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Synthesis and catalytic activities of Ni complexes bearing a novel N–C–N pincer ligand containing NHC with a bicyclic motif



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1. Introduction

Ligands equipped with multi-coordination sites are effective in stabilizing metal complexes via chelating effects as well as in controlling the electron density of the supporting metal ions [1]. Among them, N-heterocyclic carbenes (NHCs) possessing other Lewis basic site(s) are being actively investigated because of their high electron-donating ability [2]. NHCs are structurally diverse, and numerous types of ligands containing one or more NHC motifs have been developed. For example, CNC [3], PCP [4], CCC [5], and NCN [6] pincer types of tridentate ligands containing at least one NHC site have been effective in enhancing the activity of several transitional metal catalysts. In these studies, the fine tuning of additional Lewis basic sites and linker parts has often been attempted, but the NHC core structure has typically been limited to imidazolylidene, presumably because of the ease of synthesis (Fig. 1). The development of pincer NHC ligands bearing varied core NHC structures should expand the opportunity for the development of NHC-metal complexes that show unique catalytic activity [7]. Here, we report the development of a novel NCN type of pincer ligand bearing our original NHC motif, which is equipped with non-

ABSTRACT

A novel N–C–N pincer ligand bearing an NHC with a bicyclic framework, namely NHC(CH₂Py)₂, was developed and successfully applied to the syntheses of air- and moisture-stable silver and nickel complexes. The silver complex was identified as {[NHC(CH₂Py)₂]₂Ag}⁺(AgCl₂)⁻, and the AgCl₂ anion was coordinated with one of four pyridines. Transmetallation from silver to nickel using NiCl₂(PPh₃)₂ in toluene and a subsequent anion exchange gave us {[NHC(CH₂Py)₂]NiCl}⁺(PF₆)⁻ and {[NHC(CH₂Py)₂]NiCl}⁺(BF₄)⁻ in good yields. These complexes were active and highly stable catalysts when used for Kumada-Tamao-Corriu coupling between 3-bromo-/3-chloropyridine and PhMgBr.

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carbenic carbons that have a bicyclic architecture.

Our group developed our original NHCs, which we refer to as DHASI, and revealed that the aromatic ring on the bicyclic architecture has an effective shielding effect on bound metals [8]. Cu and Ni complexes supported by original NHCs showed high catalytic activity during the borylation of aryl bromide [8b], allylic arylation with Grignard reagents [8c], Kumada-Tamao-Corriu (KTC) coupling [8d], Suzuki-Miyaura coupling [8e], and Chan-Lam coupling [8f]. We also successfully isolated some stable silver, copper, and nickel complexes using DHASI ligands, and most of the structures were confirmed by X-ray crystallography. It must be emphasized that DHASIs have simple alkyl groups such as methyl, isopropyl, or cyclohexyl on their nitrogen elements adjacent to the carbenic carbon. In general, substituents on the nitrogen(s) of NHC ligands must be bulky, particularly imidazolinylidene ligands, in order to suppress the decomposition of metal complexes. On the other hand, DHASIs have demonstrated a great capacity for the stabilization of metal complexes even in the case of the silver complex in N,N'-dimethyl-DHASI (DHASIMe). We envisioned a pincer ligand with our motif showing good stability and activity during the catalysis of transitional metal complexes, and decided to synthesize *N*,*N*'-bis(pyridylmethyl)-DHASI, which is one of the most simple examples of an NCN type of pincer ligand. The synthesized pincer DHASI was applied to the syntheses of silver and nickel complexes, and the nickel complex was found to be an active catalyst for KTC coupling between 3-bromopyridine and PhMgBr.



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2. Material and methods

2.1. General procedure and chemicals

All reactions were carried out under an argon atmosphere with freshly distilled solvents under anhydrous conditions, unless otherwise noted. 1,4-Dioxane was distilled from sodium benzophenone ketyl. Toluene was distilled from CaH₂. Anhydrous THF and acetonitrile were purchased and used without further purification. PhMgBr was prepared from Mg and PhBr in THF, and the resultant solution was titrated with 1,10-phenanthroline for the determination of the concentration. Reagents were used without further purification. Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous materials, unless otherwise stated.

