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Acetylacetonato-based pincer-type nickel(II) complexes: synthesis and catalysis in cross-couplings of aryl chlorides with aryl Grignard reagents†

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In this work, three different types of acetylacetonato-based pincer-type nickel(II) complexes (**2**) were prepared. Complex **2a** possessed the tridentate ONN ligand, which was constructed by the condensation reaction of acetylacetone with *N,N*-diethylethylenediamine. Complex **2b** contained the PPh₂ donor group in contrast to the NEt₂ group in **2a**, i.e., an ONP ligand framework. Complex **2c** was composed of the NNN ligand, which was prepared by the reaction of 4-((2,4,6-trimethylphenyl)amino)pent-3-en-2-one with *N,N*-diethylethylenediamine. In addition to X-ray diffraction analysis, these complexes were characterized spectroscopically. Their catalytic activity for a cross-coupling reaction of aryl halides with aryl Grignard reagents was also evaluated. Among these complexes, **2b** acted as an effective catalyst for the cross-coupling reaction using aryl chlorides as electrophiles. The electronic properties of these Ni(II) complexes were investigated by cyclic voltammetry and density functional theory calculations.

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Introduction

Nickel-catalyzed cross-coupling reactions of an organic halide with a Grignard reagent were first described independently by Kumada/Tamao and Corriu.¹ Subsequently, such transition metal-catalyzed cross-coupling reactions of organic halides with organometallic reagents have developed into reliable and versatile tools for modern synthetic organic chemistry.² In these reactions, organic chlorides are less frequently employed as electrophiles in comparison with the corresponding bromides and iodides. This is because of the poor reactivity of the C–Cl bond. However, organic chlorides are useful substrates because of their low cost and the wide diversity of available compounds. Therefore, the development of highly active catalysts for organic chlorides in cross-coupling reactions has

received significant attention.³ In order to achieve the activation and smooth scission of the C–Cl bond in an electrophile on the metal, ancillary ligands are often used to provide an appropriate steric and electronic environment around the metal center. Naturally, such ligands play an important role in determining the catalytic properties. To date, several effective ligand systems for cross-coupling reactions have been reported. In recent years, tridentate pincer-type complexes have generated a lot of interest because the pincer-type ligand stabilizes the metal complexes and its properties can be tuned to achieve the best reactivity of the complex.^{4,5} Consequently, extensive attention has been focused on the combination of pincer-type ligands with Ni,^{5–14} which is one of the most attractive metals because of its significantly low cost as compared to precious metals such as palladium, rhodium, etc.

We have recently reported the synthesis of iron complexes bearing the tridentate β-aminoketonato ligand,¹⁵ which was easily prepared by the condensation reaction of acetylacetone with a primary amine tethering an additional donor unit. These iron complexes proved to be highly effective catalysts for the cross-coupling reaction of alkyl halides and aryl Grignard reagents¹⁶ and the atom-transfer radical polymerization reaction of styrenes.¹⁷ In order to elucidate both the generality and the availability of this type of ligands for constructing pincer-type complexes, novel Ni(II) complexes bearing β-aminoketonato- and β-diketiminato-based tridentate ligands

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were prepared. The cross-coupling reaction of aryl halides with aryl Grignard reagents was also investigated using these Ni(II) complexes as catalysts. It was found that the modifications of the ligand framework had a significant influence on the catalytic performance. In this paper, we have described the synthesis and structures of the pincer-type Ni(II) complexes and their application as catalysts for the cross-coupling reactions. Furthermore, the electronic properties of the Ni(II) complexes were estimated by cyclic voltammetry (CV) and density functional theory (DFT) calculations.

Results and discussion

Synthesis and characterization

The synthetic procedures for the acetylacetonate-based tridentate pro-ligands **1-H** are shown in Scheme 1. The pro-ligands **1a-H**¹⁶ and **1b-H**¹⁸ were prepared according to the literature reported method of a condensation reaction of acetylacetonate with the appropriate primary amine tethering an additional donating group such as NEt₂ or PPh₂ in the presence of a catalytic amount of H₂SO₄ in toluene at reflux. Pro-ligand **1c-H** was prepared by the reaction of 4-((2,4,6-trimethylphenyl)amino)pent-3-en-2-one with *N,N*-diethylethylenediamine. The former compound was prepared by the condensation of acetylacetonate with 2,4,6-trimethylaniline. Compound **1c-H** was isolated as a brown liquid in 72% yield. These compounds were characterized by NMR spectroscopy. In the ¹H NMR spectrum of **1-H**, the characteristic signals of the N–H proton atom were downfield at ~10–11 ppm.

Single crystals of **1b-H** were obtained by recrystallization from toluene/hexane and analyzed by X-ray diffraction. The ORTEP drawing of **1b-H** is shown in Fig. 1. The position of the hydrogen atom (H1) bonded to the nitrogen atom (N1) was

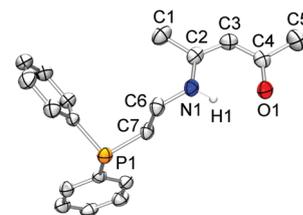
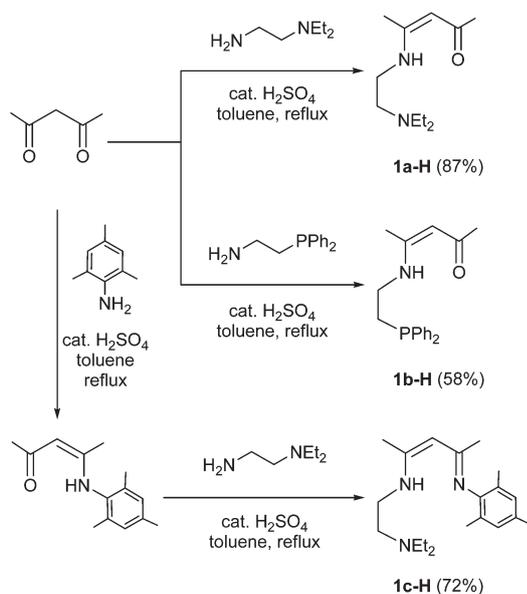


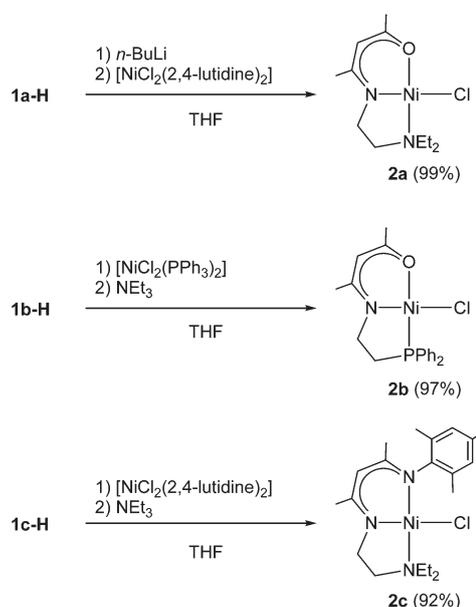
Fig. 1 ORTEP drawing of **1b-H** (30% probability of thermal ellipsoids). All hydrogen atoms except for H1 have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1–C2, 1.507(4); C2–C3, 1.374(4); C3–C4, 1.408(4); C4–C5, 1.511(4); O1–C4, 1.241(3); N1–C2, 1.324(4); N1–C6, 1.454(3); N1–H1, 0.90(3); N1...O1, 2.687(3); O1...H1, 1.94(4); N1–C2–C1, 117.7(2); N1–C2–C3, 122.3(2); C1–C2–C3, 120.0(3); C2–C3–C4, 124.5(3); O1–C4–C3, 123.2(2); O1–C4–C5, 118.5(3); C3–C4–C5, 118.3(3); C2–N1–C6, 127.4(2); C2–N1–H1, 112.3(15); C6–N1–H1, 119.8(15); N1–H1...O1, 139(2).

