



## Doctoral Thesis

# Syntheses and applications of innovative mono- and bidentate phosphorus ligands in coordination chemistry and in catalytic reactions

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**SYNTHESES AND APPLICATIONS OF INNOVATIVE MONO- AND BIDENTATE  
PHOSPHORUS LIGANDS IN COORDINATION CHEMISTRY AND IN  
CATALYTIC REACTIONS**

A dissertation submitted to the  
**Swiss Federal Institute of Technology Zurich**

for the degree of  
**Doctor of Natural Sciences**

presented by

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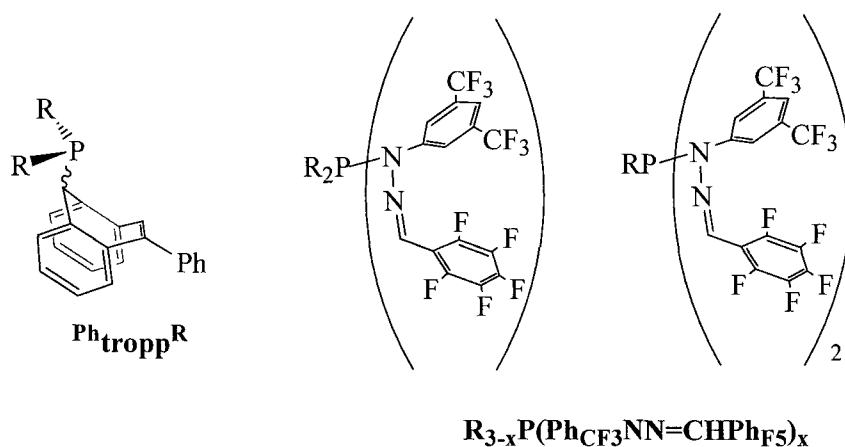
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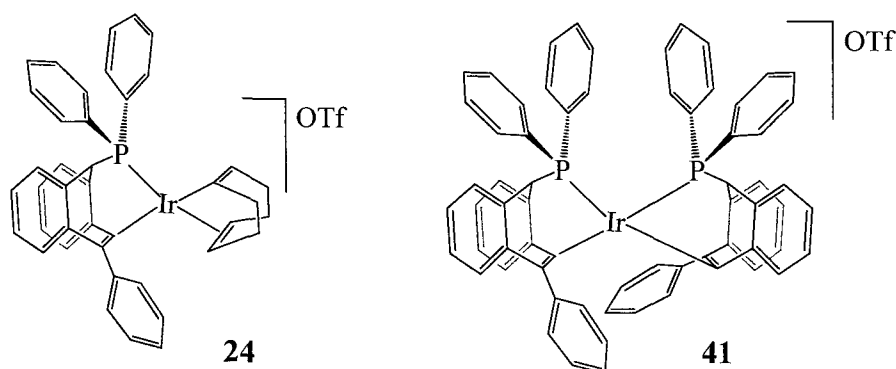
Zurich, 2005

## Summary

In this thesis, we describe the syntheses and the applications in coordination chemistry of the enantiomerically pure bidentate phosphanes, 10-phenyl-5*H*-dibenzo[*a,d*]cycloheptene-5-yl phosphanes (**Ph<sub>t</sub>tropp<sup>R</sup>**, R = phenyl, cyclohexyl, methyl substituents on the phosphorus), and the monodentate phosphones (**R<sub>3-x</sub>P(Ph<sub>CF3</sub>NN=CHPh<sub>F5</sub>)<sub>x</sub>**, R = aryl, alkyl, x = 1, 2).

