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Chelating Palladium Complexes Containing Pyridine/pyrimidine Hydroxyalkyl Di-functionalized N-Heterocyclic Carbenes: Synthesis, Structure, and Catalytic Activity towards C-H Activation

Liangru Yang,* Jinwei Yuan, Pu Mao,* and Qi Guo

The synthesis of novel chelating palladium complexes containing pyridine/pyrimidine hydroxyalkyl di-functionalized N-heterocyclic carbenes (NHCs) via direct metallation of the precursor imidazolium salts is presented. The structure has been characterized unambiguously by X-ray single crystal analysis. Catalytic activity investigation showed that the complexes catalyse the direct C-H bond arylation of (benzo)oxazoles efficiently when using ¹BuOLi as base and DMF as solvent.

Introduction

N-Heterocyclic carbenes (NHCs) have been widely used as ancillary ligands in coordination chemistry and organic catalysis since the successful isolation and characterization of the first stable NHC by Arduengo et al. in 1991. As a class of non-phosphine ligands and alternative to tertiary phosphines, their unique properties such as strong σ-donating ability, robustness, and sterically demanding character have been well documented. Numerous NHC metal complexes have been synthesized, characterized and applied successfully to organic transformations, including C-C, C-hetero atom coupling, polymerization, hydrogenation and oxidation reactions. As chelating/pincer ligands might control the stability of the active species and improve the catalytic activity, the chelating/pincer NHC metal complexes have drawn especially much attention in recent years. Chelating NHC metal complexes containing heteroatom donors, such as P, N, O and S, have been synthesized, characterized and employed as catalysts for catalytic organic transformations (Fig. 1). The preliminary research demonstrated that C_{NHC,P} and C_{NHC,N} chelating palladium, iridium, rhodium, and ruthenium complexes to be highly efficient catalyst for the Heck reaction of vinyl compounds with aryI bromides and chlorides, Suzuki-Miyaura cross-coupling of aryI bromides and chlorides, hydrogenation of alkenes or ketones, dimerization of alkenes and C-H activation of methane. Alcohol-functionalized imidazolium salts have been reported to afford different type of C_{NHC,O} chelating palladium or nickel complexes upon certain metallation conditions, and the comparatively weak C_{NHC,O} chelate dissociate easily. Hydroxyethyl substituted C_{NHC,O} chelating complexes have been demonstrated to catalyse the Heck reaction and asymmetric addition of diethylzinc to benaldehyde efficiently.

Our group have developed an efficient procedure to synthesize chiral hydroxyalkyl functionalized imidazole derivatives. Quaternization of the hydroxyalkyl functionalized imidazole with halides containing N, P, et al. heteroatom would produce di-functionalized imidazolium salts, which should be ideal precursors for the hybrid pincer NHC ligands (NC_{NHC,O} or PC_{NHC,O}) or chelating NHC ligands (C_{NHC,N} or C_{NHC,P}). Owing to the comparatively strong stability and coordination capability of nitrogen compounds, we prepared hetero-functionalized
imidazolium salts through the quaternization of hydroxyalkyl substituted imidazoles by 2-bromopyridine or 2-chloropyrimidine. Direct metallation of the hetero-difunctionalized imidazolium salts by Pd(OAc)_2 under mild reaction condition produced the CNH-C catalyzed complexes smoothly.

2-Aryl substituted (benzo)oxazoles are very important backbones for the synthesis of natural products, pharmaceutically active compounds, and functional materials. Recently, the transition metal-catalysed direct C–H bond arylation has been noticed to be a potentially more efficient and convenient alternative for the straightforward synthesis of such compounds. However, in most cases, excessive free tertiary phosphines were used as ligands with transition metal salts. Besides air-, thermal-, and moisture-sensitive tertiary phosphine ligands and metal salts systems, Arslan and co-workers reported a mixed-halide NHC complex, (NHC)PdX_2 (X=Cl,Br) and established its efficient catalytic activity toward the direct C–H bond arylation of (benzo)oxazoles.

