless of whether an electron-rich or an electron-poor aryl group was used (i.e., Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ph, *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; Scheme 2).

Given the discrepancy between the products we observe and the oxidative addition product prepared by McGuiness and Cavell,<sup>12a</sup> the oxidative addition of unhindered aryl halides was also evaluated with tetramethylimidazol-2-ylidene (tmiy). When Ni(COD)<sub>2</sub> was subjected to *p*-bromoanisole and then tmiy, (tmiy)<sub>2</sub>Ni(*p*-MeOC<sub>6</sub>H<sub>4</sub>)(Br) (7) was isolated (47% yield, eq 1). Furthermore, Ni(II) aryl halide complexes (**8**, **9**) were obtained from both electron-neutral and electron-poor aryl halides (52%



Figure 3. ORTEP diagram of the molecular structure of Ni(IMes)<sub>2</sub>(Cl) (4). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)-C(1) = 1.911(2), Ni(1)-C(22) = 1.922(2), Ni(1)-Cl(1A) = 2.192(9); C(1)-Ni(1)-Cl(1A) = 83.8(3), C(22)-Ni(1)-Br(1A) = 82.7(3), C(1)-Ni(1)-C(22) = 166.47(10).

Scheme 2. Ligand Displacement of PPh<sub>3</sub> by IMes



and 40% yields, respectively). Thus, formation of Ni(I) halides appear to be a distinct feature of Ni complexes bound by sterically hindered NHC ligands (such as IMes and IPr).<sup>13</sup>



**Cross-Coupling Chemistry.** Ni<sup>1</sup>(IMes)<sub>2</sub>X complexes 3 and 4 were evaluated as potential cross-coupling catalysts and compared to the conventional catalysts Ni(IMes)<sub>2</sub> and Ni-(IMes)<sub>2</sub>X<sub>2</sub><sup>11a</sup> for Kumada and Suzuki cross-coupling reactions (eqs 2 and 3, Tables 1 and 2). Specifically, chlorobenzene and mesitylmagnesium bromide were subjected to 3 mol % Ni catalyst and allowed to react at room temperature for 20 h (eq 2, Table 1). When reactions were run in THF, all Ni complexes displayed similar catalytic activity (Table 1, entries 1–4). The biaryl product was obtained in good yields (73–79%)

 Table 1. Ni-Catalyzed Kumada Cross-Coupling Reactions<sup>a</sup>

×	MgBr + <u>3 mol %</u> r.t	Ni cat		(2)
entry	Ni cat.	Х	solvent	yield $(\%)^b$
1	$Ni^{0}(IMes)_{2}(1)$	Cl	THF	73
2	Ni <sup>I</sup> (IMes) <sub>2</sub> Br (3)	Cl	THF	73
3	Ni <sup>I</sup> (IMes) <sub>2</sub> CI (4)	Cl	THF	77
4	$Ni^{II}(IMes)_2Br_2$ (5)	Cl	THF	79
5	$Ni^{0}(IMes)_{2}(1)$	Cl	$C_6H_6$	54
6	Ni <sup>I</sup> (IMes) <sub>2</sub> Br (3)	Cl	$C_6H_6$	64
7	$Ni^{II}(IMes)_2Br_2$ (5)	Cl	$C_6H_6$	25
8	Ni <sup>I</sup> (IMes) <sub>2</sub> Br (3)	Br	$C_6H_6$	82
a				

 $^a$  Reaction conditions: 0.25 M PhCl, 0.375 M MesMgBr, 3 mol % Ni catalyst, room temperature, 20 h.  $^b$  Isolated yields (average of two runs).

