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Verstile silver(I) and nickel(II) NHC complexes bearing benzotriazole-function: Synthesis, fluorescence and catalytic property

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ABSTRACT

The imidazolium salts [(N-alkyl-imidazolyl) methyl] benzotriazole hexafluorophosphate (**L1H**: alkyl = n-C4H9, **L2H**: alkyl = picoly, **L3H**: alkyl = 9-anthrylmethyl, **L4H**: alkyl = 1-naphthylmethyl) have been prepared. Mononuclear N-Heterocyclic carbene silver complexes: L1AgPF6 (**1**), L2AgPF6 (**2**), L3AgPF6 (**3**) were synthesized in DMSO. Transmetalation reactions afford the synthesis of the nickel(II) complex L2Ni(PF6)2 (**4**). Furthermore, **L2H**, **L3H** and **L4H** were treated with silver oxide in CH3CN to afford other complexes (**5**, **6** and **7**). The complexes **5** and **6** formed 1D and 2D supramolecular chains by Ag—N bond and intermolecular π-π interactions, respectively, which were found that the carbene carbon atoms of NHCs are not coordinated to silver atom. However, in Complex **7**, silver atoms selectly bind to nitrogen atoms of benzotriazoles and carbon atoms of imidazoles, which afford the dinuclear Ag metallamacrocycles. Complexes **1**–**7** were characterized by single crystal X-ray diffraction, NMR spectroscopy, elemental analysis and powder X-ray diffraction. The catalytic activity of NHC—Ni complex **4** for Suzuki–Miyaura cross-coupling was studied.

1. Introduction

N-Heterocyclic carbenes (NHCs) have been developed rapidly in organometallic chemistry, since Arduengo and co-workers first isolated a free N-heterocyclic carbene (NHC) [1]. The unique electronic and steric ligand properties of N-heterocyclic carbenes ligands [2] have inspired burgeoning research activities. Since then, NHCs have become vitally important ligands in organometallic chemistry [3] compared with phosphine derivatives [4]. Metal NHC complexes which are easily synthesized through the reaction metal compounds with free carbene [5], transmetalation reaction [6], the direct reaction of metal precursors with imidazolium salts [7] and electrolysis [8] have comprehensive applications in catalysis [9], luminescent components [10], medicine [11] and supramolecuar chemistry [12]. As is known to us, Ni—NHCs become extremely significant due to nickel is less expensive and easier to remove from final products [13], which have been found to be efficient catalysts for numerous organic transformations [14]. In order to further explore the structure of metal-NHCs with fascinating properties, we find that benzotiazole is an unexceptionable ligand which possesses appropriate N-coordination sites so as to construct excellent metal complexes. Meng et al. have reported the self-assembly of three Cd(II) complexes and the syntheses, structures and thermal stabilities of metal-organic frameworks which contain benzotriazole [15]. Additionally, other applications of benzotriazole derivatives in organic solar cells [16], corrosion inhibition [17] and biological activity [18] are also studied. However, metal NHCs containing benzotriazole-functionalized have been few reported.

Herein, we report the synthesis and structural characterization of silver(I) complexes and a nickel(II) complex based on benzotriazole-functionalized NHC ligands. The fluorescent emission spectra and powder X-ray diffraction measurements of silver(I) complexes are studied, and the nickel-NHC complex **4** is highly efficient catalyst for Suzuki coupling reactions under mild conditions. Additionally, we also report two diverse conformations of the silver coordination complexes **5** and **6**, the silver atom selectively binds to the N-atoms of acetonitrile and benzotriazole not to the C2 of the imidazolium rings. More importantly, the dinuclear Ag metallamacrocycles NHC Complex **7** is achieved.

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2. Results and discussion

2.1. Synthesis and characterization of the imidazolium salts and complexes **1**–**4**

The imidazolium salts **L1H-L4H** could be obtained by the reaction of corresponding N-substituted imidazole with 1-(choromethyl)benzotriazol, and an anionic exchange with ammonium hexafluorophosphate in methanol (Scheme 1). The imidazolium salts **L1H-L4H** were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analyses. The ^{1}H NMR spectra for **L1H-L4H** in DMSO-d_6 show resonances signals at $\delta = 9.40$–9.71 ppm assignable to the acidic NCHN protons of imidazolium rings, which are consistent with the chemical shifts of reported imidazolium salts [19].

The synthetic routes for the silver complexes **1**–**4** are illustrated in Scheme 1. The reactions of the imidazolium salts **L1H**, **L2H** and **L4H** with Ag$_2$O in DMSO give the corresponding silver-NHC complexes **1**–**3** under nitrogen atmosphere for 2 days in the dark, respectively. Transmetalation reactions obtain the preparation of nickel(II) complex L2Ni(PF$_6$)$_2$ (**4**).

