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A four-coordinate Cu(I)–*N*-heterocyclic carbene complex: Synthesis, structure, properties, and application in amination for the synthesis of 1-(2-*N*-heteroaryl)-1*H*-pyrazoles

Chen Xu[1], Hong-Mei Li[1], Zhi-Qiang Wang[2] and Wei-Jun Fu[2]

Abstract

A new luminescent, cationic, heteroleptic, four-coordinate Cu(I)–*N*-heterocyclic carbene complex [Cu(Br-Pyim)(POP)](PF_6) is successfully prepared and characterized, where Br-Pyim and POP are 1-(6-bromopyridin-2-yl)imidazole-3-benzyl-2-ylidene and bis[2-(diphenylphosphino)phenyl]ether, respectively. Its detailed structure is determined by single-crystal X-ray analysis. It exists as a crystalline powder at room temperature and exhibits bright yellow-green emission. The use of the Cu(I)–*N*-heterocyclic carbene complex as a catalyst for amination reactions is also investigated and is found to be very efficient for the amination of 2-*N*-heteroaryl chlorides with pyrazoles, giving the desired substituted 1-(2-*N*-heteroaryl)-1*H*-pyrazoles in good yields.

Keywords

amination, copper-catalyzed, Cu(I)–*N*-heterocyclic carbene complex, *N*-arylpyrazole

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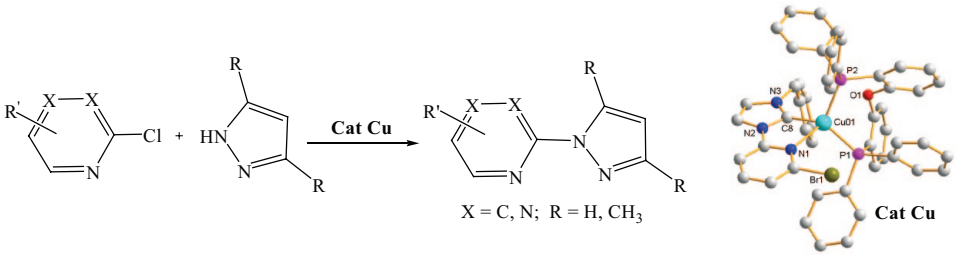


Introduction

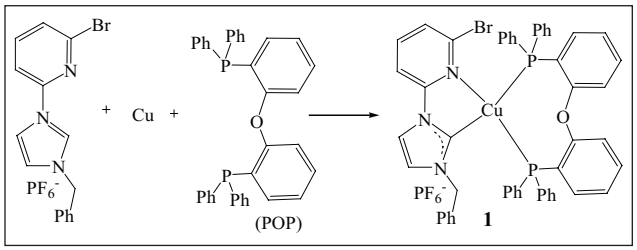
N-Arylpyrazoles are important intermediates used in the synthesis of many agrochemicals, pharmaceuticals, and functional materials.[1,2] The *N*-arylpyrazole structural unit can be obtained by several synthetic methods, among which transition-metal-catalyzed amination of aryl halides is one of the most direct and powerful.[3–5] In contrast to expensive catalysts such as palladium and rhodium complexes, low-cost copper catalysts are attracting considerable attention due to their potential use in industrial and practical applications.[6–9] Many copper/ligand systems have been reported, most of which utilize CuI as the catalyst and other Cu sources (e.g. Cu_2O, CuCl). However, the copper/ligand catalytic processes have not been well-determined; in particular, the structures of the Cu(I) pre-catalysts are rarely investigated.[8,9]

It is well-known that *N*-heterocyclic carbenes (NHCs) have strong σ-donating and modest π-accepting abilities, which make them widely used as ligands in catalysis and materials science.[10–13] Recently, Thompson's group reported luminescent Cu(I)–NHC complexes, and these complexes exhibited moderate-to-high emission efficiency.[14,15] We have also reported several cationic, heteroleptic, four-coordinate

[1]School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, P.R. China
[2]College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang, P.R. China

Corresponding authors:
Chen Xu, School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang Mengxi Road 3, Zhenjiang 212003, P.R. China.
Email: chenxu@just.edu.cn

Zhi-Qiang Wang, College of Chemistry and Chemical Engineering, Luoyang Normal University, Longmeng Road 72, Luoyang 471022, Henan, P.R. China.
Email: wzq197811@163.com



Scheme 1. Synthesis of four-coordinate Cu(I)–NHC complex **1**.

