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Synthesis, Structure, and Reactivity of Ferrocenyl-NHC Palladium Complexes

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Abstract. palladium complexes of ferrocenyl-functionalized N-heterocyclic carbenes with different substituents were synthesized. The molecular structures of selected complexes were determined by X-ray diffraction and show a pseudo-square-planar structure with a central palladium atom surrounded by carbene, pyridine, and two chloride ligands. The influence of the different substituents on the structure and reactivity of the complexes was studied. The catalytic properties of the complexes were investigated in the Larock indolization reactions of 2-bromoanilines with diphenylacetylene. Their performances slightly varied in this reaction, but the complex with mesityl substituent showed the best activity.

Introduction

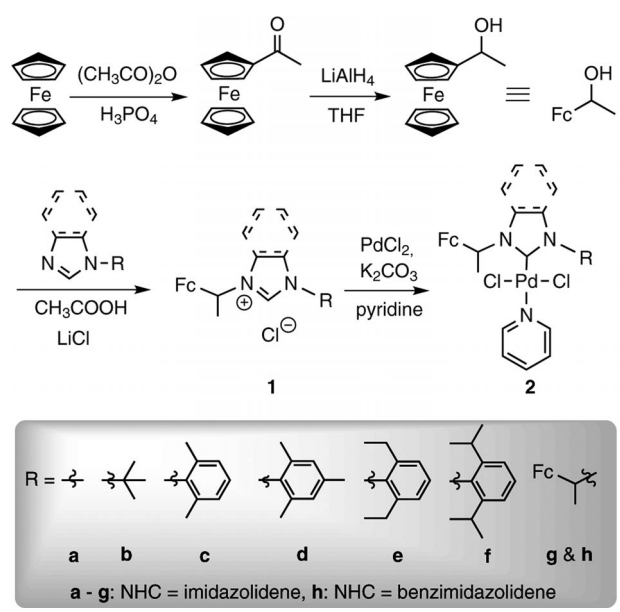
Over the past few decades, N-heterocyclic carbenes (NHCs) have attracted considerable attention and become an important class of ligands, due to their successful application in organometallic chemistry and homogeneous catalysis.[1,2] It was known that the monodentate NHC with steric hindrance would create more active catalysts for palladium-catalyzed cross-coupling reactions.[3] We are interested in the steric influences exhibited by ferrocenyl substituents, as the ferrocenyl moiety represents a quite bulky group with unique spatial requirements due to its cylindrical shape. Various complexes of ferrocenyl-functionalized NHCs and their applications in catalysis have been explored.[4] For over a century, the synthesis and functionalization of indoles has been a major area of focus for synthetic organic chemists, and numerous methods for the preparation of indoles have been developed. In recent years, the palladium-catalyzed indolization discovered by *Larock* has emerged as a powerful tool to prepare indoles.[5]

Herein we present the synthesis and structural characterization of several ferrocenyl functionalized NHC ligands with different N-substituents and we investigate the influence of substitution on solid structure and on reactivity in the Larock indolization reaction.

Results and Discussion

Synthesis of the Imidazolium Chlorides 1

The ferrocenyl imidazolium chlorides **1** can be efficiency synthesized starting from ferrocene according to the literature method (Scheme 1).[4a,6] The reduction of acetylferrocene prepared by Friedel-Crafts acylation reaction of ferrocene gave 1-ferrocenylethanol in excellent yield. Treatment of 1-ferrocenylethanol with 1-substituted imidazole (benzimidazole) in



Scheme 1. Synthesis of palladium(II) complexes **2a**–**2h**.

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acetic acid at 60 °C for 6 h gave an imidazolium salt with the hydroxide as a counter anion. Subsequently, addition of excess LiCl to the reaction mixture resulted in anion exchange to give ferrocenyl imidazolium chlorides **1**. The imidazolium chlorides **1a** and **1f**–**1h** have been reported previously,[4a,7] however, imidazolium chlorides **1b**–**1e** are new compounds and were characterized by their spectroscopic data and elemental analyses.

Synthesis and Characterization of Ferrocenyl NHC-Palladium Complexes 2

The synthesis of ferrocenyl NHC-palladium complexes **2** are achieved by refluxing of the corresponding imidazolium salt **1a**–**1h**, with palladium chloride (1.1 equiv.) in presence of K_2CO_3 in pyridine in an argon atmosphere, as shown in Scheme 1. All of these palladium complexes are air and moisture stable and can be stored under air in solid state for more than six months without any noticeable decomposition. These complexes **2** were fully characterized by NMR spectroscopy and gave satisfactory elemental analyses.

