

## Multinuclear Coinage Metal Complexes of Bis(diphenylphosphinyl)-functionalized Dipyrido-annulated N-heterocyclic Carbene

(ビス(ジフェニルホスフィニル)官能基を有するジピリド縮環 N-ヘテロサイクリックカルベンの多核貨幣金属錯体)

### 1. General Introduction (Chapter 1)

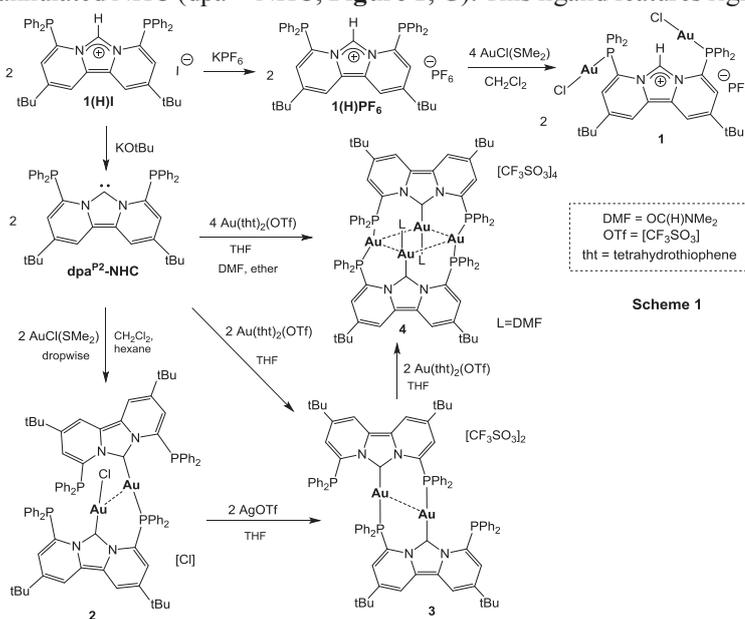
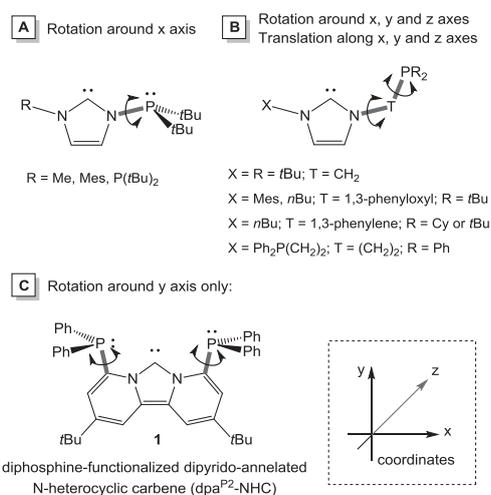
Phosphine-functionalized N-heterocyclic carbene (NHC) supported multinuclear coinage metal complexes attract considerable attention owing to their diverse structures, metal-metal interactions and interesting photoluminescence properties. Generally, two types of ancillary ligands that most are based on the Arduengo type imidazole scaffold are found in these complexes, namely the phosphine-functionalized NHC ligands with and without spacers between phosphine and carbene moieties (**Figure 1, A and B**). The type **A** whose carbene and phosphine donors are in close proximity usually form multinuclear complexes with intramolecular metal-metal interactions. While oftentimes, the structural diversity is absent in these complexes due to the rigid 2-D structure and limited rotation along the N-P bond of **A** (rotation around x axis only). The type **B** allowing the rotation of phosphine arms in all directions form multinuclear complexes with diversified coordination geometries. However, intramolecular metal-metal interactions which have been proved to affect photoluminescence properties of resulting complexes usually can not be found in these complexes, due to the long distance between carbene and phosphine donors and the flexibility of the phosphine arms.

In this context, our group designed and achieved a diphosphine-functionalized NHC, bis(diphenylphosphinyl)-functionalized dipyrido-annulated NHC (dpa<sup>P2</sup>-NHC, **Figure 1, C**). This ligand features rigid structure, whose carbene and phosphine donors are in close proximity. More importantly, the characteristic of the phosphine arms rotating freely around y axis enable access to different coordination geometries.

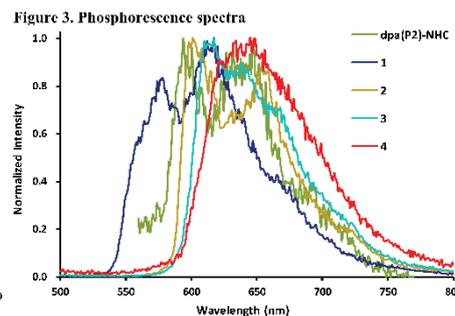
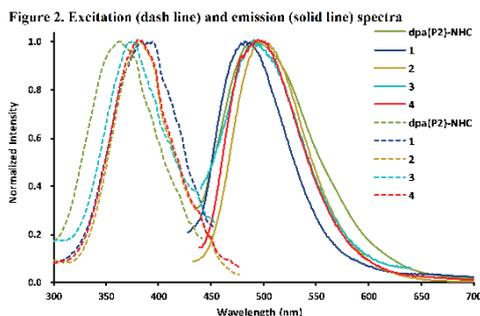
### 2. Di- and tetranuclear Au(I) complexes of bis(diphenylphosphinyl)-functionalized dipyrido-annulated NHC (Chapter 2)

Starting from dpa<sup>P2</sup>-NHC and its imidazolium salt precursor **L(H)I**, three dinuclear and one tetranuclear Au(I) complexes (**1-4**) have been synthesized and structurally characterized (**Scheme 1**). Specially, dpa<sup>P2</sup>-NHC supported gold(I) complexes (**2-4**) feature intramolecular aurophilic interactions, in which