All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25-mm E. Merck silica gel plates (60F–254) using UV-light (254 nm) for visualization or using phosphomolybdic acid in EtOH and cerium sulfate in 15% sulfuric acid for developing agents and heat for visualization. Fuji silysia silica gel (PSQ60B) was used for flash chromatography.

Melting points were measured using a Yanako micro melting point apparatus and are uncorrected. The NMR spectra were recorded on Bruker Avance 600 (600 MHz) instruments and calibrated using solvent and TMS peaks as internal references. The following abbreviations were used to indicate the multiplicities; s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, br = broad, and app = apparent. MS and HRMS (FAB) were obtained with a JEOL JMS-700 mass spectrometer. Highresolution mass spectra were obtained using EBE geometry.

2.2. Syntheses of ligand and metal complexes

N,N'-Bis(2-pyridylmethyl)-imidazolidine **2**; *meso*-3,5-Bis(2-pyridylmethyl)-3,5-diazadibenzo[h,k]tricyclo[5.2.2.2.^{2,6}]undeca-8,10-diene. Compound **2**: A flask was charged with *meso*-3,5-

Design of most pincer ligands with NHC(s)



Fig. 1. Design of the NCN pincer ligand with a DHASI core structure.

diazadibenzo[*h*,*k*]tricyclo[5.2.2.2.^{2,6}]undeca-8,10-diene [8b] (124 mg, 0.50 mmol) and a magnetic stir bar, and the resultant flask was evacuated and backfilled with argon, 1,4-Dioxane (2.5 mL) was added to the flask, and NaH (60% in oil, 100 mg, 2.50 mmol) was added in small portions to the flask, followed by an addition of freshly desalted 2-pyridylmethylchloride hydrochloride (246 mg. 1.50 mmol). The resultant flask was heated at reflux for 15 h under argon, and then the reaction was quenched with sat, NH₄Cl aq. (20 mL) at 0 °C. The mixture was extracted with EtOAc (15 mL \times 3), and the organic layers were washed with brine (30 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (10-40% EtOAc/nhexane) on amino-silica gel (100 mL) to afford the title compound 2 (159 mg, 74%) as an off-white powder. mp: 176–178 $^{\circ}$ C; ¹H NMR (600 MHz, CDCl₃, 300 K) δ = 8.53 (m, 2H), 7.65 (ddd, J = 7.6, 7.6, 1.7 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.20-7.12 (m, 8H), 7.04 (dd, J = 5.4, 3.2 Hz, 2H), 3.99 (d, J = 14.2 Hz, 2H), 3.95 (s, 2H), 3.84 (d, J = 14.2 Hz, 2H), 3.53 (d, J = 4.1 Hz, 1H), 3.35 (s, 2H), 3.15 (d, J = 4.1 Hz, 1H) ppm; ¹³C{¹H} NMR (151 MHz, CDCl₃, 300 K) $\delta = 159.5, 148.8, 142.0, 141.4, 136.5, 126.0, 125.7, 125.5, 124.5, 123.2,$ 122.1, 78.3, 69.0, 58.9, 48.6 ppm; HRMS (FAB+): m/z calcd. for C₂₉H₂₇N₄: 431.2236 [M+H]⁺; found 431.2239.