The proton signal of NCHN from the imidazolium chlordies at ca. 10–12 ppm was absent in the ^{1}H NMR of palladium complexes, confirming carbene generation. In addition, the formation of the metal complexes was evident from the distinctive Pd–$C_{carbene}$ peak ca.150–160 ppm, which significantly shifted downfield relative to that of the imidazolinium NCHN peak of the starting ligand precursor ca. 138 ppm. The molecular structures of **2a**, **2b**, and **2f** were determined by X-ray diffraction studies. The molecular diagrams of **2a**, **2b**, and **2f** are shown in Figure 1, Figure 2, and Figure 3, respectively, and selected bond lengths and angles are given below the Figures. All complexes show slightly distorted square-planar arrangement around the central palladium atom, which is surrounded by imidazolylidene, two chloride ligands in a *trans* configuration, and one pyridine. The two chlorides in the complexes are in a slightly bent arrangement, with Cl–Pd–Cl angles of 176.28(3)° for **2a** and **2b**, and 170.45(8)° for **2f**. The angle between the planes of imidazolylidene ring and pyridyl ring is different with different substitution on imidazole (46.40° for **2a**, 37.09° for **2b** and 53.93° for **2f**). The ferrocenyl substituent in these complexes is twisted with respect to the imidazol-2-ylidene ligand, with angles ranging from 77.10° to 80.23°. The Pd–$C_{carbene}$ distance is 1.952(2) Å for **2a**, 1.959(3) Å for **2b**, and 1.956(6) Å for **2f**, similar to that shown by other palladium-related species.[7] The Pd–$N_{pyridine}$ distance in complexes

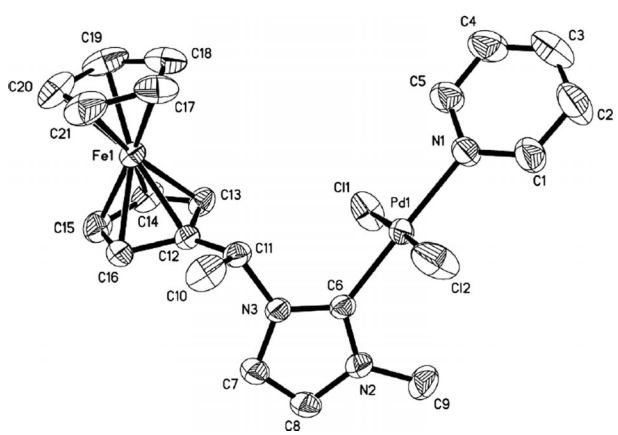


Figure 1. ORTEP structure of complex **2a** with the probability ellipsoids drawn at the 50 % level. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: Pd1–C6 1.952(2), Pd1–Cl1 2.2880(8), Pd1–Cl2 2.3009(8), Pd1–N1 2.096 (2), C6–N2 1.340(3), C6–N3 1.343(3), C6–Pd1–Cl1 86.72(8), C6–Pd1–Cl2 89.71(8), Cl1–Pd1–N1 91.13(7), Cl2–Pd1–N1 92.48(7), N2–C6–N3 105.8(2).

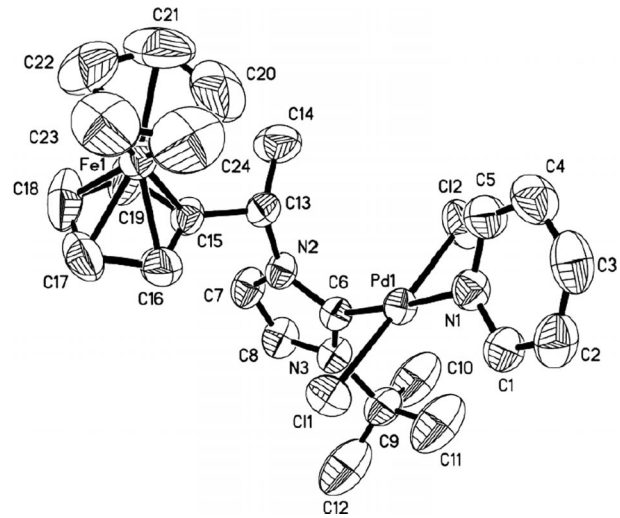


Figure 2. ORTEP structure of complex **2b** with the probability ellipsoids drawn at the 50 % level. Hydrogen atoms and solvent are omitted for clarity. Selected bond lengths /Å and angles /°: Pd1–C6 1.959(3), Pd1–Cl1 2.3155(8), Pd1–Cl2 2.3005(9), Pd1–N1 2.109(3), C6–N2 1.344(4), C6–N3 1.353(4), C6–Pd1–Cl1 88.22(8), C6–Pd1–Cl2 88.14(8), Cl1–Pd1–N1 92.09(8), Cl2–Pd1–N1 91.61(8), N2–C6–N3 105.5(2).

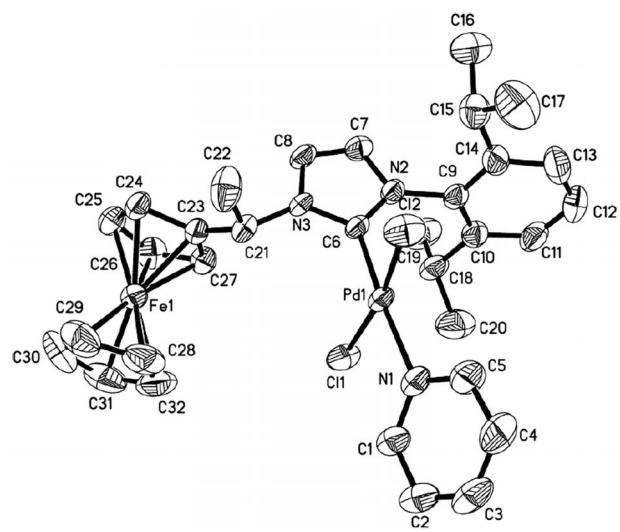
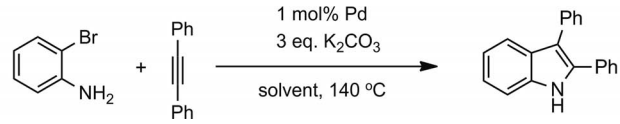