Cu(I)−NHC complexes with high emission efficiency and tunable emission wavelengths by modifying the structure of NHC ligands.[16,17] In view of these findings and our continuing interest in the synthesis of NHC complexes as well as their application in coupling reactions,[18,19] we were interested to investigate whether the obtained Cu(I)–NHC complexes were active for aminations. Thus, we prepared a new photoluminescence Cu(I)–NHC complex and examined its catalytic activity in the amination of pyrazoles.

Results and discussion

Synthesis and structure

The new four-coordinate Cu(I)–NHC complex **1** was prepared using the method reported by our group (Scheme 1)[16,17] and characterized by elemental analysis, mass spectroscopy (MS), and ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. It is very stable to air and moisture in a solid state at room temperature. The nuclear magnetic resonance (NMR) spectrum of **1** was consistent with the proposed structure, and the signal for the carbene carbon atom was observed at 158.7 ppm in the ^{13}C NMR spectrum. Furthermore, its detailed structure was confirmed by X-ray diffraction analysis. Single crystals were obtained through slow evaporation of an acetone solution at room temperature. The crystal structure of **1** is shown in Figure. 1. The Cu in the complex is in a typical distorted tetrahedral environment and is bonded to two P atoms of POP, a C atom, and the N atom of the NHC (Br-Pyim) ligand. The imidazolylidene ring and the pyridine ring of the NHC ligand are nearly coplanar and the dihedral angle is 6.4°. The bond lengths of Cu−C, Cu−N, and Cu(I)−P are similar to those of reported related four-coordinate Cu complexes.[14–17]

Absorption and emission

In CH_2Cl_2 solution, complex **1** exhibits three absorption bands as shown in Figure. 2. The intense high-energy absorption bands at 232 and 280 nm are ligand-centered (LC) π-π* transitions. The weaker absorption band at 340 nm can be assigned to the charge transfer (CT) transitions, which should include metal-to-ligand charge transfer (MLCT) and ligand-to-ligand (LLCT) transitions, according to previous reports.[16,17] It does not show luminescence in organic solutions at room temperature;[20] however, as a crystalline powder it shows intense yellow-green emission with a photoluminescence (PL) spectrum at 555 nm at room temperature (298 K). The absolute PL quantum yield and

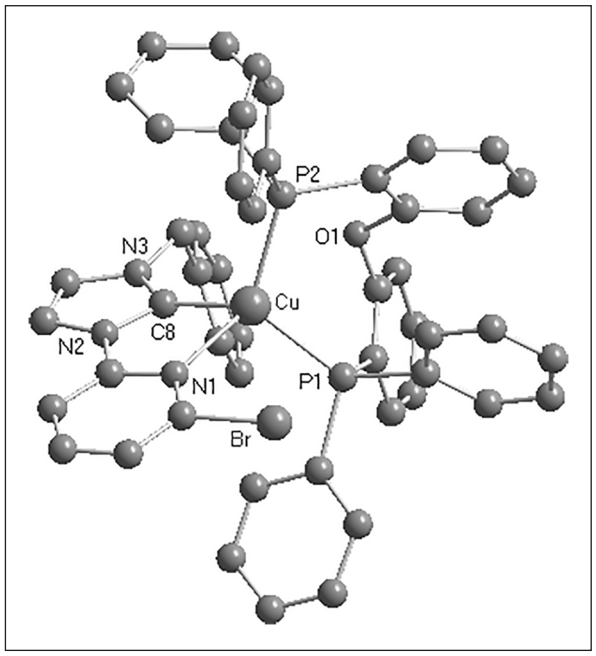


Figure 1. X-ray crystal structure of **1**. H atoms, CH_3COCH_3, and PF^{6-} are omitted for clarity. Selected bond lengths (Å) and angles (°) are as follows: Cu–N1 2.309(3), Cu–C8 1.964(3), Cu–P1 2.2566(9), Cu–P2 2.2693(10), and N1–Cu–C8 77.55(13), C8–Cu–P1 122.89(10), P1–Cu–P2 114.41(3), and P2–Cu–N1 121.96(8).