N,N'-Bis(2-pyridylmethyl)-imidazolinium chloride 3; meso-1,3-Bis(2-pyridylmethyl)-4,5-dihydro- 4,5-(9,10-dihydroanthraceno)-1H-imidazole-3-ium chloride. Compound 3: A flask was charged with meso-3,5-bis(2-pyridylmethyl)-3,5-diazadibenzo[h,k]tricyclo [5.2.2.2.^{2,6}]undeca-8,10-diene (646 mg, 1.50 mmol) and a magnetic stir bar. DME (37.5 mL) was added to the flask. followed by an addition of NCS (401 mg, 3.0 mmol). The resultant flask was darkened with aluminum foil and stirred for 16 h at ambient temperature. The white precipitate was filtered, washed with Et₂O (5 mL \times 3), and dried under reduced pressure to afford the title compound as a white powder (656 mg, 94%). mp: $176-178 \circ C$; ¹H NMR (600 MHz, CDCl₃, 300 K) $\delta = 10.36$ (s, 1H), 8.59 (ddd, J = 4.9, 1.1, 1.1 Hz, 2H), 7.80–7.75 (m, 8H), 7.36–7.30 (m, 4H), 7.22–7.15 (m, 6H), 5.17 (d, J = 14.6 Hz, 2H), 4.98 (s, 2H), 4.65 (d, J = 14.6 Hz, 2H), 4.54 (s, 2H) ppm; ${}^{13}C{}^{1}H$ NMR (151 MHz, CDCl₃, 300 K) $\delta = 160.4$, 152.8, 149.4, 138.6, 137.9, 137.1, 127.8, 127.6, 125.7, 125.3, 124.7, 123.9, 65.4, 51.2, 44.5 ppm; HRMS (FAB+): *m*/*z* calcd. for C₂₉H₂₅N₄: 429.2079 [M–Cl]⁺; found 429.2078.

[(Pincer NHC)₂AgCl][AgCl₂] 7; Complex 7: A flask was charged with meso-1,3-Bis(2-pyridylmethyl)- 4,5-dihydro- 4,5-(9,10dihydroanthraceno)-1H-imidazole-3-ium Chloride (232 mg, 0.50 mmol), Ag₂O (174 mg, 0.75 mmol), and a magnetic stir bar. CH₂Cl₂ (5.0 mL) was added to the flask, which was then darkened with aluminum foil and stirred for 16 h at ambient temperature. The resultant mixture was filtered through a short pad of Celite, washed with CH₂Cl₂, and the combined filtrate and washings were concentrated under reduced pressure to ca. 3 mL. n-Hexane (1.5 mL) was added to the flask to precipitate the title complex 7 as a beige powder (280 mg, 98%). A single crystal for X-ray diffraction analysis was grown by the slow diffusion of *n*-hexane into a CH₂Cl₂ solution. mp: 192-195 °C (decomp.); ¹H NMR (600 MHz, CDCl₃, 300 K $\delta = 8.60 \text{ (dd, } J = 4.9, 0.6 \text{ Hz}, 2\text{H}), 7.70 \text{ (ddd, } J = 7.6, 7.6, 1.7 \text{ Hz},$ 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.29–7.24 (m, 6H), 7.22–7.20 (m, 4H), 7.20-7.16 (m, 4H), 7.09 (dd, J = 5.5, 3.2 Hz, 2H), 4.89 (d, J = 15.3 Hz, 2H), 4.78 (s, 2H), 4.61 (d, J = 15.3 Hz, 2H), 4.36 (s, 2H) ppm; ¹³C{¹H} NMR (151 MHz, CDCl₃, 300 K) δ = 155.0, 149.6, 139.3, 137.8, 137.2, 127.1, 127.0, 125.4, 124.9, 123.2, 122.7, 66.7, 54.5, 45.2 ppm (carbenic carbon was not observed); HRMS (FAB+): m/z calcd. for C₅₈H₄₈N₈Ag: 963.3053 [(NHC)₂Ag]⁺; found 963.3063.

