

Preparations of a series of coinage metal complexes with pyridine-based bis(*N*-heterocyclic carbene) ligands including transmetalation to palladium complexes

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Abstract

A silver complex bearing 2,6-bis(3-*tert*-butylimidazol-2-ylidene)pyridine (CNC) ligands was easily prepared from the reaction of the CNC ligand precursor with Ag₂O. The CNC ligand contains relatively bulky substituents, *tert*-butyl, on nitrogen atoms. Use of the silver complex as a carbene transfer reagent gave rise to a copper and a gold complex, completing a series of coinage metal complexes [M₂(CNC)₂](BF₄)₂ (M = Cu, Ag, Au). In all the coinage metal complexes, the X-ray crystallographic analyses showed that the two CNC ligand strands are intertwined each other and surround the metal ions in a double helical fashion. Moreover, the carbene transfer reactions afforded a monomeric palladium complex [Pd(CNC)Cl]BF₄ and a CNC-bridged dipalladium complex [{Pd(η^3 -C₃H₅)Cl}₂(μ -CNC)]. Facile chloride ligand abstraction from the dipalladium complex yielded a chlorido-bridged dipalladium complex [{Pd(η^3 -C₃H₅)₂(μ -CNC)(μ -Cl)]BF₄.

Keywords: Bis(carbene) ligand; *tert*-Butyl substituents; Carbene transfer; Coinage metal complexes; Palladium.

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1. Introduction

Recently, pincer-type ligands, which coordinate to the metal center meridionally, have attracted great attention, because many tremendous reactions using the pincer complexes have been reported [1]. Chemistry of NHC (*N*-heterocyclic carbene) has spread explosively, due to

the strong σ -donating ability. We are interested in both combination, that is, pincer-type carbene ligands, in particular pyridine-based bis(carbene) ligands (CNC ligands) [2]. Complexation of the pyridine-based CNC ligand was first reported by I. J. B. Lin in 2000 [3]. Although complexes of the pyridine-based CNC ligands are known in many metals, those of *tert*-butyl derivatives are relatively unexplored [4]. We now report the preparation of a Ag(I) complex bearing the bis(carbene)pyridine ligand as a carbene transfer reagent. And treatment of the silver complex with $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$ and $[\text{AuCl}(\text{SC}_4\text{H}_8)]$ resulted in the corresponding Cu(I) and Au(I) complexes, respectively. The X-ray crystal structural analyses revealed that these coinage metal complexes exist as dinuclear complexes with double helical structures. Moreover, the carbene transfer reactions from Ag(I) to Pd(II) also proceeded to give monomeric and dimeric palladium complexes. The X-ray crystal structural analysis of the monomeric complex exhibited steric repulsion of the *tert*-butyl substituents.

2. Results and Discussion

The silver complex $[\text{Ag}_2(\text{CNC})_2](\text{BF}_4)_2$ (**1**) was prepared from the reaction of the CNC ligand precursor with Ag_2O (Scheme 1). This synthetic method is very useful because free carbene ligand, which is often hard to handle, does not need to be isolated [5]. The mixture of the CNC ligand precursor and Ag_2O in $\text{MeOH}/\text{CH}_2\text{Cl}_2$ (1/10) was stirred for 6h. After work up including anion exchange, complex **1** was isolated as white powder in 87% yield. The ^1H NMR spectrum of **1** shows the disappearance of a signal of hydrogen at the carbene carbons. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** also shows the presence of the carbene carbons at δ 181.2 ppm. The ESI-MS spectrum exhibits the molecular ion signal at m/z 949.3 ascribed to $[\mathbf{1}-\text{BF}_4]^+$, indicating a dimer complex, and finally the structure of **1** was determined by the X-ray crystallographic analysis (Fig. 1).

The copper and gold complexes ($[\text{Cu}_2(\text{CNC})_2](\text{BF}_4)_2$ (**2**) and $[\text{Au}_2(\text{CNC})_2](\text{BF}_4)_2$ (**3**)) were prepared by treatment of $[\text{Ag}_2(\text{CNC})_2]^{2+}$ generated *in situ* as a carbene transfer reagent with $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$ and $[\text{AuCl}(\text{SC}_4\text{H}_8)]$, respectively (Scheme 1). Although complexes **1** and **3** are relatively stable in air, complex **2** is easily decomposed. The NMR spectra of **2** and **3** indicate coordination of the carbene carbon to the metal center. The ESI-MS data support the formation of their dimer complexes, and the structures were confirmed by the X-ray crystallographic analyses (Fig. 1).

In complexes **1**, **2**, and **3**, the two CNC ligand strands are intertwined each other and surround the metal ions in a double helical fashion. Twisting of the NHC rings, with respect to the middle pyridyl ring, are not much different (torsion angles $\text{C}_{\text{NHC}}-\text{N}-\text{C}-\text{N}1$, 18.9(16), 23.7(15) (**1**); -21.2(5), -21.1(5) (**2**); 22.9(6), 18.9(6) (**3**)). In each metal complexes, the

metal-C_{NHC} bond distances are comparable to those of the complexes bearing the pyridine-based CNC ligands, and the order of the metal-C_{NHC} bond distances are Cu (av. 1.910 Å) < Au (av. 2.021 Å) < Ag (av. 2.105 Å). The distortion of the C_{NHC}-M-C_{NHC} bond angles (169.3(5)° (**1**), 163.03(16)° (**2**), and 172.57(18)° (**3**)) away from linearity occurs, probably as a result of the metal-metal interactions as shown below.

