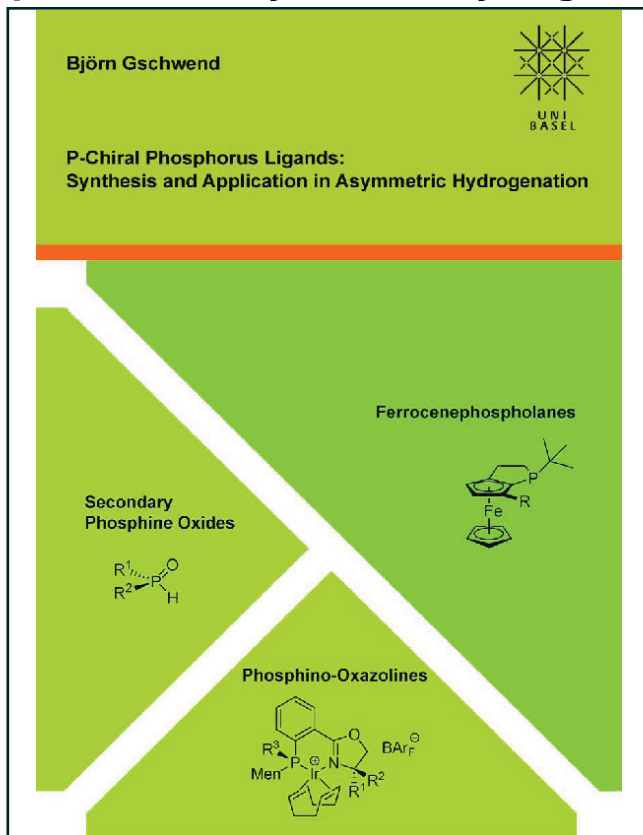




Björn Gschwend (Autor)
P-Chiral Phosphorus Ligands: Synthesis and Application in Asymmetric Hydrogenation



<https://cuvillier.de/de/shop/publications/949>

Copyright:
Cuvillier Verlag, Inhaberin Annette Jentsch-Cuvillier, Nonnenstieg 8, 37075 Göttingen,
Germany
Telefon: +49 (0)551 54724-0, E-Mail: info@cuvillier.de, Website: <https://cuvillier.de>

Table of Contents

1	Ferrocenephospholanes as Ligands in the Transition-Metal Catalyzed Asymmetric Hydrogenation	1
1.1	Introduction	3
1.1.1	P-Stereogenic Ligands in Asymmetric Catalysis	3
1.1.1.1	Chirality at Phosphorus Atoms	3
1.1.1.2	Preparation of P-Stereogenic Phosphines	4
1.1.1.3	Transition Metal-Catalyzed Asymmetric Hydrogenation of Functionalized Olefines	5
1.1.2	Cyclic Phosphines	10
1.1.2.1	Synthesis of Cyclic Phosphines	10
1.1.2.2	Phospholanes in Catalysis	12
1.1.3	Ferrocene	13
1.1.3.1	Structural Properties	13
1.1.3.1	Ligands with a Ferrocenyl Backbone	14
1.1.4	Objectives of this Work	16
1.1.5	References	17
1.2	Synthesis of Ferrocenephospholanes	21
1.2.1	<i>Ugi's</i> Amine	21
1.2.2	Formation of a Simple Ferrocenephospholane	21
1.2.3	Approaches to a Secondary Ferrocenephospholane	24
1.2.4	Functionalized Ferrocenephospholanes	33
1.2.5	Attempted Synthesis of a Ferrocene-Based P,N-Ligand with only Planar Chirality	39
1.2.6	Conclusions	42
1.2.7	References	43
1.3	Rhodium-Complexes and their Application in the Asymmetric Hydrogenation of Olefins	45
1.3.1	Coordination Behaviour	45
1.3.2	Hydrogenations	50
1.3.2.1	Substrate Screening	50
1.3.2.2	Ligand Screening	58
1.3.3	Conclusions	66
1.3.4	References	67

1.4	Iridium-Complexes and their Application in the Asymmetric Hydrogenation of Olefins	67
1.4.1	Hydrogenation with <i>in situ</i> Generated Complexes	67
1.4.1.1	Substrate Screening	67
1.4.1.2	Ligand Screening	75
1.4.2	Hydrogenation with Isolated Complexes	82
1.4.3	Hydrogenation of Unfunctionalized Olefins with a Ferrocenephospholane-Pyridine-Iridium Complex	90
1.4.4	Conclusions	92
1.4.5	References	93
1.5	Properties of Ferrocenephospholane-Complexes	95
1.5.1	X-Ray Observations	95
1.5.2	Competition Experiments in Solution	100
1.5.2.1	Competition Experiments in Methanol	100
1.5.2.2	Competition Experiments in Dichloromethane	103
1.5.3	Conclusions	109
1.5.4	References	110
2	Phosphines with Additional Functional Group as Ligands in Catalysis	111
2.1	Introduction	113
2.1.1	Secondary Phosphine Oxides	113
2.1.1.1	Properties of Secondary Phosphine Oxides	113
2.1.1.2	Synthesis of Secondary Phosphine Oxides	115
2.1.1.3	Metal Complexes	117
2.1.1.4	Application in Catalysis	119
2.1.2	Miscellaneous Functionalized Phosphines	121
2.1.3	Objectives of this Work	122
2.1.4	References	123
2.2	Synthesis and Catalysis Experiments	125
2.2.1	Secondary Phosphine Oxides	125
2.2.1.1	SPO-Phosphine Ligands	125
2.2.1.2	Terpene-Derived Secondary Phosphine Oxides	128
2.2.2	Hydroxyethyl-Functionalized Phosphines	138
2.2.3	Conclusions	142
2.2.4	References	144

3	P-Chiral Phosphino-Oxazolines as Ligands in the Iridium-Catalyzed Asymmetric Hydrogenation	145
3.1	Introduction	147
3.1.1	Historical Overview	147
3.1.2	Mechanism	151
3.1.2.1	The Catalytic Cycle	151
3.1.2.2	The Counter-Ion Effect	154
3.1.3	Objectives of this Work	156
3.1.4	References	157
3.2	Synthesis and Hydrogenation Experiments	159
3.2.1	Preparation of P-Chiral Phosphino-Oxazoline-Iridium Complexes	159
3.2.2	Asymmetric Hydrogenation	163
3.2.3	Influence of Temperature in the Reduction of 2-(4-Methoxyphenyl)-1-butene	173
3.2.4	Conclusions	174
3.2.5	References	175
4	Experimental	177
4.1	Working Techniques and Reagents	179
4.2	Analytical Methods	179
4.3	Experimental Procedures	181
4.3.1	Preparation of Ferrocenephospholanes	181
4.3.2	Preparation of Terpene-Derived Phosphorus Compounds	218
4.3.3	Preparation of P-Chiral Iridium-PHOX Complexes	232
4.3.4	Preparation of Single Crystals	244
4.3.5	Procedure for the Competition Experiments	244
4.3.6	Hydrogenation Procedures	245
4.3.6.1	Automated Parallel Hydrogenations (<i>SYMYX</i>)	245
4.3.6.2	Hydrogenations with Iridium-Complexes	246
4.3.6.3	Analytical Data of Hydrogenation Substrates	247
4.4	References	250

5	Appendix	251
5.1	Crystallographic Data	253
5.2	List of Abbreviations	262
5.3	References	265
6	Summary	267