Figure 3. ORTEP structure of complex **2f** with the probability ellipsoids drawn at the 50 % level. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and bond angles /°: Pd1–C6 1.956(6), Pd1–Cl1 2.3086(19), Pd1–Cl2 2.291(2), Pd1–N1 2.122(6), C6–N2 1.336(8), C6–N3 1.351(8), C6–Pd1–Cl1 88.51(19), C6–Pd1–Cl2 88.21(19), Cl1–Pd1–N1 92.48(17), Cl2–Pd1–N1 91.41(17), N2–C6–N3 105.4(5).

Table 1. Larock indolization of 2-bromoaniline with 1,2-diphenylethyne by palladium complexes.



Entry[a)]	Catalyst (1 mol-%)	Additive	Solvent	Temp /°C	Time /h	Yield[b)]
1	**2a**	TBAB	DMF	140	24	45
2	**2b**	TBAB	DMF	140	24	49
3	**2c**	TBAB	DMF	140	24	50
4	**2d**	TBAB	DMF	140	24	60
5	**2e**	TBAB	DMF	140	24	53
6	**2f**	TBAB	DMF	140	24	54
7	**2g**	TBAB	DMF	140	24	56
8	**2h**	TBAB	DMF	140	24	58
9	**2d**	TBAB	DMSO	140	24	0
10	**2d**	TBAB	DMAC	140	24	70
11	**2d**	TBAB	1,4-dioxane	140	24	78
12	**2d**	TBAB	1,4-dioxane	120	24	0
13	**2d**	TBAB	1,4-dioxane	100	24	0
14	**2d**	TBAB	1,4-dioxane	140	12	51
15	**2d**	LiCl	1,4-dioxane	140	24	0
16	**2d**	none	1,4-dioxane	140	24	0
17	**2d**	$(Bu_4)NCl$	1,4-dioxane	140	24	68
18	**2c**	TBAB	1,4-dioxane	140	24	59
19	**2g**	TBAB	1,4-dioxane	140	24	68
20	**2h**	TBAB	1,4-dioxane	140	24	71

a) Reaction conditions: 2-bromoaniline (1 mmol), TBAB (1 mmol), diphenylacetylene (2 mmol) and K_2CO_3 (3 mmol) in solvent (2 mL). b) Isolated yield with average of two runs.

2a [2.096(2) Å], **2b** [2.109(3) Å] and **2f** [2.122(6) Å] is comparable to that observed in other related palladium carbene analogues.[8] All other distances and angles lie in the expected ranges.

Palladium Catalyzed Larock Indole Synthesis

To evaluate the catalytic activity of complexes **2a**–**2h** in the Larock indolization reaction, we performed the reaction of 2-bromoaniline with 1,2-diphenylethyne in DMF in presence of K_2CO_3 as base and TBAB as additive at 140 °C for 24 h, using 1 mol% catalyst loading (Table 1). From the results, the performances of these catalysts are only slightly different, whereas complex **2d** is of the best activity with 60% of yield (entry 4).

Further experiments were performed to investigate the effect of different solvents, additives, temperatures, reaction times with catalyst **2d**. The results show that the solvent has important effect on the performance of the catalyst, and 1,4-dioxane is the most suitable solvent among the solvents employed. The relatively low yield of 70% was detected with DMAC (entry 10), however, DMSO is not effective at all (entry 9). The reaction temperature and time have significant effect on the yield as well. When the reaction temperature was lowered to 120 or 100 °C, no product was obtained at all (entries 11 and 12). The yield was decreased with shorter reaction time and 51% of yield was tested in 12 h (entry 14). TBAB is necessary to achieve a good yield in the reactions. No product was observed without any additive or with LiCl as additive, while 68% of yield was observed with $(Bu_4)NCl$ as additive. In addition, when 1,4-dioxane was chosen as solvent instead of DMF, the other complexes showed better performances too, such as, the yield with **2h** increased from 58% to 71% (entry 8 versus entry 20). Form all the results showed herein, the palladium complexes **2** with ferrocenyl-functionalized NHC were an effective indolization precatalyst, and 78% of yield achieved in 1 mol% palladium. The result is quite comparable to the reported palladium catalytic system with phosphine ligand, in which the 99% isolated yield was obtained with 5 mol% palladium.[9]

Conclusions

We synthesized and characterized a series of highly stable palladium complexes with ferrocenyl-functionalized N-heterocyclic carbenes. X-ray studies show that the different substituent on carbene affects the solid-state structure of these complexes. The catalytic studies show that these complexes are good catalyst for Larock indolization reaction and the substituent slightly affects the catalytic activity of these complexes. The complex **2d** with mesityl substituent appears good activity in the indolization.