determined from the difference Fourier maps and refined isotropically. The N1...O1 and O1...H1 distances were found to be 2.687(3) and 1.94(4) Å, respectively. These distances are in good agreement with that of the reported N–H...O hydrogen bond.¹⁹ In the β-aminoketone skeleton, the N1–C2 bond length (1.324(4) Å) is within the mean value of the N–C single bond (1.48 Å) and the N–C double bond (1.24 Å). The O1–C4 bond length (1.241(3) Å) was close to the C–O double bond length (1.23 Å). The C2–C3 (1.374(4) Å) and C3–C4 (1.408(4) Å) bond lengths were within the mean value of the C–C single and double bond lengths. Although, the O1–C4 bond showed a slight double bond character, it is conceivable that the π-electrons on the N1–C2–C3–C4–O1 unit would be delocalized in this skeleton.

Next, the preparation of nickel(II) complexes **2** using these ligands was examined (Scheme 2). Treatment of the nickel(II)



Scheme 1 Preparation of pro-ligands **1-H**.



Scheme 2 Preparation of nickel complexes **2**.

complex precursor $[\text{NiCl}_2(2,4\text{-lutidine})_2]$ with the lithiated tridentate ligand (**1a-Li**), which was prepared *in situ* by the reaction of **1a-H** with *n*-BuLi in THF, led to the formation of the **2a** as a purple solid in 99% yield. A similar procedure was used for the preparation of complex **2b**, *i.e.*, the reaction of the lithiated ligand **1b-Li** with $[\text{NiCl}_2(2,4\text{-lutidine})_2]$. Complex **2b** was isolated as an orange solid in moderate yield (70%). We then examined the one-pot reaction of pro-ligand **1b-H** with $[\text{NiCl}_2(2,4\text{-lutidine})_2]$ in the presence of NEt_3 as a base. In this case, **2b** was obtained in 55% yield. The best yield of **2b** (97%) was achieved by reacting $[\text{NiCl}_2(\text{PPh}_3)_2]$ as the metal precursor instead of $[\text{NiCl}_2(2,4\text{-lutidine})_2]$ with **1b-H** in the presence of NEt_3 . Complex **2c** was isolated as a red solid in 40% yield from the reaction of the lithiated tridentate ligand **1c-Li** with $[\text{NiCl}_2(2,4\text{-lutidine})_2]$. In contrast, the one-pot reaction of **1c-H** with $[\text{NiCl}_2(2,4\text{-lutidine})_2]$ in the presence of NEt_3 afforded complex **2c** in 92% yield. Elemental analysis, NMR spectra, and X-ray diffraction studies confirmed the formation of the desired pincer-type Ni(II) complexes **2a–2c**.

In the ^1H NMR spectra of **2**, the low magnetic resonance assignable to the N–H proton atom in pro-ligands **1-H** was not

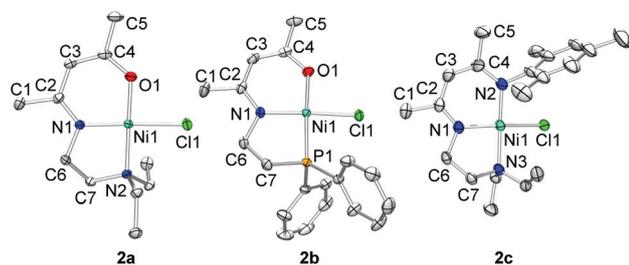


Fig. 2 ORTEP drawings of complexes **2a–2c** (30% probability of thermal ellipsoids). All hydrogen atoms have been omitted for clarity.

observed. This indicated that the ligand **1** was deprotonated and coordinated to the nickel center as a monoanionic fashion. In complex **2a**, the methylene proton atoms of the diethylamino moiety showed two sets of doublet of quartets at 2.46 and 3.18 ppm with coupling constants of 13.2 and 7.2 Hz, respectively. The corresponding methylene proton atoms in the pro-ligand **1a-H** showed a quartet at 2.57 ppm with $J = 7.3$ Hz. The nonequivalence of these methylene proton atoms in complex **2a** indicated that the ligand was coordinated to the Ni center in a tridentate fashion. Similar spectroscopic features were observed in complex **2c**, namely, two sets of doublet of quartets corresponding to the methylene proton atoms in the diethylamino group at 2.40 and 3.25 ppm with $J = 12.8$ and 7.2 Hz, respectively. Complex **2b** was characterized by comparing the ^1H NMR and ^{31}P -decoupled ^1H NMR ($^1\text{H}\{^{31}\text{P}\}$ NMR) spectra (see Experimental section). In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2b**, a singlet was observed at 37.5 ppm, which suggests that the PPh_2 moiety was coordinated to the Ni center (-20.8 ppm for **1b-H**). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2b**, two doublet signals corresponding to the OCCH_3 carbon atoms in the β -aminoketonato unit were observed at 178.8 ppm ($J = 2.7$ Hz) and 25.2 ppm ($J = 6.4$ Hz). These observations indicated that **1b** was coordinated to the Ni center in a tridentate fashion and the phosphorus atom was positioned *trans* to the oxygen atom of the β -aminoketonato unit.

The structures of the nickel(II) complexes **2a**, **2b** and **2c** were determined by X-ray analysis. The ORTEP drawings of **2a**, **2b** and **2c** are shown in Fig. 2. The selected bond lengths and angles for these complexes are listed in Table 1. These complexes have a distorted square planar geometry around the central metal, in which the ligand coordinates in a tridentate pincer-type fashion. The angles for the ligands in the mutually *cis* position bound to the Ni center were in the range $86.08(10)$ – $95.48(8)^\circ$ and the sum of the angles around the Ni

Table 1 Selected bond lengths (Å) and angles ($^\circ$) of complexes **2a**, **2b** and **2c**

2a		2b		2c	
Ni1–Cl1	2.2399(6)	Ni1–Cl1	2.1732(7)	Ni1–Cl1	2.2154(8)
Ni1–N1	1.8696(18)	Ni1–N1	1.896(2)	Ni1–N1	1.860(2)
Ni1–O1	1.8395(18)	Ni1–O1	1.8665(18)	Ni1–N2	1.891(3)
Ni1–N2	1.980(2)	Ni1–P1	2.1292(6)	Ni1–N3	1.994(3)
N1–C2	1.316(3)	N1–C2	1.321(3)	N1–C2	1.321(4)
O1–C4	1.296(3)	O1–C4	1.282(3)	N2–C4	1.339(4)
C1–C2	1.511(4)	C1–C2	1.517(4)	C1–C2	1.504(5)
C2–C3	1.408(3)	C2–C3	1.403(4)	C2–C3	1.384(5)
C3–C4	1.366(4)	C3–C4	1.369(4)	C3–C4	1.381(5)
C4–C5	1.506(4)	C4–C5	1.505(4)	C4–C5	1.527(5)
Cl1–Ni1–N1	177.20(7)	Cl1–Ni1–N1	174.50(6)	Cl1–Ni1–N1	163.43(6)
O1–Ni1–N2	178.36(9)	O1–Ni1–P1	174.16(5)	N2–Ni1–N3	169.29(9)
N1–Ni1–O1	93.68(9)	N1–Ni1–O1	95.48(8)	N1–Ni1–N2	93.27(11)
N1–Ni1–N2	87.11(9)	N1–Ni1–P1	88.10(6)	N1–Ni1–N3	86.08(10)
Cl1–Ni1–O1	87.40(6)	Cl1–Ni1–O1	88.80(6)	Cl1–Ni1–N2	93.20(8)
Cl1–Ni1–N2	91.74(6)	Cl1–Ni1–P1	87.92(3)	Cl1–Ni1–N3	90.34(7)
Ni1–N1–C2	127.51(17)	Ni1–N1–C2	123.64(18)	Ni–N1–C2	127.1(2)
Ni1–N1–C6	112.80(16)	Ni1–N1–C6	118.64(15)	Ni–N1–C6	114.36(16)
C2–N1–C6	119.49(19)	C2–N1–C6	117.4(2)	C2–N1–C6	117.8(3)
C2–C3–C4	123.9(2)	C2–C3–C4	125.9(2)	C2–C3–C4	125.8(3)
Ni1–O1–C4	126.49(16)	Ni1–O1–C4	126.94(17)	Ni1–N2–C4	125.1(2)