The Ag•••Ag distance of **1** is 3.0251(14) Å, which is shorter than the sum of the van der Waals radii of Ag (ca. 3.44 Å), indicating argentophilicity [6,7]. This distance is shorter than those of two similar pyridine-bridged bis(carbene) silver complexes (3.1585(9) [8a] and 3.7848(2) [8b] Å). The Cu•••Cu distance of **2** (2.9431(8) Å), suggesting a cuprophilic interaction [6,9], is similar to those of the previously reported C-N-C copper complexes (3.031(1) [10a] and 2.807(1) [10b] Å). The gold-gold distance (3.2563(5) Å) of **3** is in the typical range for aurophilic interactions [6,11]. The Au•••Au interactions were also observed in two crystallographically characterized gold complexes with the rigid C-N-C ligand type (3.2971(4) [12a] and 3.3000(4) [12b] Å).

The lone pair electrons of the central pyridyl nitrogen atoms are directed toward the center of the M•••M vector. Interestingly, in complex **2**, two Cu(I) atoms and two nitrogen atoms of the bridging pyridine form a rhombus. The angles of the rhombus are 65.50(7) and 114.49(9) and the length of the four sides is 2.720(3) Å. Thus, there may be very weak interaction between the middle pyridyl nitrogen atoms and the copper atoms. However, the distances between the metals and the central pyridyl nitrogen atoms in **1** (2.922(10) Å) and **3** (2.977(3) Å) are sufficiently long to indicate lack of coordination.

Easy transmetalation using the silver complex prompted us to check other metal ion, palladium. Reactions of *in situ* generated [Ag₂(CNC)₂]²⁺ with [PdCl₂(NCMe)₂] and [Pd(η³-C₃H₅)Cl]₂ gave [Pd(CNC)Cl]BF₄ (**4**) and [{Pd(η³-C₃H₅)Cl}₂(μ-CNC)] (**5**), respectively (Scheme 2). The NMR spectra of **4** show signals that indicate coordination of the carbene moiety to the metal. The ¹H NMR spectrum of **5** shows broad signals due to dynamic processes of the π-allyl ligands, but the integral ratio of the signals indicates the dipalladium complex. The FAB-MS spectrum of **5** does not show signals of the molecular ion, but there appears a fragmentation occurring with a loss of one Cl ligand [M-Cl]⁺. The molecular structures were established by the X-ray diffraction study (Fig. 2).

The central Pd atom of **4** adopts a distorted square planar coordination geometry with the tridentate CNC pincer ligand and a chlorido ligand. The Pd-C_{NHC} and Pd-N bond distances of **4** are comparable to those of similar complexes [13]. However, there is a distortion of the Cl ligand away from the idealized molecular plane (N1-Pd-Cl 167.24(11)°). Owing to no meaningful intermolecular interaction (Pd•••Pd 4.0851(8) Å), the steric hindrance between the Cl ligand and two ^tBu ligands would account for the distortion [14]. Interestingly, similar

methylpalladium complex $[\text{Pd}(\text{CNC})(\text{Me})]^+$ has not been isolated [15]. On the other hand, complex **5** consists of a dipalladium structure bridged by the CNC ligand, with the nitrogen atom of the pyridine unbound. The X-ray analysis of **5** shows that one of the π -allyl ligands is disordered over two positions. The Pd•••Pd distance of **5** (7.0544(8) Å) indicates no bonding interaction between Pd atoms. The geometry about each palladium atom is a pseudo-square-planar with the Pd-C_{NHC} bond distances of 2.046(4) and 2.061(4) Å, which are similar to those of **4** (2.061(5) and 2.064(5) Å). In complex **5**, large twisting of the NHC rings, with respect to the central pyridyl ring, occurs (torsion angles C_{NHC}-N-C-N1, -135.2(3) and 134.8(3) °).

In complex **5**, detection of loss of a Cl ligand under the FAB-MS condition prompted us to check a chloride abstraction reaction. Treatment of **5** with AgBF₄ yielded a chlorido-bridged complex $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\}_2(\mu\text{-CNC})(\mu\text{-Cl})]\text{BF}_4$ (**6**) in 80% yield. The ESI-MS spectrum of **6** exhibits the molecular ion signal at 654.1 (*m/z*), supporting the formulation. The molecular structure was confirmed by the X-ray structural analysis. The chlorido bridge shortens the Pd•••Pd distance (3.5505(7) Å), and the torsion angles (C_{NHC}-N-C-N1) are narrowed (33.7(6) and 28.1(6) °). The Pd-C_{NHC} bond distances of 2.059(5) and 2.075(5) Å are similar to those of **5**.

3. Conclusion

We obtained the pyridine-based bis(*N-tert*-butyl substituted *N*-heterocyclic carbene) (CNC) complex of Ag(I), which serves as a good carbene transfer reagent. The carbene transfer reactions yielded Cu(I) and Au(I) complexes, resulting in a series of coinage metal complexes. In all the coinage metal complexes, the two CNC ligands are arranged in a helical fashion. Moreover, the monomeric palladium complex and the CNC-bridged dipalladium complex were prepared from the carbene transfer reactions. In the dipalladium complex, facile chloride ligand abstraction afforded the chlorido-bridged dipalladium complex.