Experimental Section

Materials and General Procedures: Pyridine was distilled from calcium hydride in an argon atmosphere. Potassium carbonate was ground to a fine powder prior to use. All other reagents were commercially available and were used without further purification. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX 400 MHz spectrometer at

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room temperature and referenced to the residual signals of the solvent. Elemental analyses were performed with a EuroVektor Euro EA-300 elemental analyzer.

Synthesis of Imidazolium Chlorides 1: 1-Ferrocenylethanol (0.23 g, 1.0 mmol) and 1-substituted imidazole (or benzimidazole) (1.1 mmol) were dissolved in acetic acid (3 mL) and stirred at 60 °C for 7 h. After removed most of acetic acid, a solution of LiCl (0.17 g, 4.0 mmol) in EtOH (20 mL) was added, and stirred for 8 h at room temperature. After removed the volatiles, filtered through Celite, and rinsed by CH_2Cl_2, the crude was purified by flash column chromatography and recrystallized from CH_2Cl_2/ether.

1a: Yield: 72 % (0.24 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.90 (s, 1 H, NC*H*N), 7.07 (s, 1 H, NC*H*), 6.97 (s, 1 H, NC*H*), 5.81–5.87 (m, 1 H, C*H*), 4.36 (s, 2 H, Fc–*H*), 4.28 (s, 1 H, Fc–*H*), 4.24 (s, 5 H, Fc–*H*), 4.14 (s, 1 H, Fc–*H*), 4.08 (s, 3 H, CH_3), 1.98 (s, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 135.8, 123.4, 119.7, 85.4, 69.2, 69.0, 68.6, 68.3, 65.7, 56.2, 36.2, 21.0 ppm.

1b: Yield: 76 % (0.28 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.83 (s, 1 H, NC*H*N), 7.30 (s, 1 H, NC*H*), 7.05 (s, 1 H, NC*H*), 6.05–6.15 (m, 1 H, C*H*), 4.40 (s, 1 H, Fc–*H*), 4.34(s, 1 H, Fc–*H*), 4.19 (s, 7 H, Fc–*H*), 1.93 (d, *J* = 8.0 Hz, 3 H, CH_3), 1.86 (s, 9 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 135.3, 119.2, 118.9, 85.6, 69.4, 69.3, 68.8, 68.6, 65.8, 60.2, 56.3, 30.1, 21.4. $C_{19}H_{25}ClFeN_2$ (372.71 g·mol^{-1}): calcd. C 61.23; H 6.76; Cl 9.51; Fe, 14.98; N 7.52 %; found: C 61.11; H 6.67; N 7.64 %.

1c: Yield: 67 % (0.28 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.58 (s, 1 H, NC*H*N), 7.63 (s, 1 H, NC*H*), 7.31 (s, 1 H, NC*H*), 7.16(s, 3 H, Ph–*H*), 6.25–6.75 (m, 1 H, C*H*), 4.44 (s, 2 H, Fc–*H*), 4.28 (s, 6 H, Fc–*H*), 4.11 (s, 1 H, Fc–*H*), 2.09–2.15 (m, 9 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 137.7, 134.7, 134.5, 133.3, 130.9, 129.2, 122.4, 119.9, 85.3, 69.8, 69.5, 69.1, 68.7, 56.8, 21,2. 20.9, 17.6 ppm. $C_{23}H_{25}ClFeN_2$ (420.76 g·mol^{-1}): calcd. C 65.65; H 5.99; N 6.66 %; found: C 65.46; H 5.88; N 6.74 %.

1d: Yield: 73 % (0.32 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.71 (s, 1 H, NC*H*N), 7.42 (s, 1 H, NC*H*), 7.02 (s, 1 H, NC*H*), 6.96(s, 2 H, Ph–*H*), 6.45–6.71 (m, 1 H, C*H*), 4.56 (s, 1 H, Fc–*H*), 4.38 (s, 1 H, Fc–*H*), 4.28 (s, 7 H, Fc–*H*), 2.31 (s, 3 H, CH_3), 2.04 (s, 9 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 140.9, 139.7, 134.2, 131.0, 130.0, 124.9, 122.6, 85.6, 70.2, 70.0, 69.1, 68.7, 66.9, 57.7, 22.9, 21.4, 19.3, 18.9 ppm. $C_{24}H_{27}ClFeN_2$ (434.78 g·mol^{-1}): calcd. C 66.30; H 6.26; N 6.44 %; found: C 66.17; H 6.18; N 6.55 %.

1e: Yield: 71 % (0.32 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.34 (s, 1 H, NC*H*N), 7.63 (s, 1 H, NC*H*), 7.39 (s, 1 H, NC*H*), 7.18 (s, 2 H, Ph–*H*), 7.10 (s, 1 H, Ph–*H*) 6.52–6.57 (m, 1 H, C*H*), 4.50 (s, 1 H, Fc–*H*), 4.40 (s, 1 H, Fc–*H*), 4.24 (s, 6 H, Fc–*H*), 4,10 (s, 1 H, Fc–*H*), 2.24 (s, 4 H, CH_2), 2.04 (s, 3 H, CH_3), 1.07 (s, 6 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 140.4, 138.8, 132.1, 131.4, 127.3, 125.0, 122.3, 85.5, 70.0, 69.8, 69.1, 68.7, 68.3, 66.6, 57.5, 24.9, 24.7, 22.3, 15.4 ppm. $C_{25}H_{29}ClFeN_2$ (448.81 g·mol^{-1}): calcd. C 66.90; H 6.51; N 6.24 %; found: C 66.79; H 6.40; N 6.35 %.

