

Syntheses of Ruthenium Complexes having a Non-Innocent PNS-Type Pincer Ligand

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Transition metal complexes featuring pincer ligands play a major role in synthesis, bond activation, and homogeneous catalysis. In this work, we synthesized two ruthenium complexes having a novel PNS-type pincer ligand and we started to explore the dearomatization of the PNS ligand.

Reaction of $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$ with 1.5 equiv. of a PNS-type pincer ligand at 65 °C for 1h afforded $[(\text{PNS})\text{Ru}(\text{CO})\text{ClH}]$ (**1**) in 89 % yield. Also, $[(\text{PNS})\text{RuCl}_2(\text{PPh}_3)]$ (**2**) was synthesized by the reaction of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with a PNS-type pincer ligand. The X-ray structural analysis of **2** revealed that two chloride ligands were located in the trans position. Then, we studied the dearomatization of the PNS ligand by deprotonation. Complex **1** was reacted with 1 equiv. of $t\text{BuOK}$ in THF at r.t. for 1h to give a dearomatized species, which was confirmed by NMR spectra. However, this dearomatized species decomposed after evaporation of the reaction solution. Therefore, to avoid this decomposition treatment of **1** with 1.2 equiv. of $t\text{BuOK}$ in the presence of PMe_3 resulted in a dearomatized ruthenium complex $[(\text{PNS})\text{Ru}(\text{CO})\text{H}(\text{PMe}_3)]$ (**3**). The ^{31}P NMR spectrum showed a new additional signal and the ^1H NMR spectrum exhibited a hydride signal, which was more shielded than that of the condition without adding PMe_3 . Additionally, one PNS side arm's ^1H NMR signal disappeared. These indicated that PNS ligand was dearomatized. This complex may display metal-ligand cooperativity.

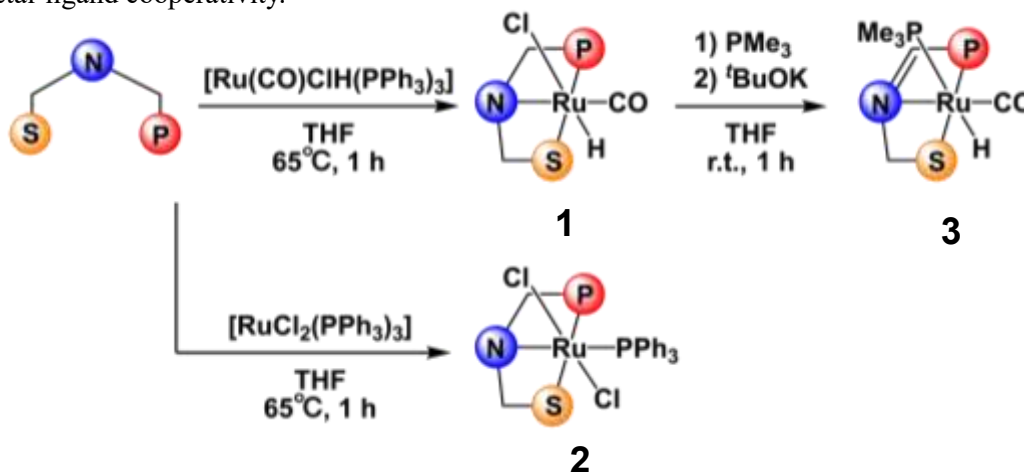


Figure 1. Syntheses of ruthenium complexes having a PNS-type pincer ligand and dearomatized reaction of **1**