[(Pincer NHC)NiCl][PF6] **8**; Complex **8**. A flask was charged with [(pincer NHC)₂AgCl][AgCl₂] **7** (120 mg, 0.21 mmol), NiCl₂(PPh₃)₂ (275 mg, 0.42 mmol), and a magnetic stir bar. The resultant flask was evacuated and backfilled with argon (repeated three times),

and toluene (20 mL) was added to the flask. The reaction mixture was then heated at reflux for 15 h under argon, and the supernatant was removed by decantation. Toluene was added to the flask, and the flask was sonicated for 10 min, followed by decantation of the supernatant. This washing process was repeated twice. KPF₆ (39 mg, 0.21 mmol) and CH₃CN (21 mL) were added to the flask, which contained a residual green nickel complex, and the mixture was stirred for 24 h at ambient temperature. The reaction mixture was then filtered through a short pad of Celite, washed with CH₃CN $(2 \text{ mL} \times 3)$, and the combined filtrate and washings were concentrated under reduced pressure. The residual yellow powder was reprecipitated from Et₂O/CH₃CN. The obtained powder was washed with H₂O, filtered, and dried under reduced pressure to afford the title complex 8 (102 mg, 73%) as a pale yellow powder. A single crystal for X-ray diffraction analysis was grown by the slow diffusion of Et₂O into a CH₃CN solution. mp: 239–242 °C (decomp.); ¹H NMR (600 MHz, acetone- d_6 , 300 K) $\delta = 8.93$ (d, J = 5.6 Hz, 2H), 8.10 (dd, J = 7.6, 7.6 Hz, 2H), 7.82 (d, J = 7.6 Hz, 2H), 7.46–7.38 (m, 4H), 7.21 (dd, J = 5.4, 3.1 Hz, 2H), 7.08 (br s, 2H), 6.84–6.77 (m, 2H), 5.41 (d, J = 16.0 Hz, 2H), 5.26 (d, J = 16.0 Hz, 2H), 5.10 (s, 2H), 4.89 (s, 2H) ppm; ¹³C{¹H} NMR (151 MHz, acetone- d_6 , 300 K) $\delta = 157.0$, 155.8, 141.1, 140.0, 138.8, 128.2, 127.3, 126.4, 126.1, 125.8, 124.5, 69.4, 50.7, 46.5 ppm (carbenic carbon was not observed); HRMS (FAB+): m/zcalcd. for C₂₉H₂₄N₄NiCl: 521.1043 [M-PF₆]⁺; found 521.1072.

[(Pincer NHC)NiCl][BF₄] **9**; Complex **9**. Complex **9** was synthesized using the same procedure detailed in the synthesis of complex **8** except for the usage of NaBF₄ instead of KPF₆. The title complex **8** was obtained as a greenish yellow powder (95 mg, 74%). A single crystal for X-ray diffraction analysis was grown by the slow diffusion of Et₂O into a CH₃CN solution. mp: 237–239 °C (decomp.); ¹H NMR (600 MHz, acetone-*d*₆, 300 K) δ = 8.93 (d, *J* = 5.6 Hz, 2H), 8.10 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.45–7.39 (m, 4H), 7.21 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.08 (br s, 2H), 6.84–6.77 (m, 2H), 5.41 (d, *J* = 16.0 Hz, 2H), 5.26 (d, *J* = 16.0 Hz, 2H), 5.11 (s, 2H), 4.89 (s, 2H) ppm; ¹³C{¹H} NMR (151 MHz, acetone-*d*₆, 299 K) δ = 157.0, 155.9, 141.1, 140.0, 138.9, 128.2, 127.3, 126.4, 126.2, 125.9, 124.5, 69.4, 50.7, 46.5 ppm (carbenic carbon was not observed); HRMS (FAB+): *m/z* calcd. for C₂₉H₂₅N₄NiCl: 521.1043 [M–BF₄]⁺; found 521.1049.

2.3. Typical procedure for a KTC coupling reaction

PhMgBr was freshly prepared from PhBr and Mg turnings in THF and titrated using 1,10-phenanthroline for determination of the concentration. Ni complex and a magnetic stir bar were added to a flask. An arylhalide in THF was added to the flask under an Ar atmosphere. The resultant flask was cooled in an ice bath, and PhMgBr in THF (2.5 eq.) was added dropwise at the same temperature. The reaction solution was stirred at ambient temperature until TLC monitoring indicated the complete consumption of the substrate, and the reaction was then quenched with sat. NH₄Cl aq. at 0 °C. The resultant mixture was extracted with EtOAc (three times), and the combined organic layers were washed with brine, dried over NaSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by a column chromatography on silica gel to afford the cross-coupled product.

