Transition Metal Complexes with P,N-Ligands and Silylenes: Synthesis and Catalytic Studies

Inauguraldissertation

zur
Erlangung der Würde eines Doktors der Philosophie

vorgelegt der
Philosophisch-Naturwissenschaftlichen Fakultät
der Universität Basel

von

Eva Neumann
aus Hannover / Deutschland

Basel 2006

Genehmigt von der Philosophisch-Naturwissenschaftlichen Fakultät auf Antrag von:

Prof. Dr. Andreas Pfaltz

Prof. Dr. Edwin Constable

Basel, den 14. Februar 2006

Prof. Dr. Hans-Jakob Wirz

Dekan

dedicated to my parents

Acknowledgments

I would like to express my gratitude to my supervisor, Professor Dr. Andreas Pfaltz for giving me the opportunity of joining his group, as well as for his constant support, confidence and encouragement over the last four years.

Special thanks to Professor Dr. Edwin Constable who agreed to co-examine this thesis, and to Professor Dr. Marcel Mayor for chairing the exam.

Furthermore, I would like to thank Professor Dr. Bernhard Breit and Dr. Evelyn Fuchs for their help with the phosphaalkyne synthesis, and sharing their glassware and expert knowledge with me.

I am grateful to Markus Neuburger for recording numerous X-ray data sets, for teaching me to refine X-ray structures, and for his constant and patient support. He and and Dr. Silvia Schaffner are also acknowledged for the refinement of some X-ray structures.

Thanks to Dr. Klaus J. Kulicke for recording ^{29}Si NMR and difference NOE spectra, introducing me to recording 2D NMR spectra, sharing his instrument time and for his help with the interpetation of the data. Dr. Daniel Häussinger is acknowledged for his valuable instructions in the ^{31}P NMR standardization and for recovering old NMR data.

Dr. Heinz Nadig recorded the EI and FAB mass spectra, my collegues Bruno Bulic, Christian Markert and Antje Teichert are acknowledged for measuring ESI mass spectra. Werner Kirsch determined all elemental analyses. I would also like to thank the crew from the workshop for their prompt and friendly help with our everyday technical troubles, and all the members of staff that run the department and made work efficient and enjoyable.

Special thanks to Dr. Valentin Köhler, Antje Teichert, Dr. Cara Humphrey and Marcus Schrems for proof-reading the manuskript.

A big thanks goes to the past and present members of the Pfaltz group for the good working atmosphere and collaboration. I especially like to thank my colleagues from lab 208 for an enjoyable time and for yummy lab dinners.

Contents

Abbreviations

3-NBA	3-nitro-benzyl alcohol (matrix for FAB-MS)
Å	Ångström (10^{-10} m)
ACPKR	asymmetric catalytic Pauson-Khand reaction
Ar	aryl
BAr_F	tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
BICP	2,2'-bis-(diphenylphosphino)-1,1'-di-cyclopentane
BINAP	2,2'-bis-(diphenylphosphino)-1,1'-bi-naphthalene
BOX	bisoxazoline
br	broad (NMR, IR)
c	concentration
CAMP	(2-methoxyphenyl)methylphenyl-phosphine
cat.	catalyst
CCDC	Cambridge Crystallographic Data Centre
cod	1,5-cyclooctadiene
conv.	conversion
COSY	correlation spectroscopy (NMR)
Cy	cyclohexyl
□	chemical shift
d	doublet (NMR)
DIOCP	2,3-*O*-isopropylidene-2,3-dihydroxy-1-(dicyclohexyl-phosphino)-4-(diphenyl-phosphino)butane
DIOP	2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenyl-phosphino)butane
DIPAMP	bis[(2-methoxyphenyl)phenylphos-phino]ethane
DMAP	dimethylaminopyridine
DMF	*N*,*N*-dimethyformamide
DMSO	dimethylsulfoxide
ebthi	ethylene-1,2-bis(□^{5}-4,5,6,7-tetrahydro-1-indenyl)
EDC	ethyl-*N,N'*-dimethylamino-propyl-carbodiimide hydrochloride
ee	enantiomeric excess
EI	elelctron impact ionization (MS)
eq.	equivalent
ESI	electrospray ionization
FAB	fast atom bombardment
FTIR	Fourier transform infra-red
GC	gas chromatography
HMBC	heteronuclear multiple-bond correlation (NMR)
HMQC	heteronuclear multiple quantum coherrence
HOBt	1-hydroxybenzotriazole
HPLC	high performance liquid chromatography
Hz	Hertz
i	iso
J	coupling constant
m	multiplet (NMR)
m.p.	melting point
MS	Mass spectroscopy
nd	not determined
NHC	*N*-heterocyclic carbene
NHS	*N*-heterocyclic silylene
NMR	nuclear magnetic resonance
NOE	Nuclear Overhauser effect
Ph	Phenyl
PHOX	phosphinooxazoline
ppm	parts per million
***pse*t**	*pseudo*-triplet (NMR)
q	quartett (NMR)
rac.	racemic
R_f	retention factor
RT	room temperature
s	singlet (NMR), strong (IR)
sat.	saturated
sh	shoulder (IR)
t	triplet (NMR)
tert	tertiary
THF	tetrahydrofurane
TLC	thin-layer chromatography
TOF	turnover frequency
TON	turnover number
t_R	retention time
w	weak (IR)
$\tilde{\nu}$	wave number (IR)

Chapter 1

Introduction

1 Introduction

1.1 Ligands - Coordination Chemistry - Catalysis

The term ligand [latin, ligare = bind] has its origin in coordination chemistry. It denotes a molecule that is able to bind to a metal center in most cases *via* one or several free electron pairs.[1] Ligands can be described by the number of electron-pair donor atoms as monodentate, bidentate, tridentate *etc.* ligands. The latter are also called chelating ligands [greek, chele = (crab's) claw]. A typical classification of ligands is according to their electronic properties. They serve either as a σ-donating, σ-donating/π-accepting, or σ,π-donating/π-accepting ligands.[2] A more practical, often encountered approach is the classification of ligands according to their donor atoms, especially when larger molecules and molecules containing heteroatoms are regarded (compare 1.2).

Coordination chemistry was already established in the 19th century. In 1893 Alfred Werner suggested an octahedral arrangement of ligands coordinated to a central metal ion for many compounds. This explained, for example, the appearance and reactivity of four different cobalt(III) complexes (Figure 1.1), when $CoCl_2$ is dissolved in aqueous ammonia and then oxidized by air to the +3 oxidation state. The formulas of these complexes can be written as depicted in Figure 1.1. Werner's work was rewarded with the Nobel prize in 1913.[3]

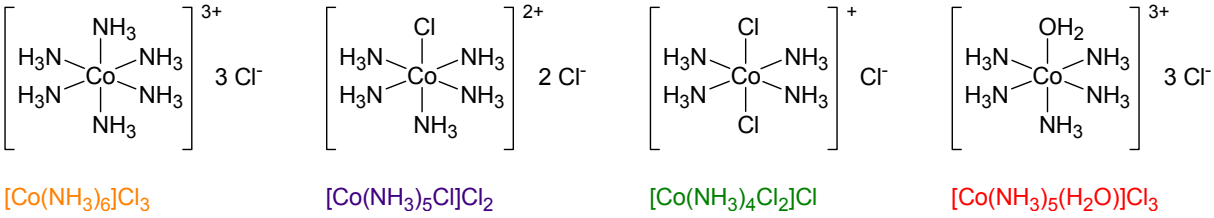


Figure 1.1: *"Werner-complexes"*

Coordination chemistry is mainly chemistry of transition metal compounds. Here, ns-, np- and nd-orbitals are valence orbitals, while the participation of nd-orbitals in main group metal chemistry is the exception. Figure 1.2 shows the different orbital interactions: σ-donating interaction takes place between s, p_z and d_z^2-orbitals of the transition metal and s and p_z orbital of the ligand. π-donating and π-accepting (retrodative) interaction occurs between p_x, p_y, d_{xz}, and d_{xy} atomic orbitals of the transition metal and p_x, p_y, d_{xz}, and d_{xy} of the ligand.

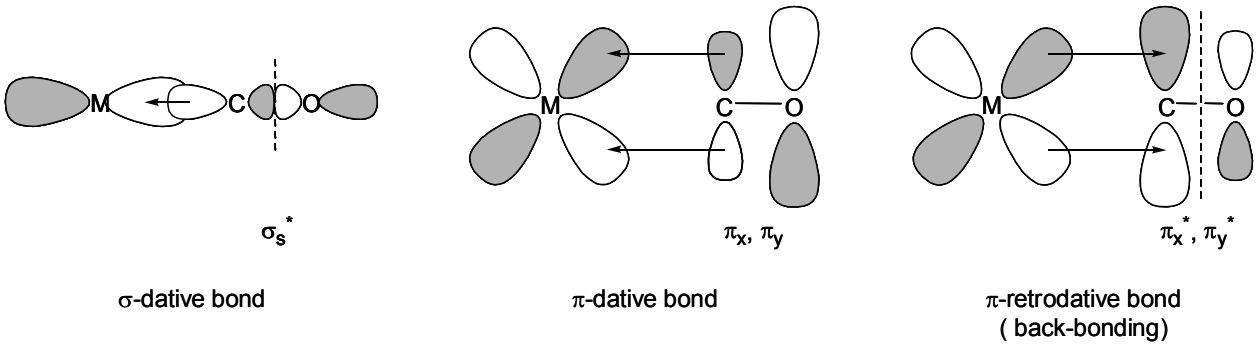


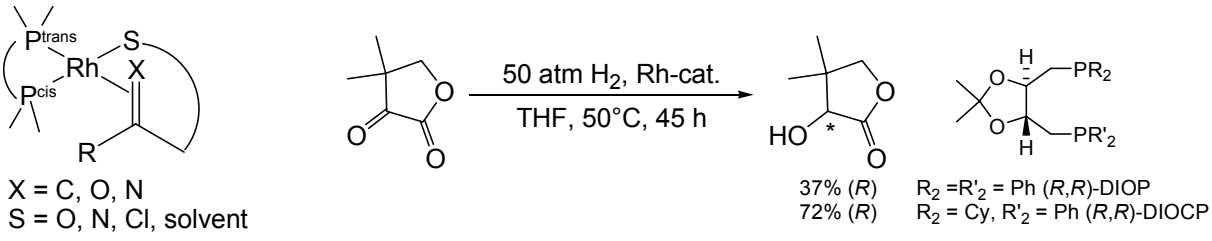
Figure 1.2: Orbital interactions in transition metal complexes

Transition metal complexes play an important role in homogeneous catalysis. Coordination at the metal center brings the reactants in close proximity and thus accelerates the reaction. Sometimes reaction can only take place when one or both reactants are activated through coordination. For example, coordination of a substrate to the metal can facilitate nucleophilic attack at the substrate. If the catalyst is chiral, *e.g.* through coordination of a chiral ligand, it can allow enantioselective syntheses through asymmetric induction. Normally, the metal component activates the reactants, while the chiral ligand is responsible for enantiocontrol.

1.2 Important Ligand-Classes

For a long time, the dominating ligands in asymmetric catalysis were C_2-symmetric.[4] C_2-symmetric ligands lead to fewer isomeric metal complexes in comparison to non-symmetric ligands, and thus to fewer transition states in catalysis. That renders them favourable objects for the determination of reaction mechanisms and the elucidation the origin of the observed asymmetric induction.

However, more recently nonsymmetrical ligands have found increasing attention. In fact, efficient nonsymmetrical ligands were in some reactions superior to C_2-symmetric ligands. This was well illustrated for rhodium-catalyzed asymmetric hydrogenation, where the intermediates in the catalytic cycle are nonsymmetrical (Scheme 1.1, left).[5]



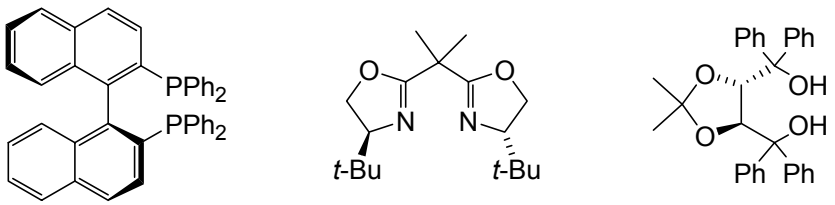
Scheme 1.1: Desymmetrized diphosphine in rhodium-catalyzed hydrogenation

In consequence the two phosphine groups interact with the substrate in a different manner. Since electronic effects are delivered preferentially to the *trans*-coordinated ligand, P^{trans} executes mainly an electronic effect. P^{cis}, in contrast, exerts mainly steric interactions with the substrate. Indeed, DIOCP ligand was more effective than DIOP in the asymmetric hydrogenation of ketopantolactone (Scheme 1.1, right).

1.2.1 P,P-Ligands: Diphosphines

Following several decades of developments, the use of asymmetric catalysis allows nowadays the enantioselective synthesis of numerous biologically active molecules or natural products.[6,7] The first breakthroughs in asymmetric catalysis have been carried out in the field of rhodium-catalyzed homogeneous hydrogenation. The use of C_2-symmetric phosphines as chiral inducers led to the formation of products with significant enantiomeric excesses. Kagan's work using the tartrate-derived diphosphine DIOP, and Knowles', using the P-chiral diphoshine DIPAMP, are the most salient pioneering examples of such catalytic systems (compare 2.1).[8,9]

The most prominent ligand among the diphosphines is probably BINAP **1**, an axially chiral ligand that was developed by Noyori *et al.* in 1980.[10] Being a so-called "privileged" ligand (Figure 1.3),[11] BINAP is used in numerous asymmetric catalytic reactions, such as hydrogenation, Diels-Alder reaction, Mukaiyama aldol reaction, *etc.*, where excellent results are obtained.[12,13,14]



BINAP **1** BOX **2** TADDOL **3**

Figure 1.3: Some "priviledged" ligands

1.2.2 N,N-Ligands: Semicorrins and Bisoxazolines

Chiral C_2-symmetric semicorrins were introduced as ligands in asymmetric catalysis by Pfaltz *et al.*.[15] These ligands were inspired by corrinoid and porphinoid metal complexes, which are known as biocatalysts. The flexibility of the semicorrin ligand framework is restricted by the inherent π-system and the two five-membered rings. The substituents at the two stereogenic centers shield the metal center from two opposite directions. They are expected to strongly influence the reaction taking place in the coordination sphere. Semicorrins were found to give

excellent results in copper-catalyzed cyclopropanation of olefins and cobalt-catalyzed conjugate reduction of α,β-unsaturated carboxylic acid derivatives.[16]

A related structural motive is found in bisoxazoline (BOX) ligands **2**, which were reported independently by several research groups.[17] BOX ligands are especially attractive, because they are easily accessible from amino alcohols which are derived from natural amino acids in enantiomerically pure form. This allows facile structural modification for different applications. More recently, related ligands (borabox, azabox) were developed, which are bearing heteroatoms in the bridge that connects the two oxazoline rings.[18,19]