Shao and co-workers reported that 2-aryl functionalized (benzo)oxazoles can be obtained efficiently via direct C–H bond arylation of (benzo)oxazoles catalysed by a well-defined imidazole coordinated NHC palladium complex. While to the best of our knowledge, the catalytic activity of chelating or pincer NH C catalyzed complexes towards the direct C–H bond arylation of (benzo)oxazoles has not been reported.

In view of the successful application of chelating palladium catalyst in classical C–C bond formation, while comparatively rare application in C–H activation, here we report the synthesis, characterization and C–H bond activation catalytic activity study of a novel type of CNH-N catalyzing complexes. As expected, the CNH-N catalyzing complexes here proved remarkably stable toward air and moisture, and showed high catalytic activity toward C–H bond arylation of (benzo)oxazoles. These results underline the high potential of this class of chelating NH C complexes in catalysis.

**Results and discussion**

**Synthesis of pyridine/pyrimidine hydroxyalkyl di-functionalized imidazolium salts**

Through slight modification of the literature reports, imidazole alcohols (1a-b) were synthesized from the condensation reaction of amino alcohols, formaldehyde, glyoxal, and ammonium chloride in relatively high yields (Scheme 1). The structure was characterized by NMR and MS analysis.

Pyridine hydroxyalkyl di-functionalized imidazolium salts (2a-b) were obtained from the neat reaction of the imidazole alcohols with excessive 2-bromopyridine at 150 °C, and pyrimidine hydroxyalkyl di-functionalized imidazolium salts (2c-d) were obtained by heating the mixture of imidazole alcohols and 2-chloropyrimidine in toluene at 110 °C (Scheme 1). The pure products were obtained by silica chromatography and characterized by NMR and MS analysis. In imidazole alcohols (1a-b), the resonances of NCH proton appeared at 7.65 and 7.48 ppm, respectively. In compounds 2a-d, single proton signals appeared within the range of 10.34-10.17 ppm, which can be attributed to the resonances of NCH proton, indicating the formation of imidazolium salts. **Additional proton signals in the range of 9.08-7.18 ppm confirmed the formation of pyridine/pyrimidine hydroxyalkyl di-functionalized imidazolium salts.**

**Synthesis of chelating NH C palladium complexes**

The chelating NH C-Pd complexes (3a-d) were prepared through the direct metallation of imidazolium salts (2a-b) by Pd(OAc)_2 in dichloromethane at room temperature (Scheme 1). The formation of the chelating NH C palladium complexes was observed from the studies of NMR spectra, showing the conspicuous absence of the NHCH resonances of imidazolium salts in the ¹H NMR spectra, and the appearance of additional signals within 160.5-149.7 ppm in the ¹³C NMR spectra, which should be attributed to the new C carbene-Pd resonance. Meanwhile, the resonances of the pyridine proton adjacent to the nitrogen atom appeared at 9.44 (3a) and 9.40 (3b) ppm, obviously downfielded compared to those of the imidazolium salts 2a (8.68 ppm) and 2b (8.65 ppm), supporting the coordination of pyridine to the palladium center. Similarly, in compounds 2c-2d, the resonances of the two pyrimidine protons adjacent to the nitrogen atom appeared as doublets at 9.08 (2e) and 9.05 (2f) ppm. While in complexes 3c-3d, those protons appeared as two magnetically unequal signals, with one shifted significantly from 9.08 (2e) and 9.05 (2f) to 9.44 (3e)
and 9.42 (3d) ppm, confirming the coordination of pyrimidine to the palladium center. The structure of complexes 3b and 3d has been further characterized unambiguously by the single-crystal X-ray diffraction studies.

Single crystals of 3b and 3d suitable for X-ray diffraction analysis were obtained from the slow diffusion of diethyl ether to concentrated dichloromethane or acetonitrile solution, respectively. The molecular structures were shown in Figure 2-3, with selected bond lengths and bond angles listed in the caption.