emission lifetime were measured to be 26% and 76.0 μs, respectively. At a low temperature of 77 K, the PL peak of **1** appears at 570 nm which is red-shifted by about 16 nm compared to that acquired at 298 K. In addition, the emission lifetime was measured to be 231.3 μs at 77 K, which increased by a factor of 3 compared to that acquired at 298 K (Figure 2, inset). These results imply that emission of this complex at room temperature is thermally activated delayed fluorescence (TADF).

Amination

1-(2-*N*-Heteroaryl)-1*H*-pyrazole derivatives as *N,N* ligands have found widespread applications in the fields of supramolecular chemistry and crystal engineering. Coupling reactions of *N*-heteroaryl halides have become one of the most valuable synthetic processes for *N*-heterocyclic compounds.[21,22] For example, 2-chloro pyridines and 2-chloropyrimidines are important coupling partners in these reactions.[23–25] However, the amination of 2-*N*-heteroaryl halides with pyrazoles has been relatively less reported.[26,27] So, we have investigated the catalytic activity of complex **1** for the *N*-arylation of 2-*N*-heteroaryl chlorides with pyrazoles.

Initially, the use of complex **1** as a catalyst for the coupling reaction of 2-chloro-5-methylpyridine with 1*H*-pyrazole was examined. Using 0.5 mol% of **1** in dioxane at 110 °C for 12 h provided the desired product **2**. The results from this study are summarized in Table 1. After screening a variety of bases (entries 1–6), KO^{t}Bu was found to give the best result, while NaO^{t}Bu gave a moderate yield. A survey of solvents indicated that dioxane was much better than other solvents such as tetrahydrofuran

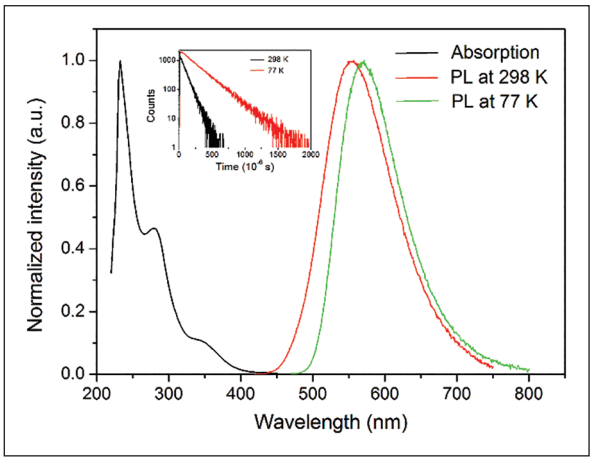
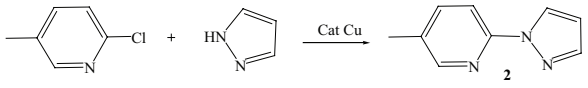


Figure 2. Absorption and photoluminescence (PL) spectra of **1**. The inset is the emission decay behavior of **1** in the solid state at 298 and 77 K.