1.2.3 P,N-Ligands: Phosphinooxazolines

Pfaltz, Helmchen[20] and Williams[21] developed independently a new class of ligands, the phosphinooxazoline (PHOX) ligands **4**. The combination of a P-ligand part and a chiral N-ligand part is another way to build up non-C_2-symmetric, chelating ligands, wherein the two ligand parts are more fundamentally distinguished, compared to the modified diphosphine ligands mentioned in 1.2. Here, the "soft" P-ligand exhibits π-acceptor properties, while the "hard" N-ligand is dominantly acting as a σ-donor. The beneficial effect of the combination of two ligands with different electronic properties is well illustrated in the palladium-catalyzed allylic alkylation (Figure 1.4, left). Crystal structure and NMR data confirmed that palladium-allyl-PHOX complexes exhibit a strong electronic differentiation of the allylic termini, and it was observed that these complexes are predisposed to be attacked at the allylic carbon atom trans to the phosphino group.[20,22] Electronic differentiation of this type has also been calculated by Ward[23] and demonstrated by Moberg *et al.* using *pseudo*-C_2-symmetric ligands (*e.g.* **5**), *i.e.* with sterical symmetry and electronic asymmetry (*e.g.* Figure 1.4, right).[24]

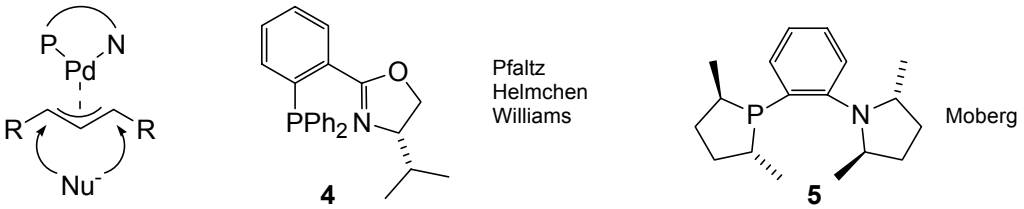


Figure 1.4: Regioselectivity in palladium-catalyzed allylic alkylation (*left*), different P,N-ligands **4** and **5**.[15,24]

PHOX ligands are modularly constructed and can be synthesized in few steps. This enables a relatively easy variation and allows to tailor the ligand according to its application. Apart from allylic alkylation, PHOX ligands were also applied in other metal-catalyzed processes, including Heck reactions,[25] silver-catalyzed 1,3 dipolar cycloaddition,[26] and iridium-

catalyzed hydrogenation.[27] The latter reaction was tested with numerous PHOX analogues, which are able to hydrogenate unfunctionalized aryl- and alkyl-substituted unfunctionalized and functionalized olefins, with high enantioselectivities and at low catalyst loadings.

1.2.4 C-Donor Ligands: *N*-Heterocyclic Carbenes

N-Heterocyclic carbenes (NHCs) were developed independently by Wanzlick[28] and Öfele in 1968.[29] However, it took about twenty years until an adamantyl-substituted carbene was isolated by Arduengo,[30] and only in the mid 1990s NHCs were finally introduced in asymmetric catalysis by Enders[31] and Herrmann.[32] Since then, the scope of catalytic reactions has largely expanded, and NHCs are now applied in a variety of metal-catalyzed asymmetric reactions, such as olefin-metathesis, allylic alkylation, transfer hydrogenation, 1,4-addition and others.[33,34,35,36]

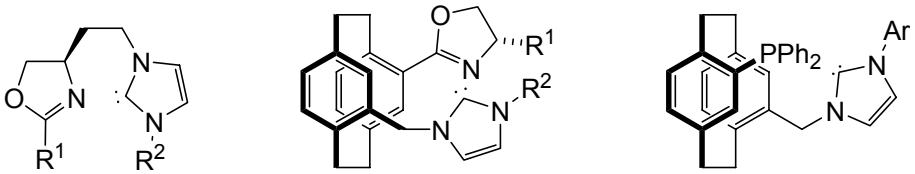


Figure 1.5: Oxazoline-NHC ligand **6** and paracyclophane based NHC chelating ligands **7** and **8**[37,38]

More recently, NHCs were incorporated in chelating P,C- and N,C-ligands, such as **6-8** (Figure 1.5), and tested in iridium-catalyzed hydrogenation. Burgess *et al*. reported high enantioselectivities for a range of olefins using a bidentate oxazoline-NHC ligand **6**.[38]

1.3 Objectives of this Work

Although many studies are carried out in order to design new catalysts on a rational basis, finding new selective ligands is also a matter of luck and intuition. Laborious screening is still the major way in obtaining taylor-made catalyst systems for a specific substrate.

Iridium-complexes derived from P,N-ligands represent a highly active class of catalysts for asymmetric hydrogenation. We were interested to extend our library of P,N-ligands (Figure 1.6), and to investigate the influence of a smaller ring-chelate **10**, since most previously tested ligands form six-ring-chelates. Another objective was to examine the effect of a strong π-accepting and planar phosphorus-moiety, as is found in λ^3-phosphinines **11**.

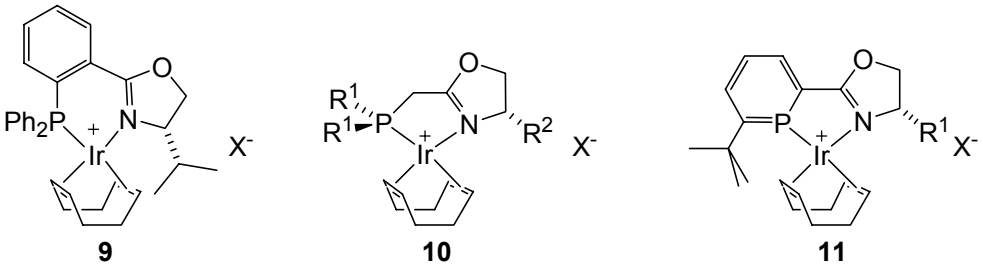
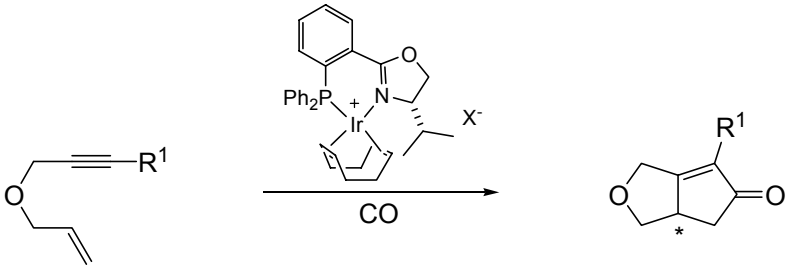


Figure 1.6: Cationic iridium-PHOX complexes

In addition, we were interested in the scope of iridium-PHOX complexes in other catalytic reactions. Initial studies towards the application of this system in asymmetric catalytic Pauson-Khand reaction have shown promising results (Scheme 1.2). The studies were to be completed regarding pressure influence, reproducability and the influence of the counteranion on the enantioselectivity of the reaction.



Scheme 1.2: Iridium-catalyzed asymmetric intramolecular Pauson-Khand reaction

The popularity of NHCs raised the question why their group 14 heavier analogues have not experienced the same attention in catalysis to date.[39] Although Fürstner *et al.* have published the application of a silylene-palladium complex **12** in Suzuki cross-coupling,[40] the actual catalytically active species remains unknown. No further attemps of using silylenes (Figure 1.7) in catalysis have been reported.

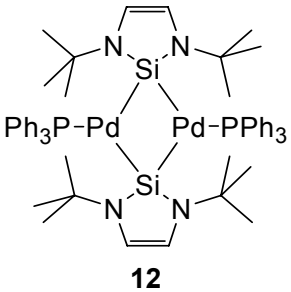


Figure 1.7: Dinuclear palladium-silylene complex **12**[40]

Inspired by the recent success of NHCs in the iridium catalyzed hydrogenation, we envisioned the synthesis of silylene containing iridium- and rhodium-complexes, suitable for hydrogenation studies.

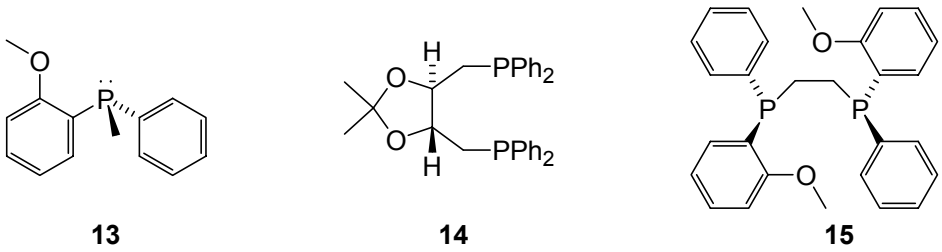
Chapter 2

New PHOX Ligands for Enantioselective Hydrogenation

2 New PHOX Ligands for Enantioselective Hydrogenation

2.1 Hydrogenation of Functionalized Alkenes

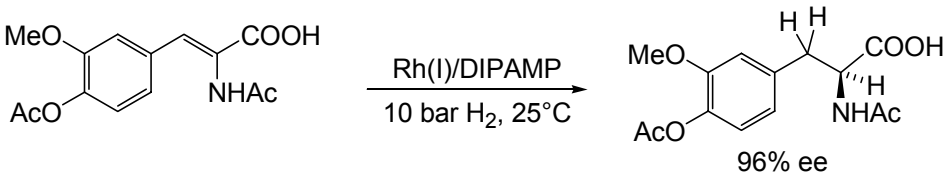
Asymmetric hydrogenation of alkenes has the longest history in enantioselective catalysis and is the best studied reaction with the largest number of industrial applications today.[41,42] Homogeneous hydrogenation catalysts were first introduced in 1961 by Halpern. [43] For the first time simple alkenes, such as maleic, fumaric, and acrylic acids, could be reduced under homogeneous conditions using a chlororuthenate(II) complex. Other significant advances were made by Wilkinson and co-workers, who developed a number of effective rhodium and ruthenium catalysts.[44] $RhCl(PPh)_3$ (*Wilkinson's* complex), was shown to effect hydrogenation reactions with site- and diastereoselectivity under mild conditions.[45] Terminal double-bonds could be efficiently reduced in the presence of hindered double-bonds and functional groups.



13 **14** **15**

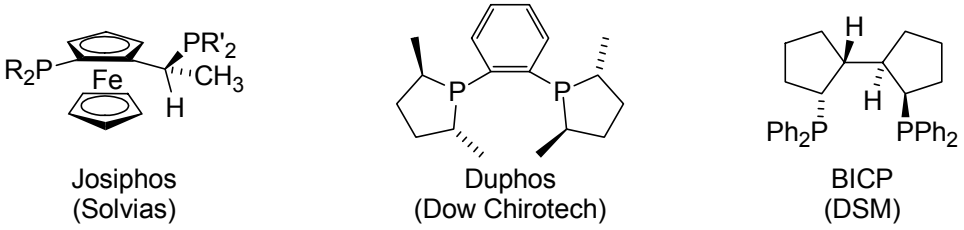
Figure 2.1: Early developments of chiral phosphines: CAMP **13**,[46,47] DIOP **14**,[8] DIPAMP **15**[9]

Knowles[46] and Horner[47] extended this method by introducing chiral phosphorus ligands. A major advance was made by the development of chiral chelating diphosphines such as Kagan's DIOP **14**, a tartric acid derived diphosphine (Figure 2.1).[8] The respective rhodium(I) catalyst was found to reduce β-substituted α-acetamidoacrylic acids with optical yields in the range of 70 to 80% ee. It was again Knowles who developed the first industrially used rhodium-catalyst.[9] The rhodium-DIPAMP catalytic system which possesses two stereogenic phosphorus atoms, and can be regarded as a second generation of the chiral monophosphine CAMP **13** (Figure 2.1). This development allowed Monsanto company the industrial scale production of an L-DOPA precursor in the 1970s using enantioselective reduction (Scheme 2.1).[48]



Scheme 2.1: Rhodium catalyzed enantioselective hydrogenation of an L-DOPA precursor

Numerous chelating diphosphines have been synthesized, a few of which are commercially available today (Figure 2.2). In the 1980s focus has changed towards chiral ruthenium catalysts,[49,50] which were applicable to a wider range of substrates, including allyl alcohols, with respectable results. However, both rhodium and ruthenium catalysts can only be applied in the reduction of functionalized olefins that bear a coordinating group next to the carbon-carbon double bond (with the exemption of 1,1-disubstituted alkenes).

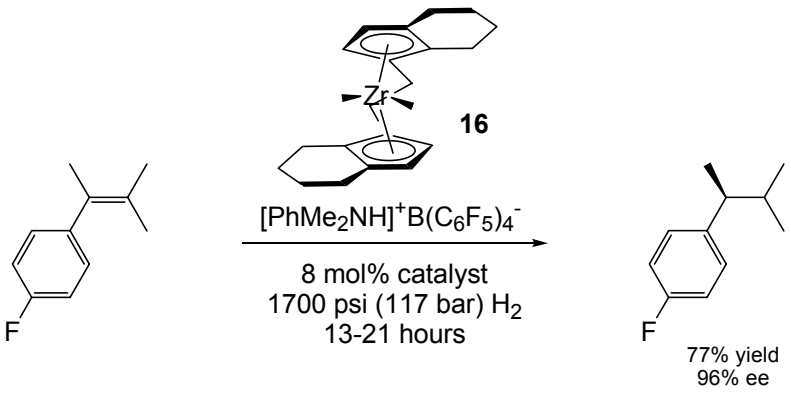


Josiphos (Solvias) | Duphos (Dow Chirotech) | BICP (DSM)

Figure 2.2: Some commercially available chelating diphosphines

2.2 Hydrogenation of Unfunctionalized Alkenes

In contrast to the enantioselective hydrogenation of functionalized alkene substrates, where the additional coordinating sites are crucial for achieving high enantioselectivity, the hydrogenation of prochiral unfunctionalized alkenes was much less delveloped. While Rhodium diphosphine catalyst systems showed only moderate selectivity,[51] very good results were achived with chiral group four metallocene complexes. A reduced form of Brintzinger's bis(tetrahydroindenyl)titanium binaphtholate catalyzed the hydrogenation of a number of trisubstituted arylalkenes with selectivities above 90% ee.[52] More recently a related cationic zirconocene **16** was found to reduce tetrasubstituted alkenes with up to 99% ee.[53] However, relatively long reaction times, high pressure and relatively high catalyst loadings are required due to the rather low catalyst activity (Scheme 2.2).



