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Cyclometalated cis-Chelated Bidentate N-Heterocyclic Carbene Palladium Complexes: Synthetic, Structural, and Catalytic Studies

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Summary: Novel cyclometalated cis-chelated bidentate N-heterocyclic carbene palladium complexes derived from binaphthyl-2,2′-diamine (BINAM) have been successfully synthesized, and the cyclometalated cis-chelated bidentate NHC−palladium(II) complex **5a** *has been characterized by X-ray crystal structure diffraction. Moreover, we found that these novel NHC−palladium(II) complexes are quite effective in Suzuki−Miyaura coupling reactions and Friedel−Crafts reactions under mild conditions.*

Recently, N-heterocyclic carbenes (NHCs) have become a very important class of ligands in organometallic chemistry and catalysis.[1] The strong σ-donating but poor π-accepting ability of these N-heterocyclic carbenes leads to the formation of many stable metal−carbene complexes, which are good catalysts in numerous organic transformations. Most significantly, a number of NHC−palladium complexes have emerged as effective catalysts for a variety of coupling reactions.[2]

Palladacycles are one of the most popular class of organopalladium derivatives. Numerous reviews have been dedicated to their synthesis, structural aspects, applications in organic synthesis, and organometallic catalysis as well as new molecular materials.[3] Palladacycles contain at least one metal−carbon bond intramolecularly stabilized by at least one donor atom, such as a N, P, As, O, Se, or S heteroatom. However, to the best of our knowledge, there has been a very limited number of spectroscopically characterized cyclometalated NHC−Pd(II) complexes reported thus far.[4]

Previously, we reported the synthesis of a novel cis-chelated NHC−Pd(II) complex derived from binaphthyl-2,2′-diamine (BINAM) and a new dimeric bidentate NHC−Pd(II) complex derived from *trans*-cyclohexane-1,2-diamine as well as their applications in the Suzuki−Miyaura coupling reaction and Heck reaction.[5] In this paper, we wish to report the synthesis and characterization of a novel class of cyclometalated cis-chelated bidentate NHC−palladium(II) complexes based on BINAM and their catalytic abilities in the Suzuki−Miyaura coupling reaction and Friedel−Crafts reaction.

Proligand Synthesis. The starting materials **1** and **2** were prepared according to previous literature.[6] The Pd-catalyzed coupling reaction of **2** with aryl bromides in toluene in the presence of NaO^{t}Bu and 2,2′-bis(diphenylphosphanyl)-[1,1′]binaphthalenyl (BINAP) at 110 °C for 3 h afforded the corresponding products **3a−c** in 86−90% yields. The desired benzimidazolium salts **4a−c** were obtained in 96−99% yields by the cyclization of **3a−c** with triethyl orthoformate in the presence of hydrochloric acid containing a catalytic amount of formic acid at 80 °C (Scheme 1).

Synthesis of Cyclometalated cis-Chelated Bidentate N-Heterocyclic Carbene Palladium Complexes. The reaction of the obtained benzimidazolium salts **4a−c** with Pd$_2$(dba)$_3$ in THF under reflux or at room temperature (20 °C) produced the corresponding cyclometalated cis-chelated N-heterocyclic carbene palladium(II) complexes **5a−c** with the metal insertion of the aromatic *o*-C−H bond in 61% and 52% yields, respectively (Scheme 2). Their structures were fully characterized by spectroscopic data, ESI-MS, and HRMS (see the Supporting Information). For example, the presence of two types of N-heterocyclic carbenes in cyclometalated cis-

