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Electronic Supporting Information for

[CNN]-Pincer Nickel(II) Complexes of N-Heterocyclic Carbene (NHC): Synthesis and Catalysis to Kumada Reaction of Unactivated C-Cl Bonds

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Contents

- 1. General.
- 2. Procedures and Experimental Data for the Ligands3, 4a-4c.
- 3. Procedures and Experimental Data for the complexes 5a-5c.
- 4. Crystal Growth and X-ray Crystallographic Data of 5b
- 5. General procedure for Ni-catalyzed Kumada cross-coupling reaction.
- 6. Analytical data of the coupling products.
- 7. References.
- Copies of ¹H, ¹³C NMR Spectra of pincer complexes and coupling products

1. General.

All experiments were carried out under N₂ atmosphere and all solvents were freshly distilled before use under an argon atmosphere. Aryl chlorides were purchased from commercial sources and Grignard reagents were prepared according to previous reported literatures^[1]. N, Ndimethylaminobromobenzene^[2], 2-(Imidazol-1-yl) phenylamine^[3], Ni(dme)Cl₂ and Ni(dme)Br₂^[4] were synthesized according to previous reported literatures. NMR spectra of ¹H and ¹³C NMR (300 and 75 MHz, respectively) were recorded on a Bruker 300 AV spectrometer. Elemental analyses were carried out on Elementar Vario ELIII. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer. GC-MS were measured on a TRACE-DSQ instrument. HRMS were recorded on an Agilent Q-TOF6510 mass spectrometer. All spectra were obtained at 25°C.

2. Procedures and Experimental Data for the Ligands3, 4a-4c.

Synthesis of **3**:

A 50 ml reaction vessel was charged with $Pd(OAc)_2$ (22.0 mg, 0.1mmol), bis(diphenylphosphino)-ferrocene (DPPF) (0.11 g, 0.2 mmol), NaO^tBu (0.62 g, 6.5 mol) and toluene (15 ml) under a N₂ atmosphere. 2-(1H-Imidazol-1-yl)phenylamine (0.80g, 5 mol) and 2-Bromo-N,N- dimethyl aniline (1.0 g, 5mmol) were degassed and added to the reaction mixture. The resulting brown solution was stirred for 24 hours at 120 °C. The solution was then cooled to room temperature and filtered through Celite. Removal of the solvent yielded a purple liquid which was then taken up in 3 ml dichloromethane and was purified through a silica chromatography ($CH_2Cl_2:CH_3OH=20:1$), dried under vacuum to give **3** (1.97 g, 91% yield) as a brown oil.



¹H NMR (300 MHz, CDCl₃): 7.66 (s, 1H, NC*H*N), 7.52 (d, J = 9.0 Hz, 1H, H_{arom}), 7.33 (t, J = 6.0 Hz, 1H, H_{arom}), 7.23-7.27 (m, 3H, H_{arom}), 7.12 (s, 1H, H_{arom}), 7.08 (d, J = 9.0 Hz, 1H, H_{arom}), 6.99 (q, J=6.0 Hz, 2H, H_{arom}), 6.91 (q, J=6.0 Hz, 1H, H_{arom}), 6.41 (s, 1H, CN*H*C), 2.53 (s, 6H, N(C*H*₃)₂). ¹³C NMR (75 MHz, CDCl₃): 143.56, 138.79, 137.72, 136.58, 130.03, 129.59, 127.42, 126.93, 124.00, 121.34, 120.63, 120.28, 120.07, 117.51, 115.75, 44.00. MS: 279.16 [M⁺]. Anal. Calc. for C₁₇H₁₈N₄: (278.36 g mol⁻¹) : C, 73.35; H, 6.52; N, 20.13. Found: C, 73.68; H, 6.39; N, 19.97.

Synthesis of **4a**:

To a solution of **3** (2.78 g, 10 mmol) in acetonitrile (30 mL) was added *n*- C_4H_9Br (2.74 g, 20 mmol), the reaction mixture was refluxed for 1 d. The solution was then cooled to room temperature, removal of the solvent under vacuum, recrystallized from CH₃OH /Et₂O to give **4a** (5.08 g, 92%)

yield based on 3) as a gray powder.