Scheme 2.2: Enantioselective hydrogenation of tetrasubstituted alkene with cationic zirconocene

In 1976 Crabtree developed a cationic iridium catalyst **17** which was found to reduce tri- and tetrasubstituted alkenes with high activity (Figure 2.3).[54] Subsequently, Pfaltz has reported a new class of chiral iridium catalysts which is structurally related to Crabtree's catalyst.[55] These chiral iridium complexes with phosphinooxazoline (PHOX) ligands catalyzed the hydrogenation of various aryl-substituted alkenes with high activity and enantioselectivity.[56,20,27]

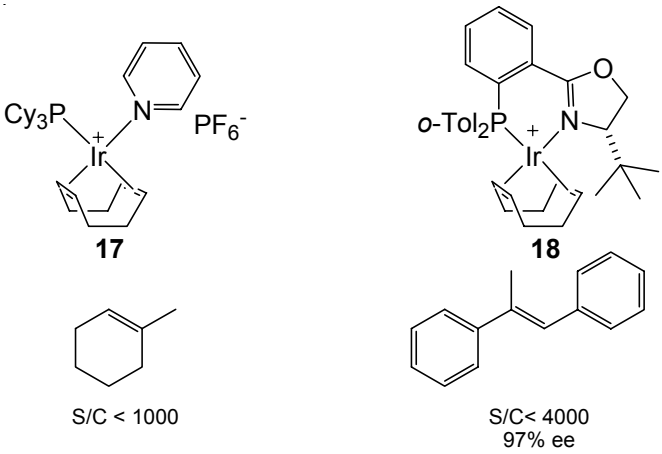
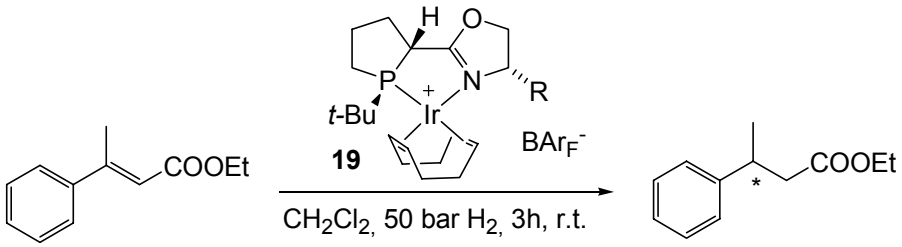


Figure 2.3: Crabtree's catalyst (*left*) and one of Pfaltz' catalyst (*right*)

Encouraged by those results, numerous related chelating ligands have been developed by Pfaltz *et al.*[57], Burgess *et al.*[58] and others.[59] Besides phosphines, more electron-poor phosphinites, phosphites and phosphoramidite ligands were employed as P-donors. Chelating *N*-heterocyclic carbenes and pyridine-based *N*-donors were also investigated. By tuning the steric and electronic properties through varying the substitution pattern, the ligands can be optimized for various substrates.

2.3 Objectives of this Chapter

Among others[60], Smidt *et al.*[61] and Zhang *et al.*[62] have prepared phosphinooxazolines ligands containing a stereogenic phosphorus atom. Zhang published the use of phospholane-oxazoline ligands for iridium-catalyzed asymmetric hydrogenation. These ligands, bearing a chiral phosphacycle next to the amino alcohol derived chiral oxazoline moiety, showed good results in the hydrogenation of methylstilbene derivatives. Furthermore, very good results were achieved in the hydrogenation of β-methylcinnamic esters.

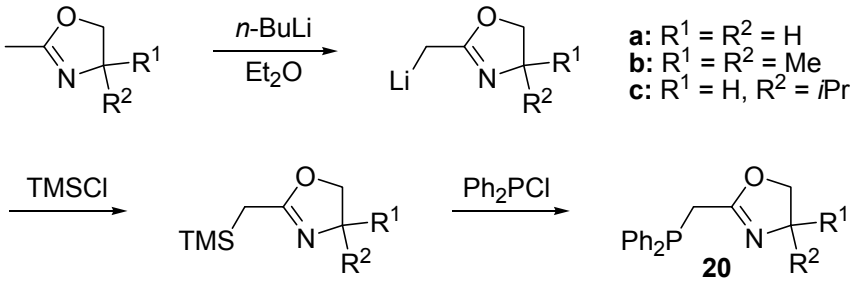


catalyst	**a**	**b**	**c**	**d**	**e**	**f**
R =	^{i}Pr	^{t}Bu	Ph	Bn	^{i}Bu	^{i}Pr
conf. ligand	*S*	*S*	*S*	*S*	*S*	*R*
ee [%]	94	91	98	92	95	93
conf. product	*R*	*R*	*R*	*R*	*R*	*S*

Scheme 2.3: Hydrogenation of (*E*)-ethyl-3-phenyl-but-2-enoate

Catalysts **a** and **f** (Scheme 2.3) are diastereoisomers and differ only at the phosphorus stereocenter. For the hydrogenation of (*E*)-ethyl-3-phenyl-but-2-enoate, essentially the same enantioselectivity is observed: 94% ee (*R*) versus 93% ee (*S*). Although the situation is somewhat different for unfunctionalized (*E*)-1,2-diphenyl-1-propene (91% ee (*R*) versus 77% ee (*S*)), it can be assumed that the influence of the chiral phospholane moiety is relatively small since only weak *matched-mismatched* behaviour is observed. It can be assumed that the absolute configuration of the phospholane is not responsible for enhanced enantioselectivity. We therefore decided to synthesize related phosphinoxazolines, containing a non-chiral phosphorus centre.

Diphenylphosphinomethyloxazolines of the same ligand-type have been previously published, and tested in palladium-catalyzed allylic alkylation and ruthenium catalyzed transfer hydrogenation.[63] These ligands were prepared according to the method depicted in Scheme 2.4. Methyloxazolines were lithiated and then transmetallated with TMS-chloride. According to Braunstein *et al*., reaction with chlorodiphenylphosphine afforded the ligands **20 a**-**c** in up to 75% yield.



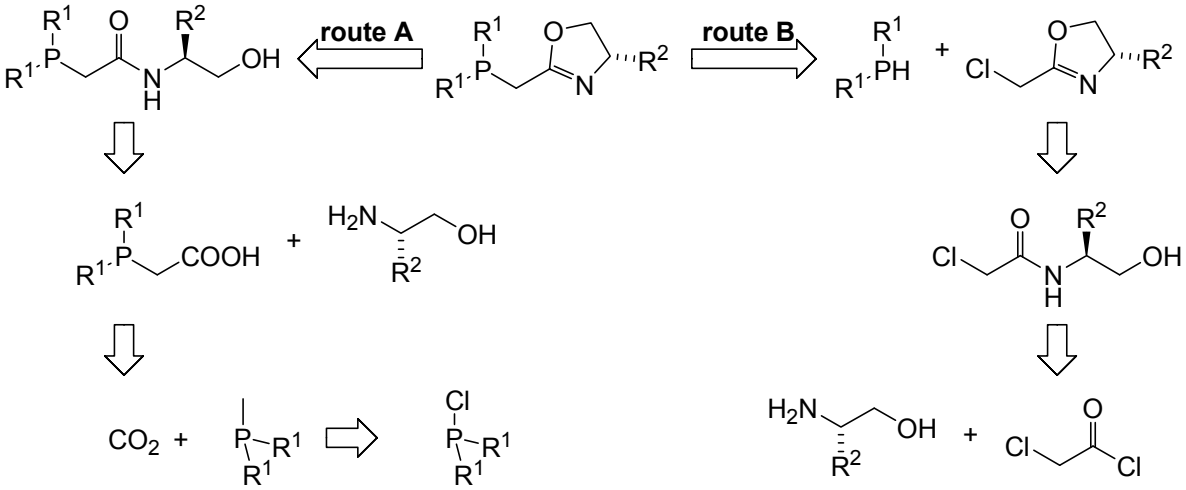
Scheme 2.4: Synthesis of diphenylphosphineoxazolines[63]

Due to the strong basic conditions of the synthesis (an excess of *n*-BuLi is used), the use of phenyl substituted oxazolines would probably lead to racemization at the stereogenic centre. A more general route to ligands of this type was therefore investigated.

During the course of this work Imamoto *et al.* published the synthesis of P-stereogenic ligands of the same type as **20**, and their application in palladium-catalyzed allylic alkylation.[64] His approach is related to route A (see below).

2.4 Ligand and Complex Synthesis

Two new routes to chiral phosphinomethyloxazolines were developed based on the retrosynthetic analysis depicted in Scheme 2.5. The ligand can be prepared by ring-closure of the respective amide, which in turn is derived from the amide coupling of a chiral amino alcohol with a phosphinoacetic acid (Scheme 2.5, route A). The latter can be obtained from the corresponding methylphosphine. In a more convergent route a secondary phosphine can be coupled with a 2-chloromethyl-2-oxaline. The latter ligand can be synthesised from chloroacetyl chloride and a chiral amino alcohol *via* amide coupling and ring-closure.



Scheme 2.5: Retrosynthesis of phosphinomethyl-oxazolines

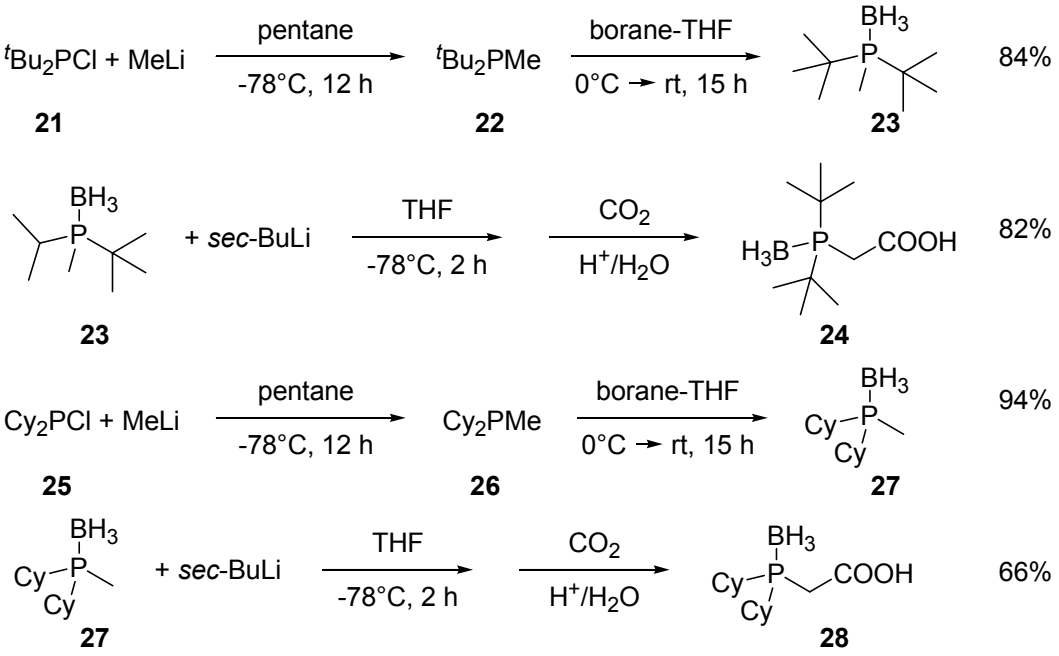
Since phosphine compounds are rather air-sensitive we chose to borane-protect the phosphino group to prevent oxidation. This facilitates the purification of the intermediates since phosphine borane-adducts are relatively air-stable and usually give crystalline compounds. The protective group was removed prior to complex synthesis. Three ligands were prepared according to route A ($R^1 = R^2 = {}^t$Bu; $R^1 = {}^t$Bu, R^2 = Ph; R^1 = Cy, R^2 = Ph). However, it was observed that ring-closure conditions also cleaved the protective group resulting in only moderate yields. Particularly in the case of R^1 = Ph deprotection was comparatively fast, so that the phosphine was almost completely oxidized. For this reason we chose route B

(Scheme 2.5) in this case. Since it was observed that the convergent route was generally higher yielding, it was also employed for the remaining dialkylphosphinomethyl-oxazolines.

2.4.1 Phosphinoacetic Acid-Borane Adducts

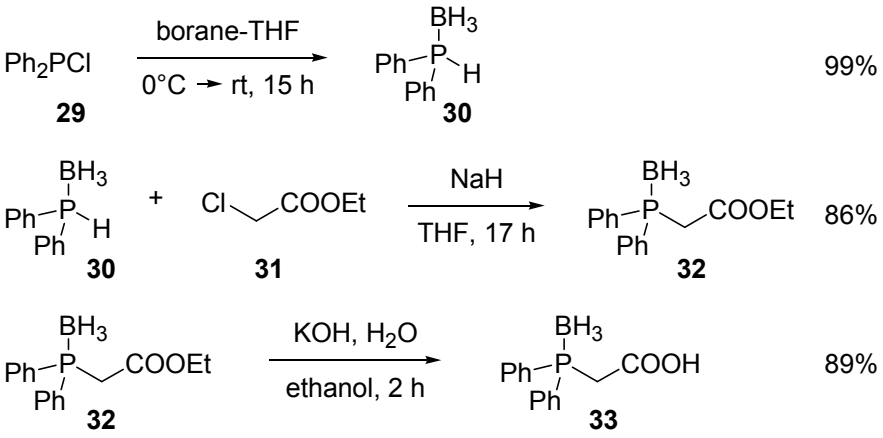
Similar to Zhang *et al.*[62] the linear approach was initially chosen (route A). It starts with the preparation of phosphinoacetic acids, which are later coupled with the amino alcohol to the corresponding amides. The latter can then be cyclized to the respective oxazolines.

The phosphinoacetic acids were prepared according to two different procedures. Di-*tert*-butylchlorophospine and chlorodicyclohexylphosphine were transformed to the corresponding methylphosphines, by use of methyl lithium, and borane-protected in one pot. In a second step, the methylphosphines were lithiated with *sec*-BuLi at low temperature. Treatment with CO_2 and acidic workup afforded the dialkylphosphinoacetic acid-borane adducts **24** and **28** in good yields.[65] (Scheme 2.6)



Scheme 2.6: Preparation of dialkylphosphinoacetic acid-borane adducts **24** and **28**

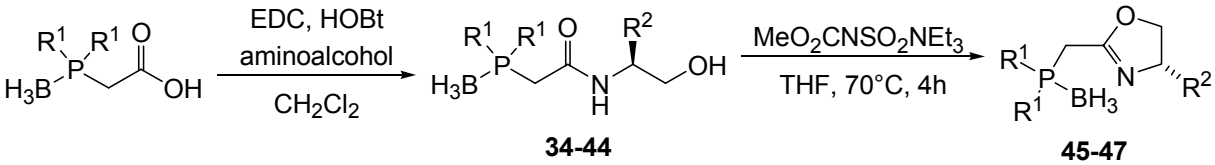
Chlorodiphenylphosphine was also transformed to the methylphosphine-borane adduct using methyl Grignard. However, the subsequent lithiation was found to be unselective. A procedure from Ebran *et al.*[66] was therefore used in which borane-protected diphenyl-phosphine was treated with chloroacetic acid ethylester in presence of NaH. Saponification of the ester **32** afforded the desired diphenylphosphinoacetic acid-borane-adduct **33** (Scheme 2.7).