4. Experimental

4.1. General

All reactions and subsequent work-up manipulations were performed in air unless otherwise noted. The starting materials, 1-*tert*-butylimidazole [16], $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$ [17], $[\text{AuCl}(\text{SC}_4\text{H}_8)]$ [18], $[\text{PdCl}_2(\text{NCMe})_2]$ [19], $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$ [20] were prepared according to

the previously reported method. Organic solvents and all other reagents were commercially available and used without further purification. NMR spectra in CDCl₃ or CD₃CN were recorded on a Varian Gemini-300 and a JEOL JNM-AL-400 spectrometers. ¹H NMR chemical shifts in CDCl₃ or CD₃CN are quoted with respect to TMS or the solvent signal, respectively, and ¹³C{¹H} NMR chemical shifts are quoted with respect to the solvent signal. Infrared spectra in KBr pellets were obtained on JASCO FT-IR-4100 spectrometer. Electrospray mass spectroscopies (ESI-MS) were carried out on a Waters ACQUITY SQD MS system. Fast atom bombardment mass spectra (FAB-MS) were recorded on a JEOL JMS-700N spectrometer. Elemental analyses (C, H, N) were performed on a Perkin Elmer 2400II elemental analyzer.

4.2. Synthesis of 2,6-bis(3-*tert*-butylimidazolium-1-yl)pyridine dichloride

This ligand was prepared according to a literature method [15] with slight modifications. A mixture of 2,6-dichloropyridine (1.5 g, 10 mmol) and 1-*tert*-butylimidazole (5.0 g, 40 mmol) was heated in an autoclave at 150 °C for 3 days. Upon cooling, the reaction mixture was dissolved in MeOH (5 mL), followed by addition of a large amount of diethyl ether. After filtration, the precipitate was washed with acetone (20 mL) and dried to give 2,6-bis(3-*tert*-butylimidazolium-1-yl)pyridine dichloride as an off-white solid (2.7 g, 68%). ¹H NMR (CD₃CN): δ 10.37 (brs, 2H, NCHN), 8.97 (brs, 2H, imid), 8.58 (t, *J* = 8.1 Hz, 1H, 4-py), 8.46 (d, *J* = 8.0 Hz, 2H, 3,5-py), 8.36 (brs, 2H, imid), 1.72 (s, 18H, ^tBu). ESI-MS (*m/z*): 360.4 [M–Cl]⁺.

4.3. Preparation of [Ag₂(CNC)₂](BF₄)₂ (**1**)

A mixture of 2,6-bis(3-*tert*-butylimidazolium-1-yl)pyridine dichloride (80.0 mg, 0.202 mmol) and Ag₂O (48.0 mg, 0.207 mmol) in MeOH/CH₂Cl₂ (v/v, 1/9) (10 mL) was stirred at room temperature for 6 h. After concentration of the mixture to about 1 mL, NaBF₄ (110 mg, 1.00 mmol) in H₂O (10 mL) was added. The resulting precipitate was filtered, washed with H₂O, and dried to afford [Ag₂(CNC)₂](BF₄)₂ (**1**) as white powder (90.6 mg, 87%). IR (KBr, pellet): ν(BF) 1084 (s) cm⁻¹. ¹H NMR (CD₃CN): δ 8.29 (t, *J* = 8.1 Hz, 2H, 4-py), 7.81 (dd, *J* = 2.0, 1.5 Hz, 4H, imid), 7.75 (d, *J* = 8.1 Hz, 4H, 3,5-py), 7.50 (t, *J* = 2.1 Hz, 4H, imid), 1.30 (s, 36H, ^tBu). ¹³C{¹H} NMR (CD₃CN): δ 181.2 (d × 2, *J* = 190, 220 Hz, C_{NHC}), 150.5 (2,6-py), 144.8 (4-py), 122.7 (d, *J* = 6.8 Hz, imid), 119.5 (d, *J* = 5.1 Hz, imid), 115.7 (3,5-py), 59.3 (CMe₃), 31.0 (CMe₃). ESI-MS (*m/z*): 949.3 [M–BF₄]⁺, 430.3 [M–(BF₄)₂]²⁺. Elemental analysis (%) calcd for C₃₈H₅₀N₁₀Ag₂B₂F₈: C, 44.05; H, 4.86; N, 13.52; found: C, 43.46; H, 4.96; N, 13.34.