Table 2. Ni-Catalyzed Suzuki Cross-Coupling Reactions<sup>a</sup>



<sup>*a*</sup> Reaction conditions: 0.15 M ArBr, 0.165 M PhB(OH)<sub>2</sub>, 0.45 M KO-*t*-Bu in benzene, 10 mol % Ni catalyst, 80 °C, 4 h. <sup>*b*</sup> Isolated yields (average of two runs).

when traditional Ni(0) and Ni(II) catalysts were employed (entries 1 and 4). Surprisingly, both Ni(I) complexes (3 and 4) catalyzed the Kumada cross-coupling reaction and afforded the biaryl product with identical yields (73-77%, entries 2 and 3). A cursory investigation on the rates of these cross-couplings suggested that reaction rates were similar regardless of which Ni catalyst (i.e., Ni(0), Ni(I), or Ni(II)) was used. Furthermore, no induction time was observed in any of the cross-coupling reactions. When the same reactions were run in benzene instead of THF, the biaryl product was still formed, but in diminished yields (entries 5-8). In fact, low yields were observed when  $Ni^{II}(IMes)_2Br_2$  (5) was used as the catalyst, which is presumably due to the low solubility of 5 in benzene (entry 7). Not surprisingly, the  $Ni^{1}(IMes)_{2}Br(3)$ -catalyzed Kumada coupling of bromobenzene successfully afforded the biaryl product in higher yield (entry 8).

The Suzuki cross-coupling reaction between aryl bromides and phenylboronic acid was also investigated (eq 3, Table 2). Again, Ni(0), Ni(I), and Ni(II) complexes were all used as catalysts (10 mol %) and the yields of biaryl product were compared. As was observed in the Kumada cross-coupling reactions, all of the Ni species, regardless of oxidation state, afforded the biaryl product in comparable yields. Interestingly, yields were better when an electron-rich aryl halide was used as the starting material (i.e., the biaryl product was formed in 72-75% yield) than when an electron-poor aryl halide was used as the starting material (i.e., the biaryl product was formed in 52-66% yield). We found that the bromo analogue of the Ni(I) complex, Ni<sup>I</sup>(IMes)<sub>2</sub>Br (3), was more effective in catalyzing the Suzuki coupling than its chloro counterpart Ni<sup>I</sup>(IMes)<sub>2</sub>Cl (4) (entry 2 vs entry 3).

Stoichiometric Reactions of Ni<sup>I</sup>(IMes)<sub>2</sub>X. Stoichiometric reactions between Ni<sup>I</sup>(IMes)<sub>2</sub>X and cross-coupling reagents were also evaluated. First, the reaction with aryl halides was evaluated.<sup>22</sup> When 1 equiv of either bromobenzene or chlorobenzene was added to Ni<sup>I</sup>(IMes)<sub>2</sub>Br (3) at room temperature, no reaction occurred even after prolonged periods of time (eqs 4–6). Similarly, no reaction occurred between aryl halides bearing either an electron-donating group (*p*-bromoanisole) or an electron-withdrawing group (*p*-bromobenzotrifluoride) and Ni<sup>I</sup>(IMes)<sub>2</sub>Br (3) at 80 °C. In fact, only decomposition of Ni<sup>I</sup>(IMes)<sub>2</sub>Br (3) was observed in less than 20 min; the aryl halide remained unchanged.

Ni<sup>l</sup>(IMes)<sub>2</sub>Br + PhBr 
$$\xrightarrow{\times}$$
 No reaction (4)  
3 RT, 24 h

Ni<sup>l</sup>(IMes)<sub>2</sub>Br + PhCl 
$$\longrightarrow$$
 No reaction (5)  
3 RT, 12 h

Ni<sup>l</sup>(IMes)<sub>2</sub>Br + R 
$$\longrightarrow$$
 Br  $\longrightarrow$  Decomposition (6)  
3 R = p-OMe  
or  
B = p-CE<sub>2</sub>