Scheme 2.7: Preparation of diphenylphosphino acetic acid-borane adduct **33**

2.4.2 Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization

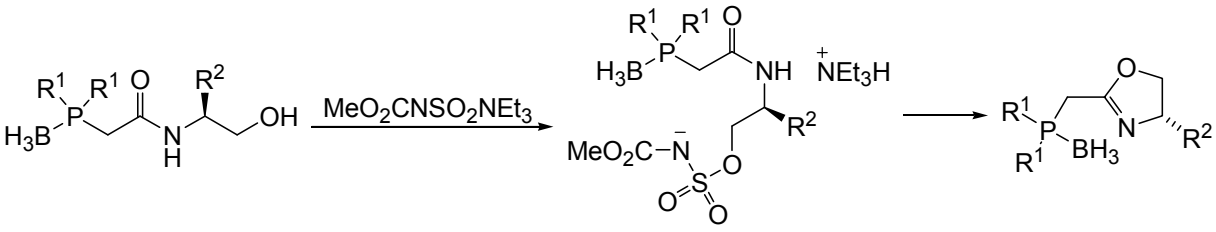
The phosphinoacetic acid-borane adduct was condensed with chiral amino alcohols using ethyl-*N,N'*-dimethylamino-propyl-carbodiimide hydrochloride (EDC) (which gives a water soluble urea by-product thus facilitating work up) and 1-hydroxybenzotriazole (HOBt) as an activating agent for the acid compound.[67] The amides obtained were used without further purification (Scheme 2.8). Ring-closure was performed with (methoxycarbonyl-sulfamoyl) triethylammonium hydroxide, inner salt (*Burgess'* reagent)[68] to give the phosphanyl-methyl-4,5-dihydro-oxazoline-borane adducts **45-47**. *Burgess'* reagent provides a reactive alcohol derivative and acts as an intramolecular base to facilitate the cyclization process. In contrast to dehydration to olefins (which is observed for secondary and tertiary alcohols) primary alcohols prefer to undergo substitution. In this case ring-closure is achieved by intramolecular S_N2 reaction of the intermediate sulfonate. (Scheme 2.9)



R^1	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph
R^2	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Ph	^{i}Pr
amide	**34**	**35**	**36**	**37**	**38**	**39**	**40**	**41**	**42**	**43**	**44**
oxazoline	**45**	-	**46**	-	-	-	**47**	-	-	-	-
$yield_{oxazoline}$	56%	-	43%	-	-	-	94%	-	-	-	-

Scheme 2.8: Phosphanyl-methyl-4,5-dihydro-oxazoline-borane adducts **45-47** *via* amides **34**, **36**, **40**

The use of *Burgess'* reagent proved to be problematic for diphenylphosphino acetamide-borane-adducts since the liberated triethylamine deprotected the less basic diphenylphosphine-derivatives. Di-*tert*-butyl- and dicyclohexyl-derivatives reacted with moderate to good yields to afford the corresponding oxazolines **45** to **47**, since deprotection of the more electron-rich phosphino groups is hampered.[69]



Scheme 2.9: Activation of phosphino acetamide-borane-adduct with *Burgess'* reagent

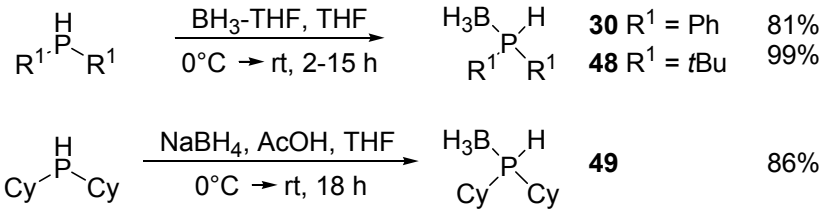
Confronted with the unwanted inherent deprotection, an alternative route was chosen (route B). This route consists of the coupling of secondary phosphine-borane adducts and a 2-chloromethyl-2-oxazoline. The borane adducts were synthesized by addition of a borane source to the secondary phosphines. 2-Chloromethyl-2-oxazolines were obtained by reaction of chloroacetyl chloride with the respective amino alcohol in the presence of triethylamine. The amide was then cyclized as described above, using *Burgess'* reagent.

2.4.3 Secondary Phosphine-Borane Adducts

According to route B (Scheme 2.5) the phosphinomethyl-oxazoline was synthesized from a secondary phosphine and 2-chloromethyl-2-oxazoline. Again we chose to borane-protect the phosphino group to prevent oxidation during work-up.

The most common approaches towards the synthesis of phosphine–boranes employ the reaction of the parent phosphine with borane sources such as borane–tetrahydrofuran and borane–dimethylsulfide.[70] The use of sodium borohydride as a borane source, in conjunction with a hydride acceptor such as acetic acid, also yields phosphine-borane adducts. The latter method was extended to the one-pot reduction-protection procedure of phosphine oxides or chlorophosphines without isolation of the intermediate phosphines, in the presence of lithium aluminium hydride and cerium trichloride.[71]

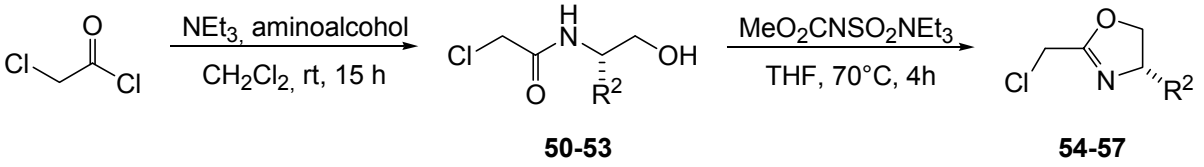
In the present case, di-*tert*-butylphosphine and diphenylphosphine were reacted with borane-THF-adduct, whereas dicyclohexylphosphine was reacted according to McNulty *et al.* with sodium borohydride in THF-acetic acid (Scheme 2.10). The respective secondary phosphine-borane adducts **30, 48** and **49** were obtained in good to very good yields.[72]



Scheme 2.10: Synthesis of secondary phosphine-borane adducts[72]

2.4.4 Chloromethyloxazolines

2-Chloromethyl-2-oxazolines detailed in Scheme 2.11 were derived from 2-chloro-*N*-(1-hydroxymethyl)-acetamides and subsequent intramolecular S_N2 reaction. The amides were prepared from chloroacetyl chloride and an amino alcohol in dichloromethane in the presence of triethylamine. The amide coupling reaction proceeded smoothly to give the 2-chloro-*N*-(1-hydroxymethyl)-acetamides **50** to **53** in 73-95% yield. Ring-closure was performed as described above (see section 2.4.2) with *Burgess'* reagent in THF to afford the oxazolines **54** to **57** in 61-89% yield.

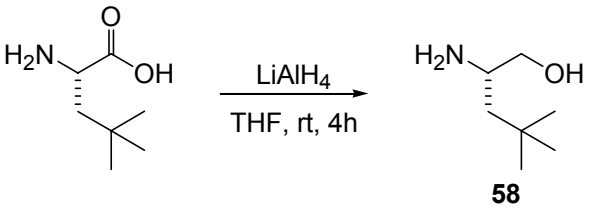


50-53 **54-57**

	50	**51**	**52**	**53**	**54**	**55**	**56**	**57**
R^2	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
yield	73%	74%	92%	95%	65%	89%	77%	61%

Scheme 2.11: Synthesis of chloromethyloxazolines **54-57**

To date, one of the best P,N-ligands for the hydrogenation of tetrasubstituted olefins is a neopentyl-substituted PHOX-ligand (compare 2.5.3, Figure 2.5). In order to test the influence of the neopentyl group in phosphinomethyl-oxazolines, the amino alcohol, derived from the non-natural amino acid (*S*)-neopentylglycine, was also synthesized (Scheme 2.12). (*S*)-Neopentylglycinol **32** was obtained by reduction of the corresponding amino acid with $LiAlH_4$ in 82% yield.[73]



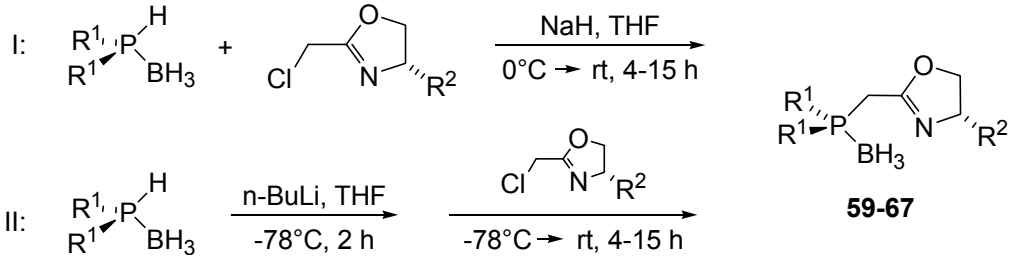
58

Scheme 2.12: Reduction of (*S*)-neopentylglycinol (*left*); neopentyl-substituted PHOX (*right*)

2.4.5 Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling

Route B (Scheme 2.5) towards phosphanyl-methyl-4,5-dihydro-oxazoline-borane adducts proceeds *via* direct coupling of a borane-protected secondary phosphine and a chloromethyloxazoline. In comparison to the linear synthesis A (2.4.2) this convergent route is more versatile. For example, it can be extended to more electron-poor phosphines which cannot tolerate the presence of a concurrent Lewis-base without suffering from deprotection and thus oxidation. In contrast to the synthesis of Sprinz *et al.*,[63] it also permits the synthesis of a broader range of oxazolines, such as phenylglycinol-derived oxazoline, without racemization of the stereogenic center.

The coupling was achieved by two slightly different variants of the same procedure (I and II in Scheme 2.13). Either borane-protected phosphine, 2-chloromethyl-2-oxazoline and NaH are reacted in one pot to give the product, or the phosphine is deprotonated at low temperature with *n*-BuLi and subsequent addition of the 2-chloromethyl-2-oxazoline gives the product in moderate to good yields. When phenylglycinol-derived oxazolines were used, a small excess of phosphine was applied to prevent racemization in the acidic benzylic position. Diphenylphosphine borane-adduct was usually deprotonated with NaH, while the protected dicyclohexylphosphine only reacted under more basic conditions. Phosphanyl-methyl-4,5-dihydro-oxazoline-borane adducts **59** to **67** were synthesized in moderate to very good yields. (Scheme 2.13)

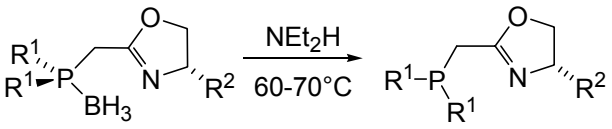


	59	**60**	**61**	**62**	**63**	**64**	**65**	**66**	**67**
R^1	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2	Np	^{i}Pr	^{t}Bu	Np	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
method:	**I**	**II**	**II**	**II**	**II**	**I**	**II**	**I**	**I**
yield:	57%	86%	89%	83%	82%	67%	35%	44%	91%

Scheme 2.13: Synthesis of phosphanyl-methyl-4,5-dihydro-oxazoline-borane adducts **33** to **41**

2.4.6 Deprotection and Complex Synthesis

Deprotection was accomplished in excess diethylamine at elevated temperature.[74] The reaction took one to five days, depending on the phosphorus substituents. Diphenylphosphine-derivatives usually reacted faster, which is in accordance to the enhanced reactivity (*i.e.* lower lewis-basicity) as discussed above (2.4.5).



68-79

Scheme 2.14: Deprotection of the phosphanyl-methyl-4,5-dihydro-oxazoline-borane adducts

The conversion was followed by ^{1}H and ^{31}P NMR. As expected, the deprotection was accompanied by a significant upfield shift of the phosphorus and the adjacent CH_2-group in ^{31}P NMR and the ^{1}H NMR spectrum, respectively. The phosphorus signal, which in the borane-protected compounds is broadened by a borane-coupling, was shifted about 20 to 35 ppm (Table 2.1). The methylene protons α to the phosphorus are upfield-shifted by 0.2 to 0.4 ppm, demonstrating the considerable electron-withdrawing nature of the Lewis-acid.

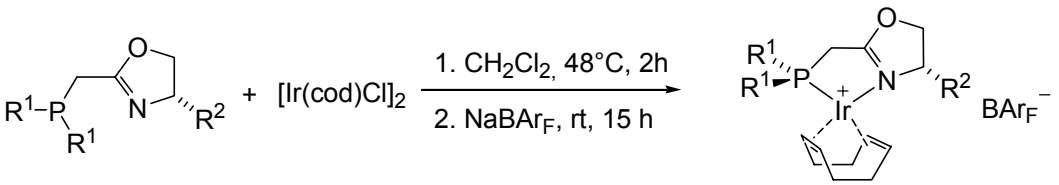
Table 2.1: $^{31}P\{^{1}H\}$ NMR resonances for all protected and free ligands in CD_2Cl_2, (For spectra that were measured on the 400 MHz NMR spectrometer, the shifts were corrected (+ 3.6 ppm))

R^1	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
$+BH_3$	**45**	**59**	**46**	**60**	**61**	**62**	**47**	**63**	**64**	**65**	**66**	**67**
δ [ppm]	48.3	48.3	49.0	48.4	28.3	28.1	28.9	28.1	17.6	17.6	17.8	17.8
$-BH_3$	**68**	**69**	**70**	**71**	**72**	**73**	**74**	**75**	**76**	**77**	**78**	**79**
δ [ppm]	27.3	27.3	28.8	27.2	-2.7	-3.1	-1.9	-2.9	-17.3	-17.3	-17.1	-19.3

If freshly distilled diethylamine was used, the ligands were formed quantitatively and cleanly. After the reaction excess diethylamine was evaporated under high-vacuum, and the amine-borane adduct at 80°C under high-vacuum. The ligands were used without further purification, since initial trials to improve the ligand purity with column-chromatography under argon, showed no great effect.

The complexes **80** to **91** were synthesized using standard procedures.[56] The ligands **68** to **79** were treated with bis[chloro-(1,5-cyclooctadiene) iridium(I)] in dichloromethane. The complexation was followed by anion exchange with a slight excess of sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate. The crude iridium-BAr_F salts were purified by column

chromatography on silica. Some complexes were recrystallized from dichloromethane and hexane at low temperature. The yields were between 29% and 96%.



80-91

R^1	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
	80	**81**	**82**	**83**	**84**	**85**	**86**	**87**	**88**	**89**	**90**	**91**
yield	80%	83%	79%	96%	78%	67%	80%	78%	77%	65%	29%	65%
δ [ppm]	42.7	46.1	41.1	41.7	21.7	25.1	25.8	22.9	24.9	23.7	19.2	21.6

Scheme 2.15: Complex Synthesis with subsequent anion-exchange

Eleven new phosphinomethyloxazoline ligands **68** to **78** were prepared *via* two different routes (Figure 2.4). In total twelve cationic iridium complexes **80** to **91** of these chelating ligands were synthesized.

