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Synthesis and structural characterization of nickel(II) complexes of 20-membered macrocyclic rings bearing chelating bis(*N*-heterocyclic carbene) ligands

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ABSTRACT

20-Membered macrocyclic rings (L_{benz} and L_{imid}) containing two amine moieties and two *N*-heterocyclic carbene (NHC) moieties coordinate in a κ^2 coordination mode to Ni(II) through the NHC moieties. Complexes **3a** and **3b** were synthesized by generating free carbenes *in situ* from bis-benzimidazolium bromide salts and subsequent addition of one equivalent of [Ni(DME)X_2] (X = Cl, Br) at 25 °C. Free carbenes of 20-membered macrocyclic ligands L_{benz} and L_{imid} can be generated *in situ* in THF-d_8 and characterized by ^{1}H and ^{13}C NMR spectroscopy. **3b** can also be synthesized by treatment of silver(I)-bis(NHC) complex **2a** with one equivalent of [$NiBr_2$(DME)] in refluxing methylene chloride for 20 h affording yields of up to70%. Complexes **3a** and **3b** were characterized by X-ray diffraction. [$NiI_2(L_{benz})$] **5c** was prepared by halogen exchange of **3a** or **3b** with NaI at 25 °C. Ni complexes of L_{imid} can be prepared and characterized *in situ* but cannot be isolated cleanly from the reaction mixtures. The cis and trans isomers of [$NiCl_2(L_{imid})$] (**4a** and **4b**) and the bromide derivative **4c** were characterized by X-ray crystallography by judicious selection of individual, high-quality crystals obtained from crude reaction mixtures.

1. Introduction

N-Heterocyclic carbenes (NHCs) are an important class of ligands that have been used widely in homogeneous catalysis since isolation of the first stable free *N*-heterocyclic carbenes by Arduengo in 1999 [1]. Their strong σ-donating properties allow NHC ligands to bind to metal ions with a variety of oxidation states [2–5]. NHC complexes have been found to be thermally stable due to the strong metal-carbon bond and are unique as a ligand class due to their lack of π-accepting properties [6–8]. Compared to classical phosphine complexes, many NHC complexes have been found to have greater thermal stability and lower sensitivity to oxygen and moisture [9,10]. The NHC moiety has been shown to coordinate to most transition metals and as a result has been used as a supporting ligand for a wide variety of catalysts that have excellent performance in a number of important reactions [7,11–13].

In recent years, nickel has become of greater interest for catalyst development, because compared to ubiquitous palladium systems, nickel is inexpensive and earth abundant. Several nickel pre-catalysts have been found to be competitive with palladium in cross-coupling reactions [14–18]. Notably, nickel catalysts have been shown to couple some electrophiles that are unreactive with palladium systems in Suzuki cross-coupling reactions [18–26].

Metal complexes supported by macrocyclic ligands containing multiple NHC moieties have been of considerable interest [27–37]. These metal complexes supported by macrocyclic ligands containing NHC's have also been shown to be competent C–C cross coupling catalysts [12,38]. Recently, we reported the synthesis and characterization of 20-membered macrocycles containing two amino and two NHC moieties [39] (Chart 1, **1a** and **1b**). Coordination of these complexes to Ag (Chart 1, **2a** and **2b**) and Pd found the ligands adopted a κ^2 coordination mode with the NHC moieties adopting a *trans* configuration at the metal. We found that the macrocyclic NHC Pd complexes were competent pre-catalysts for C–C coupling reactions. Herein, we report the synthesis and characterization of nickel complexes of proligands **1a** and **1b** and a brief survey of their reactivities.

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2. Results and discussion

Ni complexes of macrocyclic proligands **1a** and **1b** can be synthesized via several routes including transmetallation from Ag complexes to Ni and substitution of the neutral ligands of NiL_2X_2 complexes using free NHCs generated *in situ*. These Ni complexes can be synthesized as various halomers depending on the Ni starting materials used. Additionally, halogen exchange can be accomplished using salt metathesis. The Ni complexes synthesized in this work are shown in Chart 2.

2.1. Synthesis of macrocyclic bis-benzimidazolin-2-ylidene (L_{benz}) Ni complexes *3a*-*3c*

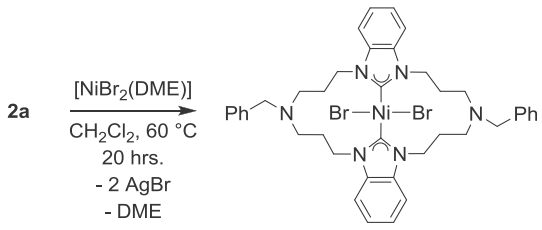
2.1.1. Transmetalation from Ag complexes

Reaction of the macrocyclic benzimidazole-based silver NHC complex **2a** and $[NiCl_2(PPh_3)_2]$ afforded a mixture of products including the $[NiCl_2(L_{benz})]$ complex **3a** and other side products. High-resolution mass spectrometry (HRMS) analysis of the reaction mixture shows the presence of nickel complex **3a** at *m*/*z* 703.2824 (calcd for $[3a\text{-}Cl]^+$ 703.283) and the $[NiBr_2(L_{benz})]$ complex produced through bromine exchange found at *m*/*z* 747.2320 (calcd for $[3b\text{-}Br]^+$ 747.2306). Halogen exchange at the metal center in NHC Ni complexes have been previously observed [40,41]. A phosphine-containing byproduct was observed in the reaction mixture by ^1H NMR (aromatic region) and ^{31}P NMR (single broad peak at 6.74 ppm, CD_2Cl_2). The tetranuclear silver complex $[Ag(PPh_3)(\mu^3\text{-}X)]_4$ (where X = Cl, Br) was characterized by X-ray crystallography (supporting information) and is a previously observed side product in the reaction of silver NHC complexes and $[Ni(PPh_3)_2X_2]$ (X = Cl, Br) [40]. The $[Ni(Cl_2(L_{benz})]$ complex **3a** could not be separated successfully from the phosphine-containing side product.

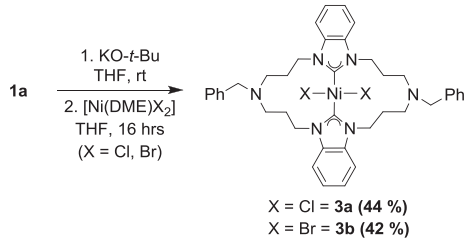
To obtain pure Ni complexes and avoid formation of multiple halomers, **2a** was reacted with $[NiBr_2(DME)]$. Equimolar amounts of $[NiBr_2(DME)]$ and **2a** were refluxed in methylene chloride for 20 h affording $[NiBr_2(L_{benz})]$ in 70% yield (Scheme 1).