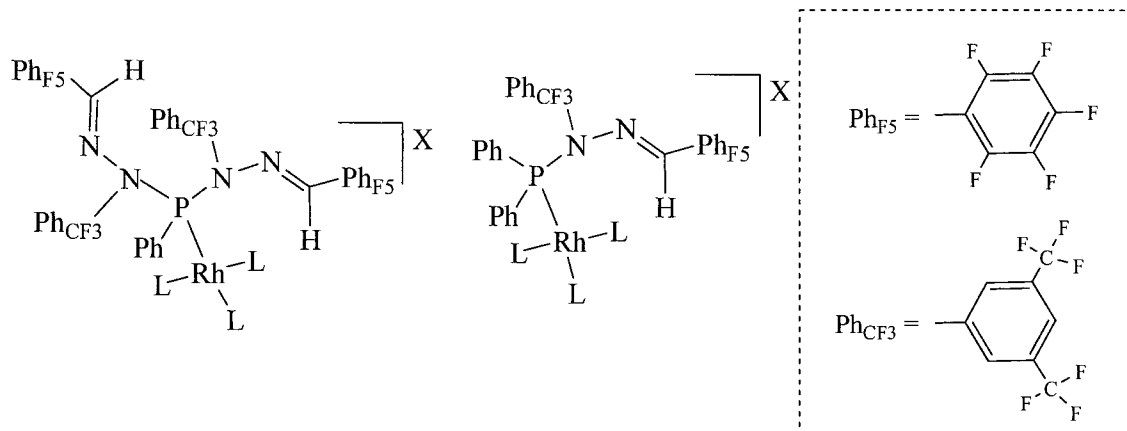


Specifically, we synthesized the iridium(I) complexes [Ir(cod)(**Ph<sub>t</sub>tropp<sup>Ph</sup>**)]OTf **24** and [Ir(**Ph<sub>t</sub>tropp<sup>Ph</sup>**)<sub>2</sub>]OTf **41** and investigated their reactivity in asymmetric olefin hydrogenation.



Using **41** a high TON of  $10^4$  was obtained for the hydrogenation of dimethylitaconate. Surprisingly, the coordinated C=C<sub>trop</sub> units of **41** were found to be reversibly hydrogenated in the presence of H<sub>2</sub>. The complex released three equivalents of dihydrogen when the atmosphere was replaced with argon.

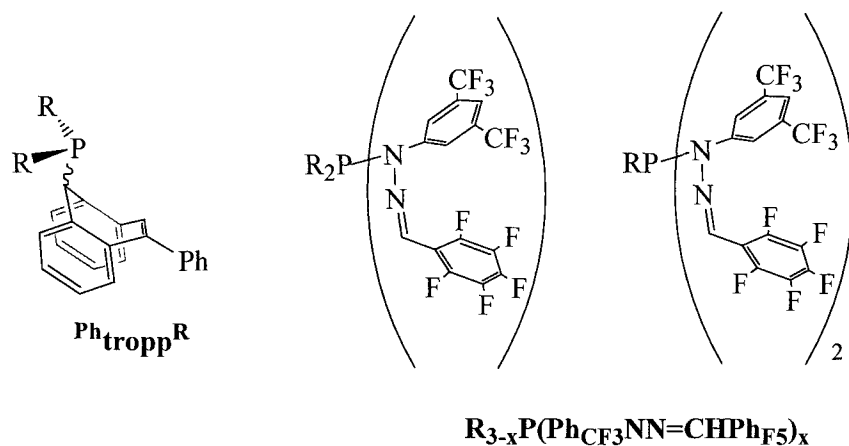
In addition, we report preliminary studies regarding the coordination properties of  $\text{PhP}(\text{Ph}_{\text{CF}_3}\text{NN}=\text{CHPh}_{\text{F}_5})_2$  **74** and  $\text{Ph}_2\text{P}(\text{Ph}_{\text{CF}_3}\text{NN}=\text{CHPh}_{\text{F}_5})$  **79** with different rhodium(I) precursors.



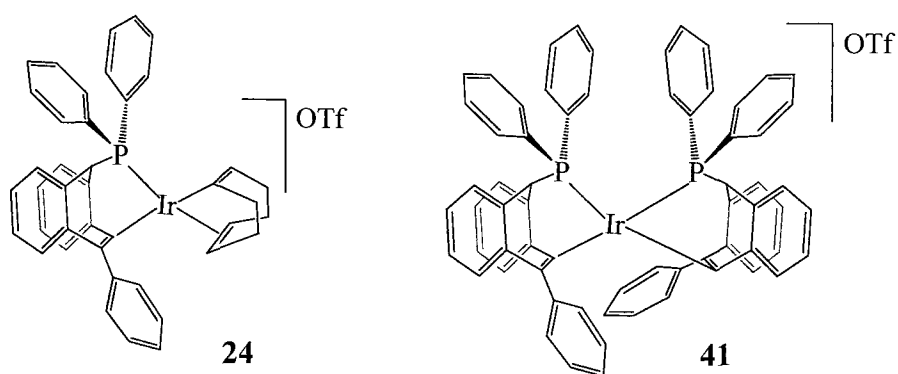
Complexes of the general formula  $[\text{Rh}(\text{L})_3(\text{PhP}(\text{Ph}_{\text{CF}_3}\text{NN}=\text{CHPh}_{\text{F}_5})_2)]\text{X}$  and  $[\text{Rh}(\text{L})_3(\text{Ph}_2\text{P}(\text{Ph}_{\text{CF}_3}\text{NN}=\text{CHPh}_{\text{F}_5}))]\text{X}$  ( $\text{L}$  = solvent,  $\text{X}$  = OTf,  $\text{PF}_6$ ) were utilized in catalytic hydroformylation. Surprisingly high TON of  $9.5 \cdot 10^6$  and TOF of  $1.1 \cdot 10^6 \text{ h}^{-1}$  were found.