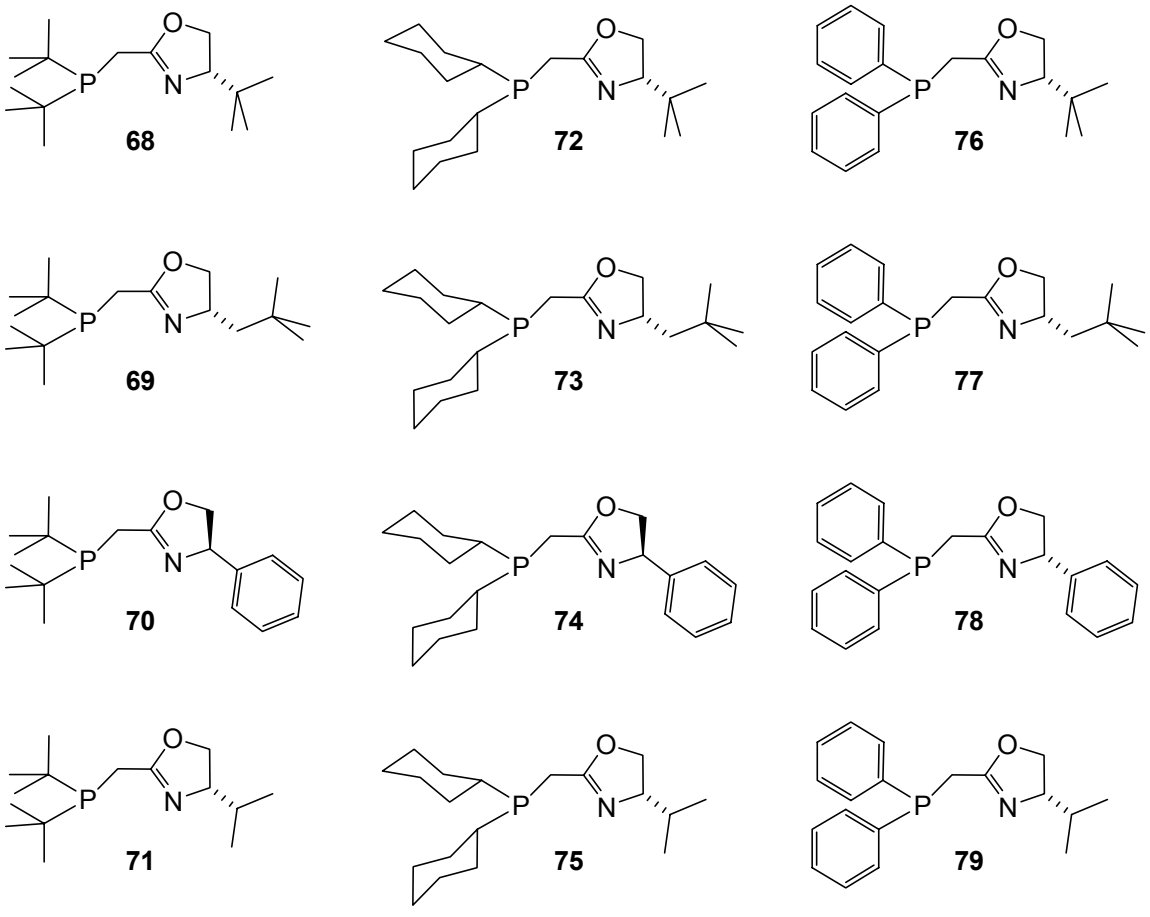


Figure 2.4: Twelve synthesized phosphinomethyloxazolines

2.5 Catalytic Hydrogenation Reactions

A number of unfunctionalized and functionalized highly-substituted substrates were tested in iridium-catalyzed enantioselective hydrogenation. The results of the hydrogenation of unfunctionalized and some functionalized alkenes are presented in the following section.

2.5.1 (*E*)-1,2-Diphenyl-1-propene

The hydrogenation of (*E*)-1,2-diphenyl-1-propene was performed with full conversion for all catalysts and gave selectivities from 37 to 99% ee. The best result was obtained for (*S*)-2-[(di-*tert*-butyl-phosphanyl)-methyl]-4-*tert*-butyl)-4,5-dihydrooxazoline **68**. Generally, the di-*tert*-butylphosphinooxazolines gave the best results with ees of >88%. The selectivity with respect to the phosphorus substituents decreased in the order *tert*-butyl > cyclohexyl > phenyl. For the substituent at the oxazoline-ring, no trend was observed. The enantioselective results for this trisubstituted alkene, with the exception of **80**, are lower than with the best PHOX ligands, where selectivities bigger 99% were obtained.[57d,75]

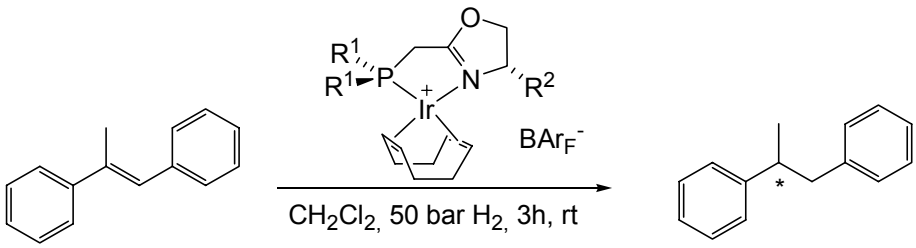


Table 2.2: Hydrogenation of (*E*)-1,2-diphenyl-1-propene

catalyst	**80**[b]	**81**[a]	**82**[b]	**83**[b]	**84**[b]	**85**[a]	**86**[b]	**87**[a]	**88**[b]	**89**[a]	**90**[a]	**91**[a]
R^1 =	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2 =	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
conf. ligand	*S*	*S*	*R*	*S*	*S*	*S*	*R*	*S*	*S*	*S*	*S*	*S*
conv. [%]	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
ee [%]	**99**	88	97	97	68	67	80	79	37	52	69	53
conf. product	*R*	*R*	*S*	*R*	*R*	*R*	*S*	*R*	*R*	*R*	*R*	*R*

[a] 1 mol% catalyst, in dichloromethane (0.5 mL); [b] 1 mol% catalyst, in dichloromethane (1 mL)

2.5.2 (*E*)-2-(4'-Methoxyphenyl)-2-butene and (*Z*) -2-(4'-methoxyphenyl)-2-butene

Full conversion was obtained for the hydrogenation of (*E*)-2-(4'-methoxyphenyl)-2-butene and (*Z*)-2-(4'-methoxyphenyl)-2-butene with any catalyst.

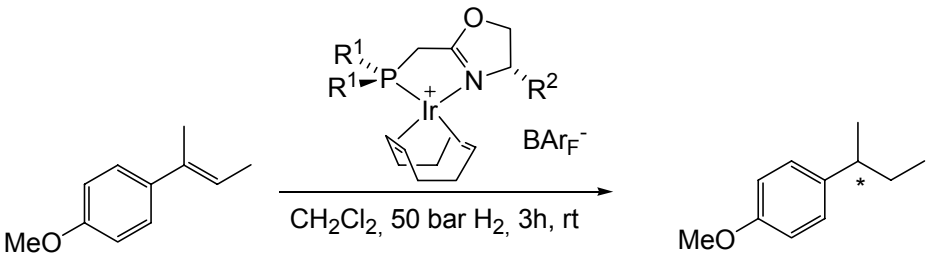


Table 2.3: Hydrogenation of (*E*)-2-(4'-methoxyphenyl)-2-butene

catalyst	**80**[b]	**81**[a]	**82**[b]	**83**[a]	**84**[b]	**85**[a]	**86**[b]	**87**[a]	**88**[a]	**89**[a]	**90**[a]	**91**[a]
R^1 =	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2 =	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
conf. ligand	*S*	*S*	*R*	*S*	*S*	*S*	*R*	*S*	*S*	*S*	*S*	*S*
conv. [%]	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
ee [%]	**96**	60	94	84	89	71	78	58	73	34	62	14
conf. product	*R*	*R*	*S*	*R*	*R*	*R*	*S*	*R*	*R*	*R*	*R*	*R*

[a] 1 mol% catalyst, in dichloromethane (0.5 mL); [b] 1 mol% catalyst, in dichloromethane (1 mL)

The selectivities for the *E*-substrate were much higher with 14 to 96% ee compared to the *Z*-substrate with only up to 16% ee. Furthermore, the absolute configuration for the hydrogenation-product of (*Z*)-2-(4'-methoxyphenyl)-2-butene could not always be predicted. Catalysts **81** and **85** gave the product with only 8% ee but with the *R*-configuration. These results suggest that the catalytic cycle involves isomerization of the double bond.

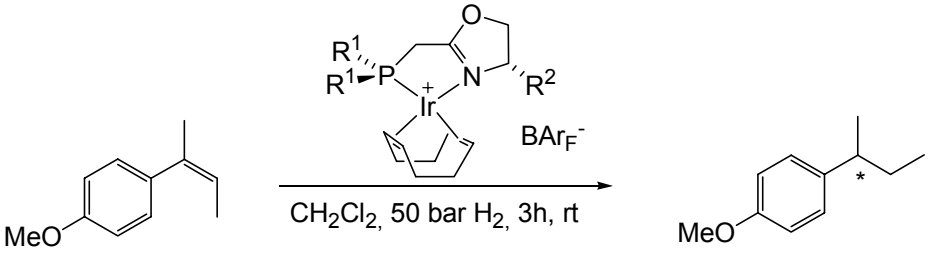


Table 2.4: Hydrogenation of (*Z*)-2-(4'-methoxyphenyl)-2-butene

catalyst	**80**[a]	**81**[a]	**82**[a]	**83**[a]	**84**[b]	**85**[a]	**86**[a]	**87**[a]	**88**[a]	**89**[a]	**90**[a]	**91**[a]
R^1 =	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2 =	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
conf. ligand	*S*	*S*	*R*	*S*	*S*	*S*	*R*	*S*	*S*	*S*	*S*	*S*
conv. [%]	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
ee [%]	rac	8	16	6	7	8	4	11	**31**	10	11	rac
conf. product	*nd*	*R*	*R*	*S*	*S*	*R*	*R*	*S*	*S*	*S*	*S*	*nd*

[a] 1 mol% catalyst, in dichloromethane (0.5 mL); [b] 1 mol% catalyst, in dichloromethane (1 mL)

2.5.3 2-(4'-Methoxyphenyl)-3-methyl-2-butene

To date, the best results for the hydrogenation of 2-(4'-methoxyphenyl)-3-methyl-2-butene with chelating P,N-ligands was 81% ee with neopentyl-substituted standard-PHOX and a pyridylsubstituted ligand (Figure 2.1). In comparison, the new phosphinomethyloxazoline-ligands performed especially well in terms of both activity and enantioselectivity. The tetrasubstituted alkene was hydrogenated with full conversion with most catalysts. In some cases, full conversion was even obtained at 50 bar hydrogen after 3 hours with 1mol% of catalyst.

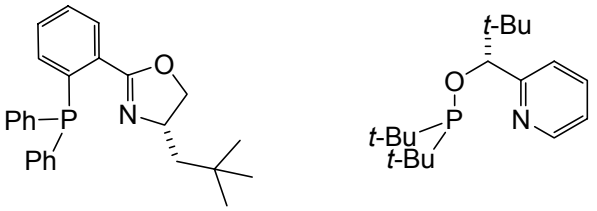


Figure 2.5: P,N-ligands for enantioselective hydrogenation of 2-(4'-methoxyphenyl)-3-methyl-2-butene

Five different catalyst outperformed the above mentioned ligands with selectivities from 84 to 93% ee. The best results were achieved with (*R*)-2-[(dicyclohexyl-phosphanyl)-methyl]-4-phenyl)-4,5-dihydrooxazo-line ligand **74**, closely followed by the corresponding neopentyl-substitud ligand **73**.

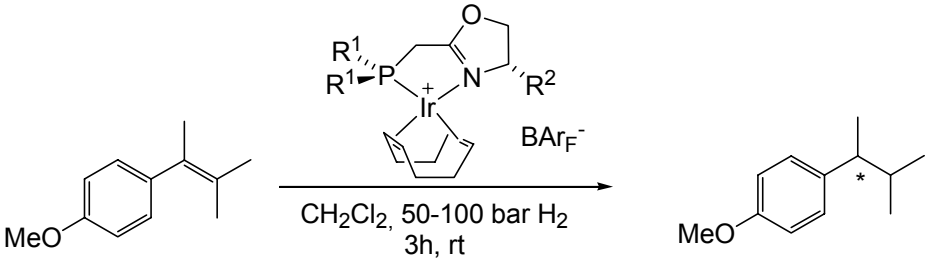


Table 2.5: Hydrogenation of 2-(4'-methoxyphenyl)-3-methyl-2-butene

catalyst	**80**[b]	**81**[a]	**82**[b]	**83**[b]	**84**[b]	**85**[a]	**86**[b]	**87**[a]	**88**[b]	**89**[a]	**90**[a]	**91**[a]
R^1 =	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2 =	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
conf. ligand	*S*	*S*	*R*	*S*	*S*	*S*	*R*	*S*	*S*	*S*	*S*	*S*
conv. [%]	93[c]	98	>99[c]	>99	>99	>99	>99	>99	66	>99	>99	>99
	(93)[c]		(>99)						28[d]			
ee [%]	27	**85**	**84**[d]	74	80	**92**	**93**[d]	**84**	30	62	74	40
	(40)		(87)						18[d]			
conf. product	-	-	+	-	-	-	+	-	-	-	-	-

[a] 2 mol% catalyst, in dichloromethane (0.5 mL); [b] 2 mol% catalyst, in dichloromethane (1 mL);
[c] 4h, [d] 1 mol%; 50 bar (100 bar)

Better results with these substrates have only be obtained with Buchwald's *ansa*-zirconocenes however these catalysts suffer from low activity, requiring in high catalyst loadings, rather drastic reaction conditions and long reaction times (compare 2.2).[53]

2.5.4 6-Methoxy-1-methyl-3,4-dihydronaphtaline

The internal alkene, 6-methoxy-1-methyl-3,4-dihydronaphtaline, was hydrogenated with full conversion by all twelve catalysts (Table 2.6). The selectivities were generally very low with only up to 55% ee for catalyst **88** (R^1 = phenyl, R^2 = *tert*-butyl). In contrast to the other unfunctionalized alkenes described above (2.5.1 to 2.5.3), diphenylphosphineoxazolines perform best with this substrate. Very high (~95%) enantioselectivities were previously obtained with di-*o*-tolylphosphinite-oxazoline ligand SimplePHOX.[57b]

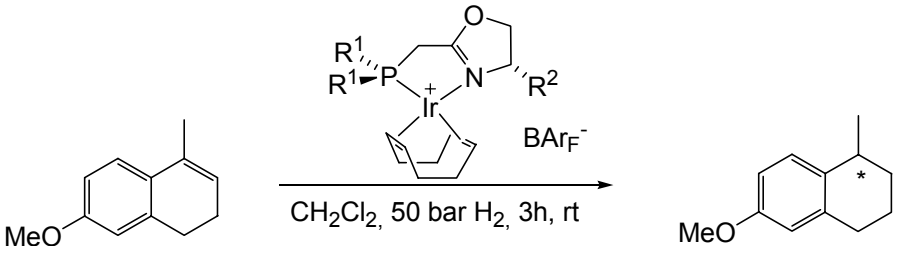


Table 2.6: Hydrogenation of 6-methoxy-1-methyl-3,4-dihydronaphtaline

catalyst	**80**[b]	**81**[a]	**82**[b]	**83**[b]	**84**[b]	**85**[a]	**86**[b]	**87**[a]	**88**[b]	**89**[a]	**90**[a]	**91**[a]
R^1 =	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2 =	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
conf. ligand	*S*	*S*	*R*	*S*	*S*	*S*	*R*	*S*	*S*	*S*	*S*	*S*
conv. [%]	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
ee [%]	5	18	rac	rac	15	rac	6	4	**55**	26	12	10
conf. product	*S*	*R*	*nd*	*nd*	*S*	*nd*	*S*	*S*	*S*	*S*	*S*	*S*

[a] 1 mol% catalyst, in dichloromethane (0.5 mL); [b] 1 mol% catalyst, in dichloromethane (1 mL)

2.6 Enantioselective Hydrogenation of Functionalized Alkenes

Crabtree showed that cationic iridium-catalysts are not only very efficient in the hydrogenation of three-and tetra-substituted alkenes, but that they also show functional group tolerance.[76] The chiral versions of Crabtree's catalyst generally give good selectivities with alkenes bearing an additional chelating functional group such as alcohols, esters or carbonyls.