2.1.2. Synthesis of Ni complexes using in situ generated free carbenes

To decrease the number of steps needed to prepare these Ni complexes, direct substitution using *in situ* generated free carbenes was attempted. Proligand benzimidazolium salt **1a** is a white solid that is stable in air, partially soluble in chloroform and methylene chloride, and insoluble in acetonitrile, THF and nonpolar solvents such as diethyl ether, pentane and hexanes. Nickel complex **3a** was obtained by the reaction of bis-benzimidazolium salt proligand **1a** with KO-*t*-Bu followed by addition of $[NiCl_2(DME)]$ in THF at 25 °C (Scheme 2). Upon addition of KO-*t*-Bu to **1a**, the colorless solution became yellow in color implying formation of free carbene *in situ*. After addition of $[NiCl_2(DME)]$, a yellow solid formed that could be conveniently handled and isolated in the glovebox. **3a** was isolated as a single product and was characterized by NMR, HRMS, elemental analysis, and X-ray crystallography.



Scheme 1. Compound **2a** is reacted with $[NiBr_2(DME)]$ to yield compound **3b**.



Scheme 2. Compound **1a** is reacted first with potassium t-butoxide in THF followed by reaction with $[Ni(DME)X_2]$ for 16 hours to yields compounds **3a** and **3b** in 44 and 42 percent respectively.

The ^1H NMR spectrum of **3a** is consistent with a molecular structure with C_2 symmetry. A fluxional structure is also implied by the observation of a single benzyl methylene peak at 3.91 ppm (59.7 ppm, ^{13}C NMR), and single resonances for the three methylene units of each arm of the macrocycle observed at 2.52 ppm, 3.27 ppm, and 5.46 ppm (CH_2 attached to the nitrogen atom of benzimidazolin-2-ylidene ring N, 2D NMR). A single ^{13}C NMR peak indicative of a nickel carbene was observed at 182 ppm. Nickel complex **3a** is soluble in polar solvents such as methylene chloride and chloroform and is insoluble in THF, acetonitrile, and nonpolar solvents.

To determine the binding mode of the ligand, crystals of $[NiCl_2(L_{benz})]$ (**3a**) were obtained by slow diffusion of diethyl ether into a saturated solution of the complex in methylene chloride at 25 °C for X-ray crystallography. The ligand was found to bind in a *trans* κ^2 fashion through the NHC moieties of the macrocycle (Fig. 1.)

Reaction of proligand **1a** and KO-*t*-Bu and subsequent addition of $[NiBr_2(DME)]$ gave $[NiBr_2(L_{benz})]$ (**3b**) as an orange solid. A single resonance in the ^1H NMR at 3.85 ppm corresponds to the benzyl CH_2 protons and a C_2 symmetric molecular structure. A characteristic single downfield ^{13}C NMR resonance for the carbene carbon of $[NiBr_2(L_{benz})]$ was observed at 185 ppm. The formation of **3b** was also confirmed by HRMS with a peak at *m*/*z* 747.2335 (calcd for $[3b\text{-}Br]^+$ 747.2306). X-ray-quality crystals of $[NiBr_2(L_{benz})]$ **3b** were

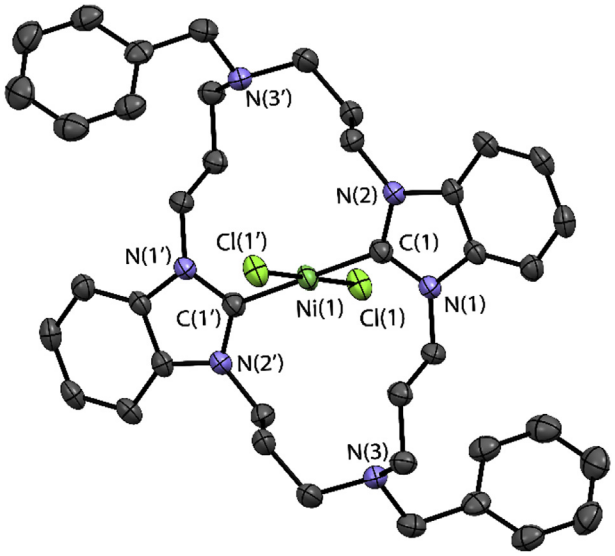


Fig. 1. Thermal ellipsoid plot of complex **3a**, (50% ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Ni(1)–C(1) = 1.909(4), Ni(1)–Cl(1) = 2.1981(10), N(1)–C(1) = 1.349(5), C(1′)-Ni(1)-C(1) = 180.0, C(1)-Ni(1)-Cl(1) = 90.07(12), C(1′)-Ni(1)-Cl(1′) = 90.07(12).

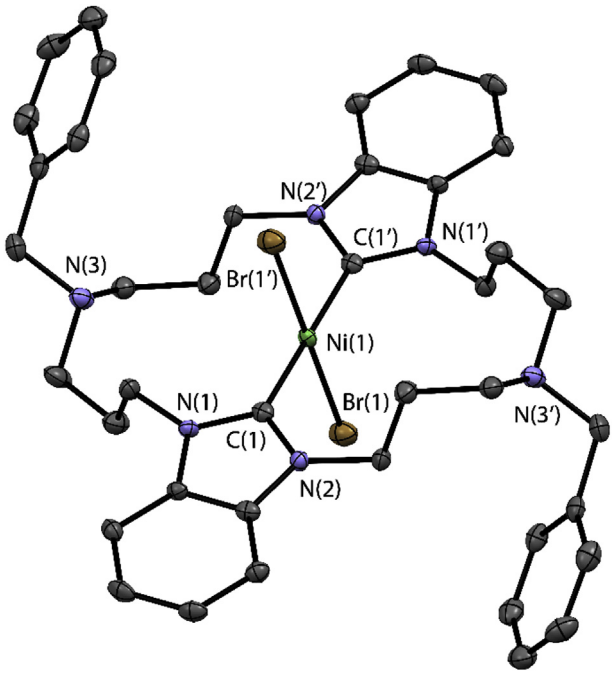
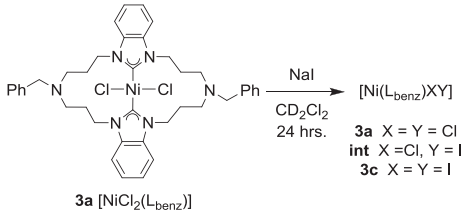


Fig. 2. Thermal ellipsoid plot of 3b (50% ellipsoids). Selected bond distances (Å) and bond angles (°.): Br(1)–Ni(1) = 2.3194(4), Ni(1)–C(1) = 1.897(3); C(1′)-Ni(1)-C(1) = 180.0, C(1′)-Ni(1)-Br(1) 91.54(10), N(2)-C(1)-N(1) = 106.2(3), N(2)-C(1)-Ni(1) = 126.7(3).

grown by slow diffusion of diethyl ether into a saturated solution of the complex in methylene chloride at 25 °C (Fig. 2). The ligand was found to bind in a *trans* κ^2 fashion through the NHC moieties of the macrocycle consistent with the X-ray structure determined for **3a**.

