Contents

1 li	ntroduction	15
1.1	Ligands - Coordination Chemistry - Catalysis	15
1.2	Important Ligand-Classes	16
1.2.1	P,P-Ligands: Diphosphines	17
1.2.2		17
1.2.3	3 P,N-Ligands: Phosphinooxazolines	18
1.2.4	4 C-Donor Ligands: N-Heterocyclic Carbenes	19
1.3	Objectives of this Work	19
2 N	New PHOX Ligands for Enantioselective Hydrogenation	25
2.1	Hydrogenation of Functionalized Alkenes	25
2.2	Hydrogenation of Unfunctionalized Alkenes	26
2.3	Objectives of this Chapter	27
2.4	Ligand and Complex Synthesis	29
2.4.	1 Phosphinoacetic Acid-Borane Adducts	30
2.4.	Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization	31
2.4.	3 Secondary Phosphine-Borane Adducts	32
2.4.	4 Chloromethyloxazolines	33
2.4.	5 Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling	34
2.4.	6 Deprotection and Complex Synthesis	35
2.5	Catalytic Hydrogenation Reactions	37
2.5.	1 (E)-1,2-Diphenyl-1-propene	37
2.5.	2 (E)-2-(4'-Methoxyphenyl)-2-butene and (Z) -2-(4'-methoxyphenyl)-2-butene	38
2.5.	3 2-(4'-Methoxyphenyl)-3-methyl-2-butene	39
2.5.	4 6-Methoxy-1-methyl-3,4-dihydronaphtaline	40
2.6	Enantioselective Hydrogenation of Functionalized Alkenes	41
2.6.	1 (E)-Ethyl-3-phenyl-but-2-enoate	41
2.6.	2 (E)-2-Methyl-3-phenyl-prop-2-enol	42
2.6.	3 N-(1-Phenylethylidene)-aniline	43
2.7	X-Ray Crystallographic Studies	45
2.8	Conclusion	48
3 1	Phosphinines as Ligands in Catalysis	51



	District Dis	- 1
3.1	Phosphinines - Phosphabenzenes - Phosphorines	51
3.1.1	•	52 53
3.1.2	•	54
3.1.3	•	55
3.1.4	••	
3.2	Objectives of this Chapter	56
3.3	Improved Synthesis of Phosphininoxazolines	57
3.3.1	Synthesis of Diene-Moiety	57
3.3.2	2 Synthesis of Phosphaalkyne	58
3.3.3	3 [4+2]-Cycloaddition of α-Pyrone and tert-Butylphosphaalkyne	59
3.3.4	4 (S)-2-(6-tert-Butylphosphinin-2-yl)-4,5-dihydro-4-isopropyloxazole	63
3.3.	5 Analogous Phosphininoxazolines	64
3.3.0	A Related Chiral Chelating Phosphininimidazoline	65
3.4	Synthesis of Phosphinine-Iridium Complexes	66
3.4.	I Iridium-Complexes with Chelating Phosphinines	66
3.4.	2 Iridium-Complexes with Monodentate Phosphinines	68
3.5	Application in Catalysis	70
3.5.	1 Hydrogenation	70
3.5.	2 Allylic Alkylation	71
3.6	Discussion of X-Ray Crystal Structures	74
3.7	Towards 6-Ring-Chelating Phosphininoxazolines	76
3.8	Conclusion	79
4	Asymmetric Catalytic Intramolecular Pauson-Khand Reaction	83
4.1	The Pauson-Khand Reaction	83
4.2	Catalytic Pauson-Khand Reaction	84
4.3	Pauson-Khand Reaction with other Metals	84
4.4	Objectives of this Chapter	86
4.5	Catalytic Intramolecular Pauson-Khand Reaction with Iridium-PHOX Catalysts	87
4.5.	1 Complex Synthesis	88
4.5.	2 Substrate Synthesis	89
4 5	3 ACPKR of Allyl-(3-phenyl-prop-2-ynyl) Ether	90
4.5	4 ACPKR of N-Allyl-N-(3-phenyl-prop-2-ynyl)-4-methylphenylsulfonamide	92
4.5	.5 ACPKR of 2-Allyl-2-(3-phenyl-prop-2-ynyl)-malonic Acid Dimethyl Ester	93

