



HOKKAIDO UNIVERSITY

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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（理学） 氏名 金 容俊

学 位 論 文 題 名

Design, Synthesis and Applications of Dumbbell-Shaped Bipyridines as Ligands for Transition Metal Catalysis

(ダンベル型ビピリジン配位子の設計、合成および 遷移金属触媒反応への応用)

2,2'-Bipyridine (bpy), 1,10-phenanthroline (phen) and their ring-substituted derivatives have been widely used in transition-metal catalysis as N,N'-bidentate ligands. Pursuing better catalytic properties of the metal complexes the bpy and phen ligands have been modified by introducing various substituents with different steric and electronic properties. For these purpose, the N- α -positions (C6, C6' in bpy and C2, C9 in phen) and the N- γ -positions (C4, C4' in bpy and C4, C7 in phen) have been the common sites of modification. The ligand modifications at the N- β -positions (C5, C5' in bpy and C3, C8 in phen), however, have attracted less attention in the research of homogeneous catalysis because both the steric and electronic effects at those positions are not significant in general. Despite its broad use in many transition metal catalysis, traditional bipyridine and phenanthroline ligands have two major problems: formation of multigated species (Figure 1) and counterproductive bimetallic pathways.

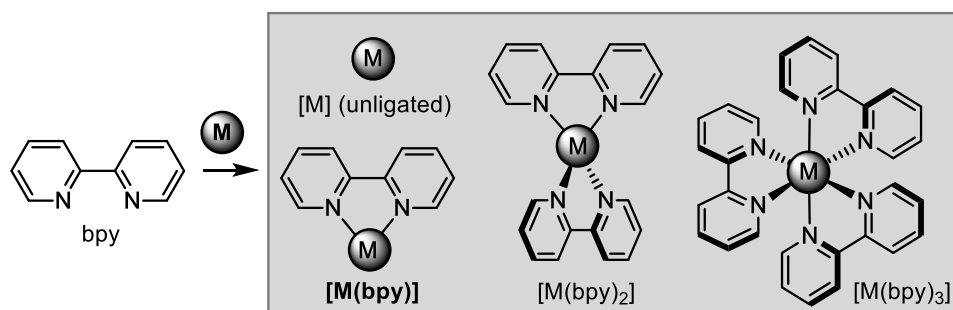


Figure 1. The formation of mulilgated species in a metal/bpy solution.

The author aimed to address those problems by developing dumbbell-shaped bipyridine and phenanthroline ligands. I envisioned that distal steric effects of the substituents at the N- β -positions, which do not hamper the catalytic reactions by steric hindrance in the vicinity of the metal but develop outside the boundary of the catalytic space, can allow the selective monochelation to the metal center and effectively suppress the bimetallic pathways while sustaining catalytic activity. Thus, I designed the ligands to have dumbbell like structures by introducing bulky substituents such as triarylmethyl and 2,6-dibenzhydryl-4-methylphenyl groups at the N- β -positions (Figure 1). Analysis of metal coordination behaviors of the bpy ligands by UV-vis absorption spectroscopy indicated the apparent monochelating nature of the dumbbell-shaped bpy/phen ligands.

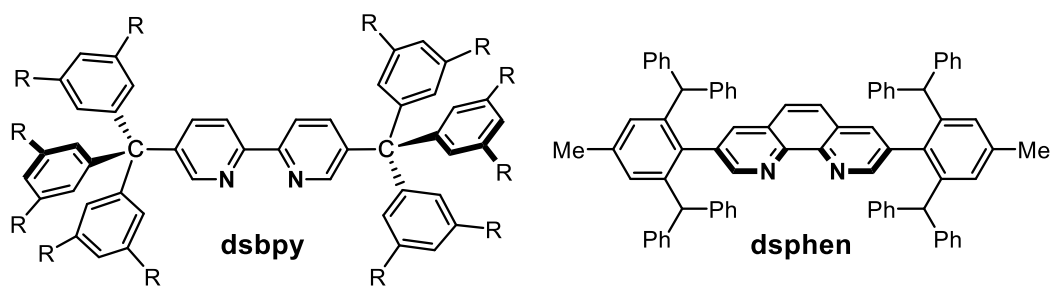


Figure 2. The dumbbell-shaped bipyridine (dsbpy) and phenanthroline (dsphen) ligands

The dumbbell-shaped bipyridines and phenanthroline showed high performance in the representative Ni-catalysis such as Ni-catalyzed cross-electrophile coupling (Scheme 1) and the Ni/photoredox synergistically catalyzed decarboxylative coupling reactions.