2.1.3. Halogen exchange studies

$[NiI_2(L_{benz})]$ **3c** was prepared by salt metathesis of the chloride or bromide anions of complex **3a**-**3b** using sodium iodide at 25 °C (Scheme 3). The conversion of $[NiCl_2(L_{benz})]$ **3a** to $[NiI_2(L_{benz})]$ **3c** was also implied by a change in the solution color from yellow to red. The progress of the halogen exchange reaction was followed for 24 h by monitoring a change in the benzyl proton resonance in the ^{1}H NMR in CD_2Cl_2 at 25 °C (Fig. 3). The benzylic CH_2 proton resonance for $[NiCl_2(L_{benz})]$ **3a** is observed at 3.93 ppm, and the resonance for complex **3c** is found at 3.83 ppm. An additional resonance is observed that is assigned to the intermediate mixed halide nickel complex (Scheme 3, "int."). Notably, the ^{13}C NMR signal for the NHC carbene carbon of **3a** was observed at 182 ppm, and after metathesis the carbene carbon of **3c** is found at 190 ppm. The carbene ^{13}C NMR chemical shifts for nickel complexes **3a, 3b**, and **3c** in $CDCl_3$ and CD_2Cl_2 are given in Table 1. Similarly, the bromide complex **3b** can be converted to **3c** by salt metathesis in 24 h (Fig. S14, supporting information).



Scheme 3. Halogen exchange of complex **3a** to **3c**.

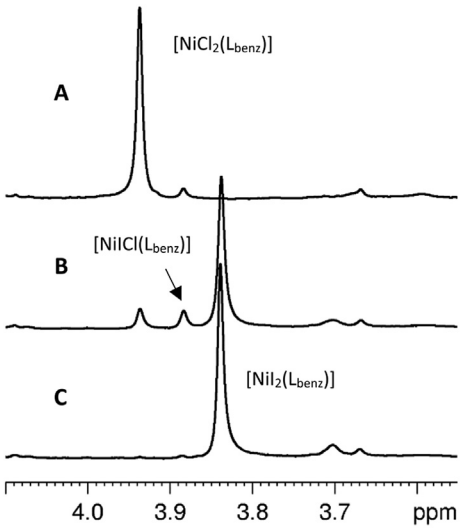


Fig. 3. Progress of the halogen exchange reaction for $[NiCl_2(L_{benz})]$ (**3a**) with NaI in CD_2Cl_2 monitored by the benzyl CH_2 proton chemical shift in ^{1}H NMR. Spectrum A after initial mixing, Spectrum B after 12 h, and Spectrum C after 24 h.

Table 1
^{13}C NMR chemical shifts of the carbene carbon of nickel complexes **3a-c** in $CDCl_3$ and CD_2Cl_2.

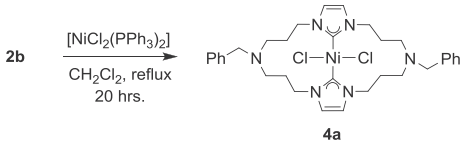
Complex	$^{13}C\{^1H\}$ $CDCl_3$	$^{13}C\{^1H\}$ CD_2Cl_2
$[NiCl_2(L_{benz})]$ (**3a**)	181.7	182.3
$[NiBr_2(L_{benz})]$ (**3b**)	184.8	185.3
$[NiI_2(L_{benz})]$ (**3c**)	189.9	190.4

2.2. Attempted synthesis of macrocyclic bis-imidazolin-2-ylidene (L_{imid}) Ni complexes ***4a-4c***

2.2.1. Attempted synthesis of Ni complexes of bis-imidazolin-2-ylidene substituted macrocycles by transmetallation from Ag

In contrast to the benzimidazolin-2-ylidene-substituted macrocyclic ligand (L_{benz}) above, the imidazolin-2-ylidene-substituted analogue (L_{imid}) does not yield convenient isolable metal complexes. Initial syntheses of Ni(II) chloride complexes of proligand **1a** were attempted by transmetallation from the silver NHC complex **2a** with $[NiCl_2(PPh_3)_2]$, as previously described in the literature [40]. Silver complex **2a** was treated with equimolar amounts of $[NiCl_2(PPh_3)_2]$ in CH_2Cl_2, and the mixture was refluxed for 20 h (Scheme 4). Notably, at ambient temperature the reaction of silver complex **2a** and $[NiCl_2(PPh_3)_2]$ does not proceed to completion. After refluxing the reaction mixture in CH_2Cl_2, a mixture of products and unreacted **2a** were observed by NMR. Ni complex **4a** was observed in the reaction mixture by HRMS at *m*/*z* 603.250 (calcd for $[4a\text{-}Cl]^+$ 603.251) in addition to other species.

The tetrameric silver complex $[Ag(PPh_3)\ (\mu^3\text{-}Cl)]_4$ was also obtained as a side product and was identified by X-ray crystallography



Scheme 4. Synthesis of macrocyclic L_{imid}Ni complex **4a**.

(supporting information) [18]. Separation of the Ni(II) complexes from other products by chromatography was not possible due to their similar solubilities. Recrystallization of the crude products from methylene chloride/pentane at 25 °C resulted in a mixture of white crystals of known tetranuclear silver complex [18] and yellow needle-shaped crystals of the *trans*-[$NiCl_2(L_{imid})$] complex **4a**. The crystals could be manually separated under a microscope. The ^{13}C NMR spectrum of solids containing **4a** isolated from the reaction mixture shows a single carbene carbon resonance for the 1-position of the NHC moiety of **4a** at 168 ppm in CD_2Cl_2. The ^{1}H and ^{13}C NMR spectra of reaction mixtures containing **4a** are consistent with components containing the macrocyclic ligand having C_2 symmetric products. The ^{1}H NMR spectrum shows three proton resonances for the 12 methylene protons of the four propyl chains in the macrocyclic ring indicating that the macrocyclic ligand in **4a** is fluxional in solution. A single proton resonance is also observed for the two benzyl methylene groups.

X-ray diffraction studies of judiciously selected crystals of **4a** shows the NHC moieties of *trans*-[$NiCl_2(L_{imid})$] complex **4a** have a C(4)-Ni(1)-C(4) bond angle of 180(0)° at the nickel center (Fig. 4). Previous DFT studies have predicted that the *cis* configuration of the NHC moieties is favorable when there are fewer than three methylene linkers between the two NHC rings [42]. The *trans* configuration has been found to be favorable in several square planar bis(NHC) metal complexes with more than three methylene groups in the linker [38,39].

Interestingly, when reaction mixtures of **4a** are not treated under rigorously anhydrous and anaerobic conditions, a crystal suitable for single-crystal X-ray studies from pentane/CH_2Cl_2 furnished the *cis*-[$NiCl_2(L_{imid})$] complex **4b** (Fig. 5) with a partially occupied water molecule incorporated in the unit cell of the crystal. The NHC moieties of **4b** were found to have a bond angle of C(4)-Ni(1)-C(13) = 93.37(7)°. The observation of the *cis*-complex **4b** is likely a result of cis/trans isomerization from associative 5-coordinate rearrangement in the presence of water.