The reactions with transmetalating agents such as mesitylmagnesium bromide and phenylboronic acid were also evaluated (eqs 7-10). In contrast to the reactions with aryl halides described above,  $Ni^{1}(IMes)_{2}Br(3)$  reacts with both the Grignard reagent and the boronic acid. When  $Ni^{I}(IMes)_{2}Br(3)$  was treated with 1 equiv of mesitylmagnesium bromide in C<sub>6</sub>D<sub>6</sub>, an immediate color change from yellow to dark brown was observed. Mesitylene was generated quantitatively, as determined by <sup>1</sup>H NMR analysis (eq 7). Unfortunately, the corresponding Ni product was unidentifiable. When the reaction was run in THF $d_8$  instead, mesitylene-d was observed by GC-MS analysis. Interestingly, when the same reaction was run with Ni<sup>II</sup>-(IMes)<sub>2</sub>Br<sub>2</sub> (5) instead, the <sup>1</sup>H NMR spectrum showed untouched  $Ni^{II}(IMes)_2Br_2(5)$  in addition to mesitylene (eq 8). It is possible that trace amounts of Ni<sup>I</sup>(IMes)<sub>2</sub>Br (3) catalyze the formation of mesityl radical, which then abstracts a proton from the solvent.<sup>23</sup> For instance, when the reaction was run in THF- $d_{8}$ , mesitylene-d was again formed. When  $Ni^{I}(IMes)_{2}Br$  (3) was subjected to 1 equiv of phenylboronic acid,  $Ni^{II}(IMes)_2Br_2$  (5) was formed in 49% yield by <sup>1</sup>H NMR (eq 9).<sup>24</sup> In addition, biphenyl was formed in less than 5 min in  $\sim$ 30% yield. The yield of biphenyl increased dramatically when 5 equiv of KO-t-Bu was added (eq 10). Taken together, the data suggest transmetalation occurs to give an unstable Ni<sup>1</sup>(IMes)<sub>2</sub>Ph species that may be



susceptible to phenyl radical formation. The phenyl radicals combine to form the observed biphenyl product.

Most cross-coupling chemistry follows an overall mechanism that includes oxidative addition of the aryl halide to the transition-metal center, transmetalation between the metal halide and main-group reagent, and reductive elimination of the product (Scheme 3).<sup>25</sup> Interestingly, our results suggest that this general mechanism may not be applicable to Ni-based cross-coupling systems when large NHC ligands are employed. The reaction of aryl halides and Ni(NHC)<sub>n</sub> complexes affords Ni<sup>1</sup>(NHC)<sub>n</sub>X complexes rather than the expected Ni aryl halides required for mechanism A. Furthermore, alternative routes, such as ligand exchange reactions, do not lead to isolable Ni aryl halide complexes. Again,  $Ni^{1}(NHC)_{n}X$  complexes are obtained. Although it is possible that oxidative addition occurs and yields an aryl halide complex that is simply too reactive to isolate,<sup>26</sup> it seems plausible that cross-coupling reactions that are mediated by Ni may involve a radical type mechanism.<sup>27</sup>

An alternative mechanism that invokes both the formation of a Ni<sup>I</sup> species as well as initial oxidative addition is shown in Scheme 4. After oxidation of the Ni<sup>0</sup> species by the aryl halide to Ni<sup>I</sup>, oxidative addition of the aryl halide occurs to afford a Ni<sup>III</sup> species bearing one aryl ligand and two halide ligands.<sup>28</sup> Transmetalation and reductive elimination completes the cycle. Although oxidative addition of aryl halides to Ni<sup>I</sup> complexes are known,<sup>20,29</sup> Ni<sup>I</sup>(IMes)<sub>2</sub>X complexes **3** and **4** appear to be unreactive toward aryl halides even under forcing conditions. In

## Scheme 4. Proposed Mechanism B



Scheme 5. Proposed Mechanism C



fact, decomposition of Ni<sup>1</sup>(IMes)<sub>2</sub>X (3, 4) occurs faster than any reaction with an aryl halide. Thus, it is unlikely that oxidative addition of an aryl halide to Ni<sup>1</sup>(NHC)<sub>n</sub>X to form Ni<sup>III</sup>(NHC)<sub>n</sub>-(Ar)(X)<sub>2</sub> would ultimately lead to the formation of a cross-coupled biaryl product.