2.6.1 (*E*)-Ethyl-3-phenyl-but-2-enoate

α-Acylaminoacrylicacids and α,β-unsaturated acids were hydrogenated with high-enantioselectivities when rhodium or ruthenium-catalysts were used. The conversion of unsaturated esters however, has only given comparatively poor results, with the exception of itaconic acid ester.[77] Over the last few years different research groups have shown, that cationic iridum-catalysts with chelating, chiral P,N-ligands can hydrogenate unsaturated esters with high enantioselectivities.

(*E*)-Ethyl-3-phenyl-but-2-enoate was tested in the enantioselective iridium-catalyzed hydrogenation with the new phosphinomethyloxazolines. All catalysts hydrogenated the unsaturated ester with full conversion. The highest enantioselectivity (96%) was obtained with catalyst **82**. The results obtained are similar to those of Zhang's phospholane-oxazolines (compare 2.3). Here, the best result was 98% ee, also using a phenyl-substituted oxazoline. Results for di-*tert*-butylphosphinomethyloxazolines were better than for the cyclohexyl and phenyl-analogs (Table 2.7). Much better results (greater than 99% ee) have already been obtained with other P,N-ligands.[78]

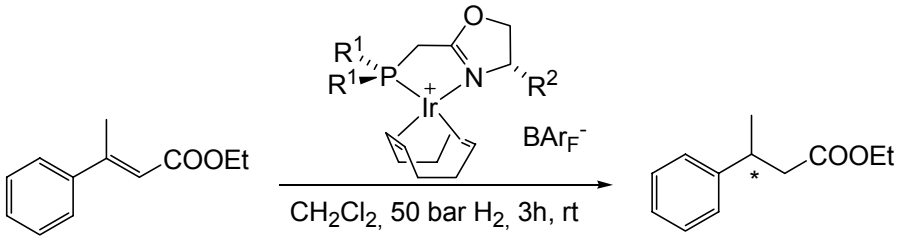


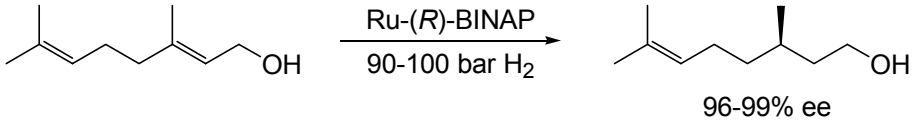
Table 2.7: Hydrogenation of (*E*)-ethyl-3-phenyl-but-2-enoate

catalyst	**80**[b]	**81**[a]	**82**[b]	**83**[a]	**84**[b]	**85**[a]	**86**[b]	**87**[a]	**88**[b]	**89**[a]	**90**[a]	**91**[a]
R^1 =	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2 =	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
conf. ligand	*S*	*S*	*R*	*S*	*S*	*S*	*R*	*S*	*S*	*S*	*S*	*S*
conv. [%]	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
ee [%]	94	91	**96**	94	86	78	92	93	65	53	74	72
conf. product	*R*	*R*	*S*	*R*	*R*	*R*	*S*	*R*	*R*	*R*	*R*	*R*

[a] 1 mol% catalyst, in dichloromethane (0.5 mL); [b] 1 mol% catalyst, in dichloromethane (1 mL)

2.6.2 (*E*)-2-Methyl-3-phenyl-prop-2-enol

Allylic alcohols can coordinate not only with the η^2 of the olefin, but also *via* the OH-group to the iridium. Some cationic rhodium- and iridium-phosphine complexes are known to catalyze diastereoselective hydrogenation of chiral allylic and homoallylic alcohols, where the preexisting chirality of the sp^3-hybridized carbons induces new asymmetry on the neighbouring olefinic diastereofaces through coordination of the hydroxyl group to the transition metals.[79]



Scheme 2.16: Enantio- and regioselective reduction of geraniol.

The enantioselective hydrogenation of prochiral substrates was first reported by Takaya *et al.*.[50c] For the enantio- and regioselective hydrogenation of geraniol they were using a BINAP-based ruthenium (II) dicarboxylate complex (Scheme 2.16).

In the present case, full conversion was obtained with 1 mol% catalyst in all cases. Lower catalyst loadings have not yet been investigated. The enantioselectivity was relatively good for those catalysts bearing a *tert*-butyl substituent at the oxazoline ring, giving 90 to 93% ee (Table 2.8, catalysts **80**, **84** and **88**). In this case, the substituent at the oxazoline seems to have a bigger effect than those at the phosphorus atom.

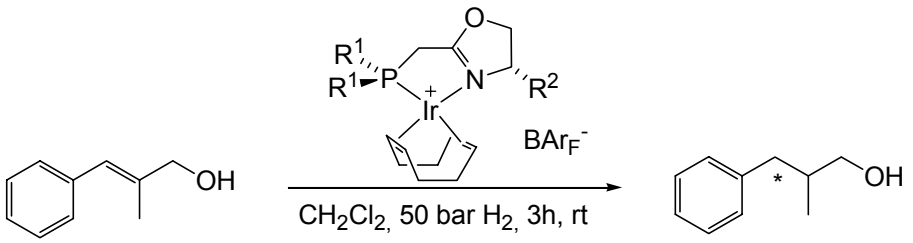


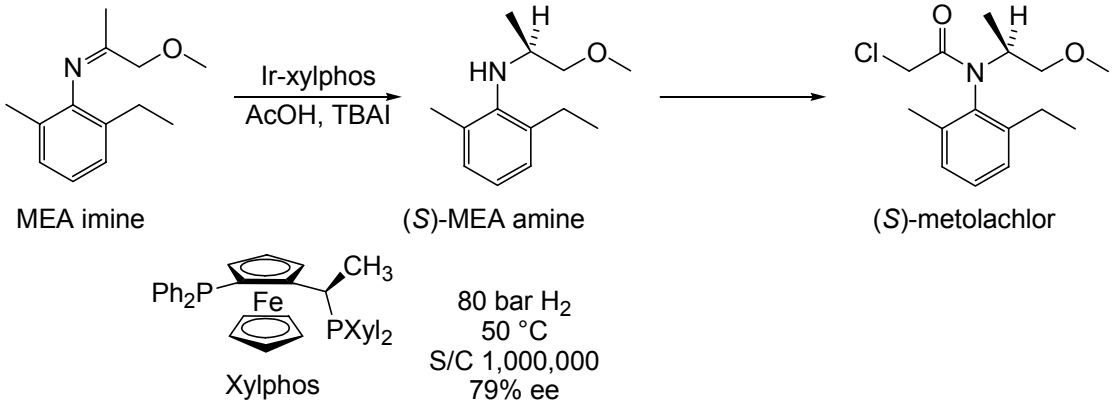
Table 2.8: Hydrogenation of (*E*)-2-methyl-3-phenyl-prop-2-enol

catalyst	**80**[b]	**81**[a]	**82**[b]	**83**[b]	**84**[b]	**85**[a]	**86**[a]	**87**[a]	**88**[b]	**89**[a]	**90**[a]	**91**[a]
R^1 =	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2 =	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
conf. ligand	*S*	*S*	*R*	*S*	*S*	*S*	*R*	*S*	*S*	*S*	*S*	*S*
conv. [%]	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
ee [%]	90	85	46	89	92	64	38	85	**93**	86	61	75
conf. product	-	-	+	-	-	-	+	-	-	-	-	-

[a] 1 mol% catalyst, in dichloromethane (0.5 mL); [b] 1 mol% catalyst, in dichloromethane (1 mL)

2.6.3 *N*-(1-Phenylethylidene)-aniline

Imines are very challenging substrates with respect to enantioselective hydrogenation meaning that there is still great demand for catalysts which can give high enantioselectivities. The nature of imines render the catalytic hydrogenation more complex. Not only can *syn*/*anti* isomers lead to low selectivity, but the strong donor character of the NH group of an amine, with its ability to compete for coordination at the catalytic site, may be one factor contributing to the more difficult hydrogenation of imines.[80]



Scheme 2.17: Industrial synthesis of (S)-metolachlor

The key-step in the synthesis of (*S*)-metolachlor (*N*-(1'-methyl-2'-methoxyethyl)-*N*-chloroacetyl-2-erhyl-6-methylanilin)[81], is the selective hydrogenation of an imine to a secondary amine.[82] (*S*)-Metolachlor is the active ingredient of Dual Magnum®, which is one of the most important grass-herbicide applied in the cultivation of maize, which was first described in 1973. The development of a diphosphino-iridium-complex is one of the industrial success stories of the last years. iridium-xylphos catalyst enables the enantioselective hydrogenation of MEA imine in 79% ee. The process is presently operated on a > 10,000 tons/year scale.

Apart from the industrially successful iridium-diphosphine catalysts, other ligand systems have been investigated. Iridium-phosphinooxazolines have been applied with success,[83] and more recently, secondary phosphine oxides have shown good results.[84] Apart from iridium catalysts, titanocene-complexes have been successfully applied by Buchwald *et al*.[85]

In the present work, *N*-(1-phenylethylidiene)-aniline has been hydrogenated as a model system. All catalysts performed equally modest with enantioselectivities up to 63% ee for **86** and **91**. However, no distinct trends were observed.

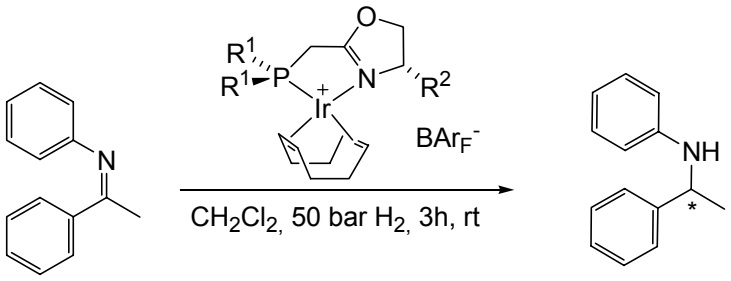


Table 2.9: Hydrogenation of *N*-(1-phenylethylidene)-aniline

catalyst	**80**[b]	**81**[a]	**82**[b]	**83**[b]	**84**[b]	**85**[a]	**86**[b]	**87**[a]	**88**[b]	**89**[a]	**90**[a]	**91**[a]
R^1 =	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Cy	Cy	Cy	Ph	Ph	Ph	Ph
R^2 =	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr	^{t}Bu	Np	Ph	^{i}Pr
conf. ligand	*S*	*S*	*R*	*S*	*S*	*S*	*R*	*S*	*S*	*S*	*S*	*S*
conv. [%]	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
ee [%]	rac	48	53	35	41	60	**63**	60	42	53	55	63
conf. product	*nd*	*R*	*S*	*R*	*R*	*R*	*S*	*R*	*R*	*R*	*R*	*R*

[a] 1 mol% catalyst, in dichloromethane (0.5 mL); [b] 1 mol% catalyst, in dichloromethane (1 mL)

2.7 X-Ray Crystallographic Studies

Single-crystals of four complexes **80**, **82**, **83**, **88**, could be obtained from dichloromethane/hexane at low temperatures. The recorded and refined crystal-stuctures were compared regarding bond lengths and angles with those of standard iridium-PHOX-complexes. The appendent crystallographic data are attached at the end of this work (page 217). All structures are depicted without the BAr_F anion. Hydrogen atoms were also omitted for clarity. The POV-Ray datasets[86] for the preparation of the pictures were generated with ORTEP.[87] The absolute configuration could be determined by refinement of the flack parameter.[88]

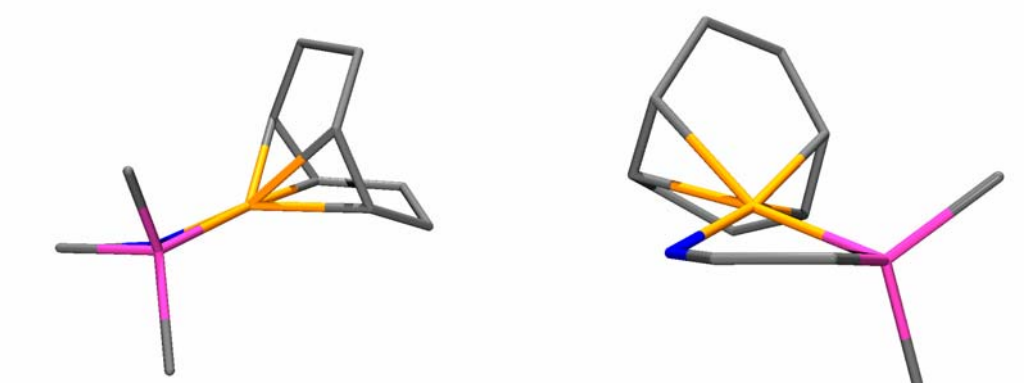
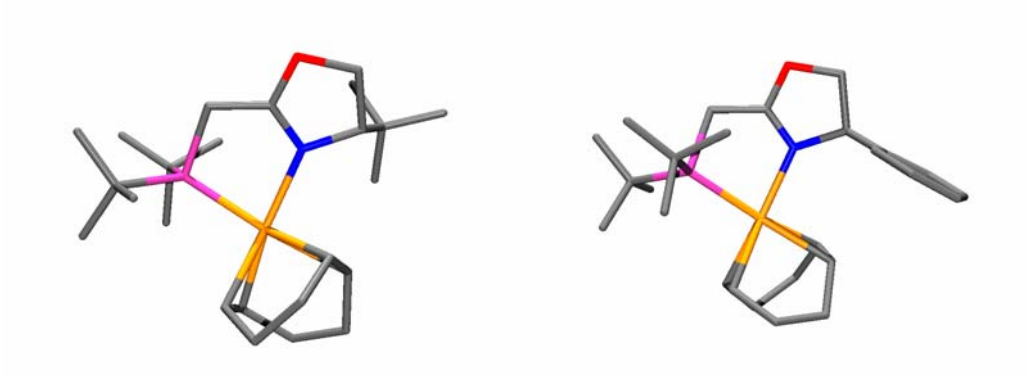


Figure 2.6: Envelope conformation of **80**. The oxazoline-rings and the phosphorus substituents are omitted for clarity.

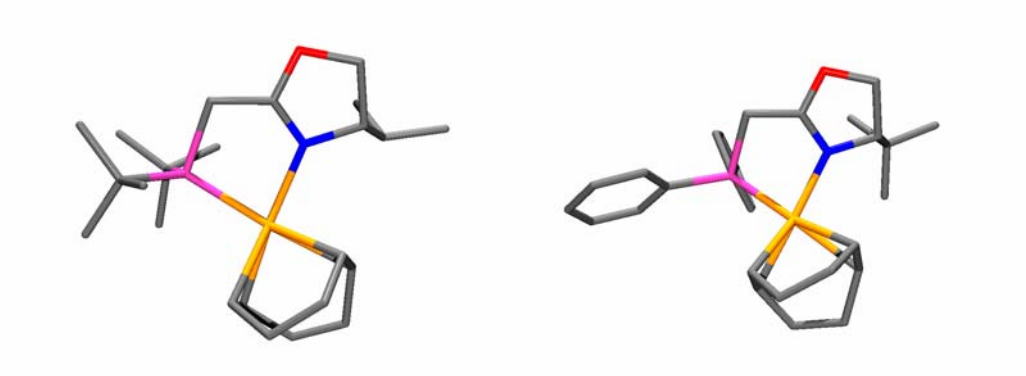
All complexes have square planar geometry with the cyclooctadiene double-bonds perpendicular to the coordination-plane. The five-membered ring which is composed of the iridium atom and the chelating ligand exhibts in all cases an envelope-conformation. In the envelope the phosphorus-substituents are occupying *pseudo*-axial and *pseudo*-equatorial positions. As can be seen in Figure 2.6 the iridium atom is pointing out of the slightly tilted plane, which is composed of the ligand P-C-C-N-atoms.