3. Results and discussion

3.1. Syntheses of a novel NCN pincer-type NHC ligand, a silver complex, and nickel complexes

We started the synthesis of a new pincer ligand from imidazolidine **1** (Scheme 1), which we had previously reported [8b]. Two pyridylmethyl groups were introduced using freshly desalted 2chloromethylpyridine hydrochloride in the presence of NaH as a base, and a subsequent oxidation of imidazolidine 2 to imidazolinium chloride 3 was accomplished via NCS in a 94% yield. The synthesized ligand precursor was briefly evaluated using KTC coupling between 3-halogenopyridines and PhMgBr (Table 1). A comparison with DHASIBn•HCl 6 [8a], which has a similar steric environment, was performed to examine the effects of additional coordination. Both NHC precursors were treated with *n*-BuLi in the presence of Ni(acac)₂ to form NHC–Ni complexes in situ, and were directly used as catalysts. Although the reaction between 3bromopyridine and PhMgBr can be catalyzed using both nickel complexes, the coupling using DHASIBn required a much longer reaction time than the reaction with the developed pincer ligand. The coupling using 3-chloropyridine 4b would not proceed using a DHASIBn-Ni catalyst, while the novel pincer NHC-Ni complex was capable of the reaction. These observations indicate that as a ligand for NHC-Ni catalysis, the DHASI with additional coordination sites is superior to the monodentate DHASI.

Encouraged by the above promising results, we next attempted the preparation of an air-stable NHC–Ni precatalyst for easy handling (Scheme 2). The imidazolinium chloride **3** was treated with Ag₂O in CH₂Cl₂ at 25 °C to afford a silver complex **7** in a 98% yield (see the following section for structural confirmation in the solid state). With the NCN pincer NHC-silver complex **7** in hand, we attempted an NHC transmetalation from silver to nickel. Although the treatment of the silver complex **7** with various nickel salts in CH₂Cl₂ at room temperature was fruitless, refluxing in toluene with NiCl₂(PPh₃)₂ gave a poorly soluble green complex [9]. After the removal of triphenylphosphine by extraction with toluene, the resultant complex was treated either with NaBF₄ or KPF₆ in acetonitrile to exchange a counter anion to tetrafluoroborate or hexafluorophosphate (74% for complex **8** and 73% for complex **9** respectively).

3.2. Structures of silver and nickel complexes in a solid state

Silver complexes of NHCs that have halide anions are aptly known to be very complex bonding motifs in the solid state; [10] therefore, we confirmed the structure by X-ray diffraction. The structure of complex 7 (CCDC# 1974276) in the solid state contained an [(NHC)–Ag–(NHC)]⁺ motif and a AgCl₂ anion bound to a nitrogen of the pyridine ring, and the absence of an Ag-Ag interaction was the most characteristic point of this complex (Fig. 2). This rare binding system had been previously reported only by Danopoulos and co-workers using an NHC equipped with a 2pyridylmethyl group on the nitrogen of an imidazolylidene ligand (Fig. 3a and Table 2) [11]. Lee and coworkers reported a related silver complex with an NHC that possessed a pyrazole instead of a pyridine (Fig. 3b) [12]. The bent structure of $(AgX_2)^-$ in this binding motif deviates from the standard structure where the $(AgX_2)^-$ is approximately linear in most $[(NHC)_2Ag]^+(AgX_2)^-$ complexes with an Ag–Ag interaction. The X–Ag–X angles of the two precedents are 154.5° (complex 10 reported by Danopoulos) and 139.8° (complex 11 reported by Lee), respectively, and the Cl1-Ag2-Cl2 in complex 4 is 123.4°. The distances between the silver and the nitrogen were 2.47 Å in complex 10, 2.35 Å in complex 11, and 2.35 Å in complex 7 (Ag2–N3). The twist angles of the two NHC planes were 33.5° in complex **10** and 24.2° in complex **7**, while complex **11** was almost planer around the NHC-Ag-NHC moiety (2.0°). In contrast to these differences, the distances between carbenic carbon and silver were similar (2.08–2.11 Å).