2.2.2. Attempted synthesis of Ni complexes of bis-imidazolin-2-ylidene-substituted macrocycles using free carbenes

Nickel(II) complexes were synthesized by substitution of phosphine ligands of [$NiCl_2(PPh_3)_2$] by free NHCs generated *in situ* [40,43]. The reaction between proligand **1a** and KO-*t*-Bu generated the free carbene *in situ* (implied by formation of a red solution). Subsequent addition of [$NiCl_2(PPh_3)_2$] afforded a mixture of products, including the desired product **4a**. Efforts to isolate the desired product from the side products were again unsuccessful. Similarly, attempts to recrystallize **4a** in various solvent systems were also unsuccessful. Reaction of solutions containing free carbenes with [$NiCl_2$(DME)] also did not yield clean products.

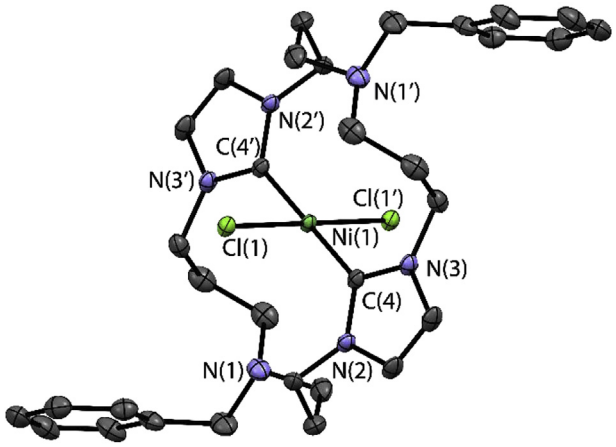


Fig. 4. Thermal ellipsoid plot of the *trans*-[$NiCl_2(L_{imid})$] complex **4a** (50% ellipsoids). Hydrogen atoms have been removed for clarity. Selected bond distances (Å) and bond angles (°.): Ni(1)–C(4) = 1.9123(16), Ni(1)–Cl(1) = 2.1963(4); Cl(1)-Ni(1)-Cl(1′) = 180.000(19), C(4)-Ni(1)-Cl(1′) = 90.49(5), C(4)-Ni(1)-Cl(1) = 89.51(5).

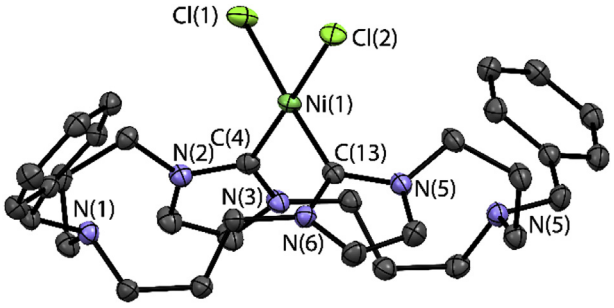
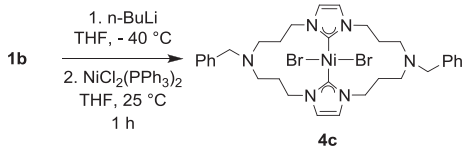


Fig. 5. Thermal ellipsoid plot of the *cis*-[$NiCl_2(L_{imid})$] complex, $C_{32}H_{42}Cl_2N_6Ni \cdot 0.30(H_2O)$ **4b** (50% ellipsoids). Hydrogen atoms and the water molecule have been removed for clarity. Selected bond distances (Å) and bond angles (°): Ni(1)–Cl(1) = 2.2431(7), N(1)–C(4) = 1.8905(18); C(4)-Ni(1)-C(13) = 93.37(7), C(4)-Ni(1)-Cl(2) = 175.81(5).

Free carbene can also be generated by reaction of proligand **1a** with *n*-BuLi in THF at −40 °C. When cold THF solutions of free carbene are combined with equimolar amounts of [$NiCl_2(PPh_3)_2$] the primary component was found to be the bromide complex (**4c**, Scheme 5). HRMS analysis of the reaction mixture shows the presence of several nickel complexes including [$NiBr_2(L_{imid})$] complex **4c** at *m/z* 729.1233 (calcd [4c + H]$^+$ 729.1264), and a mono-phosphine-substituted nickel complex (*m/z* 1290). Formation of various halomers of metal complexes is common in reactions using imidazolium halide salts [20]. Slow diffusion of diethyl ether into a saturated solution of the crude reaction mixture in methylene chloride at 25 °C again yielded a mixture of crystals both colored crystals as well as clear and colorless crystals with a variety of crystal shapes. X-ray analysis of judiciously picked crystals afforded the X-ray crystal structure (Fig. 6) of the *trans*-[$NiBr_2(L_{imid})$] complex **4c**. The ^{1}H NMR spectrum (of similar red crystals) is complicated, showing a mixture of at least two products; the other products could not be assigned. The complete disappearance of the imidazole peak (NC*H*N, 10.77 ppm) of the ligand **4a** in the ^{1}H NMR implied the reaction was complete. The ^{13}C NMR spectrum shows a characteristic single downfield carbene carbon resonance at 170 ppm. ^{31}P NMR in CD_2Cl_2 shows two peaks 17.42 and −5.55 ppm (PPh_3). The ^{31}P peak at 17.42 ppm is indicative of the phosphorus-containing byproduct (*vide supra*).

2.2.3. Catalytic study

A preliminary catalytic study tested the performance of the crude [$NiCl_2(L_{imid})$] (**4a**) as a precatalyst in the Suzuki-Miyaura C–C coupling reaction. [$NiCl_2(L_{imid})$] (**4a**) shows activity for C–C coupling between 4-bromoacetophenone and phenylboronic acid in the presence of cesium carbonate base and 1,4-dioxane as a solvent at 100 °C at ~7 mol% **4a**. The coupled product was formed in 73% yield in 24 h at 100 °C. The formation of coupled product was



Scheme 5. Synthesis of **4c** using *in situ* generated free carbenes.