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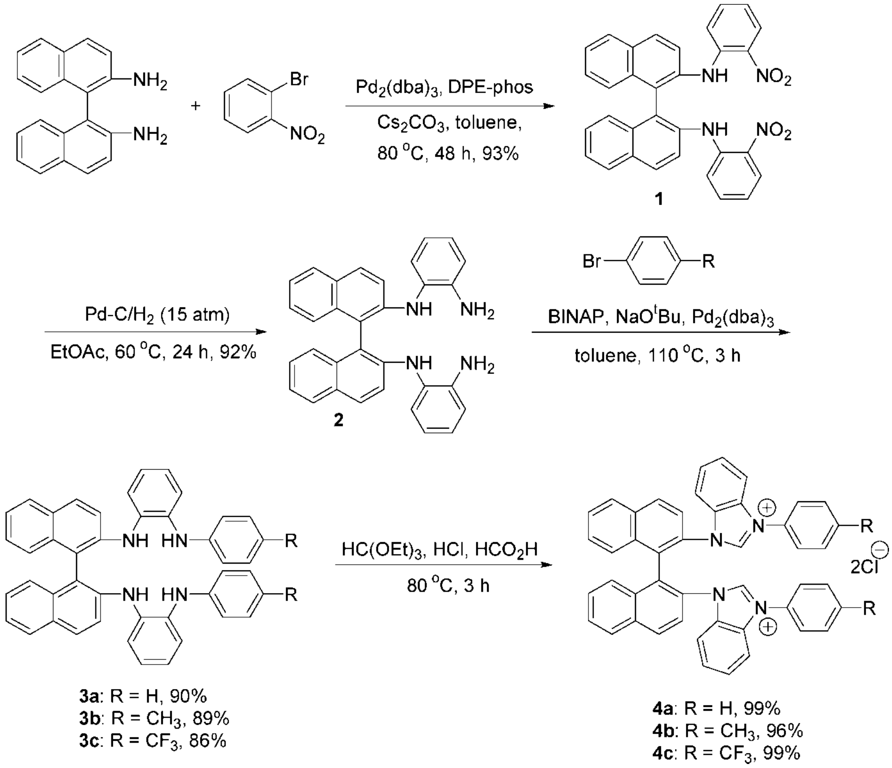
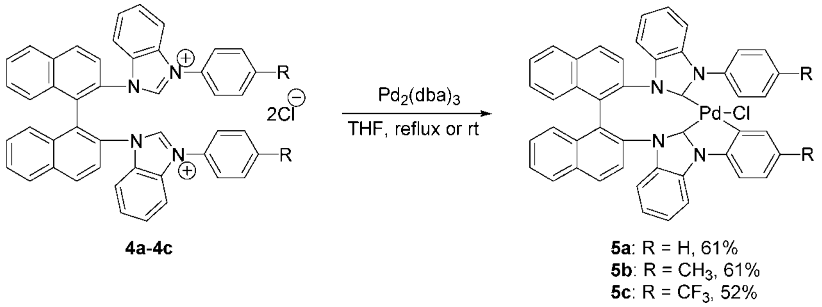
Scheme 1. Synthesis of the Benzimidazolium Salts as Ligand Precursors for the N-Heterocyclic Carbenes



Scheme 2. Synthesis of Cyclometalated cis-Chelated NHC−Palladium(II) Complexes 5a−c



chelated N-heterocyclic carbene palladium(II) complex **5a** was evidenced from its ^{13}C NMR spectrum, with two C_{NHC} signals at δ 180.4 and 197.5 ppm, respectively. In addition, single crystals of complex **5a** suitable for X-ray crystal structure analysis were grown from a mixed solvent of petroleum ether/ethyl acetate (5:1). On the basis of X-ray diffraction, the structure of complex **5a** was unambiguously determined.[7] Its ORTEP drawing is depicted in Figure 1. As for NHC−Pd(II) complexes **5b** and **5c**, the presence of two types of N-heterocyclic carbenes was identified similarly at δ 179.7 and 197.3 ppm for **5b** as well as at δ 179.6 and 196.3 ppm for complex **5c**, respectively (see the Supporting Information).

As can be seen from Figure 1, the palladium(II) center is in a slightly distorted square-planar geometry, defined by one chloride ligand and one cyclometalated bidentate NHC ligand (two carbenes and one phenyl group). The angle between the N(1)−C(1)−N(2) plane of the NHC ligand and the coordinate plane of C1−C14−C26−Pd1 is 72.81° (see the dihedral angle calculation in the Supporting Information). The bond length of Pd−C1 (2.055(6) Å) is comparable to its analogues.[5] Because of the occurrence of cyclometalation, the Pd−C14 (1.927(6) Å) bond length is shorter than that of Pd−C1 (2.055(6) Å). The $Pd-C_{phenyl}$ (2.016(6) Å) bond length falls in the range reported for similar complexes.[4d]

The mechanism that can explain the formation of these cyclometalated cis-chelated bidentate NHC−Pd(II) complexes is not obvious. But according to the mechanism in the formation of cyclometalated palladium imidazolin-2-ylidene complexes described by Danopoulos,[4d] oxidative addition of two C−H

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(7) The crystal data of **5a** have been deposited in CCDC with number 654567. Empirical formula: $C_{48}H_{33}ClN_4OPd$; formula weight: 823.63; crystal size: 0.312 × 0.300 × 0.297; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: a = 10.1191(7) Å, b = 18.5160(13) Å, c = 20.7414(14) Å, α = 90°, β = 97.9000(10)°, γ = 90°, V = 3849.3(5) Å^3; space group: $P2(1)$; Z = 4; D_{calc} = 1.421 g/cm^3; F_{000} = 1680; R1 = 0.0505, wR2 = 0.1014. Diffractometer: Rigaku AFC7R.