4.4. Preparation of [Cu₂(CNC)₂](BF₄)₂ (**2**)

A mixture of 2,6-bis(3-*tert*-butylimidazolium-1-yl)pyridine dichloride (79.3 mg, 0.200 mmol) and Ag₂O (49.2 mg, 212 μmol) in MeOH/CH₂Cl₂ (v/v, 1/9) (10 mL) was stirred at room temperature for 6 h. The mixture was filtered and evaporated to dryness. The residue was transferred to a glove-box. A mixture of the residue and [Cu(NCMe)₄]BF₄ (63 mg, 0.20 mmol) in dry MeCN (10 mL) was stirred at room temperature for 12 h. After filtration and evacuation to dryness, the crude product was recrystallized from MeCN/ether to give [Cu₂(CNC)₂](BF₄)₂ (**2**) as yellow crystals (81 mg, 85%). IR (KBr, pellet): ν(BF) 1063 (s) cm⁻¹. ¹H NMR (CD₃CN): δ 8.31 (t, *J* = 8.1 Hz, 2H, 4-py), 7.78 (d, *J* = 2.1 Hz, 4H, imid), 7.72 (d, *J* = 8.1 Hz, 4H, 3,5-py), 7.43 (d, *J* = 2.1 Hz, 4H, imid), 1.24 (s, 36H, ^tBu). ¹³C{¹H} NMR (CD₃CN): δ 178.3 (C_{NHC}), 150.6 (2,6-py), 145.1 (4-py), 122.6 (imid), 118.7 (imid), 115.1 (3,5-py), 59.1 (CMe₃), 30.8 (CMe₃). ESI-MS (*m/z*): 861.5 [M–BF₄]⁺, 387.3 [M–(BF₄)₂]²⁺. Elemental analysis (%) calcd for C₃₈H₅₀N₁₀Cu₂B₂F₈: C, 48.17; H, 5.32; N, 14.78; found: C, 47.66; H, 5.72; N, 14.46.

4.5. Preparation of [Au₂(CNC)₂](BF₄)₂ (**3**)

A mixture of 2,6-bis(3-*tert*-butylimidazolium-1-yl)pyridine dichloride (80.2 mg, 0.202 mmol) and Ag₂O (47.9 mg, 0.207 mmol) in MeOH/CH₂Cl₂ (v/v, 1/9) (10 mL) was stirred at room temperature for 6 h. After filtration and evaporation to dryness, the residue was dissolved in CH₂Cl₂ (10 mL), followed by addition of [AuCl(SC₄H₈)] (64.2 mg, 0.200 mmol). After stirring for 2 h, the mixture was filtrated and evaporated to dryness. To a MeOH (2 mL) solution of the crude product was added NaBF₄ (110 mg, 1.00 mmol) in H₂O (10 mL). After concentration of the mixture, the resulting precipitate was filtrated, washed with a small amount of H₂O, and dried to afford [Au₂(CNC)₂](BF₄)₂ (**3**) as white powder (96.0 mg, 78%). IR (KBr, pellet): ν(BF) 1084 (s) cm⁻¹. ¹H NMR (CD₃CN): δ 8.27 (t, *J* = 8.1 Hz, 2H, 4-py), 7.78 (d, *J* = 2.3 Hz, 4H, imid), 7.76 (d, *J* = 8.1 Hz, 4H, 3,5-py), 7.47 (d, *J* = 2.3 Hz, 4H, imid), 1.41 (s, 36H, ^tBu). ¹³C{¹H} NMR (CD₃CN): δ 181.8 (C_{NHC}), 149.6 (2,6-py), 144.3 (4-py), 122.4 (imid), 119.1 (imid), 115.8 (3,5-py), 60.3 (CMe₃), 30.8 (CMe₃). ESI-MS (*m/z*): 1127.3 [M–BF₄]⁺, 520.3 [M–(BF₄)₂]²⁺. Elemental analysis (%) calcd for C₃₈H₅₀N₁₀Au₂B₂F₈: C, 37.58; H, 4.15; N, 11.53; found: C, 37.04; H, 3.71; N, 11.36.

4.6. Preparation of [Pd(CNC)Cl]BF₄ (**4**)

A mixture of 2,6-bis(3-*tert*-butylimidazolium-1-yl)pyridine dichloride (80.4 mg, 0.203 mmol) and Ag₂O (48.3 mg, 0.208 mmol) in MeOH/CH₂Cl₂ (v/v, 1/9) (10 mL) was stirred at room temperature for 6 h. After filtration and evaporation to dryness, the residue was dissolved in CH₂Cl₂ (10 mL), followed by addition of [PdCl₂(NCMe)₂] (52.3 mg, 0.202 mmol). After stirring for 12 h, the mixture was filtrated and removed the solvent. To a MeOH (2 mL) solution of the crude product was added NaBF₄ (110 mg, 1.00 mmol) in H₂O (10 mL). After

concentration of the mixture, the resulting precipitate was filtrated, washed with a small amount of H₂O, and dried to give [Pd(CNC)Cl]BF₄ (**4**) as a yellow solid (69.6 mg, 62%). IR (KBr, pellet): $\nu(\text{BF})$ 1083 (s) cm⁻¹. ¹H NMR (CD₃CN): δ 8.35 (t, J = 8.3 Hz, 1H, 4-py), 7.86 (d, J = 2.4 Hz, 2H, imid), 7.72 (d, J = 8.2 Hz, 2H, 3,5-py), 7.53 (d, J = 2.4 Hz, 2H, imid), 1.87 (s, 18H, ^tBu). ¹³C{¹H} NMR (CD₃CN): δ 166.4 (C_{NHC}), 151.7 (2,6-py), 147.1 (4-py), 123.0 (imid), 117.1 (imid), 109.6 (3,5-py), 62.6 (CMe₃), 31.2 (CMe₃). ESI-MS (m/z): 466.2 [M-BF₄]⁺. Elemental analysis (%) calcd for C₁₉H₂₅N₅PdClBF₄: C, 41.33; H, 4.56; N, 12.68; Found: C, 41.20; H, 4.11; N, 12.70.