Table 1. Optimization of the reaction conditions for the amination of 2-chloro-5-methylpyridine with 1*H*-pyrazole.[a]



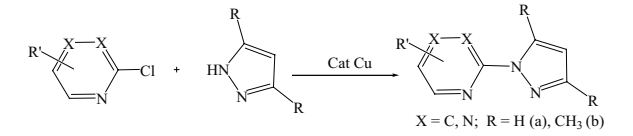
Entry	Base	Solvent	Catalyst (mol%)	Yield (%)[b]
1	Na_2CO_3	Dioxane	**1** (0.5)	28
2	K_2CO_3	Dioxane	**1** (0.5)	42
3	KOH	Dioxane	**1** (0.5)	53
4	K_3PO_4	Dioxane	**1** (0.5)	36
5	NaO^{t}Bu	Dioxane	**1** (0.5)	75
6	KO^{t}Bu	Dioxane	**1** (0.5)	91
7	KO^{t}Bu	Toluene	**1** (0.5)	86
8	KO^{t}Bu	THF	**1** (0.5)	49
9	KO^{t}Bu	DMF	**1** (0.5)	37
10	KO^{t}Bu	DMSO	**1** (0.5)	54
11	KO^{t}Bu	Dioxane	CuI (0.5)/Br-HPyimPF$_6$ (1)	38
12	KO^{t}Bu	Dioxane	CuI (0.5)/POP (1)	25
13	KO^{t}Bu	Dioxane	CuI (0.5)/Br-HPyimPF$_6$ (1)/POP (1)	72

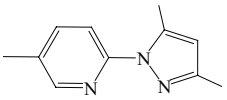
THF: tetrahydrofuran; DMF: dimethylformamide; DMSO: dimethyl sulfoxide.
[a]Reaction conditions: 2-chloro-5-methylpyridine (1.0 mmol), 1*H*-pyrazole (1.1 mmol), base (2.0 mmol), solvent (3 mL), 110 °C, 12 h.
[b]Isolated yield.

(THF), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) (entries 7–10). Toluene also afforded a good yield. In addition, CuI/Br-HPyimPF$_6$ and CuI/POP were poorly active under the same reaction conditions (entries 11 and 12). However, CuI/Br-HPyimPF$_6$/POP generated the product in a 72% yield, showing a synergistic ligand effect between the NHC and POP ligands in the amination (entry 13).[28–31]

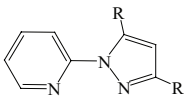
Compared with 1*H*-pyrazole, 3,5-dimethyl-1*H*-pyrazole showed no deleterious effect on these reactions. Under the optimized reaction conditions, the amination of 3,5-dimethyl-1*H*-pyrazole with 2-chloro-5-methylpyridine gave product **3** in a good yield (89%). In subsequent experiments,

Table 2. Aminations of 2-*N*-heteroaryl chlorides with pyrazoles catalyzed by **1**.[a]

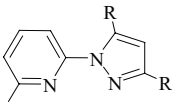




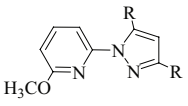
3, 89%



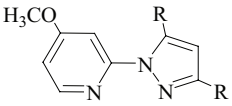
4a, 92%; **4b**, 90%



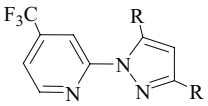
5a, 89%; **5b**, 91%



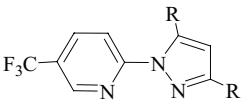
6a, 87%; **6b**, 84%



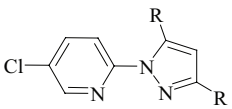
7a, 85%; **7b**, 83%



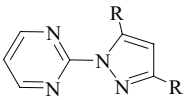
8a, 91%; **8b**, 90%



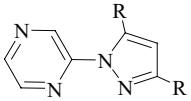
9a, 96%; **9b**, 93%



10a, 93%; **10b**, 92%



11a, 90%; **11b**, 87%



12a, 94%; **12b**, 91%

[a]Reaction conditions: 2-*N*-heteroaryl chloride (1.0 mmol), pyrazole (1.1 mmol), **1** (0.5 mol%), KO^{t}Bu (2.0 mmol), dioxane (3 mL), 110 °C, 12 h.

the coupling of a variety of electronically and structurally 2-*N*-heteroaryl chlorides with pyrazoles catalyzed by complex **1** was carried out (Table 2). Products **4a**,**b** were obtained from 2-chloropyridine in good yields (92% and 90%). For electron-rich 2-chloropyridine derivatives, the yields of the coupled products **5** and **6** were 84%–91%. As expected, the coupling reactions of activated 2-chloropyridine derivatives gave the products **7**–**10** in excellent yields (90%–96%). Finally, we investigated the couplings of 2-chloropyrimidine and 2-chloropyrazine and found them to be efficient coupling partners in this system giving products **11** and **12** in good yields.