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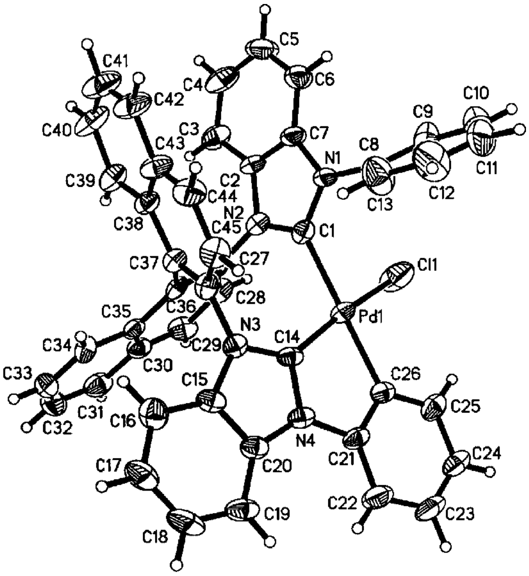


Figure 1. ORTEP drawing of cyclometalated cis-chelated bidentate NHC–Pd(II) complex **5a** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd–C1 = 2.055(6), Pd–C14 = 1.927(6), Pd–C26 = 2.016(6), Pd–Cl1 = 2.3364(19), C1–Pd–Cl1 = 83.30(16), C1–Pd–C14 = 102.3(2), C1–Pd–C26 = 178.7(2), C14–Pd–Cl1 = 168.00(17), C14–Pd–C26 = 78.8(2), C26–Pd–Cl1 = 95.5(19).

bonds in benzimidazolium salts to Pd(0) may favor the formation of a bis(NHC)–PdCl$_2$ intermediate.[8] Then, these cyclometalated bis(NHC)–Pd(II) complexes might be formed by further rearrangement through a σ-bond metathesis step. It is also notable that, in the presence of KO^{t}Bu, the reaction of benzimidazolium salt **4a** with Pd(OAc)$_2$ or PdCl$_2$ afforded complex product mixtures under standard conditions.

Catalytic Abilities in the Suzuki–Miyaura Coupling Reaction and the Friedel–Crafts Reaction. Palladacycles are among the most active catalysts in various C–C coupling reactions.[9] Therein, we turned our interest to investigate the catalytic activity of the cyclometalated cis-chelated bidentate NHC–Pd(II) complexes **5a**–**c** in the Suzuki–Miyaura coupling reaction.[4d,10] As shown in Scheme 3, **5a** is an effective catalyst in the Suzuki–Miyaura coupling reaction. The details of these results have been summarized in the Supporting Information.

In 2003, Nolan and co-workers reported NHC-modified N-palladacycles as highly effective catalysts in the Suzuki–Miyaura cross-coupling reaction as well as the coupling reaction of aryl halides with amines under mild conditions, suggesting an activation pathway involving the decomposition of palladacycle to give the catalytically active Pd(0)-imidazolin-2-ylidene species.[11] According to their assumed mechanism, NHC–Pd(II) complex **5a** might involve a similar catalyst activation pathway along with the generation of a catalytically active cis-chelated bis(NHC)–Pd(0) species in the catalytic cycle. Studies aimed at elucidating the exact mechanistic details involved in this transformation are presently being examined with these novel cyclometalated cis-chelated bidentate NHC–Pd(II) complexes.