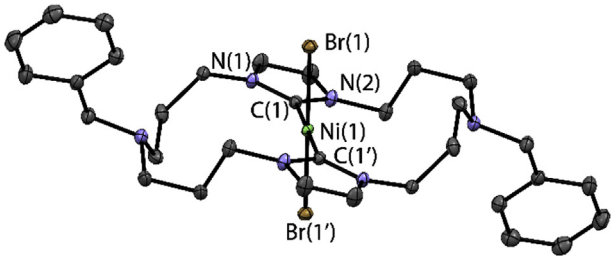
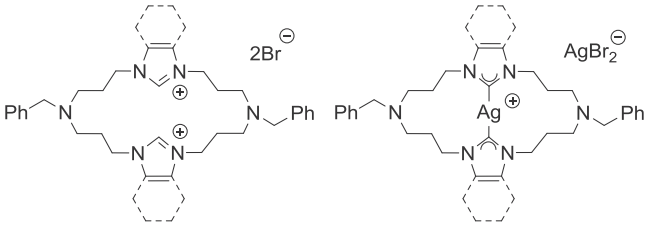


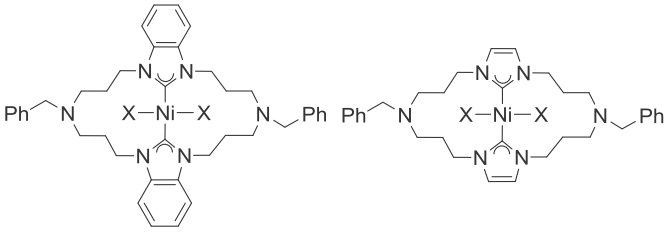
Fig. 6. Thermal ellipsoid plot of the *trans*-[$NiBr_2(L_{imid})$], **4c** (50% ellipsoids). Hydrogen atoms have been removed for clarity. Critical distances (Å) and bond angles (°): Br(1)–Ni(1) = 2.32627(12), Ni(1)–C(1) = 1.9127(11), N(2)–C(1) = 0.9500; C(1)-Ni(1)-C(1′) = 180.00(7), C(1)-Ni(1)-Br(1) = 89.73(3), Br(1)-Ni(1)-Br(1′) = 180.00.



Macrocyclic bisimidazolium salts
1a. Benzimidazolium
1b. Imidazolium

Macrocyclic bis(NHC)Ag(I) complexes
2a. Benzimidazolin-2-ylidene
2b. Imidazolin-2-ylidene

Chart 1. Macrocyclic salts used to prepare Ni complexes.



X=Cl trans-Cl **3a**
X=Br trans-Br **3b**
X=I trans-I **3c**

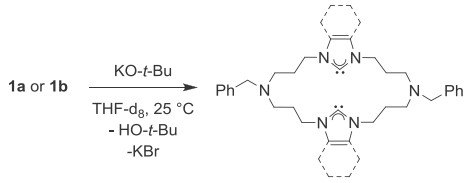
X=Cl trans-Cl **4a**
X=Cl cis-Cl **4b**
X=Br trans-Br **4c**

Chart 2. Complexes **3a** - **4c**.

confirmed by GC/MS analysis. The yield was determined by ^{1}H NMR vs. an internal standard. This reaction performance is on par with other Ni-based precatalysts previously reported for C–C coupling [44].

2.3. Attempts to isolate free carbenes

Generation of free carbenes followed by reaction with metal precursors is a common method for synthesis of metal-NHC complexes [45–50]. Free carbenes were generated by the reaction of imidazolium bromide salts **1a**-**1b** with 2 equivalents of KO-*t*-Bu in THF-d_8 at 25 °C [33,50]. The immediate formation of white precipitate (KBr) and change in solution color from colorless to yellow, for imidazolium salt **1b**, and a color change from colorless to red for benzimidazolium salt **1a**, implies formation of the carbenes. The formation of **5a** and **5b** was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy (Scheme 6). The downfield proton signals of the acidic imidazolium salts (11.3 ppm and 10.77 ppm for **5a** and **5b**, respectively) were no longer observed. Concomitant with the apparent deprotonation, a characteristic signal for the carbene carbon is



5a. Benzimidazolin-2-ylidene
5b. Imidazolin-2-ylidene

Scheme 6. Generation of free carbenes *in situ*.

observed in the ^{13}C NMR spectrum at 214 ppm and 226 ppm for **5a** and **5b**, respectively. Previous studies of related bis-carbene systems have been observed to dimerize at the 1-position of the heterocycle forming enetetramines. In these cases a red suspension was also observed, therefore we cannot preclude that an analogous dimerization reaction is occurring during the formation of **5a** and **5b** [48]. Attempts to isolate the free carbenes furnished a sensitive viscous oil that was difficult to handle, as we found in previous attempts [39].

2.4. X-ray crystal structures

Complexes **3a**, **3b**, **4a**, **4b**, and **4c** were characterized by X-ray crystallography. All of the complexes adopt a distorted square planar geometry in the solid state with two halides in a *cis* (**4b**) or *trans* (**3a**, **3b**, **4a**, **4c**) configuration. Nickel complex **4b** crystallizes in the orthorhombic system in the *Pbca* space group. Nickel complexes **4a** and **4c** crystallize in the monoclinic system in the $P2_1/c$ space group with very similar cell parameters. **3a** and **3b** crystallize in the monoclinic system in the $P2_{1/n}$ space group with similar cell parameters. The Ni–C bonds observed in these structures were found to have typical bond distances ranging from 1.89 to 1.91 Å, consistent with the reported values of known Ni–NHC complexes [43]. The carbene ligands are oriented approximately perpendicular to the coordination plane of the Ni, which is consistent with previously reported *trans*-spanning bis-NHC ligands [38,49,50]. The benzyl amine groups in the macrocyclic rings are attached to the propyl arms and are directed above and below the Ni–NHC coordination plane. The C_2-symmetric NMR resonances observed for all complexes are presumably due to the fluxional nature of the macrocycle. The details of the structure determinations for structures **3a**-**4c** are given in the experimental section, and the crystal and structure refinement data are given in Table 2.

3. Conclusions

We have synthesized a series of stable, *trans*-bis(NHC)Ni(II) complexes bearing a 20-membered macrocyclic ligand with two NHC and two amino moieties (Scheme 7). Detailed molecular structures of the nickel(II) complexes were determined by single-crystal X-ray crystallography. The *trans*-bis(NHC)nickel(II) complexes **4a**, **4c** and **3a**, **3b** possess a square planar metal center. The 20-membered bis-imidazolin-2-ylidene and bis-benzimidazolin-2-ylidene macrocycles act as bidentate ligands that coordinate to the nickel center in *trans* chelating fashion through the NHCs. Complex **4b** adopts *cis* configuration with H_2O present in the crystal lattice when crystalized under ambient atmosphere. The [$Ni(L_{benz})X_2$] complexes **3a** and **3b** are stable towards air, moisture, and heat. These complexes can be prepared by transmetallation from silver carbene complexes or by generation of free carbenes *in situ* followed by substitution at Ni. Transmetallation from silver carbenes affords yields up to 70%. (L_{imdi}))$NiCl_2$ (**4a**) was screened for the C–C coupling reaction between 4-bromoacetophenone and

Table 2
Crystal data and structure refinement parameters for **3a**-**4c**.