Conclusion

A new photoluminescent four-coordinate Cu–NHC complex has been synthesized and characterized. The complex demonstrates efficient TADF in the solid state at room temperature. In addition, we have developed an efficient method for the amination of *N*-heteroaryl chlorides with pyrazoles catalyzed by this Cu–NHC complex. This protocol provides an efficient access to a variety of substituted 1-(2-*N*-heteroaryl) -1*H*- pyrazoles.

Experimental

Materials and equipment

Solvents were dried and freshly distilled prior to use. All other chemicals were commercially available, expect for 1-(6-bromopyridin-2-yl)-3-benzylimidazolium hexafluorophosphate (Br-HPyimPF$_6$), which was prepared according to the published procedure.[16,17] Elemental analyses were determined with a Carlo Erba 1160 Elemental Analyzer. Mass spectra were measured on a LC-MSD-Trap-XCT instrument. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (400, 162, and 100 MHz, respectively) with tetramethylsilane (TMS) as an internal standard. The absorption and PL spectra were recorded on a Hitachi U-3010 UV-Vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer.

Synthesis of [Cu(Br-Pyim)(POP)](PF$_6$) **1**

Under an N_2 atmosphere, Br-HPyimPF$_6$ (1 mmol), copper powder (1.2 mmol), and bis[2-(diphenylphosphino)phenyl] ether (POP, 1 mmol) were stirred in CH_3CN (10 mL) at 70 C overnight. After cooling, the resulting mixture was filtered, and then the filtrate was collected and evaporated under vacuum. The residue was dissolved in dichloromethane/ethanol, and the product was obtained as yellow crystals by slow evaporation of the solvent. Yield: 63%. ^{1}H NMR (400 MHz, CD_3CN): δ 7.76–7.85 (m, 2H), 7.61–7.68 (m, 1H), 7.34–7.49 (m, 16H), 7.09–7.15 (m, 6H), 7.00–7.04 (m, 6H), 6.85–6.98 (m, 5H), 6.49–6.52 (s, 2H), 4.55 (s, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ 158.7, 151.6, 143.1, 141.7, 136.7, 134.6, 133.0, 131.1, 131.2, 129.8, 129.7, 129.6, 128.8, 128.0, 125.9, 125.8, 124.0, 118.3, 55.0. ^{31}P NMR (162 MHz, CD_3CN): δ −9.9 (s), −144.2 (q). MS-ESI$^+$: *m/z* = 914.1 $(M–PF_6)^+$. Anal. Calcd for $C_{51}H_{40}BrCuF_6N_3OP_3$: C, 57.7; H, 3.8; N, 4.0. Found: C, 57.9; H, 3.5; N, 4.2%.

General procedure for the amination

In a Schlenk tube, a mixture of the catalyst **1** (0.5 mol%), 2-*N*-heteroaryl chloride (1.0 mmol), pyrazole (1.1 mmol), and KO^{t}Bu (2.0 mmol) in dioxane (3 mL) was evacuated and charged with nitrogen. The reaction mixture was heated at 110 °C for 12 h. After being cooled and quenched with water, the mixture was extracted with CH_2Cl_2. The solvent was evaporated and the resulting residue was purified by flash chromatography on silica gel. The products **4a, b**,[32] **5a**,[33] **5b**,[34] **7a**,[35] **11a**,[36] **11b**,[37] and **12a**[38] are known compounds and characterized by comparison of their data with those reported in the literature. Other products were characterized by elemental analysis, MS, and ^{1}H and ^{13}C NMR.