center in complexes **2a** and **2b** was almost 360° (359.93° for **2a** and 360.30° for **2b**). On the other hand, in complex **2c**, the sum of the angles around the Ni center was 362.89° . Furthermore, a notable feature was observed in the angles for the ligands in the mutually *trans* position bound to the Ni center. The Cl1–Ni1–N1 angles decreased in the order **2a** ($177.20(7)^\circ$) > **2b** ($174.50(6)^\circ$) > **2c** ($163.43(6)^\circ$). The other mutually *trans* ligand angles showed similar features (O1–Ni1–N2 = $178.36(9)^\circ$ for **2a**, O1–Ni1–P1 = $174.16(5)^\circ$ for **2b**, and N2–Ni1–N3 = $169.29(9)^\circ$ for **2c**). This trend may be explained by the presence of the sterically bulky substituent on the tridentate ligand. Therefore, it was assumed that the Ni center in complex **2c** was sterically more crowded than in **2a** and **2b**.

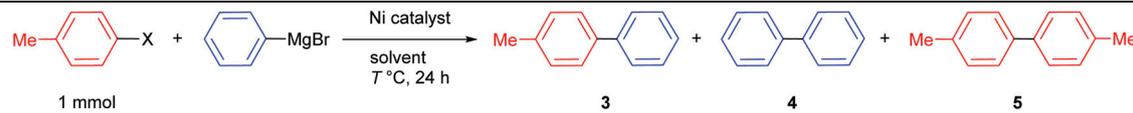
In all Ni(II) complexes, the C2–C3 and C3–C4 bond lengths were in almost the same ranges of 1.384(5)–1.408(3) Å and 1.366(4)–1.381(5) Å, respectively. The N1–C2 bond lengths in all complexes and the N2–C4 bond length for **2c** were within the mean value range of the N–C single and double bonds. Furthermore, the O1–C4 bond lengths in **2a** and **2b** were within the mean value range of the O–C single and double bonds. This implied that the π -electrons were delocalized on the N1–C2–C3–C4–O1 and N1–C2–C3–C4–N2 frameworks. The conjugated nitrogen atom N1 and the Ni center bond lengths (1.8696(18) Å for **2a**, 1.896(2) Å for **2b**, and 1.860(2) Å for **2c**) were substantially shorter than the amino nitrogen atom N2 or N3 and Ni bond lengths (Ni1–N2 = 1.980(2) Å for **2a** and Ni1–N3 = 1.994(3) Å for **2c**). Furthermore, the bond length of the other conjugated nitrogen atom N2 and Ni1 (1.891(3) Å) in **2c** was close to the Ni1–N1 bond length in complexes **2**. Therefore, it is conceivable that the monoanionic conjugated ligand system makes a considerable contribution to the formation of the stable pincer-type Ni(II) complexes.

Cross-coupling reaction catalyzed by Ni(II) complexes

The pincer-type Ni(II) complexes (**2a–2c**) were examined as catalysts in the cross-coupling reaction of 4-halotoluene with phenylmagnesium bromide. The results of the optimization experiments are summarized in Table 2.

In order to evaluate the catalytic activity of three nickel(II) complexes, the cross-coupling reaction was conducted by using 1.0 mmol of 4-chlorotoluene with 1.5 equivalents of phenylmagnesium bromide and 1 mol% of the nickel(II) complex in THF at 25°C for 24 h (entries 1–3). It was found that these complexes exhibited catalytic activity in the cross-coupling reaction and that complex **2b**, which has the β -aminoketonato skeleton with a PPh₂ moiety as the third donor, gave the best result. Complex **2b** afforded 4-phenyltoluene (**3**) in 83% yield along with the formation of homo-coupled products, biphenyl (**4**, 12%) and 4,4'-dimethylbiphenyl (**5**, 5%). To investigate the influence of the halide in as electrophile, the catalytic reactions were performed with 4-bromotoluene and 4-iodotoluene in the presence of a catalytic amount of **2b**. Similar results were obtained in the case of 4-bromotoluene (entry 4). On the other hand, with 4-iodotoluene, the yield of the cross-coupled product **3** decreased to 52% and that of the homo-coupled product **4** derived from the nucleophile increased to 37% (entry 5). In this case, 4-iodotoluene would act as not only an electrophile but also an oxidizing agent for the nickel in the catalytic cycle. Therefore, it caused the decrease in the cross-coupled product and the increase in the homo-coupled product. These results show that complex **2b** effectively catalyzed the cross-coupling reaction of aryl chloride as an electrophile. To further investigate the influence of the solvent, the reaction was conducted in different solvents. In ethereal solvents such as 1,2-dimethoxyethane (DME), Et₂O, and cyclopentyl methyl ether (CPME), poor

Table 2 Optimization of the cross-coupling reaction catalyzed by Ni(II) complexes **2**^a



Entry	Ni catalyst (mol%)	X (<i>p</i> -TolX)	PhMgBr (equiv.)	Solvent	<i>T</i> ($^\circ\text{C}$)	3 ^b (%)	4 ^b (%)	5 ^b (%)
1	2a (1)	Cl	1.5	THF	25	47	23	18
2	2b (1)	Cl	1.5	THF	25	83	12	5
3	2c (1)	Cl	1.5	THF	25	48	25	18
4	2b (1)	Br	1.5	THF	25	80	13	6
5	2b (1)	I	1.5	THF	25	52	37	5
6	2b (1)	Cl	1.5	DME	25	19	7	2
7	2b (1)	Cl	1.5	Et ₂ O	25	19	13	1
8	2b (1)	Cl	1.5	CPME	25	48	15	4
9	2b (1)	Cl	1.5	1,4-Dioxane	25	73	11	4
10	2b (1)	Cl	1.5	toluene	25	69	23	14
11	2b (1)	Cl	1.5	THF	50	84	17	9
12	2b (1)	Cl	1.5	THF	0	74	9	4
13	2b (1)	Cl	2.0	THF	25	82	14	5
14	2b (1)	Cl	2.5	THF	25	84	10	7
15	2b (2.5)	Cl	1.5	THF	25	91	14	6

^a The reaction was carried out a 1.0 mmol scale of 4-halotoluene. Phenylmagnesium bromide was added at once. ^b The yields were determined by GLC analysis using octadecane as an internal standard.

results were obtained (entries 6–8). In 1,4-dioxane, product **3** was obtained in 73% yield (entry 9). Toluene was also an effective solvent and the yield of **3** was 69% (entry 10). From these results, it was concluded that THF was a suitable solvent for this reaction. The reactions were conducted at 50 °C and 0 °C. However, the yield of **3** was not improved at higher or lower temperatures (entries 11 and 12). Regarding the optimum amounts of the Grignard reagent and the catalyst **2b**, it was found that 1.5 equivalents of the Grignard reagent and 2.5 mol% of the catalyst led to good yields of **3** (entries 13–15).