1f: Yield: 69 % (0.33 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.38 (s, 1 H, NC*H*N), 7.61 (d, *J* = 4.0 Hz, 1 H, NC*H*), 7.52 (d, *J* = 4.0 Hz, 1 H, NC*H*), 7.29 (s, 2 H, Ph–*H*), 7.05 (s, 1 H, Ph–*H*), 4.63 (s, 1 H, Fc–*H*), 4.39 (s, 2 H, Fc–*H*), 4.37 (s, 5 H, Fc–*H*), 4.10–4.29 (m, 1 H, Fc–*H*), 3.49 (s, 3 H, CH_3), 2.21–2.08 (m, 5 H, C*H*, CH_3), 1.13–1.19 (m, 9 H, CH_3) ppm.

1g: Yield: 71 % (0.37 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 11.03 (s, 1 H, NC*H*N), 6.86 (s, 2 H, NC*H*), 5.82–5.86 (m, 2 H, C*H*), 4.32 (s, 4 H, Fc–*H*), 4.20 (s, 14 H, Fc–*H*), 1.94 (d, *J* = 6.8 Hz, 6 H, CH_3). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 119.2, 85.4, 69.6, 69.5, 69.2, 68.8, 66.0, 65.8, 57.0, 21.9, 15.3 ppm.

1h: Yield: 72 % (0.42 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 11.78 (s, 1 H, NC*H*N), 7.39–7.63 (m, 4 H, Ph–*H*), 6.11–6.19 (m, 2 H, C*H*), 4.35 (s, 4 H, Fc–*H*), 4.21 (s, 14 H, Fc–*H*), 2.34 (d, *J* = 6.8 Hz, 6 H, CH_3). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 130.4, 126.6, 115.0, 84.7, 69.9, 69.5, 69.1, 68.7, 68.3, 68.0, 67.6, 66.3, 66.1, 66.0, 65.5, 57.9, 14.9 ppm.

Synthesis of Palladium Complexes 2:

2a: To an oven-dried 50 mL of r.b.f. containing **1a** (0.197 g, 0.6 mmol), $PdCl_2$ (0.117 g, 0.66 mmol), K_2CO_3 (0.829 g, 6 mmol) with a septum was injected into pyridine (15 mL) in an argon atmosphere. The reaction mixture was stirred at 75 °C for 14 h. After cooling to room temperature, the mixture was filtered through a plug of Celite and washed by DCM. After the volatile was removed under vacuum, the product was purified by flash column chromatography and subsequent recrystallization from CH_2Cl_2/ether afforded the product as yellow solid. Yield: 70 % (0.23 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.08 (d, *J* = 8.0 Hz, 2 H, Py–*H*), 7.80 (t, *J* = 8.0 Hz, 1 H, Py–*H*),7.40 (t, *J* = 8.0 Hz, 2 H, Py–*H*), 6.78 (d, *J* = 4.0 Hz, 1 H, NC*H*), 6.65–6.71 (m, 3 H, C*H*, NC*H*), 4.60 (d, *J* = 4.0 Hz, 1 H, Fc–*H*), 4.36 (s, 1 H, Fc–*H*), 4.26 (s, 5 H, Fc–*H*), 4.18 (d, *J* = 12.0 Hz, 2 H, Fc–*H*), 4.12 (s, 3 H, CH_3), 1.92 (d, *J* = 8.0 Hz, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.3, 147.0, 138.1, 124.5, 123.1, 118.5, 87.2, 69.8, 69.3, 69.1, 67.8, 65.8, 56.4, 37.9, 21.0 ppm. $C_{21}H_{23}Cl_2FeN_3Pd$ (550.60 g·mol^{-1}): calcd. C 45.81; H 4.21; N 7.63 %; found: C 45.67; H 4.14; N 7.75 %.

2b: To an oven-dried 50 mL of r.b.f. containing **1b** (0.223 g, 0.6 mmol), $PdCl_2$ (0.117 g, 0.66 mmol), K_2CO_3 (0.829 g, 6 mmol) with a septum was injected into pyridine (15 mL) in an argon atmosphere. The reaction mixture was stirred at 75 °C for 14 h. After cooling to room temperature, the mixture was filtered through a plug of Celite and washed by DCM. After the volatile was removed under vacuum, the product was purified by flash column chromatography and subsequent recrystallization from CH_2Cl_2/ether afforded the product as yellow solid. Yield: 81 % (0.29 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.08 (d, *J* = 8.0 Hz, 2 H, Py–*H*), 7.80 (t, *J* = 8.0 Hz, 1 H, Py–*H*), 7.39 (t, *J* = 8.0 Hz, 2 H, Py–*H*), 7.29–7.31 (m, 1 H, C*H*), 6.97 (d, *J* = 8.0 Hz, 1 H, NC*H*), 6.72 (d, *J* = 4.0 Hz, 1 H, NC*H*), 4.75 (s, 1 H, Fc–*H*), 4.39 (s, 1 H, Fc–*H*), 4.26 (s, 5 H, Fc–*H*), 4.19 (d, *J* = 8.0 Hz, 2 H, Fc–*H*), 2.08 (s, 9 H, CH_3), 1.97 (d, *J* = 4.0 Hz, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.5, 137.9, 124.6, 120.4, 117.8, 113.2, 87.5, 70.3, 69.3, 69.1, 67.6, 65.9, 58.8, 58.0, 32.1, 20.6 ppm. $C_{24}H_{29}Cl_2FeN_3Pd$ (592.68 g·mol^{-1}): calcd. C 48.64; H 4.93; N 7.09 %; found: C 48.53; H 4.84; N 7.19 %.