A mechanism consistent with our data that involves an initial reaction between Ni<sup>I</sup>(IMes)<sub>2</sub>X and the transmetalating agent is shown in Scheme 5. Transmetalation would afford a Ni<sup>I</sup>-(IMes)<sub>n</sub>Ar species capable of reacting with the aryl halide. Similar transmetalation reactions have been observed when organozinc reagents were added to Ni<sup>I</sup> complexes bound by terpy ligands.<sup>30</sup> After oxidative addition of the aryl halide to form Ni<sup>III</sup>(IMes)<sub>n</sub>-(X)(Ar)(Ar') occurs, facile reductive elimination of the Ar-Ar' product regenerates a Ni<sup>I</sup>(IMes)<sub>n</sub>X catalyst.<sup>14a,31</sup>

In conclusion, we have demonstrated that a series of paramagnetic Ni<sup>1</sup>(IMes)<sub>2</sub>X species can be synthesized when Ni-(IMes)<sub>2</sub> is treated with aryl halides. Oxidative addition products, Ni<sup>II</sup>(IMes)<sub>n</sub>(Ar)(X), are not observed in these cases. In contrast, the use of smaller NHCs such as timy affords the expected square-planar oxidative addition product. The Ni<sup>1</sup>-(IMes)<sub>2</sub>X complexes effectively catalyze Kumada and Suzuki coupling reactions. Stoichiometric reactions between the catalysts and the cross-coupling partners suggests that cross-coupling reactions are initiated by a transmetalation reaction between Ni<sup>1</sup>(NHC)<sub>n</sub>X and the transmetalating reagent. Further mechanistic investigations are currently underway.

#### EXPERIMENTAL SECTION

**General Information.** All experiments were carried out in a dry, oxygen-free nitrogen atmosphere glovebox. Solvents were dried, distilled, and degassed prior to use. Ni(COD)<sub>2</sub> was purchased from Strem and used without further purification. The N-heterocyclic carbenes IMes

prepared using literature procedures.<sup>21</sup> The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian VXL-300 spectrometer, an Inova-400 spectrometer, or a Varian VXR-500 spectrometer and referenced to residual protiated solvent. All <sup>13</sup>C NMR spectra were proton-decoupled. MS analyses were performed at the University of Utah Mass Spectrometry facility. The X-ray crystal structure data were collected by Dr. Atta Arif at the Department of Chemistry of the University of Utah.

Bis(1,3-dimesityl-1*H*-imidazol-2(3*H*)-ylidene)nickel(I) lodide (2). In a dry glovebox, Ni<sup>0</sup>(IMes)<sub>2</sub> (10.0 mg, 0.0150 mmol) was weighed directly into a scintillation vial equipped with a magnetic stir bar, and a solution of iodobenzene (3.1 mg, 0.015 mmol, 0.0075 M) in THF (2.0 mL) was added into the scintillation vial. The reaction mixture was stirred at room temperature for 5 min. The color changed from black to orange once iodobenzene was added. The solvent was removed under vacuum to yield the crude product (9.5 mg, 77%). Recrystallization by slow diffusion of hexane into a saturated THF solution of 2 at room temperature gave 2 as a red crystalline solid. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  8.44–8.70 (br s, 8H), 6.14–6.31 (br s, 4H), 3.54–3.73 (br s, 12H), 0.95–1.80 (br s, 24H). <sup>13</sup>C NMR (75 MHz, C6D6, ppm):  $\delta$  190.6, 154.5, 150.9, 140.8, 139.8, 94.6, 23.1. HRMS (FT-ESI): *m*/z calcd for C<sub>42</sub>H<sub>48</sub>IN<sub>4</sub>Ni [M]<sup>+</sup> 793.2272, found 793.2273.

Bis(1,3-dimesityl-1*H*-imidazol-2(3*H*)-ylidene)nickel(I) Bromide (3). In a dry glovebox, Ni<sup>0</sup>(IMes)<sub>2</sub> (10.0 mg, 0.0150 mmol) was weighed directly into a scintillation vial equipped with a magnetic stir bar, and a solution of bromobenzene (2.4 mg, 0.015 mmol, 0.0075 M) in THF (2.0 mL) was added into the scintillation vial. The reaction mixture was stirred at room temperature for 5 min. The color changed from black to orange once bromobenzene was added. The solvent was removed under vacuum to yield the crude product (9.0 mg, 80%). Recrystallization by slow diffusion of hexane into a saturated THF solution of 3 at room temperature gave the title compound as a red solid. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  9.06–9.24 (br s, 4H), 8.30–8.60 (br s, 8H), 3.29–3.50 (br s, 12H), 1.00–1.75 (br s, 24H). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  159.2, 147.2, 139.5, 138.3, 67.1, 23.5 (the NHC carbon directly connecting with Ni was not observed, due to the decomposition of 3). HRMS (FT-ESI): *m*/z calcd for C<sub>42</sub>H<sub>48</sub>BrN<sub>4</sub>Ni [M]<sup>+</sup> 745.2410, found 745.2407.