![Figure 2. Molecular structure of 3b (50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Pd(1)-C(1) 1.990(14), Pd(1)-N(1) 2.061(10), Pd(1)-Br(1) 2.47(2), Pd(1)-Br(2) 2.41(2), N(2)-C(11) 1.319(16), N(3)-C(12) 1.390(18), N(2)-C(12) 1.350(12), N(3)-C(12) 1.393(17), C(2)-C(13) 1.36(2); (C(1)-Pd(1)-Br(1) 172.7(4), C(1)-Pd(1)-Br(2) 98.7(4), C(1)-Pd(1)-N(1) 178.5(5), N(1)-Pd(1)-Br(1) 94.4(3), N(1)-Pd(1)-Br(2) 170.7(3), Br(1)-Pd(1)-Br(2) 88.59(6); N(2)-C(11)-N(3) 105.7(10).](image)

In both structures, the palladium atom adopts a slightly distorted square-planar coordination bonded to carbene, pyridine/pyrimidine nitrogen donor and two halides, with the five membered chelate ring exist a twisty conformation. The hydroyl group hangs freely, forming intermolecular hydrogen bond with the halide of another molecular (ESI), although in some NHC palladium complexes, the hydroxyl group has been reported to coordinate to the central palladium atom. 9

![Figure 3. Molecular structure of 3d (50% displacement ellipsoids). Selected bond lengths(Å) and angles (deg): Pd(1)-C(1) 1.972(4), Pd(1)-N(1) 2.043(3), Pd(1)-C(1) 2.2889(9), Pd(1)-C(2) 2.3502(11), N(2)-C(11) 1.354(4), N(3)-C(12) 1.336(5), N(2)-C(12) 1.381(5), N(3)-C(12) 1.404(5), C(2)-C(3) 1.343(6); C(1)-Pd(1)-C(1) 98.29(10), C(1)-Pd(1)-C(2) 172.55(11), C(1)-Pd(1)-N(1) 79.61(14), N(1)-Pd(1)-C(1) 175.55(10), N(1)-Pd(1)-C(2) 93.06(10), C(1)-Pd(1)-C(2) 89.12(4); N(2)-C(1)-N(3) 104.7(3).](image)

Catalytic studies

Initially, running the reaction of (benzo)oxazole and bromobenzene catalysed by complex 3a as a model, a brief screening of the base, solvent, amount of base and catalyst loading was conducted (Table 1). Among the bases tested, 'BuOLi afforded the moderate yield. 'BuONa, 'BuOK, Na2CO3, Li2CO3, and KOH all produced very low yields (table 1, entries 1-6). Tests of different solvents proved DMF to be the proper solvent. Reaction in DME, DMAC or dioxane produced the target product in a bit low yields (table 1, entries 7-10). Decreasing the amount of base resulted in low yields and the highest yield was obtained when using 5.0 equiv. of 'BuOLi with a catalyst loading of 2.5% (table 1, entries 11-13). Further decreasing of catalyst loading lead to low yield and no products was obtained in the absence of NHC-Pd catalyst (table 1, entries 14-15), implying that the introduction of the palladium catalyst was essential for this reaction, although a metal-free system for direct C-H bond arylation has been established during the past years. 15

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*Reaction condition: 1.0 mmol (benzo)oxazole, 0.5 mmol bromobenzene, 1.5-2.5 mmol base, 2 mL solvent, 130 °C, 24 h. Yields determined by HPLC.