To demonstrate the efficiency of complex **2b** as a catalyst for the biaryl cross-coupling reaction, we investigated the scope of the reaction by using different aryl chlorides and arylmagnesium bromides under the optimized reaction conditions. The results are summarized in Table 3. The aryl halide 4-chlorobenzotrifluoride, which has an electron-withdrawing group on the aromatic ring, afforded the desired product in 85% yield after 24 h (entry 1). Furthermore, the reaction was complete within 5 min (entry 2). In the case of 4-chloroanisole, which has an electron-donating substituent, the product was obtained in 88% yield after 24 h (entry 3). However, after 5 min, the yield of the product was only 35% (entry 4).

3-Chlorotoluene was effectively converted to 3-phenyltoluene (87%, entry 5). In the case of 2-chlorotoluene, the coupled product, 2-phenyltoluene, was obtained in 67% yield under the optimized conditions (25 °C, 24 h, entry 6). Under THF-refluxing conditions, the yield of 2-phenyltoluene increased to 81% (entry 7). Next, we examined the reaction of chlorobenzene with tolylmagnesium bromides. In the case of both *p*- and *m*-tolylmagnesium bromide, coupling products were formed in 91% yield (entries 8 and 9). On treating with *o*-tolylmagnesium bromide at 25 °C, 2-phenyltoluene was formed in 60% yield (entry 10). The product yield increased to 84% under refluxing conditions (entry 11). 2-Chloro-1,3,5-trimethylbenzene (mesityl chloride), as a sterically congested substrate, was examined in the reaction with phenylmagnesium bromide. When the reaction was conducted at 25 °C for 72 h, only a small amount of the desired product was obtained (5%, entry 12). The product yield did not increase to any appreciable extent (16%, entry 13) even after reflux for 72 h. In the reaction of chlorobenzene with 2-mesitylmagnesium bromide at 25 °C for 72 h, the yield of the product was not improved (2%, entry 14). On the other hand, the product was formed in 42% yield under refluxing conditions (entry 15).

Table 3 Results of cross-coupling reaction catalyzed by **2b**^a

Entry	Ar ¹ -Cl	Ar ² -MgBr	2b (2.5 mol%)		Ar ¹ -Ar ²	Yield ^b (%)
			THF, T (°C), Time			
1			25	24 h		85 ^c
2			25	5 min		86 ^c
3			25	24 h		88 ^c
4			25	5 min		35 ^c
5			25	24 h		87
6			25	24 h		67
7			Reflux	24 h		81
8			25	24 h		91
9			25	24 h		91
10			25	24 h		60
11			Reflux	24 h		84
12			25	72 h		5 ^c
13			Reflux	72 h		16 ^c
14			25	72 h		2 ^c
15			Reflux	72 h		42 ^c

^a The reaction was carried out with chloroarene (1.0 mmol) and arylmagnesium bromide (1.5 mmol) in the presence of the catalyst **2b** (0.025 mmol). Arylmagnesium bromide was added at once. ^b The yield was determined by GLC analysis using octadecane as an internal standard. ^c The yield was determined by ¹H NMR analysis using pyrazine as an internal standard.

Table 4 Results of cross-coupling reaction of dihalobenzene with PhMgBr^a

Entry	Dihalobenzene	Time	Yield ^b (%)
1		5 min	80 (88 ^c)
2		24 h	67
3		24 h	11
4		5 min	52
5		24 h	62

^aThe reaction was carried out with dihalobenzene (1.0 mmol) and PhMgBr (2.5 mmol) in the presence of the catalyst **2b** (0.025 mmol). PhMgBr was added at once. ^bIsolated yield. ^cThe yield was determined by GLC analysis using octadecane as an internal standard.

Next, we examined the reaction of dihalobenzene with 2.5 equivalents of phenylmagnesium bromide and 2.5 mol% of complex **2b**. The results are summarized in Table 4. In the case of 1,4-dichlorobenzene, *p*-terphenyl was formed within 5 min in 88% yield, as determined by gas-liquid chromatography (GLC) analysis, and the product was isolated in 80% yield (entry 1). In the case of 1,3-dichlorobenzene, *m*-terphenyl was isolated in 67% yield (entry 2), whereas the yield of *o*-terphenyl decreased to 11% using 1,2-dichlorobenzene (entry 3). In contrast, the reaction with 1,4-dibromobenzene as an electrophile gave *p*-terphenyl in 52% yield after 5 min and 62% yield after 24 h (entries 4 and 5). These results clearly show that complex **2b** can activate the C–Cl bond, and more effectively than the C–Br bond in the cross-coupling reaction.

Catalytic performance of **2** for the KTC reaction

As mentioned above, the three nickel(II) complexes (**2**) are catalytically active in the Kumada–Tamao–Corriu (KTC) reaction. Among these complexes, **2b** possesses the β -aminoketonato framework with the PPh₂ unit as the third donor and acts as an effective pre-catalyst for this reaction. In order to elucidate the catalytic performance of these complexes, the electronic properties of complexes **2** were estimated by CV. The cyclic voltammograms of these complexes were measured in a CH₂Cl₂ solution. All complexes exhibited irreversible oxidation waves, which are shown in Fig. S5 and S6 (ESI[†]). The CV of complex **2b** showed a one-electron oxidation wave at 0.61 V vs. Fc/Fc⁺. In the case of complex **2a**, a similar oxidation potential was seen at 0.64 V. On the other hand, complex **2c** showed a lower potential (0.26 V) than complexes **2a** and **2b**. These oxidation potentials are reasonable values for the pincer-type Ni(II) complexes as compared to literature values, which were independently reported by Tonzetich¹² and Zargarian.^{14a} Based on the

oxidation potentials of these complexes, it is conceivable that the electron density accumulated at the Ni center increases in the order **2a** \approx **2b** < **2c**. We assumed that the highest occupied molecular orbital (HOMO) levels of these complexes would also increase in this order. Therefore, the electronic properties of the series of Ni(II) complexes were investigated theoretically.

Computational study was carried out using Gaussian 09 at the B3LYP level with LANL2DZ basis set for the Ni atom and 6-311++G(d,p) for the other atoms. The LANL2DZ pseudo-potential was used for the Ni center. Geometry optimizations of Ni(II) complexes **2a**, **2b**, and **2c** were successful. The optimized molecular structures are shown in Fig. S7 (ESI[†]). Selected geometrical parameters of these complexes are summarized in Table S6 (ESI[†]). The geometrical parameters of the Ni(II) complexes determined by DFT were found to be in good agreement with those obtained from X-ray analysis, although the calculations predicted slightly longer bond lengths.