Bis(1,3-dimesityl-1H-imidazol-2(3H)-ylidene)nickel(I) **Chloride (4).** In a dry glovebox,  $Ni^0(IMes)_2$  (10.0 mg, 0.0150 mmol) was weighed directly into a scintillation vial equipped with a magnetic stir bar, and a solution of chlorobenzene (1.7 mg, 0.015 mmol, 0.0075 M) in THF (2.0 mL) was added into the scintillation vial. The reaction mixture was stirred at room temperature for 5 min. The color changed from black to dark red once chlorobenzene was added. The solvent was removed under vacuum to give the crude product (8.1 mg, 77%). Recrystallization by slow diffusion of hexane into a saturated THF solution of 4 at room temperature gave the title compound as a red solid. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 11.04–11.28 (br s, 4H), 8.30–8.58 (br s, 8H), 3.16–3.46 (br s, 12H), 1.15–2.15 (br s, 24H).  $^{13}\mathrm{C}$  NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 163.5, 144.2, 138.8, 137.6, 50.7, 23.7 (the NHC carbon directly connecting with Ni was not observed due to the decomposition of 4). HRMS (FT-ESI): m/z calcd for C42H48ClN4Ni [M]<sup>+</sup> 701.2916, found 701.2913.

**Comproportionation Reactions.** Bis(1,3-dimesityl-1H-imidazol-2(3H)-ylidene)nickel(1) Bromide (**3**). Ni<sup>0</sup>(IMes)<sub>2</sub> (10.0 mg, 0.0150 mmol) was weighed directly into a scintillation vial equipped with a magnetic stir bar, and a solution of Ni<sup>II</sup>(IMes)<sub>2</sub>Br<sub>2</sub> (12.5 mg, 0.0150 mmol) in THF (2.0 mL) was added. The reaction mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum to afford the product**3**as a red solid: yield 10.2 mg (91%). Bis(1,3-dimesityl-1H-imidazol-2(3H)-ylidene)nickel(1) Chloride (**4**). Ni<sup>0</sup>(IMes)<sub>2</sub> (10.0 mg, 0.0150 mmol) was weighed directly into a scintillation vial equipped with a magnetic stir bar, and a solution of Ni<sup>II</sup>(IMes)<sub>2</sub>Cl<sub>2</sub> (10.5 mg, 0.0150 mmol) in THF (2.0 mL) was added. The reaction mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum to afford the product **3** as a red solid: yield 9.5 mg (90%).

(4-Methoxyphenyl)bis(2,3,4,5-tetramethylcyclopent-3-en-1-ylidene)nickel(II) Bromide (7). In a dry glovebox, to a solution of  $Ni(COD)_2$ (10.0 mg, 0.0364 mmol, 0.0364 M) in THF (1 mL) was added a solution of p-bromoanisole (6.8 mg, 0.036 mmol, 0.036 M) in THF (1 mL) at room temperature. The reaction mixture was stirred at room temperature for 10 min. Then a solution of tetramethylimidazol-2-ylidine (tmiy; 9.0 mg, 0.073 mmol, 0.078 M) in THF (1 mL) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 30 min. THF was then removed by vacuum. Hexane (6 mL) was added to the mixture to form a brown precipitate. The solvent was pipetted out of the reaction mixture. The brown precipitate was collected and dried under vacuum to yield product 6 (7.8 mg, 47%) as a brown solid. <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ , ppm):  $\delta$  7.37 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 4.06 (s, 12H), 3.29 (s, 3H), 1.29 (s, 12H). <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ , ppm):  $\delta$  7.20 (d, J = 8.6 Hz, 2H), 6.40 (d, J = 8.6 Hz, 2H), 4.20 (s, 12H), 3.58 (s, 3H), 2.02 (s, 12H). <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 184.7, 155.9, 145.8, 137.2, 123.5, 112.6, 54.4, 34.3, 8.05. MS (ESI): m/z 413.2,  $[M - Br]^+$ .