	ACPKR of [3-(2-Methyl-allyloxy)-prop-1-ynyl]-benzene and Allyl-(3-methyl-prop	
4.5.	7 Conclusion	96
5 F	Rhodium-Silylene Complexes	99
5.1	Stable Silylenes	99
5.2	Silylene-Complexes	101
5.3	Objectives of this Chapter	102
5.4	Ligand and Complex Synthesis	103
5.4.	1 Synthesis of N-Heterocyclic Silylenes	103
5.4.	2 Rhodium Complex Synthesis	104
5.4.	3 Characterization of Rhodium-Silylene Complexes	107
5.5	Probing of Catalytic Activity	108
5.6	X-ray Crystallographic Studies	109
5.7	Conclusion	111
6 Synopsis 115		
7 Experimental 119		
7.1	Analytical Methods	119
7.1 7.2	Analytical Methods Working Techniques	119 120
	·	
7.2	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation	120
7.2 7.3	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation 1 Phosphinoacetic Acid-Borane Adducts	120 121
7.2 7.3 7.3	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization	120 121 124
7.2 7.3 7.3 7.3	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization Secondary Phosphine-Borane Adducts	120 121 124 129
7.2 7.3 7.3 7.3 7.3	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization Secondary Phosphine-Borane Adducts Chloromethyloxazolines	120 121 124 129 138
7.2 7.3 7.3 7.3 7.3 7.3	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization Secondary Phosphine-Borane Adducts Chloromethyloxazolines Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling	120 121 124 129 138 139
7.2 7.3 7.3 7.3 7.3 7.3 7.3	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization Secondary Phosphine-Borane Adducts Chloromethyloxazolines Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling	120 121 124 129 138 139
7.2 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.3	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization Secondary Phosphine-Borane Adducts Chloromethyloxazolines Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling Deprotection and Complex Synthesis Phosphinines as Ligands in Catalysis	120 121 124 129 138 139 144
7.2 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.3	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization Secondary Phosphine-Borane Adducts Chloromethyloxazolines Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling Deprotection and Complex Synthesis Phosphinines as Ligands in Catalysis Synthesis of Diene-Moiety	120 121 124 129 138 139 144 150
7.2 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.4 7.4	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization Secondary Phosphine-Borane Adducts Chloromethyloxazolines Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling Deprotection and Complex Synthesis Phosphinines as Ligands in Catalysis Synthesis of Diene-Moiety Synthesis of Phosphaalkyne	120 121 124 129 138 139 144 150
7.2 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.4 7.4 7.4	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization Secondary Phosphine-Borane Adducts Chloromethyloxazolines Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling Deprotection and Complex Synthesis Phosphinines as Ligands in Catalysis Synthesis of Diene-Moiety Synthesis of Phosphaalkyne [4+2] Cycloaddition of α-Pyrone and tert-Butylphosphaalkyne	120 121 124 129 138 139 144 150 169 171
7.2 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.4 7.4 7.4 7.4	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization Secondary Phosphine-Borane Adducts Chloromethyloxazolines Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling Deprotection and Complex Synthesis Phosphinines as Ligands in Catalysis Synthesis of Diene-Moiety Synthesis of Phosphaalkyne [4+2] Cycloaddition of α-Pyrone and tert-Butylphosphaalkyne Analogous Phosphininoxazolines	120 121 124 129 138 139 144 150 169 171 173
7.2 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.4 7.4 7.4 7.4 7.4	Working Techniques New PHOX Ligands for Enantioselective Hydrogenation Phosphinoacetic Acid-Borane Adducts Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization Secondary Phosphine-Borane Adducts Chloromethyloxazolines Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling Deprotection and Complex Synthesis Phosphinines as Ligands in Catalysis Synthesis of Diene-Moiety Synthesis of Phosphaalkyne [4+2] Cycloaddition of α-Pyrone and tert-Butylphosphaalkyne Analogous Phosphininoxazolines A Related Chiral Chelating Phosphininimidazoline	120 121 124 129 138 139 144 150 169 171 173 176

7.4.8	Towards 6-Ring-Chelating Phosphininoxazolines	194
7.5	Asymmetric Catalytic Intramolecular Pauson-Khand Reaction	201
7.5.1	Substrate Synthesis	202
7.5 2	Products of ACPKR	205
7.6	Rhodium-Silylene Complexes	208
7.6.1	Synthesis of Silylenes	208
7.6.2	Synthesis of Complexprecursors	211
7.6.3	Synthesis of Silylene Complexes	212
8 Ap	pendix	217
8.1	X-Ray Crystal Structures	217
9 Bi	bliography	225