The plots of the HOMO and LUMO orbitals of complexes **2a–2c** are illustrated in Fig. S8 (ESI[†]). These complexes had similar HOMO and LUMO orbitals. The HOMO of **2a** (–5.68 eV) was similar to that of **2b** (–5.61 eV) in energy, while the energy level of **2c** (–5.23 eV) was obviously higher than those of **2a** and **2b**. Furthermore, in these Ni(II) complexes, there was a good relationship between the HOMO energies and oxidation potentials determined by cyclic voltammetry. In these Ni(II) complexes, the HOMO orbitals are mainly located on the six-membered ring consisting of Ni and the conjugated ligand framework. Therefore, it was assumed that the conjugated ligand had an electronic influence on the Ni center and that the Ni(II) complex **2c** was more electron rich as compared to **2a** and **2b**. In general, it is known that in an electron rich metal complex, the oxidative addition reaction of an electrophile to the metal takes place quite easily.²⁰ Therefore, it was expected that complex **2c** would exhibit a high catalytic performance in the cross-coupling reactions. However, as mentioned above, the catalytic performance of complex **2b** was superior to that of **2a** and **2c**. Although, further investigation of the influence of electronic factors on the catalytic activity is necessary, the steric environment around the Ni center should be considered as the most dominant factor affecting the catalytic performance. The X-ray diffraction study of the series of Ni(II) complexes revealed that complex **2c** was more distorted from the ideal square planar geometry around the Ni center compared to complexes **2a** and **2b** (*vide supra*). This distortion arises from the steric bulkiness of the ligand skeleton. Therefore, in complex **2c**, the interaction of the substrate with the Ni center is encumbered and leads to poor catalytic activity. Compared to complex **2b**, complex **2a** also shows lower activity. These complexes show similar electronic features, as estimated by CV and DFT. The low performance of **2a** might be attributed to the different “third donor”, *i.e.*, the phosphorus or nitrogen donor atoms. Phosphorus as the third donor in complex **2b** would elicit a higher performance in the cross-coupling reaction. Further investigations of the influence of the ligand framework on the catalytic performance are currently underway.

Conclusions

In this work, we investigated the synthesis of pincer-type Ni(II) complexes and their catalytic performance for the KTC reaction. β -Aminoketonato and β -diketiminato frameworks tethering the nitrogen or phosphorus groups as the third donor to the metal center led to the desired pincer-type Ni(II) complexes **2**. The Ni(II) complexes exhibited catalytic activity for the KTC reaction; complex **2b** bearing the β -aminoketonato framework with the diphenylphosphino group as the third donor showed remarkable catalytic performance. The combination of β -aminoketonato and/or β -diketiminato frameworks with the third donor enabled the fine tuning of the electronic and steric factors around the metal center. These pincer ligand systems can be easily prepared by the condensation reaction of acetylacetonate with amines and their coordination to various transition metals is expected to produce highly active metal catalysts. Further investigations on the mechanistic aspects, the coupling reactions of various organometallic reagents with organic electrophiles, and the application of these ligand systems to other metals are currently underway.

Experimental

General procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were performed under an atmosphere of nitrogen, which was dried with SICAPENT (Merck Co., Inc.), using standard Schlenk tube or high vacuum techniques. All solvents were distilled over appropriate drying agents prior to use. 2-(Diphenylphosphino)ethylamine,²¹ **1a-H**,¹⁶ **1b-H**,¹⁸ 4-((2,4,6-trimethylphenyl)amino)pent-3-en-2-one,²² [NiCl₂(2,4-lutidine)₂],²³ and [NiCl₂(PPh₃)₂]²⁴ were prepared according to literature reported procedures. The other reagents employed in this work were commercially available and used without further purification. ¹H, ¹H{³¹P}, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on BRUKER DRX-300, DRX-500, or JEOL ECX-400 spectrometers at ambient temperature. The ¹H, ¹H{³¹P}, and ¹³C{¹H} NMR chemical shifts were recorded in ppm relative to Me₄Si as an internal standard. The ³¹P{¹H} NMR chemical shifts were recorded in ppm relative to H₃PO₄ as an external standard. All coupling constants were recorded in Hz. Multiplicity is indicated by s (singlet), d (doublet), t (triplet), q (quartet), dt (doublet of triplets), dq (doublet of quartets) and m (multiplet). Thin layer chromatography was performed using Merck silica gel 60F-254 plates and examined under UV (254 nm) irradiation. Column chromatography was performed using Silica Gel 60N (spherical, neutral, 63–210 μ m, Kanto Chemical Co., Inc.). High-resolution mass spectra (HRMS) were recorded using fast atom bombardment (FAB) ionization with a JEOL JMS-700 mass spectrometer. Elemental analyses were performed on a Vario EL elemental analyzer. GLC were recorded on a Shimadzu GC-17A gas chromatograph using a ULBON HR-1 capillary column (0.25 ID \times 25 m, Shinwa Chemical Industries Ltd).

Preparation of 1c-H

4-((2,4,6-Trimethylphenyl)amino)pent-3-en-2-one (1240 mg, 5.71 mmol), *N,N*-diethylethylenediamine (992 mg, 1.20 mL, 8.54 mmol), and toluene (60 mL) were put in a round-bottom flask. A few drops of H₂SO₄ and molecular sieves 4 Å (*ca.* 10 g) were added to the reaction mixture. The mixture was refluxed for 48 h and then cooled to room temperature. After neutralization with aq. KOH, the reaction mixture was extracted with CH₂Cl₂. The combined organic extracts were dried with Na₂SO₄, filtered, and concentrated *in vacuo* to obtain **1c-H** as a brown liquid (1300 mg, 4.12 mmol, 72%). ¹H NMR (δ , CDCl₃): 0.97 (t, *J* = 7.3 Hz, 6H, NCH₂CH₃), 1.59 (s, 3H, NCCH₃), 2.00 (s, 9H, *o*-(CH₃)₃C₆H₂ + *p*-(CH₃)₃C₆H₂, overlapped), 2.26 (s, 3H, NCCH₃), 2.51 (q, *J* = 7.3 Hz, 4H, NCH₂CH₃), 2.54 (m, 2H, NCH₂CH₂N), 3.30 (m, 2H, NCH₂CH₂N), 4.62 (s, 1H, CH), 6.84 (s, 2H, *N-m*-(CH₃)₃C₆H₂), 10.69 (broad s, 1H, NH). ¹³C{¹H} NMR (δ , CDCl₃): 11.9 (s, NCH₂CH₃), 18.3 (s, *N-o*-(CH₃)₃C₆H₂), 19.4 (s, *N-p*-(CH₃)₃C₆H₂), 20.7 (s, NCCH₃), 21.1 (s, NCCH₃), 41.9 (s, NCH₂CH₂N), 47.5 (s, NCH₂CH₃), 53.8 (s, NCH₂CH₂N), 93.1 (s, NCCCN), 127.6 (s, *N-m*-(CH₃)₃C₆H₂), 128.2 (s, *N-o*-(CH₃)₃C₆H₂), 130.8 (s, *N-p*-(CH₃)₃C₆H₂), 147.2 (s, *N-e*-(CH₃)₃C₆H₂), 155.3 (s, NCCCN), 166.0 (s, NCCCN). HRMS (FAB⁺) *m/z* [M + H]⁺ calc. for C₂₀H₃₄N₃: 316.2753; found 316.2750.