Bis(2,3,4,5-tetramethylcyclopent-3-en-1-ylidene)(p-tolyl)nickel(II) Bromide (8). In a dry glovebox, to a solution of  $Ni(COD)_2$  (10.0 mg, 0.0364 mmol, 0.0364 M) in THF (1 mL) was added a solution of p-bromotoluene (6.2 mg, 0.036 mmol, 0.036 M) in THF (1 mL) at room temperature. The reaction mixture was stirred at room temperature for 10 min. A solution of tetramethylimidazol-2-ylidine (tmiy; 9.0 mg, 0.073 mmol, 0.073 M) in THF (1 mL) was then added to the reaction mixture. The reaction mixture was stirred at room temperature for 30 min. THF was then removed by vacuum. Hexane (6 mL) was added to the reaction mixture to form a yellow precipitate. The solvent was pipetted out of the reaction mixture. The yellow precipitate was collected and dried under vacuum to yield product 7 (8.5 mg, 52%) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  7.30 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 8.5 Hz, 2H), 4.22 (s, 12H), 2.06 (s, 3H), 2.01 (s, 12H). <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 182.7, 153.9, 136.0, 129.1, 126.8, 124.4, 34.5, 20.4, 8.8. HRMS (ESI): m/z calcd for  $C_{21}H_{31}N_4NiNa$ [M+Na]<sup>+</sup> 499.0992, found 499.0983.

Bis(2,3,4,5-tetramethylcyclopent-3-en-1-ylidene)(4-(trifluoromethyl)phenyl)nickel(II) Bromide (9). In a dry glovebox, to a solution of Ni(COD)<sub>2</sub> (10.0 mg, 0.0364 mmol, 0.0364 M) in THF (1 mL) was added a solution of p-bromobenzotrifluoride (8.2 mg, 0.036 mmol, 0.036 M) in THF (1 mL) at room temperature. The reaction mixture was stirred at room temperature for 10 min. A solution of tetramethylimidazol-2-ylidine (tmiy) (9.0 mg, 0.073 mmol, 0.073 M) in THF (1 mL) was then added to the reaction mixture. The reaction mixture was stirred at room temperature for 30 min. THF was then removed by vacuum. Hexane (6 mL) was added to the reaction mixture to form a dark yellow precipitate. The solvent was pipetted out of the reaction mixture. The yellow precipitate was collected and dried under vacuum to yield product 8 (7.8 mg, 40%) as a yellow solid. <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ , ppm):  $\delta$  7.61 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 7.5 Hz, 2H), 4.21 (s, 12H), 2.06 (s, 3H), 2.01 (s, 12H). <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 180.9, 169.9, 136.3, 124.7, 126.8, 34.6, 8.8. MS (ESI): m/z  $451.1, [M - Br]^+$ .

General Procedure of Kumada Coupling. Chlorobenzene (37.1 mg, 0.330 mmol) and mesitylmagnesium bromide (0.50 mmol, 0.50 mL, 1.0 M in diethyl ether) were weighed into a scintillation vial equipped with a magnetic stir bar. A solution of the Ni catalyst (0.01 mmol, 0.005 M) in THF (0.5 mL) or benzene (0.5 mL) was added.

The reaction mixture was stirred at room temperature for 20 h. The solvent was removed under vacuum. Purification by flash column chromatography column yielded biaryl product. The NMR data of the product matched those of the literature report.<sup>34</sup>

**General Procedure of Suzuki Coupling.** *p*-Bromoanisole (18.7 mg, 0.100 mmol) and phenylboronic acid (13.4 mg, 0.110 mmol) were weighed into a scintillation vial equipped with a magnetic stir bar. A solution of the Ni catalyst (0.01 mmol, 0.007 M) in benzene (0.67 mL) was added. The reaction mixture was stirred at 80 °C for 8 h. The solvent was removed under vacuum. Purification by flash column chromatography yielded biaryl product. The NMR data of the product matched those of the literature report.<sup>35</sup>