Under the standard conditions, using 'BuOLi as base and DMF as solvent, the catalytic activity of complexes 3a-d towards the reaction of (benzo)oxazole with bromobenzene were investigated (Table 2). As shown in Table 2, the pyrimidine chelating complexes (3c-d) displayed higher activities than the corresponding pyridine chelating complexes (3a-b), which can be tentatively attributed to the stronger basicity of pyrimidine group. For complexes having the same chelating structure, the substituents near the hydroyl group also showed some effect on the catalytic activity. The complexes containing benzyl substituent (3b & 3d) were more active than those containing 'butyl substituent (3a & 3c). In general, complexes 3a-d all presented high catalytic efficiency towards the C-H activation of (benzo)oxazole when using bromobenzene as aryl source. While in literature reports, aryl iodide is used as the aryl source for most of the Pd-catalysed direct C-H bond functionalization of (benzo)oxazoles, or addition of copper salt as co-catalyst is necessary to produce the target products in moderate or high yields. 16
Using complex 3c as catalyst, BuOLi as base and DMF as solvent, the feasibility of the complex towards the C-H activation of (benzo)oxazole derivatives was further investigated (Table 3). The results showed that complex 3c presented high catalytic efficiency towards the reaction of (benzo)oxazoles with a series of aryl bromides, producing the target products in moderate to high yields. For instance, both aryl bromides bearing electron-rich, -neutral, and -poor substituents are tolerated in such conditions, and the substituents did not show any obvious electron effect on the reaction. In addition, 2-methyl-phenylbromide and 2,4,6-trimethyl-phenylbromide gave inferior results (Table 4, entries 2, 6, 10, 17 and 21), maybe partially attributed to the steric hindrance.

The alkyl substituents on the phenyl ring of (benzo)oxazoles seemed to have some effect on the reaction. For examples, in the reaction of aryl bromides bearing electron-rich substituents, 5-methyl-, and 5-tert-butyl- substituted (benzo)oxazoles gave better yields than (benzo)oxazole (Table 4, entries 9-13 and 16-21 vs entries 1-6). While in the cases of aryl bromide with electron-poor substituent, 5-methyl-, and 5-tert-butyl-substituted (benzo)oxazoles gave inferior yields (Table 4, entries 14-15 and 22-23 vs entries 7-8).

### Experimental section

#### General consideration

All solvents and chemicals were used as received or dried with standard methods and freshly distilled prior to use if needed. NMR spectra were recorded at 25 °C on a 400 MHz Bruker spectrometer. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to the residual solvent resonances. Elemental analyses were obtained from a thermo Flash 2000. ESI-MS spectra were recorded on a Bruker Esquire 3000.

#### Synthesis of imidazole alcohols (1a-b)

L-amino alcohol (60 mmol) and ammonium chloride (60 mmol, 3.21 g) were dissolved in MeOH (120 mL), and the mixture was put in an ice-bath. Aqueous HCHO solution (36%, 60 mmol) and aqueous CHOCHO solution (40%, 60 mmol) were then added dropwise before the mixture being heated to 60°C for 5 h. The mixture was then cooled to room temperature and the solvent was removed by evaporation. The residue was dissolved in NaOH solution (150 mL, 2M), and then extracted with CH₂Cl₂ (20 mL×3). The combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated successively. Purification of the residue by flash chromatography (silica, CH₂COOEt/EtOH = 10/1, v/v) afforded the pure products.

(S)-2-(1H-imidazol-1-yl)-4-methylpentan-1-ol (1a). White crystals (75.7 g, 75%). Mp: 68-70 °C. ¹H NMR (DMSO, 400 MHz): δ 7.65 (s, 1H, CH in imidazole) 7.19 (s, 1H, CH in imidazole) 6.87 (s, 1H, CH in imidazole), 4.97 (t, J = 4.9 Hz, 1H, CH₂OH) 4.16-4.11 (m, 1H, NCH) 3.57-3.53 (m, 2H, CH₂OH) 1.72-1.65 (m, 1H, CH₂CH₂CH₂) 1.54-1.47 (m, 1H, CH₂CH₂CH₂) 1.23-1.15 (m, 1H, CH₂CH₂CH₂) 0.86 (d, J = 6.6 Hz, 3H, CH₂CH₂CH₂) 0.80 (d, J = 6.6 Hz, 3H, CH₂CH₂CH₂) ppm. ¹³C NMR (DMSO, 100 MHz) δ 137.4, 128.5, 118.1 65.0, 57.8, 24.5, 23.5, 22.0 ppm. MS Calcd. for C₁₉H₂₃NO, 286.2. Found: ESI-MS, m/z: 286.2 [M+H]⁺.

