Synthesis and Characterization of Group 10 Transition Metal Complexes Bearing a NHC/Pyridyl Hybrid Ligand.

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Keywords: N-heterocyclic Carbenes (NHCs); Chelating Ligand; Group 10 Transition Metal Complexes

N-Heterocyclic carbenes (NHCs) are one of the most attractive ligands in organometallic chemistry due to their high σ-donating ability. Recently, hybrid chelating ligands combining electron-donating NHCs with π-electron accepting pyridyl sites have been developed, and several transition metal complexes with these NHC/pyridyl hybrid ligands exhibit interesting coordination geometries and catalytic properties. However, it is still unclear how the bridging groups between the moieties affect the structure and properties of the complex. Thus, we report here the synthesis of a new chelating ligand (Figure 1), **L**, in which two NHCs are linked by a rigid phenylene linker with flexible methylene-mediated pyridines, and its application to the synthesis and characterization of group 10 transition metal complexes.

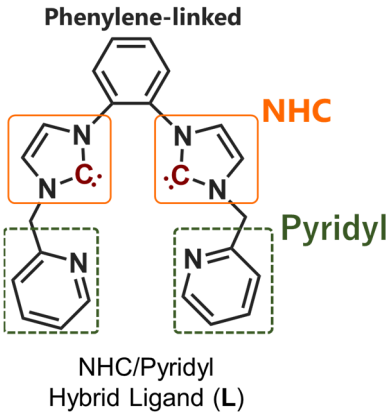

Figure 1. Ligand design

The imidazolium precursor, $H_2\mathbf{L}^{2+}$ was prepared in two steps following procedures reported for similar compounds[1,2]. This salt, $[H_2L^{2+}]Br_2.2HBr$ was treated with an excess of Ag_2O at 80° in CH_3CN to form a silver complex. X-ray structural analysis of the crystals as a $(CF_3SO_2)_2N^-$ salt revealed a $[Ag_4\mathbf{L}_2]^{4+}$ structure consisting of linear Ag_4 chains. The four silver atoms are bridged by two **L** ligands, whose Ag(I)-Ag(I) distances of 3.2628(4)-3.1653(3) Å are shorter than the van der Waals radius of silver (3.44 Å). The BF_4^- or ClO_4^- salts of this $Ag_4\mathbf{L}_2$ complex were then reacted with metal-halides ($NiCl_2$, $PdCl_2$, K_2PtCl_4) in CH_3CN at 80ºC for 4h, resulting in two different complexes depending on the equivalents of metal ions. When $Ag_4\mathbf{L}_2$ complex was reacted with two equivalents of metal ions, [ML]-type composition was observed in the ESI-MS measurement. In contrast, $[ML_2]$-type complex was obtained by using one equivalent of the metal ions. The crystal structures of a series of $[ML_2]^{2+}$ complexes were successfully determined. In all of them, the two **L** ligands coordinated to the metal center in a bidentate fashion *via* the NHC moieties, and the four pyridine sites were free without coordination. Due to the difference in the orientation of the phenylene groups, Ni(II) and Pd(II) complexes form an almost perfect square planar structure, whereas Pt(II) complex has a distorted square planar structure.

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2) S. Matsumoto, *et al*. *Org. Biomol. Chem.* **2011**, *9*, 5941–5944.

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