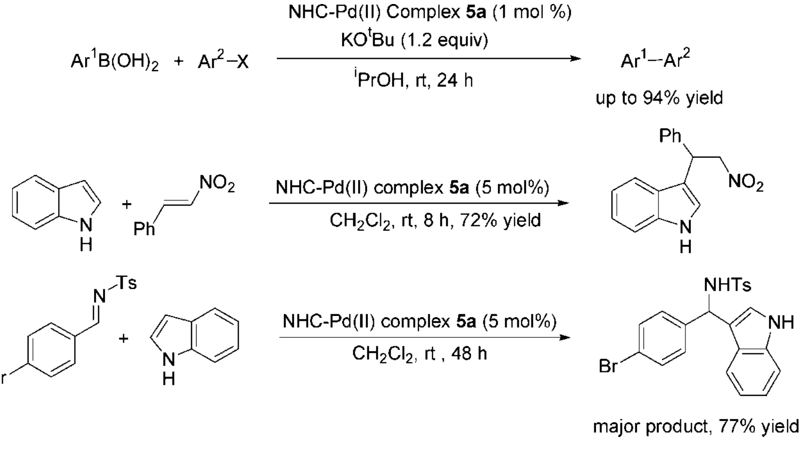
Moreover, Lewis acid-catalyzed Friedel–Crafts reaction is a powerful carbon–carbon bond-forming process in organic chemistry.[12] Pd(II) complexes serving as Lewis acids in a variety of reactions have been extensively invetigated.[13] Thus, the cyclometalated cis-chelated bidentate NHC–Pd(II) complex **5a** was also examined in the Friedel–Crafts reactions of indole with 2-nitrovinylbenzene and *N*-(4-bromobenzylidene)-4-methylbenzenesulfonamide in dichloromethane under mild conditions. As shown in Scheme 3, it is an effective catalyst in these Friedel–Crafts reactions. The details of these experiments are summarized in the Supporting Information. Efforts to apply these cyclometalated cis-chelated bidentate NHC–Pd(II) complexes to asymmetric Friedel–Crafts reaction are underway in our laboratory.

In conclusion, a novel class of cyclometalated cis-chelated bidentate NHC–Pd(II) complexes has been successfully prepared whether they have electron-donating or electron-withdrawing R group on the benzene rings, and these complexes have been fully characterized by IR, NMR spectroscopic data, and ESI-MS as well as HRMS spectroscopy. Moreover, cyclometalated cis-chelated bidentate NHC–Pd(II) complex **5a** has been further characterized by X-ray crystal structure analysis. The catalytic activities of these interesting cyclometalated cis-chelated bidentate NHC–Pd(II) complexes have been examined in the Suzuki–Miyaura coupling reaction and Friedel–Crafts reaction, and we have found that those complexes are quite effective in those reactions under mild conditions. Efforts to use these catalysts in some asymmetric reactions are ongoing.

Experimental Section

Synthesis of NHC–Pd(II) Complex 5a. Under an argon atmosphere, a mixture of compound **4a** (300 mg, 0.422 mmol) and Pd$_2$(dba)$_3$ (462 mg, 0.505 mmol) was stirred in anhydrous THF (25 mL) under reflux for 4 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate, 1:1) to give NHC–Pd(II) complex **5a** (206 mg, 61%) as a white solid. The single crystal for X-ray diffraction was obtained by recrystallization

Scheme 3. Catalytic Abilities of NHC–Pd(II) Complex 5a



from EtOAc/petroleum ether. Mp: 274−276 °C. $[\alpha]^{20}_{D} = +126.1$ (*c* 0.95, $CHCl_3$). IR (KBr): ν 3053, 2924, 2852, 1589, 1501, 1394, 1329, 744 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 6.89−7.25 (11H, m, Ar), 7.28−7.56 (11H, m, Ar), 7.67 (1H, d, $J = 8.4$ Hz, Ar), 7.86 (1H, d, $J = 8.4$ Hz, Ar), 7.90 (1H, d, $J = 8.1$ Hz, Ar), 7.97 (1H, d, $J = 9.0$ Hz, Ar), 8.08−8.14 (3H, m, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 110.5, 111.4, 112.0, 112.0, 122.6, 122.8, 123.2, 124.1, 124.67, 124.71, 125.7, 125.8, 126.6, 126.9, 127.1, 127.2, 127.3, 127.6, 128.3, 128.6, 129.1, 129.8, 130.0, 131.0, 131.8, 132.1, 132.2, 132.5, 132.6, 133.3, 133.6, 134.1, 135.0, 135.7, 136.96, 137.00, 137.7, 147.6, 150.0, 180.4, 197.5. MS (ESI): *m*/*e* 745 ($M^+ - Cl$). Anal. Calcd for $C_{46}H_{29}ClN_4Pd \cdot 1/2CH_3CO_2CH_2CH_3$: C 69.99, H 4.04, N 6.80. Found: C 69.58, H 4.02, N 6.61.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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