	[Ni(Cl_2(L_{benz})] (**3a**)	[$NiBr_2$(L_{benz})] (**3b**)	[$NiCl_2$(L_{imid})] (**4a**)	*cis*-[$NiCl_2$(L_{imid})] (**4b**)	[$NiBr_2$(L_{imid})] (**4c**)
Empirical formula	$C_{40}H_{46}Cl_2N_6Ni$	$C_{40}H_{46}Br_2N_6Ni$	$C_{32}H_{42}Cl_2N_6Ni$	($C_{32}H_{42}Cl_2N_6Ni$) (H_2O)$_{0.30}$	$C_{32}H_{42}Br_2N_6Ni$
Formula weight	740.44	829.36	640.32	645.73	729.24
Crystal system	Monoclinic	monoclinic	Monoclinic	orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	*Pbca*	$P2_1/c$
a (Å)	7.7486(9)	11.9199(7)	8.3832(5)	17.424(6)	11.3814(4)
b (Å)	24.250(3)	10.7256(6)	25.2191(17)	18.867(6)	12.2898(4)
c (Å)	10.0627(9)	14.4744(9)	7.8615(5)	19.205(6)	11.9185(3)
α (deg)	90	90	90	90	90
β (deg)	109.480(6)	106.0912(19)	107.7218(2)	90	103.2645(13)
γ (deg)	90	90	90	90	90
Volume (Å^3)	1782.6(4)	1778.02(18)	1583.18(17)	6313(4)	1622.63(9)
Z, Z'	2, 0.5	2, 0.5	2, ½	8, 1	2, 0.5
Density (calc) (Mg/m^3)	1.379	1.549	1.343	1.359	1.493
Wavelength Å	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature (K)	102(2)	100(2)	100(2)	100(2)	100(2)
F(000)	780	852	676	2728	748
Absorption coeff.	0.733 mm^{-1}	2.832 mm^{-1}	0.813 mm^{-1}	0.817 mm^{-1}	3.092 mm^{-1}
Absorption correction	Semi-emp. from equiv.	Semi-emp. from equiv.	Semi-emp. from equiv.	Semi-emp. from equiv.	Semi-emp. from equiv.
Max. & min. transmission	0.6463, 0.5265	0.781, 0.494	0.968, 0.841	0.908, 0.676	0.5312, 0.4051
θ range/°	2.305 to 25.781	2.3980 to 26.395	1.615 to 27.484	1.912 to 27.547	2.414 to 36.292
Reflection collected	23300	107596	14517	104044	21014
Independent reflection	3405[R(int) = 0.0695]	3636[R(int) = 0.0757]	3623[R(int) = 0.0369]	7281[R(int) = 0.0558]	7805[R(int) = 0.0291]
Data/restraints/param.	3405/0/223	3636/0/223	3623/0/187	7281/0/380	7805/0/187
w*R*(F^2 all data)	w*R*2 = 0.1680	w*R*2 = 0.1277	w*R*2 = 0.0771	w*R*2 = 0.1096	w*R*2 = 0.0657
R(F obsd data)	R1 = 0.0546	R1 = 0.0420	R1 = 0.0295	R1 = 0.0380	*R*1 = 0.0261
Goodness-of-fit on F^2	1.009	1.004	0.950	0.964	1.003
Observed data [I > 2σ (I)]	2704	3038	3011	6302	6420
Largest & mean shift/s.u.	0.000, 0.000	0.000, 0.000	0.001, 0.000	0.044, 0.000	0.002, 0.000
Largest diff peak and hole e/Å^3	1.860, −1.841	1.860, −1.841	1.321, −0.252	1.492, −0.363	2.664, −0.629

w*R*2 = { Σ [$w(F_o^2 - F_c^2)^2$]/Σ [$w(F_o^2)^2$] }$^{1/2}$, *R*1 = Σ ||F_o| - |F_c||/Σ |F_o

phenylboronic acid and was found to be a competent precatalyst with average activity. Further studies of the scope and catalytic activity of macrocyclic nickel(II) complexes towards a variety of catalytic reactions are underway in our laboratory.

4. Experimental methods

4.1. General comments

Reagents were obtained from common commercial sources and were used without further purification. Solvents were obtained anhydrous from Aldrich and were placed over 3 Å molecular sieves. All reactions were performed under inert atmosphere using standard Schlenk or glovebox techniques unless otherwise noted. Proligands **1a** and **1b** and Ag complexes **2a** and **2b** were synthesized by the published procedure [39]. [$NiBr_2$(DME)] and [$NiCl_2$(DME)] were prepared using literature procedures [39,51]. High-resolution mass spectra were recorded using a Bruker APEX-II FTMS instrument with an electrospray ionization source. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on 300 and 400 MHz Bruker Avance DPX spectrometers. Chemical shifts are reported in parts per million downfield shift from $SiMe_4$. ^{1}H NMR spectra were referenced internally to the residual protio solvent resonance of $CHCl_3$ (δ 7.26), CH_2Cl_2 (δ 5.32). ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0), CH_2Cl_2 (δ 53.84). ^{1}H COSY, ^{13}C HSQC, and NOESY experiments were performed using standard Bruker pulse sequences. Microanalysis of the samples was performed by the University of Rochester CENTC facility where microanalysis samples were weighed with a PerkinElmer Model AD-6 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Gas chromatography was performed on an Agilent 6890/5973 N in positive ion CI mode with a flow rate of 1 mL/min constant flow He, an inlet temperature of 250 °C, and a column temperature of 80 °C with 20 °C/min increase to 250 °C (held for 2 min) for a total time of 16 min.