Preparation of 2a

A solution of [NiCl₂(2,4-lutidine)₂] (1240 mg, 3.61 mmol) in THF (15 mL) was prepared and cooled to -78 °C. To this solution, a THF solution of the lithiated ligand (**1a-Li**), which was prepared by the reaction of **1a-H** (718 mg, 3.62 mmol) with *n*-butyllithium (1.40 mL of the 2.67 M hexane solution, 3.74 mmol) at -78 °C, was added. The reaction mixture was allowed to warm to room temperature. After 18 h, the volatiles were removed under reduced pressure. The residual solid was extracted with CH₂Cl₂ (30 mL) and the volatiles were removed under reduced pressure. The resulting purple solid was washed with hexane and dried *in vacuo* to yield **2a** (1040 mg, 3.57 mmol, 99%). Analytically pure sample of **2a** was obtained by recrystallization from CH₂Cl₂/hexane. Anal. calc. for C₁₁H₂₁ClN₂NiO: C, 45.33; H, 7.26; N, 9.61%. Found: C, 45.35; H, 7.33; N, 9.53%. ¹H NMR (δ , CDCl₃): 1.75 (s, 3H, CH₃), 1.78 (t, *J* = 7.2 Hz, 6H, NCH₂CH₃), 1.90 (s, 3H, CH₃), 2.14 (t, *J* = 6.4 Hz, 2H, NCH₂CH₂N), 2.46 (dq, *J* = 13.2, 7.2 Hz, 2H, NCH₂CH₃), 3.06 (t, *J* = 6.4 Hz, 2H, NCH₂CH₂N), 3.18 (dq, *J* = 13.2, 7.2 Hz, 2H, NCH₂CH₃), 4.92 (s, 1H, CH). ¹³C{¹H} NMR (δ , CDCl₃): 11.1 (s, NCH₂CH₃), 21.2 (s, CH₃), 24.0 (s, CH₃), 50.2 (s, NCH₂CH₂N), 52.0 (s, NCH₂CH₂N + NCH₂CH₃, overlapped), 99.6 (s, CH), 164.6 (s, CCH₃), 176.8 (s, CCH₃).

Preparation of 2b

Compound **1b-H** (191 mg, 0.61 mmol), [NiCl₂(PPh₃)₂] (405 mg, 0.62 mmol), and THF (20 mL) were mixed in a Schlenk tube. After stirring the reaction mixture for 1 h, NEt₃ (0.10 mL, 73 mg, 0.72 mmol) was added to the mixture and the solution was stirred for another 4 h at room temperature. Subsequently,

the solution was filtered through a Celite pad and the filtrate was evaporated to dryness *in vacuo*. The residual solid was washed with Et₂O and dried *in vacuo* to yield **2b** as an orange solid (237 mg, 0.59 mmol, 97%). An analytically pure sample of **2b** was obtained by recrystallization from CH₂Cl₂/hexane. Anal. calc. for C₁₉H₂₁ClNiOP: C, 56.42; H, 5.23; N, 3.46%. Found: C, 56.14; H, 5.27; N, 3.37%. ¹H NMR (δ, C₆D₆): 1.27 (dt, *J* = 10.9, 6.8 Hz, 2H, NCH₂CH₂P), 1.35 (s, 3H, NCCH₃), 1.99 (s, 3H, OCCH₃), 2.41 (dt, *J* = 25.2, 6.8 Hz, 2H, NCH₂CH₂P), 4.92 (s, 1H, CH), 6.98–7.08 (m, 6H, *P-p*-C₆H₅ + *P-m*-C₆H₅), 7.93–8.01 (m, 4H, *P-o*-C₆H₅). ¹H{³¹P} NMR (δ, C₆D₆): 1.27 (t, *J* = 6.7 Hz, 2H, NCH₂CH₂P), 1.35 (s, 3H, NCCH₃), 1.99 (s, 3H, OCCH₃), 2.42 (t, *J* = 6.7 Hz, 2H, NCH₂CH₂P), 4.92 (s, 1H, CH), 6.99–7.09 (m, 6H, *P-p*-C₆H₅ + *P-m*-C₆H₅), 7.97 (d, *J* = 7.0 Hz, 4H, *P-o*-C₆H₅). ¹³C{¹H} NMR (δ, C₆D₆): 23.1 (s, NCCH₃), 25.2 (d, ⁴*J*_{PC} = 6.4 Hz, OCCH₃), 30.6 (d, ¹*J*_{PC} = 25.7 Hz, NCH₂CH₂P), 52.0 (d, ²*J*_{PC} = 8.2 Hz, NCH₂CH₂P), 99.8 (s, OCCCN), 128.7 (d, ³*J*_{PC} = 11.0 Hz, *P-m*-C₆H₅), 129.6 (d, ¹*J*_{PC} = 52.2 Hz, *P-e*-C₆H₅), 131.1 (d, ⁴*J*_{PC} = 2.7 Hz, *P-p*-C₆H₅), 133.7 (d, ²*J*_{PC} = 9.2 Hz, *P-o*-C₆H₅), 165.1 (s, OCCCN), 178.8 (d, ³*J*_{PC} = 2.7 Hz, OCCCN). ³¹P{¹H} NMR (δ, C₆D₆): 37.5.

Preparation of 2c

This complex was prepared from **1c-H** (302 mg, 0.96 mmol), [NiCl₂(2,4-lutidine)₂] (225 mg, 0.65 mmol), and NEt₃ (0.10 mL, 73 mg, 0.72 mmol) with THF (10 mL) as the solvent in the same manner as that described for **2b**. Complex **2c** was isolated as a red solid (246 mg, 0.60 mmol, 92%). An analytically pure sample of **2c** was obtained by recrystallization from Et₂O/hexane. Anal. calc. for C₂₀H₃₂ClN₃Ni: C, 58.79; H, 7.89; N, 10.28%. Found: C, 58.48; H, 7.97; N, 10.12%. ¹H NMR (δ, CDCl₃): 1.23 (s, 3H, NCCH₃), 1.67 (t, *J* = 7.2 Hz, 6H, NCH₂CH₃), 1.92 (s, 3H, NCCH₃), 2.21 (s, 3H, *N-p*-(CH₃)₃C₆H₂), 2.22 (t, *J* = 6.4 Hz, 2H, NCH₂CH₂N), 2.46 (dq, *J* = 12.8, 7.2 Hz, 2H, NCH₂CH₃), 2.49 (s, 6H, *N-o*-(CH₃)₃C₆H₂), 3.25 (dq, *J* = 12.8, 7.2 Hz, 2H, NCH₂CH₃), 3.39 (t, *J* = 6.4 Hz, 2H, NCH₂CH₂N), 4.56 (s, 1H, CH), 6.75 (s, 2H, *N-m*-(CH₃)₃C₆H₂). ¹³C{¹H} NMR (δ, CDCl₃): 11.2 (s, NCH₂CH₃), 19.3 (s, *N-o*-(CH₃)₃C₆H₂), 21.0 (s, *N-p*-(CH₃)₃C₆H₂), 22.8 (s, NCCH₃), 23.4 (s, NCCH₃), 49.9 (s, NCH₂CH₂N), 51.3 (s, NCH₂CH₃), 52.1 (s, NCH₂CH₂N), 99.3 (s, NCCCNC), 127.8 (s, *N-m*-(CH₃)₃C₆H₂), 132.7 (s, *N-o*-(CH₃)₃C₆H₂), 133.2 (s, *N-p*-(CH₃)₃C₆H₂), 149.1 (s, *N-e*-(CH₃)₃C₆H₂), 157.7 (s, NCCCNC), 158.0 (s, NCCCNC).

Typical procedure for the cross-coupling reaction (Table 2, entry 15): GLC analysis

Complex **2b** (10.2 mg, 0.025 mmol), octadecane (145.8 mg, 0.57 mmol), THF (5 mL), and 4-chlorotoluene (130.1 mg, 0.122 mL, 1.03 mmol) were placed in a Schlenk tube. Phenylmagnesium bromide (1.5 mL of the 1.0 M THF solution, 1.5 mmol) was added at once to the reaction mixture. After stirring for 24 h at 25 °C, 1 M hydrochloric acid (5 mL) was added to quench the reaction. The products were extracted with Et₂O and the yields of the products were determined by GLC analysis using octadecane as an internal standard.