4a:

¹H NMR (300 MHz, CDCl₃): 10.49 (s, 1H, NC*H*N), 7.60-7.68 (m, 2H, H_{arom}), 7.37-7.48 (m, 3H, H_{arom}), 7.19 (t, *J* = 6.0 Hz, 1H, H_{arom}), 7.09 (d, *J* = 9.0 Hz, 1H, H_{arom}), 6.84-6.94 (m, 3H, H_{arom}), 6.52 (s, 1H, CN*H*C), 4.61 (t, *J* = 6.0 Hz, 2H, NC*H*₂CH₂), 2.61 (s, 6H, N(C*H*₃)₂), 1.89 (m, 2H, CH₂C*H*₂CH₂), 1.31 (m, 2H, CH₂C*H*₂CH₃), 0.94 (t, *J* = 9.0 Hz, 3H, CH₂C*H*₃). ¹³C NMR (75 MHz, CDCl₃): 142.92, 137.68, 137.64, 136.92, 131.78, 127.10, 126.76, 124.26, 123.82, 122.77, 122.64, 122.33, 121.59, 120.11, 115.15, 50.22, 44.21, 32.20, 19.37, 13.58. MS: 335.22 [M⁺-Br]. Anal. Calc. for C₂₁H₂₇N₄Br: (415.38 g mol⁻¹) : C, 60.72; H, 6.55; N, 13.49. Found: C, 60.48; H, 6.47; N, 13.71.

Synthesis of 4b:

To a solution of **3** (2.78 g, 10 mmol) in acetonitrile (30 mL) was added *i*-PrBr(2.46 g, 20 mmol), the reaction mixture was refluxed for 2 d. The solution was then cooled to room temperature, removal of the solvent under vacuum, recrystallized from CH₃OH /Et₂O to give **4b** (4.08 g, 78% yield based on 3) as a white powder.





¹H NMR (300 MHz, CDCl₃): 10.58 (s, 1H, NC*H*N), 7.69 (d, J = 6.0 Hz, 1H, H_{arom}), 7.37-7.52 (m, 4H, H_{arom}), 7.21 (t, J = 6.0 Hz, 1H, H_{arom}), 7.08 (d, J = 9.0 Hz, 1H, H_{arom}), 6.82-6.95 (m, 3H, H_{arom}), 6.56 (s, 1H, CN*H*C), 5.39 (m, 1H, C*H*(CH₃)₂), 2.62 (s, 6H, N(C*H*₃)₂), 1.62 (d, 6H, CH(C*H*₃)₂). ¹³C NMR (75 MHz, CDCl₃): 142.85, 137.59, 137.14, 137.01, 131.79, 127.15, 127.04, 124.32, 124.06, 123.15, 123.02, 121.51, 120.11, 119.20, 115.14. MS: 321.20 [M⁺-Br]. Anal. Calc. for C₂₀H₂₅N₄Br: (401.35 g mol⁻¹) : C, 59.85; H, 6.28; N, 13.96. Found: C, 60.04; H, 6.32; N, 14.01.

Synthesis of **4c**:

To a solution of **3** (2.78 g, 10 mmol) in acetonitrile (30 mL) was added Benzyl chloride (2.53 g, 20 mmol), the reaction mixture was refluxed for 1 d. The solution was then cooled to room temperature, removal of the solvent under vacuum, recrystallized from CH_3OH / Et_2O to give **4c** (1.97 g, 90% yield based on **3**) as a gray powder.



4c:

¹H NMR (300 MHz, CDCl₃): 10.81 (s, 1H, NC*H*N), 7.33-7.59 (m, 10H, H_{arom}), 7.08-7.15 (m, 2H, H_{arom}), 6.93(s, 3H, H_{arom}), 6.64 (s, 1H, CN*H*C), 5.85 (m, 2H, NC*H*₂Ph), 2.57 (s, 6H, N(C*H*₃)₂). ¹³C NMR (75 MHz, CDCl₃): 138.33, 137.96, 136.67, 133.39, 131.70, 129.33, 129.27, 127.22, 126.36, 124.43, 124.30, 124.10, 123.29, 122.99, 122.59, 122.44, 121.96, 121.80, 120.04, 116.06, 115.89, 53.65, 44.13. MS: 369.28[M⁺-Cl]. Anal. Calc. for $C_{24}H_{25}N_4Cl$: (404.94 g mol⁻¹) : C, 71.19; H, 6.22; N, 13.84. Found: C, 71.29; H, 6.36; N, 13.91.