The obtained NCN pincer NHC–Ni complexes were subsequently analyzed by X-ray diffraction (CCDC numbers are 1974274 for complex **8** and 1974275 for complex **9**). Complexes **8** and **9** were recrystallized from n-hexane/acetonitrile into yellow plates



Scheme 1. Synthesis of an NCN pincer ligand with a DHASI coordination site.





1	4a	3	2.5	2.5	75
2	4a	6	2.5	20.5	64
3	4b	3	3.0	6.0	67
4	4b	6	3.0	21.0	NR ^a
aNo road	tion				

^aNo reaction.

(complex **8**, Fig. 4) or blocks (complex **9**), respectively. Both structures are basically identical in the solid state except for the counter anions. We compared the structure of complex **8** with a similar nickel complex **12** that was reported by Lee and co-workers (Table 3) [12]. These complexes bind to Ni with a carbene and two nitrogens of pyridine rings, and the coordination geometry of nickel is square planar in both structures. Bond lengths around the bound nickel as well as the twist angles between the N^1-C-N^2 planer and a planer around the bound nickel are located in close proximity. One of the most characteristic differences was observed around a heterocycle containing a carbenic carbon, which amounted to the imidazolylidene ring on complex **12** was planer, while the imidazolinylidene of DHASI appeared to have an



Fig. 2. ORTEP diagram of complex **7**. Thermal ellipsoids are shown at the 50% probability level (CCDC 1974276). H atoms are omitted for clarity.

envelope conformation with a 5.8° bend toward the aromatic ring on the bicyclic architecture. The steric maps and $%V_{bur}$ of these complexes were also calculated using the SambVca program developed by Nolan and Caballo (Fig. 5) [13], which indicated that the bicyclic architecture resulted in a slight increase in the steric pressure ($%V_{bur}$: 61.4 on complex **8**; 58.1 on complex **12**). This steric pressure from the bicyclic architecture might have caused the higher catalytic activity and stability of the nickel complex during the KTC coupling shown in Table 4 (vide infra).

3.3. Structures of nickel complexes in a solution state

In the X-ray diffraction studies of Ni complexes **8** and **9**, pairs of asymmetric conformers were observed in a unit cell. In theory, the two pyridylmethyl groups are unequivalent in a single conformer in a solid state. In a solution state, however, the NMR spectra of these complexes showed symmetric features (see the supplementary material), which suggested the presence of a rapid conformational exchange between the enantiomeric conformers in an NMR time scale at 300 K. The experimental observations from silver complexe **7** showed the same situation, but we could not predict the structure in a solution state at this point, because the NHC–Ag complexes with a halogen counter anion have a substantial amount of possible equilibria [10].



Scheme 2. Syntheses of NCN pincer NHC-Ni complexes.



Fig. 3. Structure of NHC-AgX complexes related to complex 7.

Table 2											
Selected	bond	length	and	angles	of	complex	7,	complex	10	[11],	and
complex	11 [12	1.									

Distance (Å)/angle	Complex 8	Complex 10	Complex 11
(deg)		[11]	[12]
C _{carbene} –Ag1 N–Ag2	2.11 (1), 2.08 (1) 2.35 (6)	2.07 (4), 2.07 (6) 2.47 (4)	2.09 (9), 2.09 (8) 2.35 (1)
C _{carbene} —Ag1—C _{carbene}	173.3 (4)	175.9 (2)	179.5 (5)
Cl1—Ag2—Cl1	123.4 (1)	154.5 (3)	139.8 (2)



With the well-defined novel NHC–Ni complexes in hand, we investigated their catalytic activity during KTC coupling between 3-bromopyridine **4a** and PhMgBr. Both complexes **8** and **9** were activated *in situ* presumably by a Grignard reagent, and the resultant complex catalyzed the KTC coupling shown in Table 4 with a 0.5 mol % catalyst loading, which resulted in 52 and 64% yields, respectively (entries 1 and 2). Complex **12** was also a catalytically active complex, but its activity was somewhat lower than complexes possessing the DHASI core structure (entry 3). Albeit with the requirement of longer reaction time, 0.1 mol% of complex **9** was capable of catalyzing this

Table 3

Comparison of an NCN pincer with imidazolylidene-Ni complex 12.