4.7. Preparation of [$\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}\}_2(\mu\text{-CNC})$] (**5**)

A mixture of 2,6-bis(3-*tert*-butylimidazolium-1-yl)pyridine dichloride (79.4 mg, 0.200 mmol) and Ag₂O (47.0 mg, 0.203 mmol) in MeOH/CH₂Cl₂ (v/v, 1/9) (10 mL) was stirred at room temperature for 6 h. After filtration and evaporation to dryness, the residue was dissolved in CH₂Cl₂ (10 mL), followed by addition of [Pd(η^3 -C₃H₅)Cl]₂ (73.2 mg, 0.200 mmol). The mixture was stirred for 12 h, filtrated, and removed the solvent. The crude product was washed with benzene and recrystallized from CH₂Cl₂/ether to give [$\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}\}_2(\mu\text{-CNC})$] (**5**) as light yellow crystals (97.2 mg, 71%). ¹H NMR (CDCl₃): δ 9.00 (br, 2H, 3,5-py), 8.02 (t, J = 8.0 Hz, 1H, 4-py), 7.83 (brs, 2H, imid), 7.35 (d, J = 2.1 Hz, 2H, imid), 5.05 (br, CH_{allyl}), 4.18 (br, CH_{allyl}), 3.06 (br, CH_{allyl}), 1.87 (s, 18H, ^tBu). ¹³C{¹H} NMR (CDCl₃): δ 180.7 (C_{NHC}), 151.3 (2,6-py), 140.3 (4-py), 120.3 (imid), 120.1 (imid), 59.3 (CMe₃), 50.1, 31.6 (CMe₃); we couldn't assign the carbon signals of the η^3 -C₃H₅. FAB-MS (m/z): 654.1 [M-Cl]⁺, 429.2 [Pd(CNC)]⁺. Elemental analysis (%) calcd for C₂₅H₃₅N₅Cl₂Pd₂: C, 43.56; H, 5.12; N, 10.16; found: C, 43.19; H, 5.30; N, 9.76.

4.8. Preparation of [$\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\}_2(\mu\text{-CNC})(\mu\text{-Cl})$]BF₄ (**6**)

A mixture of [$\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}\}_2(\mu\text{-CNC})$] (**5**) (69.3 mg, 0.101 mmol) and AgBF₄ (20.3 mg, 0.104 mmol) in acetone (10 mL) was stirred at room temperature for 1 h. After filtration and evaporation to dryness, the crude product was extracted with CHCl₃. The extract was filtrated and evaporated to give [$\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\}_2(\mu\text{-CNC})(\mu\text{-Cl})$]BF₄ (**6**) as a light yellow solid (60.2 mg, 80%). ¹H NMR (CDCl₃): δ 8.29 (t, J = 7.9 Hz, 1H, 4-py), 7.89 (d, J = 2.1 Hz, 2H, imid), 7.82 (br, 2H, 3,5-py), 7.45 (brs, 2H, imid), 5.10 (br, CH_{allyl}), 3.61 (br, CH_{allyl}), 3.30 (br, CH_{allyl}), 2.23 (br, CH_{allyl}), 1.80 (s, 18H, ^tBu). ¹³C{¹H} NMR (CDCl₃): δ 181.8 (Pd-C_{NHC}), 150.2 (2,6-py), 143.7 (4-py), 121.3 (imid), 119.5 (imid), 115.3 (3,5-py), 59.3 (CMe₃), 31.3 (CMe₃); we couldn't assign the carbon signals of the η^3 -C₃H₅. ESI-MS (m/z): 654.2 [M-BF₄]⁺. Elemental analysis (%) calcd for C₂₅H₃₅N₅Pd₂ClBF₄·H₂O: C, 39.58; H, 4.92; N, 9.23; found: C, 39.26; H, 5.45; N, 9.02.

4.9. X-ray crystal structural analyses

Crystallographic data are summarized in Table 1. X-ray quality single crystals were obtained from CH₃CN/ether (for **1**·(MeCN) and **2**), CH₂Cl₂/hexane (for **3**), CH₃CN (for **4**·(MeCN)), CHCl₃/pentane (for **5**·(CHCl₃)), and acetone/ether (for **6**·(OH₂)), respectively. Diffraction data were collected at -180°C under a stream of cold N₂ gas on a Rigaku RA-Micro7 HFM instrument equipped with a Rigaku Saturn724+ CCD detector by using graphite-monochromated Mo-K α radiation. The intensity images were obtained at the exposure of 16.0 s/° (**1**·(MeCN), **2**, and **6**·(OH₂)), 8.0 s/° (**3** and **4**·(MeCN)), and 4.0 s/° (**5**·(CHCl₃)). The frame data were integrated using a Rigaku CrystalClear program package, and the data sets were corrected for absorption using a REQAB program.