3. Procedures and Experimental Data for the complexes 5a-5c. Synthesis of **5a**:

A 100 ml reaction vessel was charged with **4a** (1.2 g, 3.0 mmol) and THF (30 ml) under a N₂ atmosphere. n-BuLi (2.6 ml, 2.5 M in hexane, 6.6 mmol) was slowly added to the suspension at -50°C, the reaction was stirred back to room temperature until the suspension turned to brown solution, Ni(dme)Br₂ (0.92 g, 3.0 mmol, dme = dimethoxyethane) suspended in THF(10 ml) was added to the solution slowly. The reaction mixture was stirred over night at room temperature. After remove of the solvent under vacuum, the green residue was washed with n-pentane (30 ml), then taken up with Et₂O (3×20 ml) and filtered through Celite. Evaporation of the solvent yielded a green solid and dried under vacuum.

Yield: (1.14g, 80% based on 4a).



5a:

¹H NMR (300 MHz, CDCl₃): 7.57 (d, J = 9.0 Hz, 1H, H_{arom}), 7.32 (s, 1H, H_{arom}), 7.26 (s, 1H, H_{arom}), 7.16 (dd, J = 9.0 Hz, 2H, H_{arom}), 6.90-7.02 (m, 3H, H_{arom}), 6.74 (t, 1H, J = 6.0 Hz, H_{arom}), 6.64 (t, 1H, J = 6.0 Hz, H_{arom}), 4.82 (m, 1H, NCH₂CH₂), 4.25 (m, 1H, NCH₂CH₂), 3.18 (s, 3H, N(CH₃)₂), 2.70 (s, 3H, N(CH₃)₂), 2.25 (m, 2H, CH₂CH₂CH₂), 1.57 (m, 2H, CH₂CH₂CH₃), 1.07 (t, 3H, CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): 149.79, 148.02, 147.42, 142.37, 130.53, 127.11, 126.68, 123.94, 120.58, 120.26, 119.63, 118.48, 117.39, 117.21, 116.13, 51.47, 51.36, 47.58, 33.72, 20.03, 13.92. Anal. Calc. for C₂₁H₂₅N₄BrNi: (472.06 g mol⁻¹) : C, 53.43; H, 5.34; N, 11.87. Found: C, 53.58; H, 5.42; N, 11.77.

Synthesis of 5b:

A 100 ml reaction vessel was charged with **4b** (1.25 g, 3.0 mmol) and THF (20 ml) under a N₂ atmosphere. n-BuLi (2.6 ml, 2.5 M in hexane, 6.6 mmol) was slowly added to the suspension at -50°C, the reaction was stirred back to room temperature until the suspension turned to brown solution, Ni(dme)Br₂ (0.92 g, 3.0 mmol) suspended in THF(10 ml) was added to the solution slowly. The reaction mixture was stirred overnight

at room temperature. After remove of the solvent under vacuum, the green residue was washed with n-pentane (30 ml), then taken up with Et_2O (3×20 ml) and filtered through Celite. Evaporation of the solvent yielded a green solid and dried under vacuum. Yield: (1.23 g, 87% based on **4b**).