Distance (Å)/angle (deg)	Complex 8	Complex 12
C–Ni	1.84 (3)	1.84 (3)
N ³ -Ni, N ⁴ -Ni	1.93 (2), 1.93 (2)	1.94 (4), 1.94 (3)
Ni-Cl	2.23 (7)	2.24 (1)
N^1-C-N^2	110.4 (2)	106.9 (3)
$C-Ni-N^3$, $C-Ni-N^3$	87.4 (9), 87.4 (8)	86.7 (1), 87.0 (2)
C–Ni–Cl	179.2 (7)	179.0 (1)

N2 N1 N1 C N3

Fig. 4. ORTEP diagram of complex 8. Thermal ellipsoids are shown at the 50% probability level (CCDC 1974274). H atoms and counter anion are omitted for clarity.

coupling (entry 4). Even with this lowered catalyst loading system, complex 9 showed better activity than complex 12 (entry 5), and the bicyclic motif effectively stabilized the catalytically active nickel species. To demonstrate this stabilizing effect, we attempted the experiment shown in Fig. 6. In this experiment, we performed the same coupling using a 0.5 mol% catalyst for 24 h, and then an additional 3-bromopyridine and PhMgBr solution was added to the reaction flask and stirred at 25 °C for a further 42 h (Fig. 6a). After the isolation procedure, we obtained the product in a 69% yield, suggesting that the active species maintained its level of activity in the reaction vessel after 24 h. Further investigation using a second addition (first addition was after 24 h and second was addition after 66 h, Fig. 6b) obviously indicated that the catalyst remained active even after 66 h, although the activity seemed to decrease somewhat. These data verified that our NCN pincer NHC preserved the activity of the bound nickel under the reaction conditions for as long as several days.



Fig. 5. The steric maps of a) complex 8 and b) complex 12. Calculation parameters: Bondi radii scaled by 1.17; 3.5 Å for the sphere radius; 0.0 Å for the distance from the center of the sphere; 0.10 Å for the mesh spacing.

Table 4

KTC coupling using an NCN pincer NHC-Ni precatalyst.



4. Conclusions

We developed a novel NCN pincer NHC ligand that bears a bicyclic architecture on its non-carbenic carbons. The synthesized pincer ligand was successfully applied to the syntheses of silver and nickel complexes, and we unambiguously confirmed the structures of complexes 7, 8, and 9 via X-ray crystallography. The silver complex **7** in the solid state is a rare $[(NHC)_2Ag][AgCl_2]$ type of binding system that is without Ag–Ag interaction. The NHC-Ni complexes $\mathbf{8}$ and $\mathbf{9}$ with PF₆ and BF₄ counter anions were also analyzed, and the results indicated that the binding systems were almost identical to the reported NCN imidazolylidene-Ni complex 12 with the exception of differences between imidazolinylidene and imidazolylidene. Calculation using the SambVca program suggested that our DHASI-based pincer ligand has a somewhat higher $%V_{bur}$ than complex **12**. The welldefined nickel complexes were used as precatalysts for KTC coupling between 3-bromo-/3-chloropyridine and PhMgBr, where the complex 9 was found to be the best catalyst among the three complexes we tested. The robustness of an in situ-formed catalyst was also investigated, and the performance of complex 9 showed it to be a long-lived active species. Further investigations to find a unique reaction for the synthesized novel NCN pincer NHC-Ni complex are being conducted in our laboratory.



Fig. 6. Investigation of the robustness of the in situ-formed catalyst.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2020.121200.

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