Conflicts of interest

There are no conflicts of interest to declare.

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Notes and references

- (a) K. Tamao, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.*, 1972, **94**, 4374–4376; (b) R. J. P. Corriu and J. P. Masse, *J. Chem. Soc., Chem. Commun.*, 1972, 144.
- Review articles: (a) *Cross-Coupling Reactions: A Practical Guide*, ed. N. Miyauro, Springer-Verlag, Berlin, Heidelberg, 2002; (b) *Metal-Catalyzed Cross-Coupling Reactions*, ed. A. de Meijere and F. Diederich, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2nd edn, 2004; (c) A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 4176–4211; (d) A. C. Frisch and M. Beller, *Angew. Chem., Int. Ed.*, 2005, **44**, 674–688; (e) J.-P. Corbet and G. Mignani, *Chem. Rev.*, 2006, **106**, 2651–2710; (f) J. Terao and N. Kambe, *Acc. Chem. Res.*, 2008, **41**, 1545–1554; (g) X. Hu, *Chem. Sci.*, 2011, **2**, 1867–1886; (h) R. Jana, T. P. Pathak and M. S. Sigman, *Chem. Rev.*, 2011, **111**, 1417–1492.
- (a) K. Tamao, A. Minato, N. Miyake, T. Matsuda, Y. Kiso and M. Kumada, *Chem. Lett.*, 1975, 133–136; (b) V. P. W. Böhm, T. Weskamp, C. W. K. Gstöttmayr and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2000, **39**, 1602–1604; (c) G. Y. Li and W. J. Marshall, *Organometallics*, 2002, **21**, 590–591; (d) L. Ackermann, R. Born, J. H. Spatz and D. Meyer, *Angew. Chem., Int. Ed.*, 2005, **44**, 7216–7219; (e) L. Ackermann, R. Born, J. H. Spatz, A. Althammer and C. J. Gschrei, *Pure Appl. Chem.*, 2006, **78**, 209–214; (f) D. Sémeril, M. Lejeune, C. Jeunesse and D. Matt, *J. Mol. Catal. A: Chem.*, 2005, **239**, 257–262; (g) L. Monnereau, D. Sémeril and D. Matt, *Chem. Commun.*, 2011, **47**, 6626–6628; (h) N. Şahin, H. El Moll, D. Sémeril, D. Matt, İ. Özdemir, C. Kaya and L. Toupet, *Polyhedron*, 2011, **30**, 2051–2054; (i) N. Şahin, D. Sémeril, E. Brenner, D. Matt, İ. Özdemir, C. Kaya and L. Toupet, *Eur. J. Org. Chem.*, 2013, 4443–4449; (j) K. Matsubara, K. Ueno and Y. Shibata, *Organometallics*, 2006, **25**, 3422–3427; (k) Z. Xi, B. Liu and