The calculations were performed with a CrystalStructure software package. The structures were solved by direct methods, and refined on F^2 by the full-matrix least squares methods. For **1**·(MeCN) and **4**·(MeCN), a CH₃CN crystal solvent is included, and the CH₃CN crystal solvent molecule of **1**·(MeCN) is disordered over two positions in a 1/1 ratio. For **5**·(CHCl₃) and **6**·(OH₂), there are one CHCl₃ and one H₂O crystal solvents, respectively. In the case of **5**, one carbon atom of a η^3 -C₃H₅ ligand is disordered over two positions with occupancy factors of 0.6/0.4. Anisotropic refinement was applied to all non-hydrogen atoms with the exception of the crystal solvents (**1**·(MeCN) and **4**·(MeCN)). Hydrogen atoms for all structures were put at calculated positions, while those of the solvent molecules (**1**·(MeCN) and **6**·(OH₂)) and the disordered η^3 -C₃H₅ ligand of **5**·(CHCl₃) were not included in the calculations.

(Table 1 here)

Supplementary material

CCDC 1419784 – 1419789 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 1. Crystallographic data for **1 – 6**.

	1·(MeCN)	2	3	4·(MeCN)
formula	C ₄₀ H ₅₀ N ₁₁ Ag ₂ B ₂ F ₈	C ₃₈ H ₅₀ N ₁₀ Cu ₂ B ₂ F ₈	C ₃₈ H ₅₀ N ₁₀ Au ₂ B ₂ F ₈	C ₂₁ H ₂₈ N ₆ ClPdBF ₄
fw	1074.25	947.58	1214.42	593.15
cryst system	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	<i>Pnna</i> (No. 52)	<i>C222</i> ₁ (No. 20)	<i>C222</i> ₁ (No. 20)	<i>P2</i> ₁ / <i>c</i> (No. 14)
color of crystal	colorless	yellow	colorless	colorless
crystal size (mm)	0.08 x 0.04 x 0.02	0.1 x 0.1 x 0.09	0.13 x 0.03 x 0.03	0.1 x 0.1 x 0.05
<i>a</i> (Å)	25.570(7)	9.9193(18)	10.0219(12)	10.460(2)
<i>b</i> (Å)	18.781(5)	22.236(5)	22.476(3)	9.1161(18)
<i>c</i> (Å)	9.915(3)	19.779(4)	19.643(2)	25.623(5)
α (deg)	90	90	90	90
β (deg)	90	90	90	96.668(3)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	4761(2)	4362.5(14)	4424.6(9)	2426.7(8)
<i>Z</i>	4	4	4	4
ρ_{calc} (g cm ⁻³)	1.498	1.443	1.823	1.623
μ (cm ⁻¹)	8.925	10.499	67.212	9.279
$2\theta_{\text{max}}$ (deg)	55.0	54.9	54.9	55.0
no. of all reflns collected	37109	18337	18435	19496
no. of unique reflns	5472	5001	5056	5505
<i>R</i> _{int}	0.1262	0.0700	0.0305	0.0413
no. of obsd reflns ^a	4202	4198	4556	4563
no. of parameters	281	277	277	292
<i>R</i> ₁ ^{a, b}	0.1444	0.0556	0.0205	0.0559
<i>R</i> _w (all data) ^c	0.2565	0.1001	0.0285	0.1287
GOF (all data) ^d	1.261	1.060	0.866	1.040

^a $I > 2\sigma(I)$. ^b $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^c $R_w = \{\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2\}^{1/2}$.

^d $GOF = [\{\Sigma w (F_o^2 - F_c^2)^2\} / (No - Np)]^{1/2}$, where *No* and *Np* denote the number of data and parameters.

Table 1. (Continued)

	5·(CHCl₃)	6·(OH₂)
formula	C ₂₆ H ₃₆ N ₅ Cl ₅ Pd ₂	C ₂₅ H ₃₇ N ₅ OClPd ₂ BF ₄
fw	808.67	758.66
cryst system	monoclinic	monoclinic
space group	<i>P2₁/c</i> (No. 14)	<i>P2₁/c</i> (No. 14)
color of crystal	colorless	yellow
crystal size (mm)	0.15 x 0.08 x 0.06	0.1 x 0.1 x 0.03
<i>a</i> (Å)	17.632(3)	13.169(3)
<i>b</i> (Å)	8.9571(12)	13.172(2)
<i>c</i> (Å)	20.249(3)	17.069(3)
α (deg)	90	90
β (deg)	97.272(3)	91.149(3)
γ (deg)	90	90
<i>V</i> (Å ³)	3172.3(8)	2960.2(9)
<i>Z</i>	4	4
ρ_{calc} (g cm ⁻³)	1.693	1.702
μ (cm ⁻¹)	15.801	13.590
$2\theta_{\text{max}}$ (deg)	55.0	54.9
no. of all reflns collected	25536	24071
no. of unique reflns	7572	6711
<i>R</i> _{int}	0.0363	0.0544
no. of obsd reflns ^a	5709	5474
no. of parameters	358	358
<i>R</i> ₁ ^{a, b}	0.0405	0.0513
<i>R</i> _w (all data) ^c	0.0858	0.0949
GOF (all data) ^d	1.087	1.108

^a $I > 2\sigma(I)$. ^b $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^c $R_w = \{\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2\}^{1/2}$.

^d $\text{GOF} = [\{\Sigma w (F_o^2 - F_c^2)^2\} / (N_o - N_p)]^{1/2}$, where *N_o* and *N_p* denote the number of data and parameters.