5-Methyl-2-(1H-pyrazol-1-yl)pyridine (**2**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, J = 2.4 Hz, 1H), 8.22 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.72 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 6.45 (d, *J* = 1.6 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 148.0, 141.8, 139.4, 131.0, 126.9, 112.1, 107.6, 18.0. MS-ESI$^+$: *m/z* = 159.1. Anal. Calcd for $C_9H_9N_3$: C, 67.9; H, 5.7; N, 26.4. Found: C, 68.2; H, 5.3; N, 26.9%.

5-Methyl-2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (**3**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.70 (d, *J* = 6.8 Hz, 1H), 7.60 (d, *J* = 6.8 Hz, 1H), 5.99 (s, 1H), 2.36 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 146.1, 139.4, 131.0, 126.9, 112.1, 110.8, 107.6, 29.8, 15.7, 13.8. MS-ESI$^+$: *m/z* = 187.1. Anal. Calcd for $C_{11}H_{13}N_3$: C, 70.6; H, 7.0; N, 22.4. Found: C, 71.0; H, 6.7; N, 22.6%.

2-Methoxy-6-(1H-pyrazol-1-yl)pyridine (**6a**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.72 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.46 (d, *J* = 1.2 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 149.6, 142.0, 141.1, 127.1, 107.8, 107.4, 103.9, 53.6. MS-ESI$^+$: *m/z* = 175.1. Anal. Calcd for $C_9H_9N_3O$: C, 61.7; H, 5.2; N, 24.0. Found: C, 61.9; H, 4.9; N, 24.3%.

2-Methoxy-6-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (**6b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 5.99 (s, 1H), 3.93 (s, 3H), 2.69 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 151.6, 149.9, 141.3, 140.7, 109.1, 107.1, 107.0, 53.9, 15.0, 13.8. MS-ESI$^+$: *m/z* = 203.1. Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.0; H, 6.5; N, 20.7. Found: C, 65.3; H, 6.1; N, 20.9%.

4-Methoxy-2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (**7b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 6.0 Hz, 1H), 7.36 (s, 1H), 6.68 (t, *J* = 5.6 Hz, 1H), 5.98 (s, 1H), 3.90 (s, 3H), 2.61 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 155.4, 149.7, 141.8, 141.1, 109.0, 107.9, 100.3, 55.5, 14.6, 13.7. MS-ESI$^+$: *m/z* = 203.1. Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.0; H, 6.5; N, 20.7. Found: C, 65.4; H, 6.2; N, 21.1%.

4-(Trifluoromethyl)-2-(1H-pyrazol-1-yl)pyridine (**8a**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.99 (t, *J* = 7.7 Hz, 1H), 7.78 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 148.6 (q, *J* = 36.2 Hz), 142.9, 140.2, 127.7 (q, *J* = 285.6 Hz), 117.7 (q, *J* = 2.2 Hz), 115.4 (q, *J* = 1.0 Hz), 108.6. MS-ESI$^+$: *m/z* = 213.1. Anal. Calcd for $C_9H_6F_3N_3$: C, 50.7; H, 2.8; N, 19.7. Found: C, 50.9; H, 2.5; N, 19.9%.

4-(Trifluoromethyl)-2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (**8b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 4.4 Hz, 1H), 8.20 (s, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 6.03 (s, 1H), 2.68 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 150.9, 148.6, 142.3, 141.2 (q, *J* = 33.6 Hz), 129.0, 124.6 (q, *J* = 276.4 Hz), 115.8 (q, *J* = 1.2 Hz), 111.5 (q, *J* = 1.6 Hz), 15.0, 13.7. MS-ESI$^+$: *m/z* = 241.1. Anal. Calcd for $C_{11}H_{10}F_3N_3$: C, 54.8; H, 4.2; N, 17.4. Found: C, 55.1; H, 4.0; N, 17.7%.

