Synthesis of PNN Phenanthroline Pincer Complexes of Ruthenium and Their Reactivity in Ester Reduction

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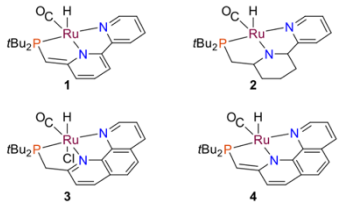
The Milstein bipyridyl PNN pincer complex of ruthenium **1** (Scheme 1) and metal-ligand cooperation by ligand aromatization-dearomatization have been extensively discussed over the past decade.[1] Recently, it has been revealed that the PNN ligand of **1** undergoes hydrogenation under H_2 resulting in the formation of the structurally related and highly catalytically active piperidine complex **2**.[2] This has led to some ambiguity about the nature of the active species in the hydrogenation and dehydrogenation reactions where complex **1** was utilized as the catalyst.



Scheme 1. The bipyridyl and phenanthroline pincer complexes of ruthenium

To gain a better understanding of the chemistry of coordination compounds of N-heterocyclic ligands, we have designed a phenanthroline PNN pincer complex **3**.

We compared the hydrogenation of bipyridyl and phenanthroline PNN pincer ligands on ruthenium under reducing conditions. This process is facile for the dearomatized PNN ligand of the Milstein catalyst **1**, and the related dearomatized phen-PNN ligand of **4** is also reduced by ethanol or H_2 under ambient conditions. A number of complexes, some of which are catalytically active were isolated and characterized.

Both experimental and computational evidence, together with previous research contradicts metal-ligand cooperation by aromatization-dearomatization of the PNN ligand of **1** as a mechanistic pathway for catalytic ester reduction under H_2 pressure. Unlike **2,** the newly introduced dearomatized phen-PNN complex **4** in this study is inactive in the reduction of methyl hexanoate, though non-methyl esters are readily reduced.

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2) Dawe, L.N.; Karimzadeh-Younjali, M.; Dai, Z.; Khaskin, E.; Gusev, D.G., *J.Am.Chem.Soc.*, **2020**, *142*, 19510-19522.