2c: To an oven-dried 50 mL of r.b.f. containing **1c** (0.285 g, 0.6 mmol), $PdCl_2$ (0.117 g, 0.66 mmol), K_2CO_3 (0.829 g, 6 mmol) with a septum was injected into pyridine (15 mL) in an argon atmosphere. The reaction mixture was stirred at 75 °C for 12 h. After cooling to room temperature, the mixture was filtered through a plug of Celite and washed by DCM. After the volatile was removed under vacuum, the product was purified by flash column chromatography and subsequent recrystallization from CH_2Cl_2/ether afforded product as yellow solid. Yield: 68 % (0.26 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 4.0 Hz, 2 H, Py–*H*), 7.72 (t, *J* = 4.0 Hz, 1 H, Py–*H*), 7.23–7.35 (m, 5

H, Py–*H*, Ph–*H*), 7.03–7.09(m, 1 H, C*H*), 6.91 (s, 1 H, NC*H*), 6.80 (s, 1 H, NC*H*), 4.76 (s, 1 H, Fc–*H*), 4.45 (s, 1 H, Fc–*H*), 4.31 (s, 5 H, Fc–*H*), 4.26 (s, 2 H, Fc–*H*), 2.32 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.05 (t, J = 8.0 Hz, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.4, 137.7, 137.3, 136.9, 136.8, 129.3, 128.4, 124.3, 123.9, 118.7, 87.4, 70.0, 69.4, 69.2, 67.7, 65.9, 56.9, 20.8, 19.1,19.0 ppm. $C_{28}H_{29}Cl_2FeN_3Pd$ (640.72 g·mol^{-1}): calcd. C 52.49; H 4.56; N 6.56 %; found: C 52.34; H 4.44; N 6.65 %.

2d: To an oven-dried 50 mL of r.b.f. containing **1d** (0.260g, 0.6 mmol), $PdCl_2$ (0.117 g, 0.66 mmol), K_2CO_3 (0.829 g, 6 mmol) with a septum was injected into pyridine (15 mL) in an argon atmosphere. The reaction mixture was stirred at 75 °C for 12 h. After cooling to room temperature, the mixture was filtered through a plug of Celite and washed by DCM. After the volatile was removed under vacuum, the product was purified by flash column chromatography and subsequent recrystallization from CH_2Cl_2/ether afforded product as yellow solid. Yield: 77 % (0.30 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.86 (d, J = 4.0 Hz, 2 H, Py–*H*), 7.69 (t, J = 8.0 Hz, 1 H, Py–*H*), 7.25–7.29 (m, 2 H, Py–*H*), 7.00–7.06 (m, 3 H, Ph–*H*, C*H*), 6.87 (d, J = 2.0 Hz, 1 H, NC*H*), 6.75 (d, J = 2.0 Hz, 1 H, NC*H*), 4.73 (s, 1 H, Fc–*H*), 4.42 (s, 1 H, Fc–*H*), 4.29 (s, 5 H, Fc–*H*), 4.21–4.23 (m, 2 H, Fc–*H*), 2.35 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.20 (s, 3H CH_3), 2.02 (d, J = 4.0 Hz, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.4, 148.7, 139.0, 137.8, 136.5, 136.4, 134.9, 129.2, 124.3, 118.6, 87.5, 70.0, 69.4, 69.2, 67.7, 65.9, 56.9, 21.2, 20.8, 19.0,15.3 ppm. $C_{29}H_{31}Cl_2FeN_3Pd$ (654.75 g·mol^{-1}): calcd. C 53.20; H, 4.77; N, 6.42 %; found: C 53.09; H, 4.66; N, 6.51 %.

