

DOCTORAL THESIS

The syntheses and reactivity of polydentate PNNP ligands and macrocyclic polyphosphine ligands

Chen, Yang

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**The Syntheses and Reactivity
of
Polydentate PNNP Ligands
and
Macrocyclic Polyphosphine Ligands**

CHEN Yang

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ABSTRACT

A series of novel and chiral diimino-diphosphine (PNNP) ligands were synthesized in good yields *via* the condensation of *o*-(diphenylphosphino)benzaldehyde with the appropriate diamine. The corresponding diamino-diphosphine (PNNP) ligands were synthesized in good yields by the reduction of the diimino-diphosphino ligands with NaBH_4 . The reactions of such novel and chiral PNNP ligands with Ru(II), Fe(II), Pd(II), Cu(I) produced bis-chelate/single-bridged dinuclear complexes, tri-dentate and tetra-dentate mononuclear complexes. All of the complexes were characterized by analytical and spectroscopic methods. Some of them were further confirmed by the X-ray crystal structures.

The reactions of *trans*- $\text{RuCl}_2[\text{P}_2\text{N}_2\text{H}_4]$, *trans*- $\text{RuCl}_2[\text{R,R-cyclohexyl-P}_2\text{N}_2]$ and *trans*- $\text{RuCl}_2[\text{R,R-cyclohexyl-P}_2\text{N}_2\text{H}_4]$ with Ag^+ , CuCl or $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ result in *trans*→*cis* isomerization giving *cis* analogues in near quantitative yields which have been isolated and characterized. Photolytical *cis*→*trans* isomerizations of the *cis* species were observed by $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring. The pathway of the isomerization has been addressed experimentally.

The first selective-functionalized tritertiary 1,5,9-triphosphacyclododecane Mo complexes with one or three pendant ether functions were prepared from the trisecondary 1,5,9-triphospha-cyclododecane precursor. All the compounds have been characterized analytically and spectroscopically.

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