	80	**82**
Ir-P [Å]	2.3376 (12) / 2.3365 (14)	2.3410 (19)
Ir-N [Å]	2.095 (4) / 2.085 (4)	2.101 (6)
P-Ir-N [deg]	81.71 (12) / 82.72 (12)	81.54 (17)

Figure 2.7: Selected bond lengths and angles of complexes **80** and **82**

The asymmetric units of **80** and **83** each contain two complexes, in **82** and **88** they are only occupied by one complex. Structure **88** also includes one molecule of dichloromethane. The P-Ir-N angles of complexes **80** to **83** are all around 82° - although the two angles of **80** differ by 1°. The P-Ir-N angle of **88** is considerably smaller (78.65°). This might be due to the smaller size of the phenyl groups compared to the bulky *tert*-butyl substituents.



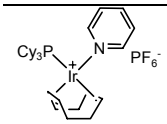
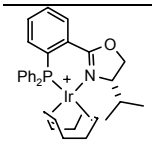
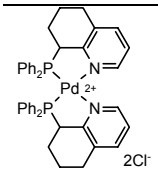
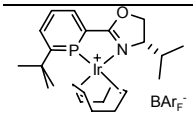
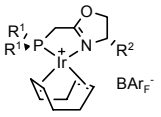
	83	**88**
Ir-P [Å]	2.337(2) / 2.340(2)	2.262(2)
Ir-N [Å]	2.097(5) / 2.068(4)	2.117(4)
P-Ir-N [deg]	81.31(14) / 82.01(14)	78.65(14)

Figure 2.8: Selected bond lengths and angles of complexes **83** and **88**

In comparison with Crabtree's catalyst **17**, standard iridium-PHOX complex **9** and the new phosphinomethyl-oxazolines have considerably smaller P-Ir-N angles. Apparently, this is due to the ring that is formed by the chelating ligand and the metal-center. The ring-size influences the width of this angle. For the six-membered ring chelating PHOX ligand the angle is around 3 to 6° wider than for the five-membered ring chelating phosphinomethyl-

oxazolines. The P-Pd-N angle in palladium-complex **92** which also contains a five-membered ring compares well with these structural data.[78] The corresponding P-Ir-N angle of complex **87** (compare chapter 3.4.1, page 66) is 80.45°, and thus also is in line with the angles of **80**, **82**, **83**, and **88**. Bond lengths are all in the same range with ~2.1Å for the iridium-nitrogen bond and ~2.3Å for the iridium-phosphorus bond.

Table 2.10: Comparison of x-ray structural data

	complex	R^1	R^2	Ir-P [Å]	Ir-N [Å]	Ir-C trans to P [Å]	Ir-C trans to N [Å]	P-Ir-N [deg]
	**17**	-	-	2.37	2.09	2.18	2.15	92.2
	**9**	-	-	2.274(2) 2.258(3)	2.119(7)	2.10 2.11	2.01 2.03	84.95
	**92**	-	-	-	-	-	-	81.32(6)
	**87**			2.295 (9)	2.084 (3)	2.180 (3) 2.151 (3)	2.167 (3) 2.134 (3)	80.45 (8)
	**80**	^{t}Bu	^{t}Bu	2.338(2) 2.337(2)	2.095(4) 2.085(4)	2.202(5) 2.172(5)	2.144(5) 2.128(5)	81.71(12) 82.72(12)
	82	^{t}Bu	Ph	2.341(2)	2.101(6)	2.221(8) 2.182(9)	2.151(7) 2.139(5)	81.54(17)
	83	^{t}Bu	^{i}Pr	2.337(2) 2.340(2)	2.097(5) 2.068(4)	2.165(6) 2.192(6)	2.130(7) 2.134(7)	81.31(14) 82.01(14)
	88	Ph	^{t}Bu	2.262(2)	2.117(4)	2.212(5) 2.214(5)	2.112(6) 2.113(5)	78.65(14)

2.8 Conclusion

Twelve new phosphinomethyl-oxazoline-borane adducts were prepared by two different syntheses. The corresponding ligands could be obtained after deprotection with diethylamine. In contrast to the method reported by Sprinz *et al.*[63] for diphenylphosphinomethyl-oxazolines, these routes also allowed the preparation of phenylsubstituted ligands **70, 74** and **78**.

After deprotection to the free ligands, the corresponding iridium-complexes **80**-**91** were synthesized as their BAr_F salts. Single crystals were obtained for four complexes **80**, **82**, **83**, and **88**. The crystal structures were compared with previously crystallized complexes. As expected, the P-Ir-N angle of these 5-membered-ring chelating iridium-complexes is somewhat smaller than those of the standard PHOX ligands.

The new iridium complexes **80**-**91** were successfully tested in the enantioselective hydrogenation of unfunctionalized and functionalized olefins. Generally, the results are in the same range as those of existing P,N-ligands. The tetrasubstituted olefin, 2-(4'-methoxyphenyl)-3-methyl-2-butene, was reduced with higher enantioselectivity than reported for other iridium catalysts. Better results were only observed for *ansa*-zirconocenes however these catalysts showed comparatively low activity.

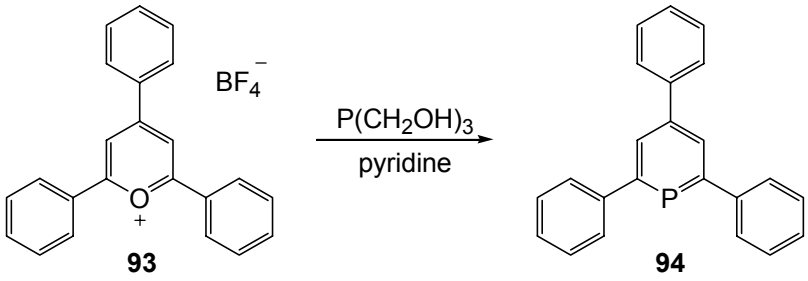
Chapter 3

Phosphinines as Ligands in Catalysis

3 Phosphinines as Ligands in Catalysis

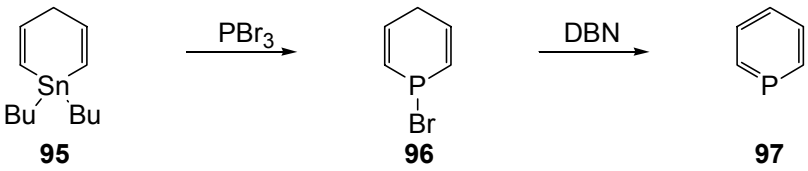
3.1 Phosphinines - Phosphabenzenes - Phosphorines

For a considerable time the "double bond rule" has been established in chemistry textbooks. It states that elements outside the first row of the periodic table do not form multiple bonds either with themselves or with other elements. However, this rule was disproved by the spectroscopic detection of a compound having a multiple P-C bond in 1961.[89] Another fundamental breakthrough in maingroup-metal chemistry was achieved by Märkl.[90] In 1966 he succeeded in preparing 2,4,6-triphenyl- λ^3-phosphabenzene **93** (2,4,6-triphenyl- λ^3-phosphinine[i]).[91]



Scheme 3.1: Original Synthesis of 2,4,6-triphenyl- λ^3-phosphabenzene[90]

The synthesis was achieved by the formal exchange of O^+ against P from the respective substituted pyrylium salt **93** using $P(CH_2OH)_3$ as a phosphine equivalent (Scheme 3.1). Other sources of PH_3 (*e.g.*, $P(TMS)_3$, PH_4I)[92] can also be employed. However, the synthesis starting from pyrylium salts is restricted to 2,4,6-trisubstituted derivatives. The unsubstituted "parent" phosphinine **97** was obtained by an entirely different route. It was obtained from reaction of 1,4-dihydro-1,1-dibutylstannabenzene **95** with PBr_3 and liberation of the phosphinine from 1,4-dihydrophosphinine **96** by HBr elimination with DBN (Scheme 3.2).[93]

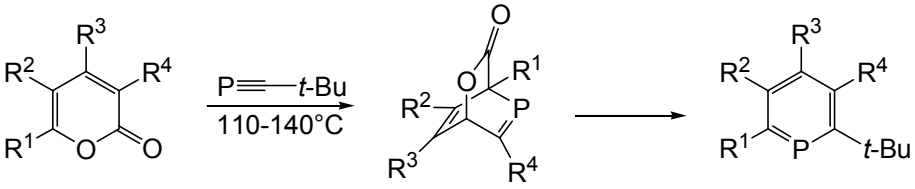


Scheme 3.2: Synthesis of "parent"-phosphinine **65** by Ashe[93]

[i] According to IUPAC-nomenclature the phosphabenzene ring system was named λ^3-phosphorin until 1982, now it is termed λ^3-phosphinine. The λ convention was introduced in 1979 to describe compounds containing skeletal atoms that can occur in two or more valence states. λ is written with a superscript number that gives the valence state of the heteroatom. In addition, the symbol δ^c was introduced. c gives the number of double bonds in the skeletal structure terminating at the heteroatom. Earlier the symbol σ^m, where m is the number of bonds terminating at the heteroatom was suggested in conjunction with the λ^n symbol. However, this symbolism was not included in the revision of the Section D rules for the 1979 edition of the *IUPAC Organic Rules*.

Later, Märkl, Dimroth, and Bickelhaupt prepared a variety of highly substituted λ^3-phosphinines and began to illuminate their chemistry.[94] A number of related λ^5-phosphinines have also been investigated.[95]

There are several other methods to obtain λ^3-phosphinines. For example, λ^5-phosphinines can serve as precursors for the respective λ^3-phosphinines that are generated by thermal elimination.[96] Another general approach implies the ring-construction of the λ^3-phosphinine by [4+2]-cycloaddition reaction. An already established phosphacycle, e.g. 1,3-azaphosphinines can react with an alkyne.[97,98] The reverse scheme involves cycloaddition of a conjugated diene with phosphaalkyne or a suitable phosphaalkene.[99,100]



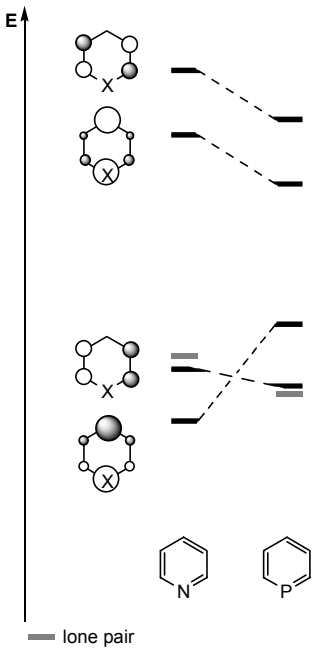
Scheme 3.3: [4+2]-cycloaddition from α-pyron[99a]

3.1.1 Aromaticity of λ^3-Phosphinines

Aromaticity cannot be described with a sole definition. In fact, it is associated with a set of properties, comprising planarity, lack of bond alternation, and multiple bond character of all ring bonds. More important are probably the magnetic criteria that characterize aromatic species. Aromaticity is indicated by large downfield NMR shifts (due to the presence of a diamagnetic ring current) and negtive NICS values (nucleus-independent chemical shift).[101]

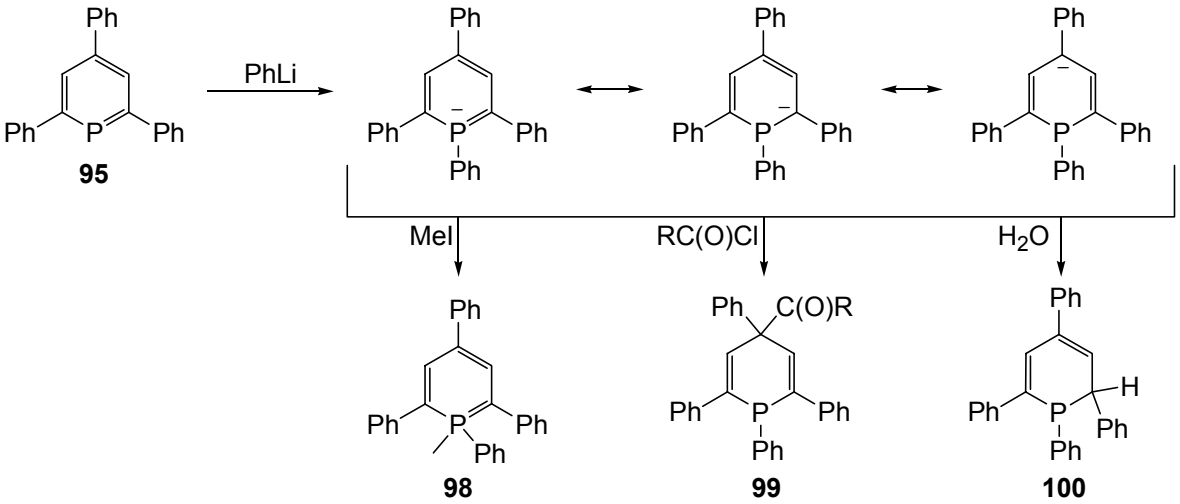
Already early articles about λ^3-phosphinines mentioned typical features of aromaticity, such as planarity, no carbon-carbon bond lenghts alteration and short carbon-phosphorus bonds.[102] Aromatic character was also assigned because the peripheral protons of the planar molecule showed a considerable downfield shift.[103] The calculated Hückel-aromaticity of parent λ^3-phosphinine was calculated to be as high as 88% compared with benzene.[104] More advanced, recent studies even assigned an aromaticity of 97% compared with benzene.[105] NICS values, *i.e.* the ring-current contributions to the chemical shift of a central atom, were calculated to be -9.5 (*vs* -8.9 in benzene) for NICS(0) (atom at the center of the ring) and -11.4 (*vs* -10.6 in benzene) for NICS(1) (atom 1Å above the center of the ring).[101,106]

3.1.2 Chemical Reactivity



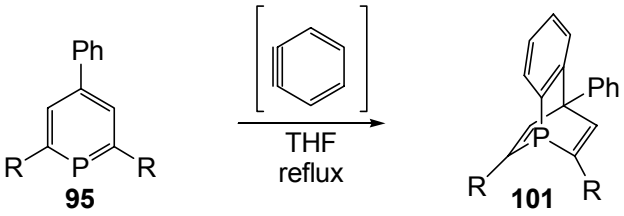
The chemical consequences of aromaticity are far different from those observed in pyridines. In contrast to the nitrogen atom in pyridine, the phosphorus atom in λ^3-phosphinine is less electronegative than the adjacent carbon atoms. Since the lone pair of pyridine occupies the HOMO, pyridine has good σ-donating ability. Photoelectron spectroscopy[107] and *ab initio* calculations[108] have shown that the lone pair of λ^3-phosphinine is located at a lower energy level. The HOMO and LUMO of λ^3-phosphinine are the π and π^* orbitals, respectively. Consequently, λ^3-phosphinine posseses at least qualitatively an ideal frontier molecular-orbital situation for an efficient overlap with filled metal d-orbitals and the ability to function as π-acceptor ligand (compare orbital diagram). The phosphorus atom in λ^3-phosphinine exhibits a strong s-orbital character (63.8% versus 29.1% found for the nitrogen atom in pyridine),[109] and is due to the low basicity comparatively inert towards electrophilic attack.[110]

For the above reasons electrophilic attack at the phosphorus does not occur. Neither stable PH^+ nor PR^+ phosphininium salts are known. Reaction of λ^3-phosphinines with nucleophiles leads to phosphininylanions by addition of the nucleophile to the phosphorus.[111] Subsequent reaction with soft electrophiles give λ^5-phosphinines. Hard electrophiles lead to *ortho*- or *para*-substituted 1,2- or 1,4-dihydrophosphinines.[112] Functionalization is generally difficult.