6-(Trifluoromethyl)-2-(1H-pyrazol-1-yl)pyridine (**9a**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (m, 2H), 8.28 (s, 1H), 7.80 (s, 1H), 7.41 (d, *J* = 4.8 Hz, 1H), 6.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 146.8 (q, *J* = 32.2 Hz), 142.8, 140.5, 127.6, 123.0 (q, *J* = 272.6 Hz), 117.6 (q, *J* = 2.6 Hz), 115.3 (q, *J* = 1.4 Hz), 108.4. MS-ESI$^+$: *m/z* = 213.1. Anal. Calcd for $C_9H_6F_3N_3$: C, 50.7; H, 2.8; N, 19.7. Found: C, 50.9; H, 2.3; N, 20.0%.

Table 3. Crystallographic data for complex **1**.

Empirical formula	$C_{54}H_{46}BrCuF_6N_3O_2P_3$
Fw	1119.30
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	17.9246(4)
b (Å)	21.3341(4)
c (Å)	14.7201(3)
α (°)	90
β (°)	113.918(3)
γ (°)	90
Volume (Å^3)	5145.7(2)
Goodness-of-fit (GOF)	1.068
F(000)	2280.0
Reflections collected	93,565
Independent reflections	9476
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0536$, $wR_2 = 0.1638$
R indices (all data)	$R_1 = 0.0677$, $wR_2 = 0.1725$

6-(Trifluoromethyl)-2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (**9b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J=8.4 Hz, 1H), 7.93 (t, J=8.2 Hz, 1H), 7.49 (d, J=7.6 Hz, 1H), 6.04 (s, 1H), 2.71 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 155.4, 153.0, 151.8, 150.5, 149.8, 141.8 (q, J=30.8 Hz), 122.4 (q, J=268.2 Hz), 114.0 (q, J=1.8 Hz), 109.1 (q, J=1.0 Hz), 100.3, 14.6, 13.7. MS-ESI$^+$: *m/z*=241.1. Anal. Calcd for $C_{11}H_{10}F_3N_3$: C, 54.8; H, 4.2; N, 17.4. Found: C, 55.0; H, 3.8; N, 17.8%.

5-Chloro-2-(1H-pyrazol-1-yl)pyridine (**10a**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.37 (s, 1H), 7.96 (d, J=8.8 Hz, 1H), 7.80–7.75 (m, 2H), 6.49 (d, J=1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 146.7, 142.5, 138.5, 129.1, 127.2, 113.4, 108.3. MS-ESI$^+$: *m/z*=179.0. Anal. Calcd for $C_8H_6ClN_3$: C, 53.5; H, 3.4; N, 23.4. Found: C, 53.7; H, 3.0; N, 23.9%.

5-Chloro-2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (**10b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.86 (d, J=8.8 Hz, 1H), 7.75 (d, J=7.2 Hz, 1H), 6.01 (s, 1H), 2.63 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 151.2, 146.1, 141.8, 138.0, 128.4, 116.5, 109.5, 14.7, 13.7. MS-ESI$^+$: *m/z*=207.1. Anal. Calcd for $C_{10}H_{10}ClN_3$: C, 57.8; H, 4.9; N, 20.2. Found: C, 57.6; H, 4.6; N, 20.6%.

2-(3,5-Dimethyl-1H-pyrazol-1-yl)pyrazine (**12b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (s, 1H), 8.39 (d, J=3.0 Hz, 2H), 6.06 (s, 1H), 2.66 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 149.9, 142.5, 141.2, 140.7, 138.4, 110.0, 14.6, 13.8. MS-ESI+: *m/z*=174.1. Anal. Calcd for $C_9H_{10}N_4$: C, 62.1; H, 5.8; N, 32.2. Found: C, 62.5; H, 5.5; N, 32.6%.

Crystal structure determination

Crystallographic data for complex **1** were collected on an Xcalibur Eos Gemini diffractometer with Mo-Kα radiation (λ=0.71073 Å) at ambient temperature. The data were corrected for Lorentz polarization factors as well as for absorption. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELX-97 program.[39] Crystal data, as well as details of data collection and refinements of **1**, are summarized in Table 3. The Cambridge Crystallographic Data Centre (CCDC) deposition number is 1583423. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/datarequest/cif.

Declaration of conflicting interests

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ORCID iD

Chen Xu https://orcid.org/0000-0003-1589-736X

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