(S)-2-(1H-imidazol-1-yl)-3-phenylpropan-1-ol (1b). White crystals (9.71 g, 80%). Mp: 74-76 °C. ¹H NMR (DMSO, 400 MHz): δ 7.48 (s, 1H, CH in imidazole), 7.23-7.14 (m, 4H, PhH), 7.08 (d, J = 4 Hz, 2H, CH in imidazole, & PhH), 5.10 (s, 1H, CH₂OH) 4.38-4.32 (m, 1H, NCH) 3.65 (bs, 2H, CH₂OH) 3.15-3.10 (m, 1H, PhCH₂) 3.00-2.94 (m, 1H, PhCH₂) ppm. ¹³C NMR (DMSO, 100 MHz) δ 138.5, 137.3, 129.3, 128.7, 128.4, 126.7, 118.3, 64.0, 61.1, 37.9 ppm. MS Calcd. for C₁₇H₂₁NO₂, 292.1. Found: ESI-MS, m/z: 292.1 [M+H]⁺.

#### Synthesis of pyridine hydroxalkyl di-functionalized imidazolium bromides (2a-b)

...
A Schlenk tube containing imidazole alcohol (1a or 1b, 5 mmol) and 2-bromopyridine (3 mL) was heated at 150 °C for 72 h. The mixture was then cooled to room temperature and added to diethyl ether (30 mL) dropwise, leading to the formation of deep yellow precipitate, which was then collected and purified by flash chromatography (silica, CH₂Cl₂/EtOH = 15/1–8/1, v/v) to produce the pure products.

(S)-1-(1-hydroxy-4-methylpentan-2-yl)-3-(pyridin-2-yl)-1H-imidazol-3-ium bromide (2a). Viscous oil (1.42 g, 87%). 1H NMR (400 MHz, DMSO): δ 10.25 (s, 1H, CH in imidazole), 8.68-8.66 (m, 1H, CH in pyridine), 8.62 (t, J = 1.8 Hz, 1H, CH in imidazole), 8.26-8.22 (m, 1H, CH in pyridine), 8.21 (t, J = 1.8 Hz, 1H, CH in imidazole), 8.11 (d, J = 8.3 Hz, 1H, CH in pyridine), 7.68-7.65 (m, 1H, CH in pyridine), 5.26 (bs, 1H, CH₂OH), 4.64-4.60 (m, 1H, NCH), 3.77-3.70 (m, 2H, CH₂OH), 1.97-1.91 (m, 1H, CH₂CH(CH₃)₂), 1.70-1.63 (m, 1H, CH₂CH(CH₃)₂), 1.45-1.38 (m, 1H, CH₂CH(CH₃)₂), 0.93 (d, 3H, J = 6.5 Hz, CH₂CH(CH₃)₂), 0.89 (d, 1H, J = 6.6 Hz, CH₂CH(CH₃)₂) ppm. 13C NMR (100 MHz, DMSO): δ 149.7, 146.9, 141.0, 135.2, 125.7, 122.8, 120.1, 114.8, 63.5, 62.3, 38.6, 24.4, 23.2, 22.0 ppm. MS Calcd. for C₁₂H₂₀BrN₂O, 325.1. Found: ESI-MS, m/z: 246.08 [M+Br]⁺.

Synthesis of palladium complexes (3a-d)

A mixture of imidazolium salt (2a, 2b, 2c or 2d, 1.0 mmol), Pd(OAc)₂ (1.0 mmol, 0.22 g) in CH₂Cl₂ (10 mL) was stirred at room temperature for 12 h. The solvent was then evaporated and purification of the residue by column chromatography (silica, CH₂Cl₂-acetone, gradient elution, 15/1–4/1, v/v) produced the pure palladium complexes 3a-d.

