

## Effect of tritopic ligands on the formation mechanism of self-assembled $\text{Pd}_6\text{L}_4$ complexes

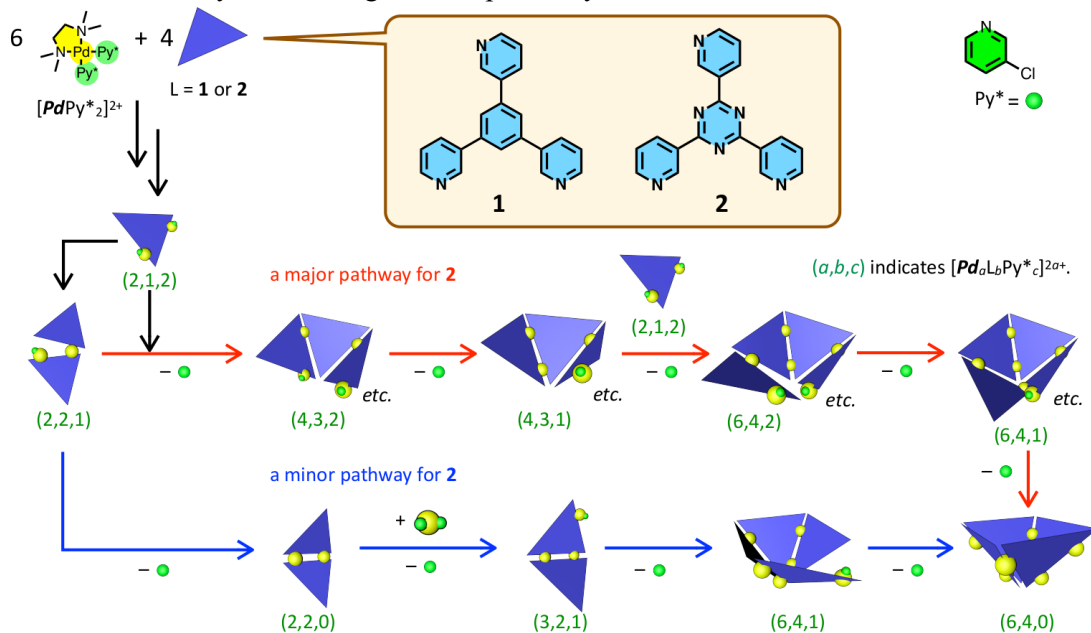
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Although the relation between the stability of coordination self-assemblies and their components, organic multitopic ligands, can be discussed based on thermodynamics, the effect of multitopic ligands on the formation mechanisms has scarcely been investigated. Previously, taken  $\text{Pd}_6\text{L}_4$  assemblies consisting of tritopic ligands (L) and  $[\text{PdPy}^*_2](\text{BF}_4)_2$ , as examples, the self-assembly pathway to the  $[\text{Pd}_6\text{L}_4]^{12+}$  complexes was investigated for the tritopic ligands L with a triazine ring by quantitative analysis of self-assembly process (QASAP).<sup>1</sup>

In this study, the self-assembly pathway to the  $[\text{Pd}_6\text{1}_4]^{12+}$  complex from the tritopic ligand **1** with a benzene ring, which is geometrically similar to **2**, was investigated. It was found that the major self-assembly pathway to  $[\text{Pd}_6\text{1}_4]^{12+}$  is different from that of  $[\text{Pd}_6\text{2}_4]^{12+}$ , whose self-assembly mainly takes place through the intermolecular reaction between  $[\text{Pd}_2\text{2}_2\text{Py}^*]^{4+}$  and  $[\text{Pd}_2\text{2}_2\text{Py}^*]^{4+}$  as a key reaction.<sup>1b</sup> This difference is discussed based on the planarity, the coordination ability, and the negative cooperativity of the three coordination sites in **1** and **2**.



**Figure** Self-assembly pathways of  $[\text{Pd}_6\text{L}_4]^{12+}$ .

- 1) (a) S. Komine, S. Takahashi, T. Kojima, H. Sato, S. Hiraoka, *J. Am. Chem. Soc.* **2019**, *141*, 3178; (b) T. Tateishi, S. Takahashi, I. Kikuchi, K. Aratsu, H. Sato, S. Hiraoka, *Inorg. Chem.* **2021**, *60*, 16678.