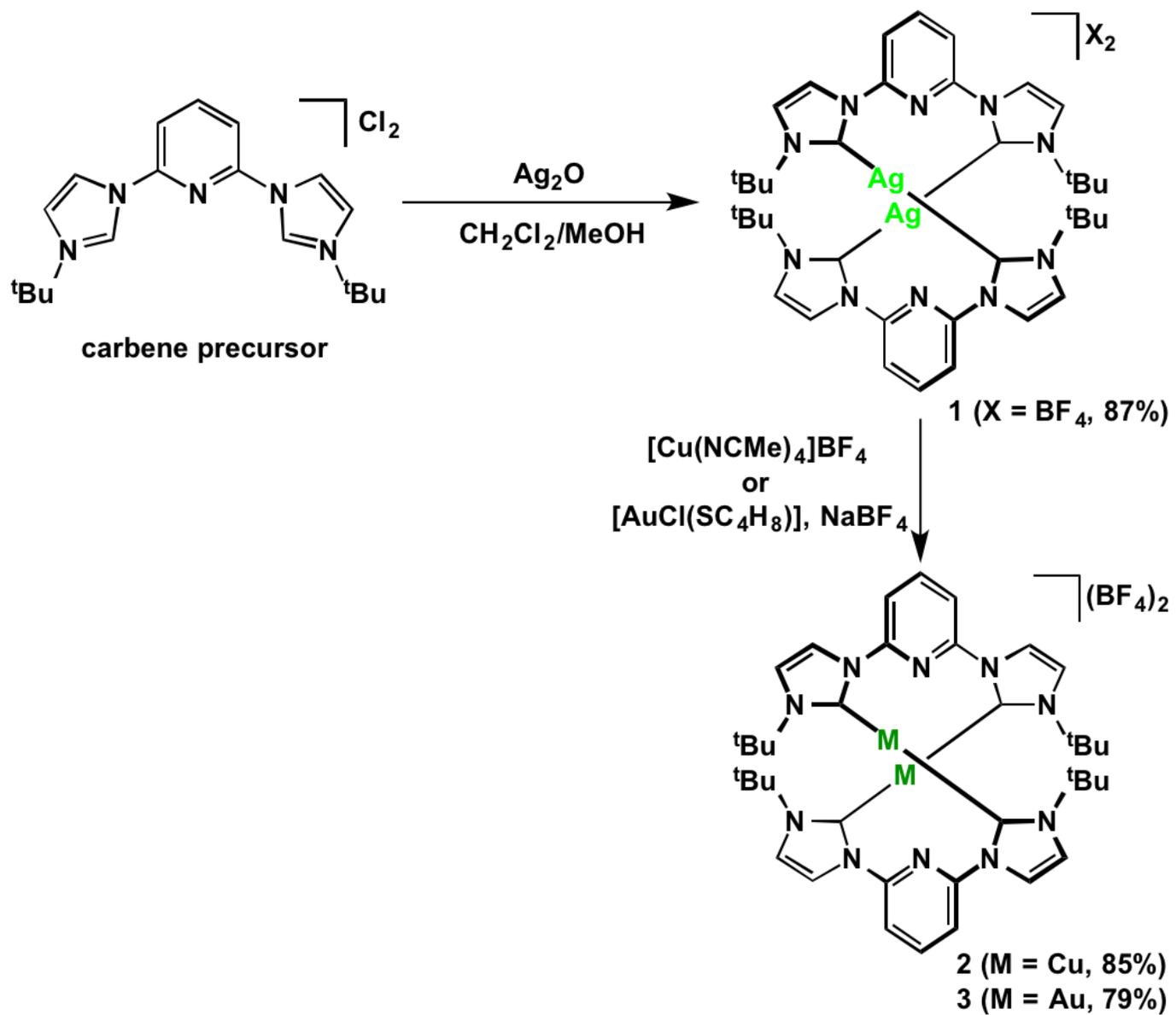
[Captions]

Scheme 1. Preparations of a series of coinage metal complexes $[M_2(CNC)_2](BF_4)_2$ ($M = Cu, Ag, Au$).

Scheme 2. Preparations of palladium complexes using the carbene transfer reactions.

Fig. 1. Molecular structures of **1** (left), **2** (middle), and **3** (right) with thermal ellipsoids at the 50% probability level. Hydrogen atoms, solvent molecules of **1**, and BF_4 counter ions are omitted for clarity.

Fig. 2. Molecular structures of **4** (left), **5** (middle), and **6** (right) with thermal ellipsoids at the 50% probability level. Hydrogen atoms, the disordered carbon atom of **5**, solvent molecules, and BF_4 counter ions for **4** and **6** are omitted for clarity.



Scheme 1.

Scheme 2.