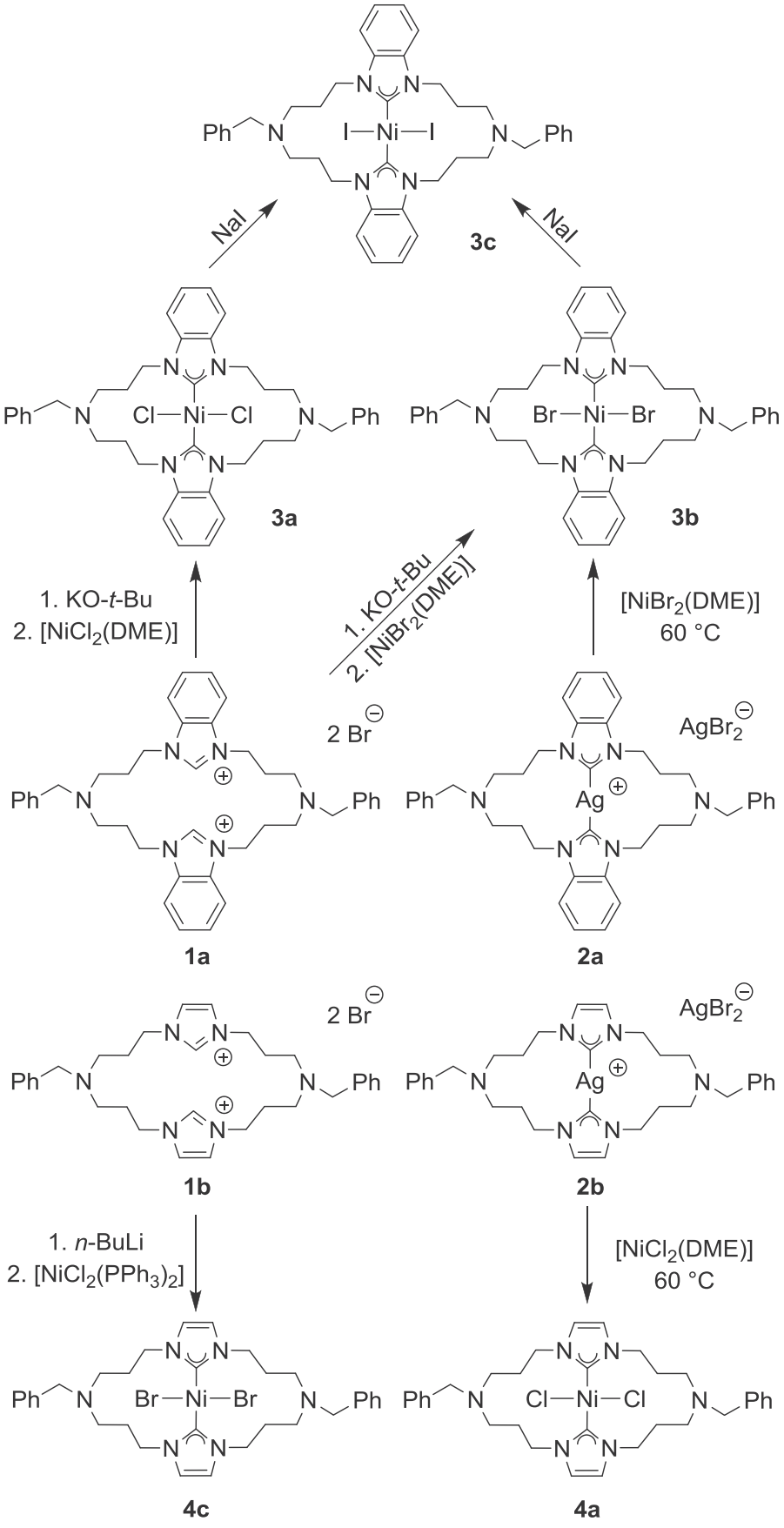
4.2. X-ray crystallography

Crystals of stable shape and dimension were selected for structural analysis. Intensity data were collected using a diffractometer with a Bruker APEX CCD area detector [52,53] and graphite-monochromated radiation. The data were corrected for absorption by the empirical method [54] giving minimum and maximum transmission factors. The space group was determined by systematic absences and statistical tests and was verified by subsequent refinement. The structure was solved by direct methods and was refined by full-matrix least-squares methods [55,56] on F^2. The positions of hydrogens bonded to carbons were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms.

4.3. Synthesis and characterization of compounds

4.3.1. Synthesis of [Ni(Cl_2(L_{benz})] (**3a**)

Benzimidazolium bromide salt **1a** (190.4 mg, 246 mmol) was dissolved in 5 mL of THF and was stirred in a scintillation vial. A mixture of 2.5 equiv. of KO-*t*-Bu (69.12 mg, 616 mmol) suspended in 5 mL of THF was added to the vial. The solution was stirred for 20 min and was filtered through Celite. [$NiCl_2$(DME)] (54.14 mg, 247 mmol), was added to the resultant solution and was stirred for 1 h. The resultant suspension was filtered, and **3a** was isolated as a yellow solid (80 mg) in 44% yield after being dried under vacuum. Crystals suitable for X-Ray diffraction analysis were grown by slow diffusion of diethyl ether into a saturated solution of complex **3a** in methylene chloride at 25 °C. ^{1}H NMR (CD_2Cl_2): δ 7.61 (d, *J* = 7.32,



Scheme 7. Summary of the syntheses of complexes **3a** – **4a**, **4c**.

ortho, 4H, -C_6H_5), 7.42 (t, $J = 7.4$, meta, 4H, -C_6H_5), 7.32–7.23 (m, meta, 2H, -C_6H_5, and 4H, benzimi -C*H*=C*H*), 7.21–7.18 (m, 4H, benzimi), 5.41 (bs, 8H, -benzimi-NCH_2), 3.90 (s, 4H, -NCH_2Ph), 3.23 (bs, 8H, Ph$CH_2CH_2CH_2$), 2.49 (t, $J = 5.72$, 8H, CH_2NCH_2Ph). ^{1}H NMR ($CDCl_3$): δ 7.62 (d, $J = 7.2$, ortho, 4H, -C_6H_5), 7.42 (t, $J = 7.6$, meta, 4H, -C_6H_5), 7.32–7.23 (m, meta, 2H, -C_6H_5, and 4H, benzimi-C*H*=C*H*), 7.19–7.15 (m, 4H, benzimi), 5.46 (bs, 8H, -benzimi NCH_2), 3.90 (s, 4H, -NCH_2Ph), 3.27 (bs, 8H, Ph$CH_2CH_2CH_2$), 2.52 (t, $J = 5.6$, 8H, CH_2NCH_2Ph. ^{13}C NMR ($CDCl_3$): δ 182, 140.5, 135, 129, 128.6, 127, 122, 110, 60, 53.5, 45, 29. ^{14c} NMR (CD_2Cl_2): δ 182.3, 141, 135, 129, 128.7, 127.2, 122, 109, 60, 54, 45, 29. HR FT-ICR MS: found 703.2824 (calcd for $C_{40}H_{46}ClN_6Ni$, *m/z* [3a-Cl]$^+$ 703.2826); Elemental analysis was attempted several times and our results are consistent with the compound absorbing water from atmosphere during transit. Anal. Calcd [$C_{40}H_{46}Cl_2N_6Ni \cdot H_2O$]: C 63.34, H 6.38, N 11.08. Anal. Found C 63.434, H 6.115 N 11.112.

4.3.2. Synthesis of [Ni(Br_2(L_{benz})] (**3b**)

Benzimidazolium bromide salt **1a** (153 mg, 198 mmol) was dissolved in 5 mL of THF and stirred in a scintillation vial. A mixture of 2.5 equiv. of KO-*t*-Bu (56 mg, 499 mmol) suspended in 5 mL of THF was added to the vial. The solution was stirred for 20 min and was filtered through Celite. [$NiBr_2$(DME)] (61 mg, 198 mmol) was added to the resultant solution and was stirred for 1 h. The suspension was filtered through Celite, and **3b** was isolated as an orange solid (69 mg) in 42% yield after the volatiles were removed under vacuum. Crystals suitable for X-Ray diffraction analysis were grown by slow diffusion of diethyl ether into a saturated solution of complex **3b** in methylene chloride at 25 °C. ^{1}H NMR (CD_2Cl_2): δ 7.61 (d, $J = 7.2$, ortho, 4H, -C_6H_5), 7.39 (t, $J = 7.6$, meta, 4H, -C_6H_5), 7.29–7.27 (m, meta, 2H, -C_6H_5, and 4H, benzimi -C*H*=C*H*), 7.20–7.19 (m, 4H, benzimi), 5.37 (bs, 8H, -benzimiNCH_2), 3.85 (s, 4H, -NCH_2Ph), 3.17 (bs, 8H, Ph$CH_2CH_2CH_2$), 2.54 (bs, 8H, CH_2NCH_2Ph). ^{13}C NMR (CD_2Cl_2): δ 185, 141, 135, 129.4, 128.8 127, 122, 110, 60, 54, 45, 28. ^{13}C NMR ($CDCl_3$): δ 184.8, 140.5, 135, 129, 128.7, 127, 122, 109, 60, 53.5, 45, 28. HR FT-ICR MS: found 829.1605 (calcd for $C_{40}H_{46}Br_2N_6NiH$, *m/z* [3b + H]$^+$ 829.1577); found 749.2303 (calcd for $C_{40}H_{46}BrN_6Ni$, *m/z* [3b-Br]$^+$ 749.2306).