2e: To an oven-dried 50 mL of r.b.f. containing **1e** (0.269 g, 0.6 mmol), $PdCl_2$ (0.117 g, 0.66 mmol), K_2CO_3 (0.829 g, 6 mmol) with a septum was injected into pyridine (15 mL) in an argon atmosphere. The reaction mixture was stirred at 75 °C for 13 h. After cooling to room temperature, the mixture was filtered through a plug of Celite and washed by DCM. After the volatile was removed under vacuum, the product was purified by flash column chromatography and subsequent recrystallization from CH_2Cl_2/ether afforded product as yellow solid. Yield: 85 % (0.34 g). **^{1}H NMR** (400 MHz, $CDCl_3$) : δ = 8.80 (d, J = 8.0 Hz, 2 H, Py–*H*), 7.67 (t, J = 8.0 Hz, 1 H, Py–*H*), 7.43 (t, J = 8.0 Hz, 1 H, Py–*H*), 7.24–7.28 (m, 4 H, Py–*H*, Ph–*H*), 7.00–7.05 (m, 1 H, C*H*), 6.87 (d, J = 2.0 Hz, 1 H, NC*H*), 6.81 (d, J = 4.0 Hz, 1 H, NC*H*), 4.74 (s, 1 H, Fc–*H*), 4.43 (s, 1 H, Fc–*H*), 4.29 (s, 5 H, Fc–*H*), 4.24 (s, 2 H, Fc–*H*), 2.72–2.83 (m, 2 H, CH_2), 2.31–2.46 (m, 2 H, CH_2), 2.03 (d, J = 8.0 Hz, 3 H, CH_3), 1.15 (t, J = 8.0 Hz, 3 H, CH_3), 1.10 (t, J = 8.0 Hz, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.4, 149.3, 142.4, 142.3, 137.7, 135.9, 129.7, 126.2, 124.7, 124.3, 118.3, 87.4, 70.1, 69.4, 69.2, 67.7, 65.9, 56.9, 24.7, 20.9, 14.9 ppm. $C_{30}H_{33}Cl_2FeN_3Pd$ (668.77 g·mol^{-1}): calcd. C 53.88; H 4.97; N 6.28 %; found: C 53.75; H 4.88; N 6.34 %.

2f: To an oven-dried 50 mL of r.b.f. containing **1f** (0.285 g, 0.6 mmol), $PdCl_2$ (0.117 g, 0.66 mmol), K_2CO_3 (0.829 g, 6 mmol) with a septum was injected into pyridine (15 mL) in an argon atmosphere. The reaction mixture was stirred at 75 °C for 12 h. After cooling to room temperature, the mixture was filtered through a plug of Celite and washed by DCM. After the volatile was removed under vacuum, the product was purified by flash column chromatography and subsequent recrystallization from CH_2Cl_2/ether afforded product as yellow solid. Yield: 68 % (0.28 g). **^{1}H NMR** (400 MHz, $CDCl_3$,): δ = 8.85 (d, J = 4.0 Hz, 2 H, Py–*H*), 7.68 (t, J = 8.0 Hz, 1 H, Py–*H*), 7.47 (t, J = 8.0 Hz, 1 H, Py–*H*), 7.28–7.32 (m, 4 H, Py–*H*, Ph–*H*), 7.08 (d, J = 4.0 Hz, 1 H, C*H*), 6.86 (d, J = 4.0 Hz, 1 H, NC*H*), 6.81 (d, J = 4.0 Hz, 1 H, NC*H*), 4.74 (s, 1 H, Fc–*H*), 4.43 (s, 1 H, Fc–*H*), 4.30 (s, 5 H, Fc–*H*), 4.24 (s, 2 H, Fc–*H*), 2.82–2.93 (m, 2 H, C*H*), 2.05 (d, J = 8.0 Hz, 3 H, CH_3), 1.41 (t, J = 4.0 Hz, 6 H, CH_3), 1.03 (d, J = 8.0 Hz, 3 H, CH_3), 0.96 (d, J = 8.0 Hz, 3 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.3, 147.1, 137.7, 130.1, 125.7, 124.3, 123.9, 117.9, 87.6, 70.1, 69.3, 69.2, 67.7, 66.0, 57.0, 28.4, 28.3, 26.5, 23.2, 21.0 ppm. $C_{32}H_{37}Cl_2FeN_3Pd$ (696.83 g·mol^{-1}): calcd. C 55.16; H 5.35; N 6.03 %; found: C 55.07; H 5.28; N 6.12 %.

2g: To an oven-dried 50 mL of r.b.f. containing **1g** (0.316 g, 0.6 mmol), $PdCl_2$ (0.117 g, 0.66 mmol), K_2CO_3 (0.829 g, 6 mmol) with a septum was injected into pyridine (15 mL) in an argon atmosphere. The reaction mixture was stirred at 75 °C for 13 h. After cooling to room temperature, the mixture was filtered through a plug of Celite and washed by DCM. After the volatile was removed under vacuum, the product was purified by flash column chromatography and subsequent recrystallization from CH_2Cl_2/ether afforded product as yellow solid. Yield: 80 % (0.36 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.17 (d, J = 4.0 Hz, 2 H, Py–*H*), 7.82 (t, J = 8.0 Hz, 1 H, Py–*H*), 7.43 (t, J = 8.0 Hz, 2 H, Py–*H*), 6.67–6.72 (m, 2 H, C*H*), 6.58 (s, 2 H, NC*H*), 4.59 (s, 2 H, Fc–*H*), 4.32 (s, 2 H, Fc–*H*), 4.25 (s, 1 H, Fc–*H*), 4.24 (s, 9 H, Fc–*H*), 4.15 (d, J = 8.0 Hz, 4 H, Fc–*H*), 1.91 (d, J = 8.0 Hz, 6 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.4, 145.2, 138.1, 124.6, 118.6, 113.2, 87.5, 69.9, 69.1, 67.6, 65.8, 56.4, 20.9 ppm. $C_{32}H_{33}Cl_2Fe_2N_3Pd$ (748.64 g·mol^{-1}): calcd. C 51.34; H 4.44; N 5.61 %; found: C 51.21; H 4.35; N 5.70 %.