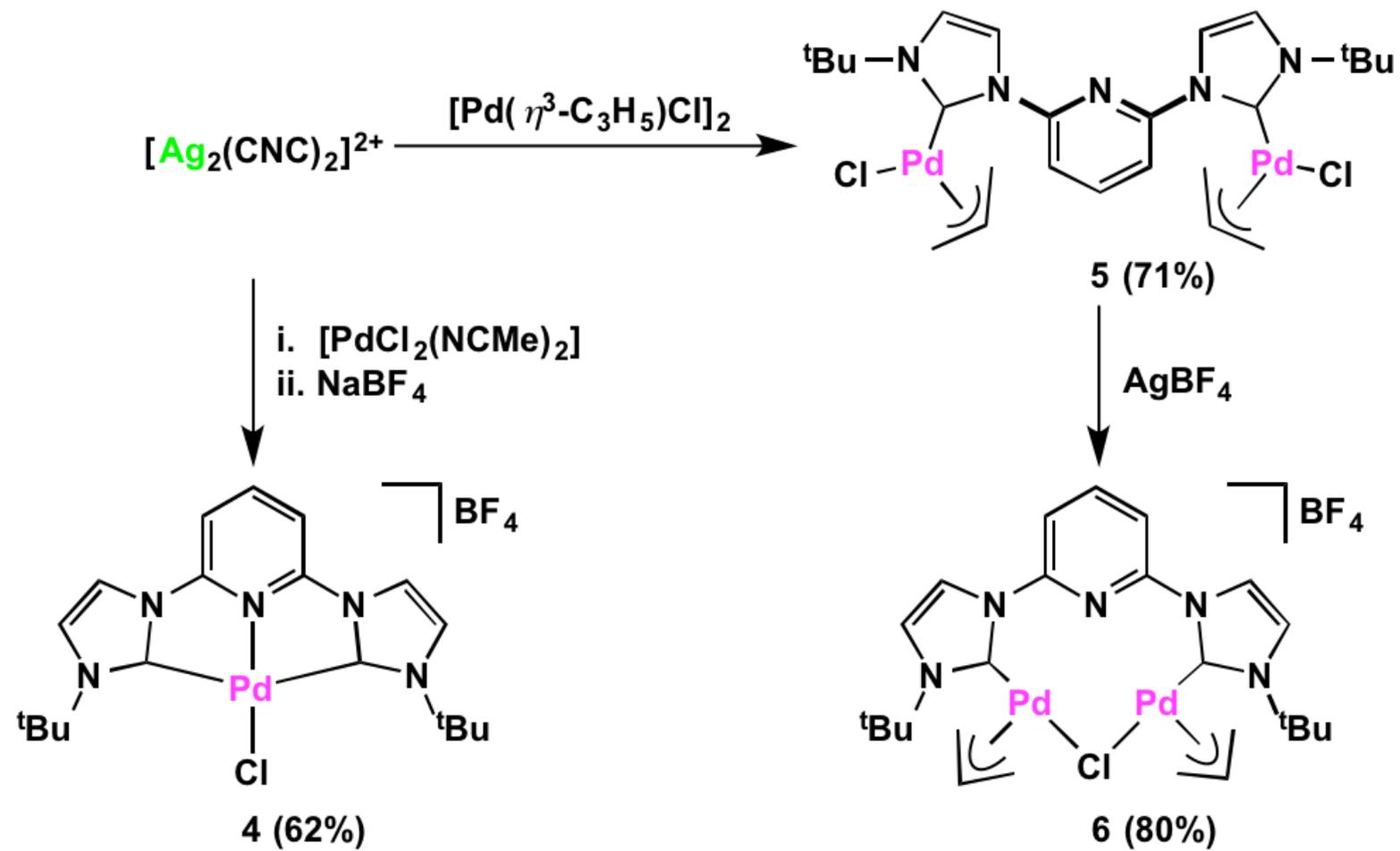


Figure 1.

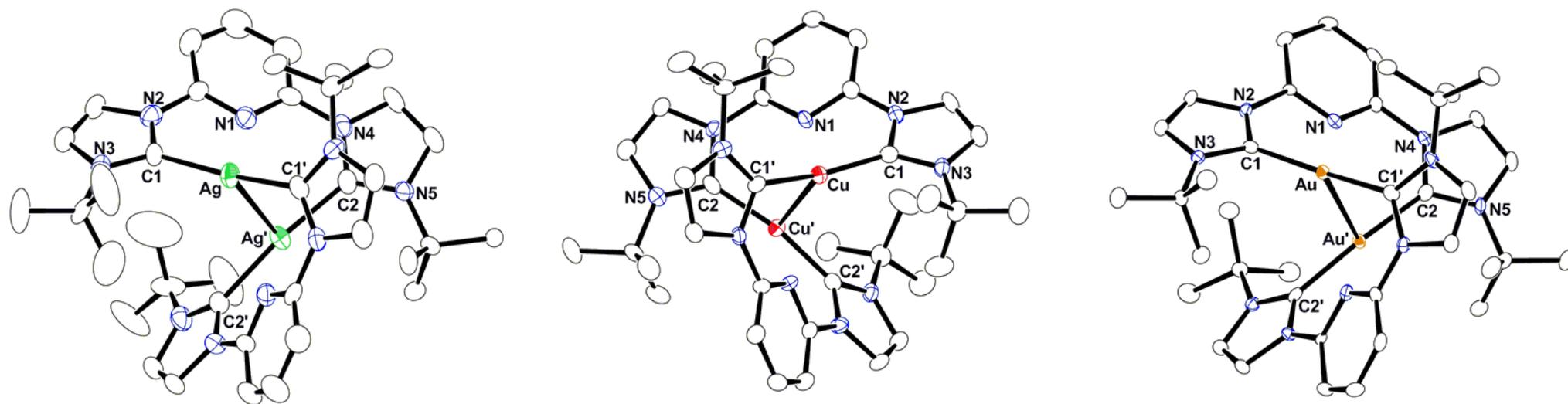


Figure 2.