5b:

¹H NMR (300 MHz, CDCl₃): 7.55 (d, J = 9.0 Hz, 1H, H_{arom}), 7.36 (s, 1H, H_{arom}), 7.28 (d, J = 9.0 Hz, 1H, H_{arom}), 7.21 (d, J = 9.0 Hz, 1H, H_{arom}), 7.09 (m, 2H, H_{arom}), 6.96 (m, 2H, H_{arom}), 6.75 (t, J = 6.0 Hz, 1H, H_{arom}), 6.66 (t, J = 6.0 Hz, 1H, H_{arom}), 5.81 (m, 1H, CH(CH₃)₂), 3,19 (s, 3H, N(CH₃)₂), 2.70 (s, 3H, N(CH₃)₂), 1.73(d, J = 6.0 Hz, 3H, CH(CH₃)₂), 1.45(d, J = 6.0 Hz, 3H, CH(CH₃)₂). ¹³C NMR (75 MHz, CDCl₃): 149.85, 148.14, 146.77, 142.38, 130.53, 127.12, 126.65, 120.68, 120.25, 119.92, 119.61, 118.48, 117.88, 117.12, 116.10, 52.65, 51.43, 47.32, 24.71, 22.86. Anal. Calc. for C₂₀H₂₃N₄BrNi: (458.03 g mol⁻¹) : C, 52.45; H, 5.06; N, 12.23. Found: C, 52.24; H, 5.12; N, 12.11.

Synthesis of 5c:

A 100 ml reaction vessel was charged with 4c (1.21 g, 3.0 mmol) and THF (20 ml) under a N_2 atmosphere. n-BuLi (2.6 ml, 2.5 M in hexane, 6.6 mmol) was slowly added to the suspension at -50°C, the reaction was

stirred back to room temperature until the suspension turned to brown solution, Ni(dme)Cl₂ (0.66 g, 3.0 mmol) suspended in THF(10 ml) was added to the solution slowly. The reaction mixture was stirred overnight at room temperature. After remove of the solvent under vacuum, the green residue was washed with n-pentane (30 ml), then taken up with Et_2O (3×20 ml) and filtered through Celite. Evaporation of the solvent yielded a green solid and dried under vacuum. Yield: (1.11 g, 80% based on **4c**).



5c:

¹H NMR (300 MHz, CDCl₃): 7.60 (d, J = 6.0 Hz, 1H, H_{arom}), 7.52 (d, J = 6.0 Hz, 2H, H_{arom}), 7.29-7.37 (m, 5H, H_{arom}), 7.13-7.21 (m, 2H, H_{arom}), 6.94-7.00 (m, 2H, H_{arom}), 6.84 (s, 1H, H_{arom}), 6.69 (td, J = 9.0 Hz, 2H, H_{arom}), 5.79 (dd, J = 81.0, 15.0 Hz, 2H, NCH₂Ph), 2.96 (s, 3H, N(CH₃)₂), 2.68 (s, 3H, N(CH₃)₂). ¹³C NMR (75 MHz, CDCl₃): 149.83, 148.62, 148.08, 142.43, 136.93, 130.16, 128.83, 128.43, 128.09, 127.06, 126.73, 124.04, 120.48, 120.15, 119.63, 118.51, 117.40, 117.31, 116.18, 54.49, 50.92, 46.38. Anal. Calc. for C₂₄H₂₃N₄ClNi: (461.62 g mol⁻¹) : C, 62.45; H, 5.02; N, 12.14. Found: C, 62.39; H, 4.96; N, 11.99.

4. Crystal Growth and X-ray Crystallographic Data of 5b

Compound 5b was easily obtained from 4b through one step, and the

green single crystal was obtained by solvent evaporation from Et₂O.

5b: C₂₀ H₂₁ Cl N₄ Ni, Mr = 411.57, orthorhombic, space group Pna2(1), *a* = 19.216(6) Å, *b* = 10.729 (4) Å, *c* = 9.506(3) Å, β = 90°, *V* = 1959.8(11) Å³, T = 293(2) K, *Z* = 4, Dc = 1.395g/cm³, μ = 1.137 mm⁻¹. A total of 9190 reflections were collected, 3341 unique (Rint = 0.0556), R1 = 0.1322 (for 3341 reflections with I > 2 sigma(I)), wR2 = 0.3219 (all data), CCDC No. 981371.