- W. Chen, *J. Org. Chem.*, 2008, **73**, 3954–3957; (l) N. Yoshikai, H. Matsuda and E. Nakamura, *J. Am. Chem. Soc.*, 2009, **131**, 9590–9599; (m) T. Hatakeyama, S. Hashimoto, K. Ishizuka and M. Nakamura, *J. Am. Chem. Soc.*, 2009, **131**, 11949–11963; (n) J. Berding, T. F. van Dijkman, M. Lutz, A. L. Spek and E. Bouwman, *Dalton Trans.*, 2009, 6948–6955; (o) R. Ghosh and A. Sarkar, *J. Org. Chem.*, 2010, **75**, 8283–8286; (p) F. Li, J. J. Hu, L. L. Koh and T. S. A. Hor, *Dalton Trans.*, 2010, **39**, 5231–5241; (q) M. J. Iglesias, A. Prieto and M. C. Nicasio, *Org. Lett.*, 2012, **14**, 4318–4321; (r) S. G. Rull, R. J. Rama, E. Álvarez, M. R. Fructos, T. R. Belderrain and M. C. Nicasio, *Dalton Trans.*, 2017, **46**, 7603–7611; (s) I. Stamatopoulos, M. Plaček, V. Psycharis, A. Terzis, J. Svoboda, P. Kyritsis and J. Vohlidial, *Inorg. Chim. Acta*, 2012, **387**, 390–395; (t) Z. Jin, Y.-J. Li, Y.-Q. Ma, L.-L. Qiu and J.-X. Fang, *Chem. – Eur. J.*, 2012, **18**, 446–450; (u) J. Guo, L. Lv, X. Wang, C. Cao, G. Pang and Y. Shi, *Inorg. Chem. Commun.*, 2013, **31**, 74–78; (v) Y.-C. Xu, J. Zhang, H.-M. Sun, Q. Shen and Y. Zhang, *Dalton Trans.*, 2013, **42**, 8437–8445; (w) J. Zhang, J. Xu, Y. Xu, H. Sun, Q. Shen and Y. Zhang, *Organometallics*, 2015, **34**, 5792–5800; (x) J. Zhang, G. Lu, J. Xu, H. Sun and Q. Shen, *Org. Lett.*, 2016, **18**, 2860–2863; (y) M.-T. Chen, W.-Y. Lee, T.-L. Tsai and L.-C. Liang, *Organometallics*, 2014, **33**, 5852–5862; (z) Ł. Banach, P. A. Guńka and W. Buchowicz, *Dalton Trans.*, 2016, **45**, 8688–8692.
- 4 Review articles: (a) M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759–1792; (b) H. Nishiyama, *Chem. Soc. Rev.*, 2007, **36**, 1133–1141; (c) P. Bhattacharya and H. Guan, *Comments Inorg. Chem.*, 2011, **32**, 88–112; (d) J. Choi, A. H. R. MacArthur, M. Brookhart and A. S. Goldman, *Chem. Rev.*, 2011, **111**, 1761–1779; (e) N. Selander and K. J. Szabó, *Chem. Rev.*, 2011, **111**, 2048–2076; (f) J.-L. Niu, X.-Q. Hao, J.-F. Gong and M.-P. Song, *Dalton Trans.*, 2011, **40**, 5135–5150; (g) S. Schneider, J. Meiners and B. Askevold, *Eur. J. Inorg. Chem.*, 2012, 412–429; (h) M. Asay and D. Morales-Morales, *Dalton Trans.*, 2015, **44**, 17432–17447.
- 5 Review articles: (a) R. A. Gossage, L. A. van de Kuil and G. van Koten, *Acc. Chem. Res.*, 1998, **31**, 423–431; (b) M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750–3781; (c) J. T. Singleton, *Tetrahedron*, 2003, **59**, 1837–1857; (d) L.-C. Liang, *Coord. Chem. Rev.*, 2006, **250**, 1152–1177; (e) *The Chemistry of Pincer Compounds*, ed. D. Morales-Morales and C. M. Jensen, Elsevier, Amsterdam, 2007; (f) D. Benito-Garagorri and K. Kirchner, *Acc. Chem. Res.*, 2008, **41**, 201–213; (g) Z.-X. Wang and N. Liu, *Eur. J. Inorg. Chem.*, 2012, 901–911; (h) Top. Organomet. Chem., in *Organometallic Pincer Chemistry*, ed. G. van Koten and D. Milstein, Springer, Berlin, 2013, vol. 40; (i) *Pincer and Pincer-Type Complexes: Applications in Organic Synthesis and Catalysis*, ed. K. J. Szabó and O. F. Wendt, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2014; (j) S. Murugesan and K. Kirchner, *Dalton Trans.*, 2016, **45**, 416–439.
- 6 K. Inamoto, J.-I. Kuroda, K. Hiroya, Y. Noda, M. Watanabe and T. Sakamoto, *Organometallics*, 2006, **25**, 3095–3098.
- 7 (a) L.-C. Liang, P.-S. Chien, J.-M. Lin, M.-H. Huang, Y.-L. Huang and J.-H. Liao, *Organometallics*, 2006, **25**, 1399–1411; (b) L.-C. Liang, W.-Y. Lee, Y.-T. Hung, Y.-C. Hsiao, L.-C. Cheng and W.-C. Chen, *Dalton Trans.*, 2012, **41**, 1381–1388.
- 8 (a) Z.-X. Wang and L. Wang, *Chem. Commun.*, 2007, 2423–2425; (b) Z.-X. Wang and Z.-Y. Chai, *Eur. J. Inorg. Chem.*, 2007, 4492–4499; (c) K. Sun, L. Wang and Z.-X. Wang, *Organometallics*, 2008, **27**, 5649–5656; (d) C. Zhang and Z.-X. Wang, *Organometallics*, 2009, **28**, 6507–6514; (e) L.-G. Xie and Z.-X. Wang, *Chem. – Eur. J.*, 2010, **16**, 10332–10336; (f) N. Liu and Z.-X. Wang, *J. Org. Chem.*, 2011, **76**, 10031–10038; (g) W.-J. Guo and Z.-X. Wang, *J. Org. Chem.*, 2013, **78**, 1054–1061; (h) X.-Q. Zhang and Z.-X. Wang, *Synlett*, 2013, 2081–2084; (i) D. Wu and Z.-X. Wang, *Org. Biomol. Chem.*, 2014, **12**, 6414–6424.
- 9 (a) Z. Csok, O. Vechorkin, S. B. Harkins, R. Scopelliti and X. Hu, *J. Am. Chem. Soc.*, 2008, **130**, 8156–8157; (b) O. Vechorkin, A. Godinat, R. Scopelliti and X. Hu, *Angew. Chem., Int. Ed.*, 2011, **50**, 11777–11781; (c) J. Breitenfeld, J. Ruiz, M. D. Wodrich and X. Hu, *J. Am. Chem. Soc.*, 2013, **135**, 12004–12012; (d) J. Breitenfeld, M. D. Wodrich and X. Hu, *Organometallics*, 2014, **33**, 5708–5715; (e) P. M. P. Garcia, T. D. Franco, A. Epenoy, R. Scopelliti and X. Hu, *ACS Catal.*, 2016, **6**, 258–261; (f) T. D. Franco, M. Stojanovic, S. C. Keller, R. Scopelliti and X. Hu, *Helv. Chim. Acta*, 2016, **99**, 830–847.
- 10 (a) Y. Zhou, Z. Xi, W. Chen and D. Wang, *Organometallics*, 2008, **27**, 5911–5920; (b) S. Gu and W. Chen, *Organometallics*, 2009, **28**, 909–914; (c) A. Liu, X. Zhang and W. Chen, *Organometallics*, 2009, **28**, 4868–4871; (d) C. Chen, H. Qiu and W. Chen, *J. Organomet. Chem.*, 2012, **696**, 4166–4172.
- 11 (a) M. Shen, P. Hao and W.-H. Sun, *J. Organomet. Chem.*, 2008, **693**, 1683–1695; (b) J. Sanford, C. Dent, J. D. Masuda and A. Xia, *Polyhedron*, 2011, **30**, 1091–1094.
- 12 (a) G. T. Venkanna, T. V. M. Ramos, H. D. Arman and Z. J. Tonzetich, *Inorg. Chem.*, 2012, **51**, 12789–12795; (b) G. T. Venkanna, S. Tammineni, H. D. Arman and Z. J. Tonzetich, *Organometallics*, 2013, **32**, 4656–4663.
- 13 (a) Y. Sun, X. Li and H. Sun, *Dalton Trans.*, 2014, **43**, 9410–9413; (b) Y. Sun, X. Li and H. Sun, *Inorg. Chim. Acta*, 2014, **415**, 95–97.
- 14 (a) A. Castonguay, A. L. Beauchamp and D. Zargarian, *Organometallics*, 2008, **27**, 5723–5732; (b) Y. Zhang, G. Song, G. Ma, J. Zhao, C.-L. Pan and X. Li, *Organometallics*, 2009, **28**, 3233–3238; (c) M. M. Tamizh and R. Karvembu, *Inorg. Chem. Commun.*, 2012, **25**, 30–34; (d) V. Kuchtanin, L. Kleščíková, M. Šoral, R. Fischer, Z. Růžičková, E. Rakovský, J. Moncol' and P. Segl'a, *Polyhedron*, 2016, **117**, 90–96; (e) M. Mastalir and K. Kirchner, *Monatsh. Chem.*, 2017, **148**, 105–109; (f) A. G. Nair, R. T. McBurney, M. R. D. Gatus, D. B. Walker, M. Bhadbhade and B. A. Messerle, *J. Organomet. Chem.*, 2017, **845**, 63–70; (g) P. Hasche, M. Joksch,

- G. Vlachopoulou, H. Agarwala, A. Spannenberg and T. Beweries, *Eur. J. Inorg. Chem.*, 2018, 676–680.
- 15 Although this ligand is often described as “ β -ketiminato” in other manuscripts, we consider it to be an anionic ligand derived from β -aminoketone **1**. Therefore, we have used the term ‘ β -aminoketonato’ to refer to this ligand in our paper.
- 16 Y. Yamaguchi, H. Ando, M. Nagaya, H. Hinago, T. Ito and M. Asami, *Chem. Lett.*, 2011, **40**, 983–985.
- 17 (a) H. Hinago, Y. Shidara, T. Sato, Y. Yamaguchi and T. Ito, *Kobunshi Ronbunshu*, 2011, **68**, 484–492; (b) T. Sakayori, T. Sato, M. Nagaya, T. Yamaguchi, S. Ishihara, T. Kaneko and Y. Yamaguchi, *Kobunshi Ronbunshu*, 2015, **72**, 306–317.
- 18 K. Hiraki, T. Masumoto, Y. Fuchita and Y. Zegi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1044–1047.
- 19 R. Taylor, O. Kennard and W. Versichel, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1984, **40**, 280–288.
- 20 J. F. Hartwig, in *Organotransition Metal Chemistry from Bonding to Catalysis*, University Science Books, Mill Valley, California, 2010, ch. 6.1.
- 21 D. Spasyuk and D. G. Gusev, *Organometallics*, 2012, **31**, 5239–5242.
- 22 (a) D. V. Vitanova, F. Hampel and K. C. Hultsch, *J. Organomet. Chem.*, 2005, **690**, 5182–5197; (b) D. M. Granum, P. J. Riedel, J. A. Crawford, T. K. Mahle, C. M. Wyss, A. K. Begej, N. Arulsamy, B. S. Pierce and M. P. Mehn, *Dalton Trans.*, 2011, **40**, 5881–5890.
- 23 H. L. Wiencko, E. Kogut and T. H. Warren, *Inorg. Chim. Acta*, 2003, **345**, 199–208.
- 24 L. M. Venanzi, *J. Chem. Soc.*, 1958, 719–724.