General Procedure for Stoichiometric Reaction of Ni(I) Complex with Aryl Halide. In a glovebox, stock solution 1 was prepared by dissolution of Ni<sup>1</sup>(IMes)<sub>2</sub>Br (40.0 mg, 0.0535 mmol, 0.0535 M) and ferrocene (10.0 mg, 0.0535 mmol, 0.0535 M) in  $C_6D_6$  (1 mL) in a 5 mL glass vial. Stock solution 2 was prepared by dissolution of aryl halide (0.054 mmol, 0.054 M) in  $C_6D_6$  (1 mL) in a 5 mL glass vial. A 0.25 mL portion of stock solution 1 and 0.25 mL of stock solution 2 were added into an NMR tube. The NMR tube was equipped with a screwthread cap with a PTFE/silicone septum and taken out of the glovebox. The NMR spectra were obtained every 1 h.

General Procedure for Stoichiometric Reaction of Ni Complexes with Aryl Grignard Reagent. In a glovebox, stock solution 1 was prepared by dissolution of Ni<sup>I</sup>(IMes)<sub>2</sub>Br (40.0 mg, 0.0535 mmol, 0.0535 M) and ferrocene (10.0 mg, 0.0535 mmol, 0.0535 M) in  $C_6D_6$  (1 mL) in a 5 mL glass vial. Stock solution 2 was prepared by adding a mesitylmagnesium bromide solution (0.0535 mmol, 0.0535 mL, 1.0 M in diethyl ether) in  $C_6D_6$  (1 mL) into a 5 mL glass vial. A 0.25 mL portion of stock solution 1 and 0.25 mL of stock solution 2 were added into an NMR tube. The NMR tube was equipped with a screw-thread cap with a PTFE/silicone septum and taken out of the glovebox. The NMR spectrum was obtained immediately.

Stoichiometric Reaction of Ni(I) Complex with Phenylboronic Acid without KO-t-Bu. In a glovebox, stock solution 1 was prepared by dissolution of Ni<sup>I</sup>(IMes)<sub>2</sub>Br (40.0 mg, 0.0535 mmol, 0.0535 M) and ferrocene (10.0 mg, 0.0535 mmol, 0.0535 M) in C<sub>6</sub>D<sub>6</sub> (1 mL) in a 5 mL glass vial. Stock solution 2 was prepared by dissolution of phenylboronic acid (6.5 mg, 0.054 mmol, 0.054 M) in C<sub>6</sub>D<sub>6</sub> (1 mL) in a 5 mL glass vial. A 0.25 mL portion of stock solution 1 and 0.25 mL of stock solution 2 were added into an NMR tube. The NMR tube was equipped with a screw-thread cap with a PTFE/silicone septum and taken out of the glovebox. The NMR spectrum was obtained immediately.

Stoichiometric Reaction of Ni Complex with Phenylboronic Acid with KO-t-Bu. In a glovebox, stock solution 1 was prepared by dissolution of Ni<sup>I</sup>(IMes)<sub>2</sub>Br (40.0 mg, 0.0535 mmol, 0.0535 M) and ferrocene (10.0 mg, 0.0535 mmol, 0.0535 M) in  $C_6D_6$  (1 mL) in a 5 mL glass vial. Stock solution 2 was prepared by dissolution of phenylboronic acid (6.5 mg, 0.054 mmol, 0.054 M) and KO-t-Bu (29.9 mg, 0.267 mmol, 0.267 M) in  $C_6D_6$  (1 mL) in a 5 mL glass vial. A 0.25 mL portion of stock solution 1 and 0.25 mL of stock solution 2 were added into an NMR tube. The NMR tube was equipped with a screw-thread cap with a PTFE/silicone septum and taken out of the glovebox. The NMR spectrum was obtained immediately.

## ASSOCIATED CONTENT

**Supporting Information.** Figures giving EPR spectra for compounds 2–4 and CIF files, tables, and figures giving crystallographic data and structural details for 2–4, 7, and 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on Apr 1, 2011, with errors in the labels in Scheme 1. The corrected version was reposted on Apr 8, 2011.