3a. Yellow solids (0.20 g, 39%). 1H NMR (400 MHz, DMSO): δ 9.44 (s, 1H, CH in pyridine), 8.46 (d, 1H, J = 2.2 Hz, CH in imidazole), 8.40-8.36 (m, 1H, CH in pyridine), 8.18 (d, 1H, J = 8.2 Hz, CH in pyridine), 7.78 (d, 1H, J = 2.3 Hz, CH in imidazole), 7.62 (t, 1H, J = 7.0 Hz, CH in pyridine), 6.25 (bs, 1H, NCH), 5.01 (t, 1H, J = 5.2 Hz, CH₂OH), 3.70-3.60 (m, 2H, CH₂OH), 1.90-1.82 (m, 1H, CH₂CH(CH₃)₂), 1.64-1.57 (m, 1H, CH₂CH(CH₃)₂), 1.41-1.35 (m, 1H, CH₂CH(CH₃)₂), 0.95 (d, 3H, J = 6.5 Hz, CH₂CH(CH₃)₂), 0.89 (d, 3H, J = 6.5 Hz, CH₂CH(CH₃)₂) ppm. 13C NMR (100 MHz, DMSO): δ 151.8, 150.8, 143.4, 123.6, 126.2, 117.5, 112.9, 64.2, 59.3, 30.1, 24.7, 23.4, 22.8 ppm. Anal Calcd for C₁₂H₁₄Br₂N₂O₂Pd (511.55): C, 32.87; H, 3.74; N, 8.21. Found: C, 32.68; H, 3.56; N, 8.42.

3b. Yellow solids (0.24 g, 44%). 1H NMR (400 MHz, DMSO): δ 9.40 (s, 1H, CH in pyridine), 8.42 (d, 1H, J = 1.6 Hz, CH in imidazole), 8.37 (t, 1H, J = 8.2 Hz, CH in pyridine), 8.13 (d, 1H, J = 8.2 Hz, CH in pyridine), 7.91 (d, 1H, J = 2.0 Hz, CH in imidazole), 7.61 (t, 1H, J = 6.6 Hz, CH in pyridine), 7.34-7.26 (m, 4H, PhH), 7.18 (t, 1H, J = 7.3 Hz, PhH), 6.55 (bs, 1H, NCH), 5.12 (t, 1H, J = 5.0 Hz, CH₂OH), 3.75-3.65 (m, 2H, CH₂OH), 3.20 (d, 2H, J = 7.9 Hz, C₂H₆₂OH) ppm. 13C NMR (100 MHz, DMSO): δ 151.7, 143.4, 137.4, 129.6, 128.8, 127.0, 123.7, 122.7, 117.4, 112.8, 68.9, 63.0, 56.3, 36.7 ppm. Anal Calcd for C₁₂H₁₂Br₂N₂O₂Pd (545.56): C, 37.43; H, 3.14; N, 7.70. Found: C, 37.28; H, 2.97; N, 7.89.

3c. Yellow solids (0.18 g, 42%). 1H NMR (400 MHz, DMSO): δ 9.44 (s, 1H, CH in pyrimidine), 9.07 (s, 1H, CH in pyrimidine), 8.14 (d, 1H, J = 2.3 Hz, CH in imidazole), 7.75 (d, 1H, J = 2.4 Hz, CH in imidazole), 7.72 (t, 1H, J = 5.3 Hz, CH in imidazole), 6.11-6.07 (m, 1H, NCH), 5.02 (t, 1H, J = 5.0 Hz, CH₂OH), 3.65 (t, 2H, J = 4.6 Hz, CH₂OH), 1.89-1.82 (m, 1H, CH₂CH(CH₃)₂), 1.62-1.55 (m, 1H, CH₂CH(CH₃)₂), 1.39-1.34
the complexes catalyse the direct C-H bond arylation of (benzo)oxazoles efficiently when using BuOLi as base and DMF as solvent. The catalytic activity of this novel type of NHC complexes towards other organic transformations, especially asymmetric catalysis, are currently in progress in our group.

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Notes and references


Chelating Palladium Complexes Containing Pyridine/pyrimidine Hydroxyalkyl Di-functionalized N-Heterocyclic Carbenes: Synthesis, Structure, and Catalytic Activity towards C-H Activation

Liangru Yang,* Jinwei Yuan, Pu Mao,* Qi Guo

Chelating palladium complexes containing pyridine/pyrimidine hydroxyalkyl di-functionalized NHCs were synthesized, characterized and tested for C-H activation of (benzo)oxazoles.