



# **LIGAND PLATFORMS IN HOMOGENOUS CATALYTIC REACTIONS WITH METALS**

PRACTICE AND APPLICATIONS FOR  
GREEN ORGANIC TRANSFORMATIONS

RYOHEI YAMAGUCHI & KEN-ICHI FUJITA

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**Practice and Applications for  
Green Organic Transformations**

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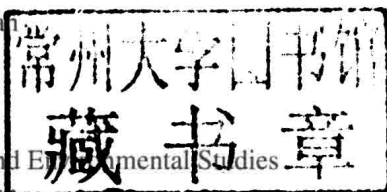
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IN HOMOGENOUS  
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WITH METALS**



# PREFACE

The developments of higher atom-economical methodologies and usage of less harmless reactants and reagents are increasingly important in modern organic synthesis from environmental points of view. In this context, catalytic organic transformations based on the hydrogen transfer catalyzed by metal-complexes have been attracting considerable attention and are widely investigated. Thus, it is indispensable to design and create the metal complexes exhibiting high catalytic performance for the hydrogen transfer between organic substances. It has been well recognized that the catalytic performance of metal-complexes depends on not only the inherent nature of the metal but also the ligand that stabilizes the atomic metal and also governs the catalytic activity of the metal center. In addition, the metal-ligand cooperative catalysis and functional ligands have been widely recognized for the important role especially in the hydrogen transfer processes [1].

This monograph aims to survey the notable ligand platforms in homogeneous transition metal complexes those catalyze organic transformations based on the hydrogen transfer and consists of 4 parts including 10 chapters. Topics of N-heterocyclic carbene ligands are described in the part I, those of  $\eta^4$ -cyclopetadienone/ $\eta^5$ -hydroxycyclopentadienyl and related ligands in the part II, those of pincer ligands in the part III, and bidentate and miscellaneous functional ligands in the part IV. Owing to limited space, this monograph is focused on the recent progress (ca. 2000~the beginning of 2012) of homogeneous catalytic organic transformations based on the hydrogen transfer catalyzed by well-defined transition metal complexes, but asymmetric reactions are not included in most cases. R. Y. wrote the parts II and IV (Chapters 3, 4, 8–10) and K. F. wrote the parts I and III (Chapters 1, 2, 5–7).

We hope this monograph would help to understand the notable roles of the ligands, design the highly active transition metal complex catalysts, and develop the efficient green organic transformations in not only basic researches but also industrial applications.

April, 2014

RYOHEI YAMAGUCHI

KEN-ICHI FUJITA

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# ABBREVIATION

Ac	acetyl
acac	acetylacetonate
Ad	adamantyl
Ar	aryl
Ar <sup>F</sup> , Ar <sup>f</sup>	3,5-bis(trifluoromethyl)phenyl
BINAP, binap	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BIPHEP	2,2'-bis(diphenylphosphino)biphenyl
BMIM	1-butyl-3-methylimidazolium
Bn	benzyl
Boc	<i>tert</i> -butoxycarbonyl
bpy	2,2'-bipyridyl
bpym	2,2'-bipyrimidyl
BQC	dipotassium 2,2'-bisquoline-4,4'-dicarboxylate
Bu	butyl
<sup>t</sup> Bu	<i>tert</i> -butyl
CataXCium@Pcy	<i>N</i> -phenyl-2-(dicyclohexylphosphinyl)pyrrole
cod	1,5-cyclooctadiene
coe	cyclooctene
conc.	concentration
Cp	cyclopentadienyl
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
CSA	camphorsulfonic acid
Cy	cyclohexyl
Cyp	cyclopentyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DBAD	di- <i>tert</i> -butyl azodicarboxylate
DCE	dichloroethane



DCPE	1,2-bis(dicyclohexylphosphino)ethane
DFT	density functional theory
ditz	1,2,4-triazol-di-ylidene
DKR	dynamic kinetic resolution
DMBQ	2,6-dimethoxy-1,4-benzoquinone
DME	dimethoxyethane
DMF	dimethylformamide
DMHQ	2,6-dimethoxy-1,4-hydroquinone
DMSO	dimethyl sulfoxide
DPEphos	bis(2-diphenylphosphinophenyl)ether
DPPB, dppb	1,3-bis(diphenylphosphino)butane
DPPF, dppf	1,1'-bis(diphenylphosphino)ferrocene
DPPM, dppm	bis(diphenylphosphino)methane
DPPP, dppp	1,3-bis(diphenylphosphino)propane
EDA, eda	ethylenediamine
EDTA, edta	ethylenediaminetetraacetic acid
ee	enantiomeric excess
Et	ethyl
GC	gas chromatography
'Hex	<i>tert</i> -hexyl (1,1-dimethylbutyl)
IPr	<i>N,N'</i> -bis(2,6-diisopropylphenyl)imidazol-2-ylidene
Me	methyl
Mes	mesityl (2,4,6-trimethylphenyl)
MMA	methyl methacrylate
Ms	methansulfonyl
MS	molecular sieves
MTBE	methyl <i>tert</i> -butyl ether
MW	microwave
NBE, nbe	norbornene
NHC	N-heterocyclic carbene
NHPI	<i>N</i> -hydroxyphthalimide
Np	neopentyl
1-Oct	1-octene
2-Oct	2-octene
PEG	polyethylene glycol
Ph	phenyl
Pr	propyl
'Pr	<i>iso</i> -propyl
Py	pyridyl
rt	room temperature
tba	<i>tert</i> -butylethane
tbe	<i>tert</i> -butylethylene
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
Tf	trifluoromethanesulfonyl
TFA	trifluoromethylacetic acid
THF	tetrahydrofuran
THQ	1,2,3,4-tetrahydroquinoline
TMEDA, tmeda	tetramethylethylenediamine

TMS	trimethylsilyl
TOF	turnover frequency
Tol	4-methylphenyl
TON	turnover number
<sup>t</sup> Pent	<i>tert</i> -pentyl (1,1-dimethylpropyl)
Ts	<i>p</i> -toluenesulfonyl
Xantphos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene



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## **PART I**

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# **N-HETEROCYCLIC CARBENE LIGANDS IN TRANSITION METAL CATALYZED HYDROGEN TRANSFER AND DEHYDROGENATIVE REACTIONS**