**Figure 1.** Reported P-functionalized NHC and dpa<sup>P2</sup>-NHC



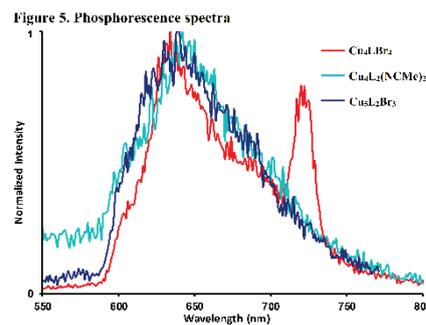
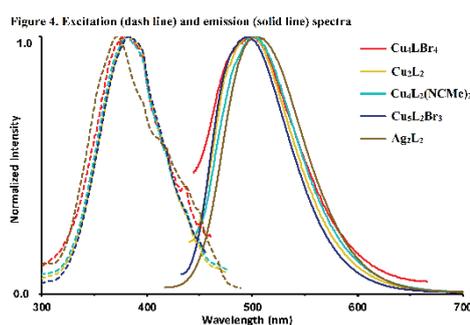
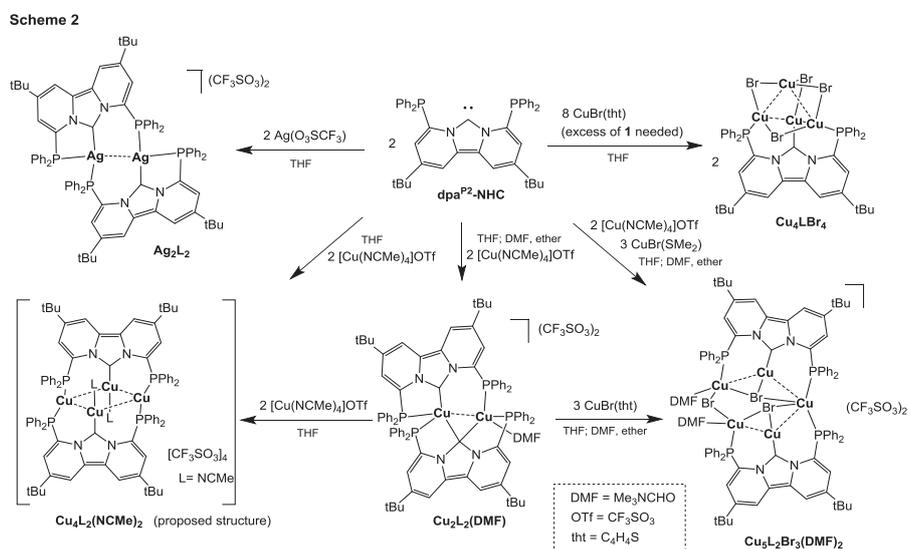
2 and 4 were found to undergo dynamic behavior in solution judging from NMR spectroscopy, suggesting weak coordination. All the complexes are fluorescent at room temperature in solution (Figure 2) and interestingly, phosphorescent at 77 K with



long lifetimes ranging from 85.1 to 772.0  $\mu\text{s}$  (Figure 3). Complexes 1-4 showed almost same emissions centered at around 500 nm, which are comparable to that of the carbene ligand  $\text{dpa}^{\text{P}2}\text{-NHC}$ , indicating that the electronic transition of these gold(I) complexes are mostly attributed to ligand-centered (LC) transitions.

### 3. Multinuclear Cu and Ag Complexes of Bis(diphenylphosphinyl)-functionalized Dipyrido-annulated N-heterocyclic Carbene (Chapter 3)

A series of homonuclear complexes of  $\text{dpa}^{\text{P}2}\text{-NHC}$  have been achieved (Scheme 2), including two dinuclear silver and copper complexes ( $\text{Ag}_2\text{L}_2$  and  $\text{Cu}_2\text{L}_2$ ), two tetranuclear copper complexes [ $\text{Cu}_4\text{L}_2(\text{NCMe})_2$  and  $\text{Cu}_4\text{LBr}_4$ ] and a pentanuclear copper complex ( $\text{Cu}_5\text{L}_2\text{Br}_3$ ). Judging from their NMR spectroscopy, all the complexes show fluxional behavior in solution, in which, particularly,  $\text{Ag}_2\text{L}_2$  underwent a dissociative process according to the calculated Eyring plot. Interestingly,  $\text{Cu}_2\text{L}_2$  contains two different carbenes, namely a  $\mu$ -bridging carbene and a terminal carbene. All the complexes were found to be fluorescent at room temperature in solution (Figure 4), in which



three homonuclear copper complexes [ $\text{Cu}_4\text{L}_2(\text{NCMe})_2$ ,  $\text{Cu}_4\text{LBr}_4$  and  $\text{Cu}_5\text{L}_2\text{Br}_3$ ] can provide phosphorescence at 77 K (Figure 5). Same with aforementioned gold complexes, the electronic transitions of these complexes are also mostly attributed to LC transitions, due to their similar emissions with that of  $\text{dpa}^{\text{P}2}\text{-NHC}$ .

#### Publications

- S. Zhang, R. Shang, M. Nakamoto, Y. Yamamoto, Y. Adachi and J. Ohshita, *Inorg. Chem.*, **2019**, 58(9), 6328–6335.  
S. Zhang, R. Shang, M. Nakamoto, Y. Yamamoto, Y. Adachi and J. Ohshita, *Dalton Trans.*, **2019**, accepted.