2h: To an oven-dried 50 mL of r.b.f. containing **1h** (0.346 g, 0.6 mmol), $PdCl_2$ (0.117 g, 0.66 mmol), K_2CO_3 (0.829 g, 6 mmol) with a septum was injected into pyridine (15 mL) in an argon atmosphere. The reaction mixture was stirred at 75 °C for 13 h. After cooling to room temperature, the mixture was filtered through a plug of Celite and washed by DCM. After the volatile was removed under vacuum, the product was purified by flash column chromatography and subsequent recrystallization from CH_2Cl_2/ether afforded product as yellow solid. Yield: 75 % (0.36 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.18 (d, J = 8.0 Hz, 2 H, Py–*H*), 7.84 (t, J = 8.0 Hz, 1 H, Py–*H*), 7.51–7.59 (m, 2 H, Py–*H*), 7.45 (t, J = 8.0 Hz, 2 H, Ph–*H*), 7.07–7.10 (m, 2 H, Ph–*H*), 6.85–6.89 (m, 2 H, C*H*), 4.79 (s, 1 H, Fc–*H*), 4.74 (s, 1 H, Fc–*H*), 4.56 (s, 2 H, Fc–*H*), 4.32 (d, J = 4.0 Hz, 10 H, Fc–*H*), 4.19 (d, J = 8.0 Hz, 2 H, Fc–*H*), 4.14 (d, J = 8.0 Hz, 2 H, Fc–*H*), 2.03–2.07 (m, 6 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 160.6, 151.2, 138.3, 132.8, 124.8, 122.1, 112.5, 86.1, 70.9, 69.6, 69.4, 67.3, 66.7, 57.6, 17.8 ppm. $C_{36}H_{35}Cl_2Fe_2N_3Pd$ (798.69 g·mol^{-1}): calcd. C 54.14; H 4.42; N 5.26 %; found: C 54.02; H 4.33; N 5.37 %.

Procedure for the Pd-catalyzed Indolization: 2-Bromoaniline (1 mmol), alkyne (2 mmol), palladium catalyst (1 mol %), TBAB (1 mmol), and K_2CO_3 (3 mmol) were dissolved in dioxane (2 mL) in a 5 mL vial in air and heated at 140 °C for 24 h. After the reaction was complete (monitored by GC-MS or TLC), the mixture was diluted with ethyl acetate (10 mL), filtered through a pad of Celite, and the Celite pad was washed multiple times with ethyl acetate. The combined organic layer was dried with anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the pure product.

X-ray Crystallography: Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode by using Mo-K_α radiation (λ = 0.71073 Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given by full-matrix least-squares procedures based on F^2.[10] All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically (C–H bond lengths fixed at 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride

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Table 2. Crystallographic data for complexes **2a**, **2b**, and **2f**.

	2a	**2b**	**2f**
Empirical formula	$C_{21}H_{23}Cl_2FeN_3Pd$	$C_{48}H_{58}Cl_4Fe_2\ N_6Pd_2{\cdot}CH_3CN$	$C_{32}H_{37}Cl_2FeN_3Pd$
Formula weight	550.57	1226.36	696.80
Temperature /K	296(2)	296(2)	296(2)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$C2/c$	$P21/c$
Crystal size /mm	$0.29 \times 0.27 \times 0.22$	$0.35 \times 0.33 \times 0.25$	$0.28 \times 0.26 \times 0.20$
a /Å	7.4163(6)	31.547(5)	18.859(5)
b /Å	11.7509(9)	10.8116(16)	10.675(3)
c /Å	25.1829(19)	15.831(2)	15.679(4)
α /°	90	90	90
β /°	90	90.979(4)	104.011(3)
γ /°	90	90	90
V /Å^3	2194.6(3)	5398.6(14)	3062.6(14)
Z	4	4	4
$D_{calcd.}$ /mg·cm^{-3}	1.666	1.509	1.511
Absorption coefficient /mm^{-1}	1.735	1.420	1.261
F(000)	1104	2488	1424
θ range /°	1.62–28.01	2.38–26.37	3.59–25.35
Reflections collected / unique	29398 / 5146 [R(int) = 0.0206]	33528 / 5492 [R(int) = 0.0283]	20532 / 5547 [R(int) = 0.0595]
Data / restrains / parameters	5146 / 0 / 253	5492 / 78 / 295	5547 / 0 / 357
Goodness-of-fit on F_2	1.145	1.037	1.074
Final R indices [$I > 2\sigma$ (I)]	R_1 = 0.0221 wR_2 = 0.0584	R_1 = 0.0343 wR_2 = 0.0903	R_1 = 0.0709 wR_2 = 0.2091
R indices (all data)	R_1 = 0.0226 wR_2 = 0.0591	R_1 = 0.0401 wR_2 = 0.0961	R_1 = 0.0804 wR_2 = 0.2206

on their parent carbon atoms. All the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structure was solved by directed methods using the SHELXS-97 program and absorption correction was performed by the SADABS program. Selected crystallographic data are shown in Table 2. Crystals of complex **2a**, **2b**, and **2f** suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated solution of acetonitrile and DCM (15:1) at room temperature.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-922470 (**2a**), CCDC-922471 (**2b**), and CCDC-922472 (**2f**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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