5. General procedure for Ni-catalyzed Kumada cross-coupling reaction.

(1). General procedure for the Kumada coupling of 1-chloro-4-methoxybenzene with benzenemagnesium bromide catalyzed by **5a-5c**. A Schlenk tube was charged with pincer nickel complex **5a-5c** (0.0025 mmol), THF (1.5 mL), and 1-chloro-4-methoxybenzene (0.056 g, 0.5 mmol). To the solution was added dropwise a solution of C_6H_5MgBr (0.5 mL, 1.5 M in THF, 0.75 mmol) at 25 °C with stirring. After stirring at this temperature for 24 h, the reaction mixture was quenched with water and extracted with diethyl ether (3 × 10 mL). The combined organic phases were dried over Na₂SO₄, concentrated by rotary evaporation, and purified by column chromatography on silica gel to afford 4-Methoxybiphenyl, the yields were assessed based on the amount of 1chloro-4-methoxybenzene.

The reactions in toluene, Et_2O or DME followed the same procedure, only THF was replaced with the required solvent.

(2). General procedure for the Kumada coupling of aryl chlorides with Grignard reagents catalyzed by **5b**. A Schlenk tube was charged with

pincer nickel complex **5b** (0.01 mmol), THF (1.5 mL), and aryl chlorides (0.5 mmol). To the mixture was added dropwise a solution of Grignard reagent (0.75 mmol) in THF at 25 °C with stirring. After the resulting solution was stirred at 25 °C for 24 h, the reaction mixture was quenched with water and extracted with diethyl ether (3×10 mL). The combined organic phases were dried over Na₂SO₄, concentrated by rotary evaporation, and purified by column chromatography on silica gel to afford the desired products, the yields were assessed based on the amount of aryl chlorides.

(3). General procedure for the Kumada coupling of aryl dichlorides with Grignard reagents catalyzed by **5b**. A Schlenk tube was charged with pincer nickel complex **5b** (0.015 mmol), THF (1.5 mL), and aryl dichlorides (0.5 mmol). To the mixture was added dropwise a solution of Grignard reagent (1.25 mmol) in THF at 25 °C with stirring. After the resulting solution was stirred at 25 °C for 24 h, the reaction mixture was quenched with water and extracted with diethyl ether (3×10 mL). The combined organic phases were dried over Na₂SO₄, concentrated by rotary evaporation, and purified by column chromatography on silica gel to afford the desired products, the yields were assessed based on the amount of aryl dichlorides.

6. Analytical data of the coupling products.



4-Methylbiphenyl^[5] (Table2, entry 1 and 4). ¹H NMR (300 MHz, CDCl₃): δ 2.39 (s, 3H), 7.24 (d, *J* = 9 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H) ppm. MS (EI, m/z): 168 [M⁺].



4-Methoxybiphenyl^[5] (Table1, Table2, entry 3 and 7).

¹H NMR (300 MHz, CDCl₃): δ 3.85 (s, 3H), 6.98 (d, J = 9 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.51–7.57 (m, 4H) ppm. MS (EI, m/z): 184 [M⁺].



2-Methylbiphenyl^[5], (Table2, entry 2). ¹H NMR(300 MHz, CDCl₃): δ 2.27 (s, 3H), 7.24 (m, 4H), 7.33 (m, 3H), 7.41 (m, 2H) ppm. MS (EI, m/z): 168 [M⁺].



4-Methoxy-4'-methylbiphenyl^[5] (Table2, entry 6 and 9). ¹H NMR (300 MHz, CDCl₃): δ 2.38 (s, 3H), 3.84 (s, 3H), 6.97 (d, J = 9 Hz, 2H), 7.23 (d, J = 9 Hz, 2H), 7.45 (d, J = 9 Hz, 2H), 7.51 (d, J = 9 Hz, 2H) ppm. MS (EI, m/z): 198 [M⁺].



4-Methyl-2'-methylbiphenyl^[6] (Table2 entry 5). ¹H NMR (300 MHz, CDCl₃): δ 2.30 (s, 3H), 2.40 (s, 3H), 7.22-7.27 (m, 8H) ppm. MS (EI, m/z): 182 [M⁺].



4-Methoxy-2'-methylbiphenyl^[7] (Table2, entry 8).

