論 文 審 査 の 要 旨
(Summary of Dissertation Review)

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論文題目（Title）

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
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〔論文審査の要旨（Summary of Dissertation Review)〕

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. The type **A** whose carbene and phosphine donors are in 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 (rotation around one 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 cannot 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^{P2}-NHC, type **C**). This ligand features a rigid structure, whose carbene and phosphine donors are in proximity. More importantly, the characteristic of the phosphine arms rotating freely around one axis, enables access to different coordination geometries.

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

Starting from dpa^{P2}-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. Specially, based on interatomic distances in the solid-state structures, dpa^{P2}-NHC supported gold(I) complexes (**2-4**) feature intramolecular aurophilic interactions. Complexes **2** and **4** were found to exhibit dynamic behavior in solution judging from NMR spectroscopy, suggesting weak metal-ligand coordination. All the complexes are fluorescent at room temperature in solution. More interestingly, phosphorescence were observed for all complexes at 77 K with long lifetimes ranging from 85.1 to 772.0 μs. Complexes **1-4** showed almost same emissions centered at around 500 nm, which are comparable to that of the carbene ligand dpa^{P2}-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 dpa^{P2}-NHC have been achieved, including two dinuclear silver and copper complexes (Ag_2L_2 and Cu_2L_2), two tetranuclear copper complexes [$Cu_4L_2(NCMe)_2$ and Cu_4LBr_4] and a pentanuclear copper complex ($Cu_5L_2Br_3$). Judging from their NMR spectroscopy, all the complexes show fluxional behavior in solution, in which, particularly, Ag_2L_2 underwent a dissociative process according to the calculated Erying plot. Interestingly, Cu_2L_2 contains two carbenes with different coordination modes, namely a μ-bridging carbene and a terminal carbene. All the complexes were found to be fluorescent at room temperature in solution. Three homonuclear copper complexes [$Cu_4L_2(NCMe)_2$, Cu_4LBr_4 and $Cu_5L_2Br_3$] showed phosphorescence at 77 K. Same as aforementioned gold complexes, the electronic transitions of these complexes are also mostly attributed to LC transitions, due to their similar emissions with that of dpa^{P2}-NHC.

Finally, it is agreed from the above review result that the author of the present thesis has enough credentials to be awarded the doctoral degree (Science).

公表論文

[1] Luminescent Di- and Tetranuclear Gold Complexes of Bis(diphenylphosphinyl)-Functionalized Dipyrido-Annulated N-Heterocyclic Carbene
S. Zhang, R. Shang, M. Nakamoto, Y. Yamamoto, Y. Adachi and J. Ohshita, *Inorg. Chem*, **2019**, 48, 12250-12256

[2] Bis(diphenylphosphinyl)-functionalized dipyrido-annulated NHC towards copper(i) and silver(i)
S. Zhang, R. Shang, M. Nakamoto, Y. Yamamoto, Y. Adachi and J. Ohshita, *Dalton Trans.*, **2019,** 58(9), 6328–6335