4.3.3. Synthesis of [$NiBr_2$(L_{benz})] (**3b**) via transmetallation from Ag salts

Silver carbene salt **2a** (210 mg, 0.213 mmol) was dissolved in 10 mL of CH_2Cl_2 and [$NiBr_2$(DME)] (66 mg, 0.213 mmol) in 10 mL of CH_2Cl_2 was added dropwise. The mixture was refluxed for 20 h, and the resultant solution was filtered through Celite, and the volatiles were removed under vacuum. The crude solid was triturated with 5 mL of EtOH and was dried under vacuum to afford 155 mg of 3b as an orange solid (70% yield). The spectroscopic properties of this solid were consistent with samples prepared using the free carbene method described in section 4.3.2.

4.3.4. Synthesis of [NiI_2(L_{benz})] (**3c**)

NaI (73 mg, 0.487 mmol) in CH_2Cl_2 (5 ml) was added to [Ni(Cl_2(L_{benz})] **3a** (90 mg, 121 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred 24 h, was filtered over Celite and was concentrated by ½ volume to afford 100 mg (90%) of **3c** as a red solid that was isolated by filtration. ^{1}H NMR ($CDCl_3$): δ 7.62 (d, $J = 7.2$, ortho, 4H, -C_6H_5), 7.40 (t, $J = 7.6$, meta, 4H, -C_6H_5), 7.31 (t, $J = 7.6$, para, 2H, -C_6H_5), 7.19–7.22 (m, 4H, benzimi -C*H*=C*H*), 7.13–7.15 (m, 4H, benzimi), 5.29 (bs, 8H, -benzimi-NCH_2), 3.75 (s, 4H, -NCH_2Ph), 3.11 (bs, 8H, Ph$CH_2CH_2CH_2$), 2.59 (t, $J = 5.6$, 8H, CH_2NCH_2Ph). ^{13}C NMR (CD_2Cl_2): δ 190.4, 141, 136, 129.5, 128.8, 127, 122, 109.6, 60, 54, 46, 30, 28. ^{13}C NMR ($CDCl_3$): δ 190, 140, 136, 129, 128.7, 127, 122, 109, 59.5, 53, 46, 27. HR FT-ICR MS: found 462.0680 (calcd for $C_{40}H_{46}I_2N_6NiH$, *m/z* [3c + H]$^{2+}$ 462.0686).

4.4. Generation of free carbenes in situ

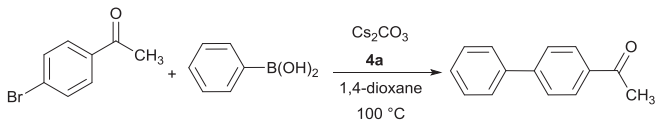
4.4.1. Free carbene (**5a**)

Benzimidazolium bromide salt **1a** (20 mg, 26 mmol) and KO-*t*-Bu (6 mg, 53 mmol) were combined in a vial in the glove box1 mL of THF-d_8 was added at 25 °C. The reaction mixture was stirred for 2 min. The reaction mixture immediately became a red suspension. The reaction mixture was filtered and was transferred to a J-Young tube. ^{1}H NMR (C_4D_8O): δ 7.40 (d, $J = 7.2$, ortho, 4H, -C_6H_5), 7.29 (t, $J = 7.2$, meta, 4H, -C_6H_5), 7.21 (m, para, 2H, -C_6H_5 and 4H, benzimi) 7.00 (m, 4H, benzimi), 4.14 (t, $J = 6.8$, 8H, -benzimiNCH_2), 3.79 (s, 4H, -NCH_2Ph), 2.50 (t, $J = 6.8$, Ph$CH_2CH_2CH_2$), 1.98 (t, $J = 6.8$, 8H, CH_2NCH_2Ph). ^{13}C NMR (C_4D_8O): δ 226.6, 141, 135, 129, 128.7, 127,121, 110, 59, 51, 45, 28.

4.4.2. Free carbene (**5b**)

Imidazolium bromide salt **1b** (8 mg, 12 mmol) and KO-*t*-Bu (4 mg, 34 mmol) were combined in a vial in the glove box. 1 mL of THF-d_8 was added at 25 °C. The reaction mixture was stirred for 2 min. The reaction mixture immediately became a yellow suspension. The reaction mixture was filtered and was transferred to a J-Young tube. ^{1}H NMR (C_4D_8O): δ 7.45 (d, $J = 7.2$, ortho, 4H, -C_6H_5), 7.36 (t, $J = 7.6$, meta, 4H, -C_6H_5), 7.29–7.27 (t, $J = 7.2$, meta, 2H, -C_6H_5) 6.90 (s, 4H, imi -C*H*=C*H*), 3.95 (t, $J = 7.2$, 8H, Ph$CH_2CH_2CH_2$), 3.64 (s, 4H, -NCH_2Ph), 2.48 (t, $J = 7.2$, 8H, Ph$CH_2CH_2CH_2$), 1.93 (t, $J = 7.2$, 8H, CH_2NCH_2Ph). ^{13}C NMR (C_4D_8O): δ 214, 141, 129, 128.6, 127, 119, 59, 50, 48, 29.

4.5. Ni-Catalyzed Suzuki coupling reaction



Cs_2CO_3 (196 mg, 0.60 mmol), phenylboronic acid (37 mg, 0.30 mmol), 4-bromoacetophenone (33.6 mg, 0.20 mmol), 7.6 mg (~7 mol %) of precatalyst **4a**, and the internal standard 4-methoxyphenol (12.7 mg, 102 mmol) were added to a 15 mL pressure tube with a stir bar. 1,4-Dioxane (1.5 mL) was added to the tube, and the solution was heated with stirring at 100 °C under nitrogen for 24 h. After the mixture was cooled, it was passed through a short pad of SiO_2 and the filtrate was analyzed by ^{1}H NMR and GC/MS. The presence of the coupled product was confirmed by GC/MS, and NMR showed that the coupled product formed in 73% yield.

Acknowledgments

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Appendix A. Supplementary data

NMR spectra of **3a**- **5b** and additional details of X-ray crystal refinement as well as X-ray crystal data (CIF files) are available online. X-ray data has been deposited in the CCDC (https://www.ccdc.cam.ac.uk/) deposition numbers 1953335-1953338, and 1953344.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.120937.

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