¹H NMR (300 MHz, CDCl₃): δ 2.27(s, 3H), 3.83 (s, 3H), 6.95 (d, *J* = 9 Hz, 2H), 7.21-7.25 (m, 6H) ppm. MS (EI, m/z): 198 [M⁺].



4-Trifluoromethyl-biphenyl^[5] (Table2, entry 10).

¹H NMR (300 MHz, CDCl₃): δ 7.38-7.50 (m, 3 H), 7.60 (d, *J* = 6.0 Hz, 2 H), 7.69 (s, 4 H) ppm. MS (EI, m/z): 222 [M⁺].



4-Methoxy-4'-trifluoromethyl-biphenyl^[8] (Table2, entry 11). ¹H NMR (300 MHz, CDCl₃): δ 3.86 (s, 3 H), 7.01 (d, *J*= 9 Hz, 2 H), 7.54 (d, *J* = 12 Hz, 2 H), δ 7.59 (s, 4 H) ppm. MS (EI, m/z): 252 [M⁺].



1, 2-Diphenylbenzene^[5] (Table3, entry 1). ¹H NMR (300 MHz, CDCl₃): δ 7.14 (m, 4 H), 7.19 (m, 6 H), 7.42 (m, 4 H) ppm. MS (EI, m/z): 230 [M⁺].



1, 2-Di(p-methylphenyl)benzene^[7] (Table3, entry 2). ¹H NMR (300 MHz, CDCl₃): δ 2.31 (s, 6H), 7.03 (s, 8H), 7.40 (s, 4H) ppm. MS (EI, m/z): 258 [M⁺].



1, 3-diphenylbenzene ^[5] (Table3, entry 3).

¹H NMR (300 MHz, CDCl₃): δ7.37 (t, J = 7.6 Hz, 2H), 7.46 (t, J = 7.6 Hz, 4H), 7.52 (m, 1H), 7.58 (m, 2H), 7.65 (d, J = 6.9 Hz, 4H), 7.81 (s, 1H) ppm. MS (EI, m/z): 230 [M⁺].



1, 3-di(4-methylphenyl)benzene^[6] (Table3, entry 4). ¹H NMR (300 MHz, CDCl₃): δ 2.40 (s, 6H), 7.27 (d, J = 8.1 Hz, 4H), 7.47 (m, 1H), 7.54 (d, J = 8.1 Hz, 6H), 7.77 (s, 1H) ppm. MS (EI, m/z): 258 [M⁺].



1, 3-di(4-methoxyphenyl)benzene^[5] (Table3, entry 5). ¹H NMR (300 MHz, CDCl₃): δ 3.86 (s, 6H), 7.00 (d, J = 9 Hz, 4H), 7.48 (m, 3H), 7.58 (d, J = 9 Hz, 4H), 7.72 (s, 1H) ppm. MS (EI, m/z): 290 [M⁺].



1, 4-diphenylbenzene^[5] (Table3, entry 6).

¹H NMR (300 MHz, CDCl₃): δ 7.36 (t, J = 9 Hz, 2H) 7.46 (t, J = 9 Hz, 4H), 7.65(d, J = 9 Hz, 4H), 7.68 (s, 4H) ppm. MS (EI, m/z): 230 [M⁺]



4-di(4-methylphenyl)benzene^[6] (Table3, entry 7).
¹H NMR (300 MHz, CDCl₃): δ 2.40 (s, 6H), 7.27 (d, J = 9 Hz, 4H), 7.54 (d, J = 9 Hz, 4H), 7.64 (s, 4H), ppm. MS (EI, m/z): 258 [M⁺]



1,4-di(2-methylphenyl)benzene^[7] (Table3, entry 8). ¹H NMR (300 MHz, CDCl₃): δ 2.34 (s, 6H), 7.24-7.32 (m, 8H), 7.36 (s, 4H), ppm. MS (EI, m/z): 258 [M⁺]

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8. Copies of ¹H, ¹³C NMR Spectra of pincer complexes and coupling prouducts



 $^{1}\mathrm{H}$



¹³C







¹³C







 ^{13}C







 ^{13}C













 ^{13}C



















































