## Sommario

In questa tesi, verrà riportata e descritta dettagliatamente la sintesi e l'applicazione di fosfine innovative come le fosfine bidentate ed enantiopure 10-phenyl-5*H*-dibenzo[*a,d*]cycloheptene-5-yl (<sup>Ph</sup>tropp<sup>R</sup>, R = fenile, cicloesile, metile sostituenti al fosforo) e i mododentati phossoni ( $R_{3-x}P(Ph_{CF_3}NN=CHPh_{F_5})_x$ , R = arile, alchile, x = 1, 2).

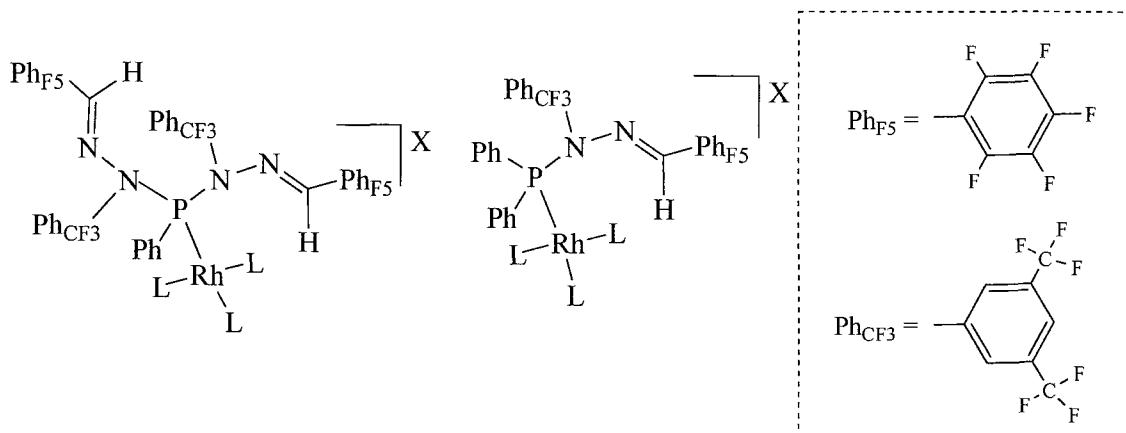


In particolare, i complessi di iridio(I) [Ir(cod)(<sup>Ph</sup>tropp<sup>Ph</sup>)]OTf **24** e [Ir(<sup>Ph</sup>tropp<sup>Ph</sup>)<sub>2</sub>]OTf **41** sono stati sintetizzati, studiati e applicati in idrogenazione asimmetrica di olefine.



Particolarmente interessante sono stati i risultati ottenuti dalla idrogenazione catalitica del dimetilitaconato in presenza di **41** con un TON di 10<sup>4</sup>. Sorprendentemente le unità C=C<sub>trop</sub>, coordinate al metallo in **41**, sono reversibilmente idrogenate in presenza di H<sub>2</sub>. Il complesso è quindi capace di rilasciare tre equivalenti di diidrogeno in presenza di argon.

In aggiunta, riportiamo gli studi preliminari delle proprietà di coordinazione di  $\text{PhP}(\text{Ph}_{\text{CF}_3}\text{NN}=\text{CHPh}_{\text{F}_5})_2$  **74** e di  $\text{Ph}_2\text{P}(\text{Ph}_{\text{CF}_3}\text{NN}=\text{CHPh}_{\text{F}_5})$  **79** con vari precursori di rodio(I).



Complessi del tipo  $[\text{Rh}(\text{L})_3(\text{PhP}(\text{Ph}_{\text{CF}_3}\text{NN}=\text{CHPh}_{\text{F}_5})_2)]\text{X}$  e  $[\text{Rh}(\text{L})_3(\text{Ph}_2\text{P}(\text{Ph}_{\text{CF}_3}\text{NN}=\text{CHPh}_{\text{F}_5}))]\text{X}$  ( $\text{L}$  = solvente,  $\text{X}$  =  $\text{OTf}$ ,  $\text{PF}_6$ ) sono stati applicati in idroformilazione catalitica. Sorprendentemente alti TON di  $9.5 \cdot 10^6$  e TOF di  $1.1 \cdot 10^6 \text{ h}^{-1}$  sono stati osservati.