The structures of complexes **1**–**4** were confirmed by ^{1}H NMR, ^{13}C NMR spectroscopy, X-ray crystallography and elemental analysis. In the ^{1}H NMR spectra of complexes **1**–**4** in DMSO-d_6 show the obviously disappearance of acidic 2H-imidazolium protons, which is diagnostic for the formation of metal carbene complexes, and the chemical shifts of the other hydrogen substituents are similar to those in the ^{1}H NMR spectra the signals of the corresponding precursors. The resonances signals of carbene carbon for the complexes **1**–**4** are not observed in the ^{13}C NMR spectra, which most likely ascribed to the dynamic behavior in solution [20].

2.2. Synthesis and characterization of the complexes **5**–**7**

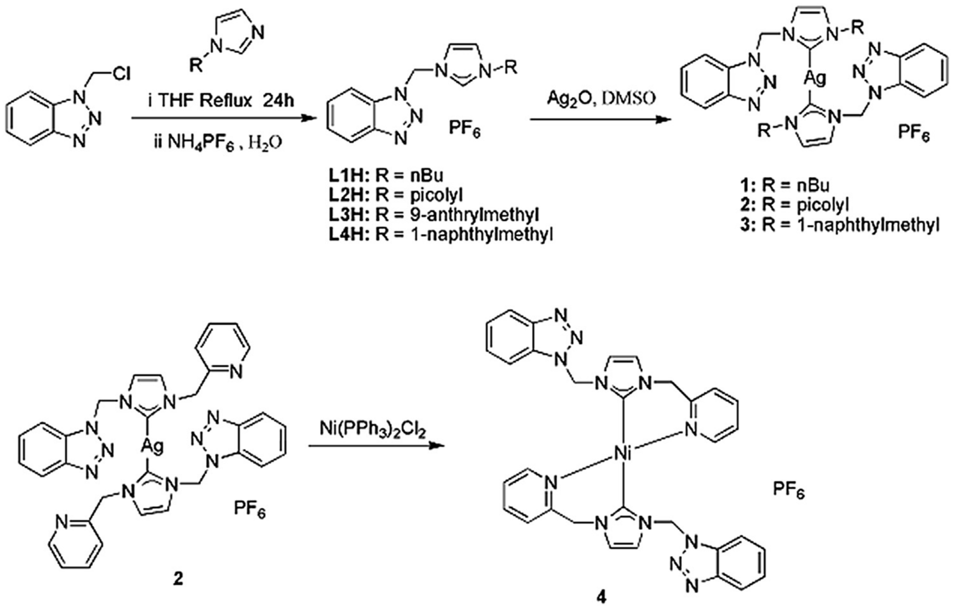
As shown in Scheme 2, treatment of **L2H**, **L3H** and **L4H** with Ag$_2$O in CH$_3$CN under exclusion of light at 50 °C for 24 h resulted in the formation of the complexes **5**–**7**, which were also confirmed by ^{1}H NMR, ^{13}C NMR spectroscopy, X-ray crystallography and elemental analysis. The characteristic resonances for the C2−H proton of imidazolium salts (**L2H**, **L3H**) at $\delta = (9.71, 9.40)$ ppm in DMSO-d_6 are found in the ^{1}H NMR spectrum of **5**–**6**. However, it is disappeared in the ^{1}H NMR spectrum of complex **7**, which is consistent with the single crystal structure. It is known to us that a great many influencing factors can result in the difference of metal complexes structures [21], while ligand and solvent are generally considered as the main factors. Different complexes **1**–**7** were obtained in different solvents, which may be ascribed to the reason that nitrogen atom of acetonitrile coordinated to metal atom of metal NHCs. Additionally, the polarity and dielectric constant of solvents may be also considered as the cause of the difference of complexes.

2.3. X-ray structure analysis

Complexes **1**–**7** suitable for single crystal X-ray diffraction were obtained by slow diffusion of diethyl ether into their CH$_3$CN solution in the dark at room temperature. The crystallographic parameters are listed in Tables 1 and 2. X-ray diffraction analysis shows that complex **1**–**3** are mononuclear silver-NHC complexes (Figs. 1–3), which afford *trans*-conformation. and silver atom has a typical liner conformation and adopts dicoordinated geometry with Ag−C bond lengths of 2.075(3)-2.088(5) Å and C−Ag−C angles of 174.05(2)-180.000°, which are quite normal compared to the corresponding values reported for other silver(I)-carbene complexes [22].

In complexes **1** and **2**, benzotriazole and N-(alkyl) arms of the same imidazole ring adopt a *cis*-conformation with the dihedron angles of 65.55(1)° and 68,67(1)° for complex **1**, 69.60(2)° and 68.25(2)° for complex **2** between imidazole rings and adjacent benzotriazole. Furthermore, in complexes **1** and **2**, the dihedron angles between two imidazole rings are 68.47(1)° and 65.51(2)°, respectively. However, the molecular structure of complex **3** is different compared with **1** and **2**, the benzotriazole and N-(alkyl) arms of the same imidazole plane adopt a *trans*-conformation with the dihedron angles of 88.85(7)° and 89.70(7)° between the imidazole and adjacent benzotriazole rings.

Transmetalation reaction has proved to be a promising procedure to obtain metal-NHC complexes [23]. The Nickel-NHC



Scheme 1. Synthesis of **L1H-L4H** and Complexes **1**–**4**.