Scheme 3.4: Nucleophilic attack at the phosphorus followed by reaction with an electrophile.

Oxidation leads to λ^5-derivatives, reaction of 2,4,6-trisubstituted-phosphinines with bromine or chlorine give 1,1-dihalo-λ^5-phosphinines.[113] In the 1990s, Mathey and co-workers developed a methodology for the synthesis of functionalized phosphinines using transition metal mediated reactions including palladium- and nickel-catalyzed coupling reactions.[114,115] Remarkably, phosphinines also function as dienes in [4+2]-cycloadditions when reacted with activated alkynes (Scheme 3.5).[116]



Scheme 3.5: Reaction of phosphinine with benzyne

3.1.3 Coordination Chemistry

The coordinative abilities of λ^3-phosphinines are not limited to monodentate binding *via* the lone-pair at the phosphorus atom. Some phosphinine-complexes also involve π-coordination. While phosphinines usually undergo κ^1-coordination with late transition metals in low oxidation states,[117] they are also able to bind η^6, typically with early transition metals in high oxidation states.[118] For some metals both coordination modes were observed.

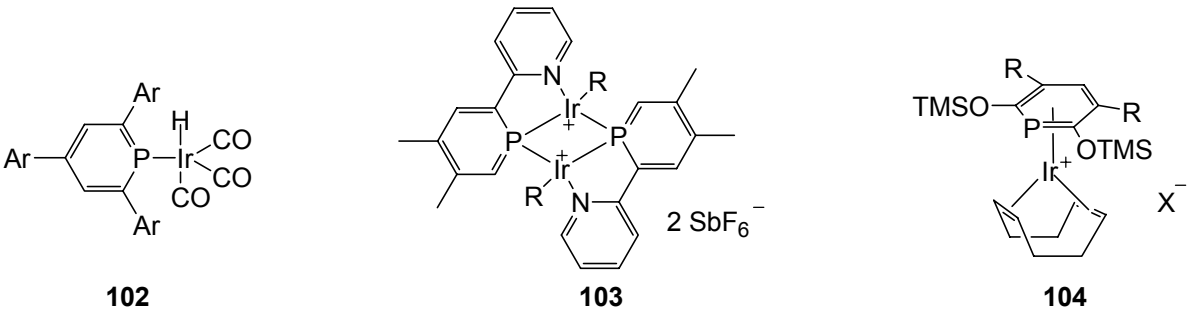


Figure 3.1: Different coordination modes of iridium-phosphinine complexes η^1 **102**, η^6 **104** (R = η^4-1,5-cyclooctadiene), μ^2-bridging **103**.

Iridium can undergo both coordination modes, although the κ^1-coordination is more typical (Figure 3.1).[119,120] According to Mathey and co-workers two very bulky groups are needed in *ortho*-position to favor η^6- versus κ^1-coordination. Interestingly, phosphinines can also serve as bridging ligands, as was shown in the case of NIPHOS ligand by Schmid *et al*.[121]

3.1.4 Application in Catalysis

As electron withdrawing (π-acceptor) ligands phosphinines are able to stabilize metals in low oxidation states and electron-rich transition metal complexes.[122] Recently, Breit and co-workers have systematically investigated the use of λ^3-phosphinine ligands in rhodium-catalyzed hydroformylation. The activity of a 2,6-dimethyl-4-phenyl-λ^3-phosphinine complexe was found to be twice as high as that of the conventional triphenylphosphine catalyst. Furthermore, exellent branched to linear ratios were observed.[123] A η^6-phosphinine iron complex was found to catalyze the cyclotrimerizaton of dimethyl acetylenecarboxylate. The co-cyclotrimerization of butyronitrile and alkynes afforded pyridine derivatives.[118a] 1,3-Butadiene dimerization lead to cycloocatdienes.[118b]

In the context of his research of the application of phosphinines in rhodium-catalyzed hydroformylation reactions, Breit investigated the use of chiral ligands in this reaction. In 1999, he published the synthesis of phosphininoxazoline **105** and another phosphininoxazoline **106** which is enabled to form a larger chelating ring.[124] The ligands were tested in the hydroformylation of styrene. While ligand **105** lead to a disappointingly low yield (5%), ligand **106** performed to full conversion and showed a respectable regioselectivity (branched-to-linear ratio 25:1). The enantioselectivity of the reaction was not discussed. The poor result obtained with ligand **105** might have been caused by an impurity of 20% starting material (*i.e.* the respective α-pyrone) in the ligand. It is reported that the catalyst was prepared *in situ*. Therefore, the pyrone-impurity might have inhibited the reaction. Probably in consideration of the poor results, no further applications of phospininoxazoline **105** were published.

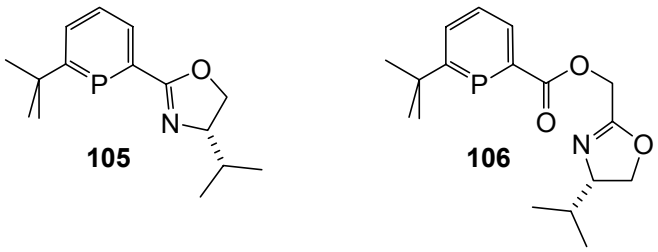


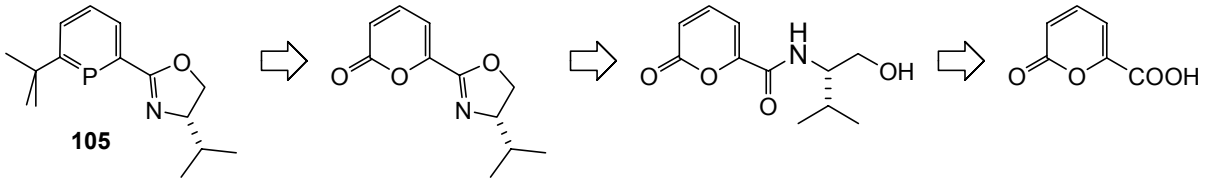
Figure 3.2: Chiral phosphininoxazoline ligands **105** and **106** for rhodium-catalyzed hydroformylation[124]

3.2 Objectives of this Chapter

Having already investigated a broad scope of related P,N-ligands in iridium-catalyzed hydrogenation,[125] we were interested in the performance of strong π-accepting ligands such as **105**. Apart from the electronic characteristics, the phosphinine system exhibits an interesting planar geometry rather than a three-dimensional sterically more demanding phosphorus moiety. Unfortunately, the system is relatively complicated to synthesize and not as versatile as other phosphinoxazolines. Still, changing the substituent at the oxazoline-ring is feasible. Ligand **105** is capable of forming a five-membered ring chelate. For better comparability with other phosphinoxazoline ligands (most of the tested ligands in iridium-catalyzed hydrogenation are forming six-membered chelate rings) the synthesis of a related phosphininoxazoline capable of forming a six-membered chelate ring was envisioned as well.

3.3 Improved Synthesis of Phosphininoxazolines

For the synthesis of ligand **105** Breit has used the [4+2]-cycloaddition procedure described above to obtain the λ^3-phosphinine moiety in the last step of the reaction sequence (Scheme 3.6).[124] As the diene moiety he chose an α-pyrone that can react with *tert*-butylphosphaalkyne in a hetero-Diels-Alder type reaction liberating carbon dioxide.

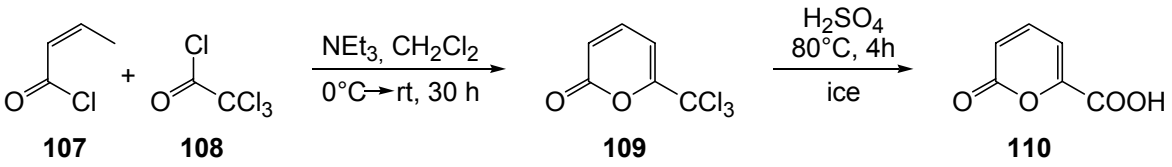


Scheme 3.6: Retrosynthesis of phosphininoxazoline **105** according to Breit[124]

As mentioned, syntheses starting from *e.g.* a pyrylium salts are only possible for 2,4,6-trisubstituted precursors. Preparation by [4+2]-cycloaddition bears the advantage that other substitution patterns can be achieved. The conditions, apart from the rather high temperature, are relatively mild, so that functional groups are tolerated. The drawbacks are the low yields of this procedure and the fact, that due to the limited number of phosphaalkynes, only variation of the second *ortho*-position is possible.

3.3.1 Synthesis of Diene-Moiety

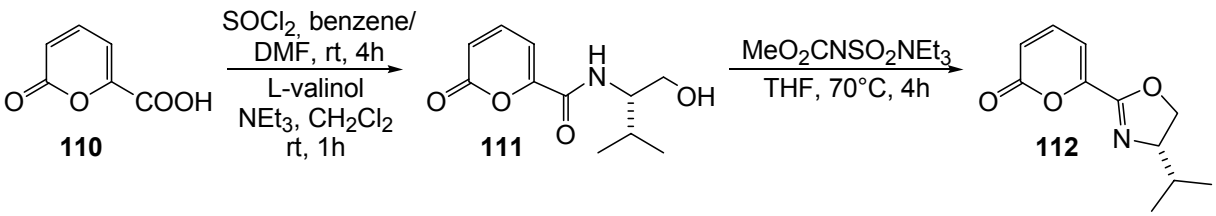
The first three steps towards ligand **105** were performed according to literature procedures.



107 **108** **109** **110**

Scheme 3.7: Preparation of 6-substituted α-pyrones **109** and **110** according to Rey *et al.*[126]

2-Pyron-6-carboxylic acid **110** was prepared according to Rey *et al.*.[126] First, trichloromethylpyrone **109** was obtained in 61% yield by condensation of crotonyl chloride **107** and trichloroacetyl chloride **108** with triethylamine in dichloromethane. Then **109** was heated to reflux for four hours with concentrated sulfuric acid. Hydrolysis of the reaction mixture in an ice-bath afforded **110** in 83% yield.

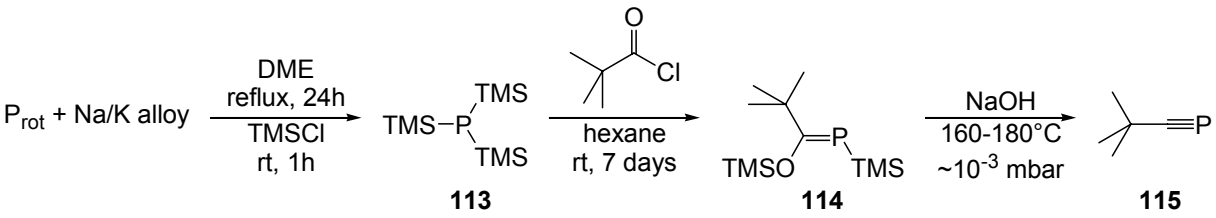


Scheme 3.8: Synthesis of pyrone-oxazoline **112**

As described by Breit,[124] **111** was prepared by amide coupling with thionyl chloride and subsequent addition of the amino alcohol and triethyl amine. Amide **111** was obtained in up to 70% yield. Instead of using Mitsunobu-conditions,[127] the following ring-closure was performed with (methoxycarbonyl-sulfamoyl) triethylammonium hydroxide, inner salt (*Burgess'* reagent) to afford the oxazoline **112** in 77% yield.[128]

3.3.2 Synthesis of Phosphaalkyne

tert-Butylphosphaalkyne was prepared according to the reaction sequence depicted in Scheme 3.9. Tris(trimethylsilyl)phosphine is prepared from sodium-potassium alloy, red phosphorus and trimethylsilyl chloride in DME.[129] The intermediately formed sodium-potassium phosphide reacts with trimethylsilyl chloride to yield **113** (58%). $P(TMS)_3$ reacts with pivaloyl chloride in pentane to a bright yellow solution of phosphaalkene **114** (88%).[130]

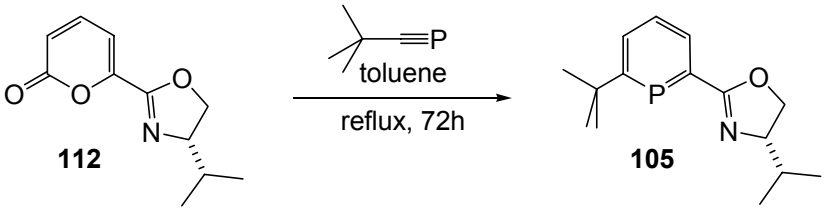


Scheme 3.9: Three-step synthesis of tert-butylphosphaalkyne **115**

According to Rösch *et al.* β-elimination of hexamethyldisiloxane from phosphaalkyne **73** was obtained under NaOH catalysis.[131] The reaction takes place in a vacuum apparatus under approximated 10^{-3} to10^{-4} mbar. An aggravating fact is the high volatility of both substrate and product, which have to be trapped seperately in individual cooling traps at -78°C and -196°C, respectively. First trials gave unsatisfactory yields, because the contact time between substrate and catalyst was too short and the trapping proved inefficient. Eventually, preparation of phosphaalkyne **115** was achieved with the kind help of Evelyn Fuchs and Bernhard Breit (University of Freiburg im Breisgau) who provided the suitable reaction apparatus and expert knowledge. Copound **115** was obtained in 61% yield as a 3.79 M solution in $(TMS)_2O$.

3.3.3 [4+2]-Cycloaddition of α-Pyrone and *tert*-Butylphosphaalkyne

The cycloaddition step was performed according to the published synthesis of **105** by mixing pyronoxazoline **112** and *tert*-butylphosphaalkyne **113** in toluene (Scheme 3.10). After heating to 140 °C for 3 to 5 days a dark brown oil was obtained. According to the publication, Kugelrohr distillation resulted in a lighter colored compound, but still separation from the starting material was not achieved. As described in the literature procedure compound **105** was obtained with residual starting material as proven by ^{1}H NMR. ^{31}P NMR showed a single peak at 205 ppm, which is in the typical range for λ^3-phosphinines.



Scheme 3.10: Synthesis of phosphininoxazoline **105**

When storing the product mixture at ambient atmosphere (the purification method applied did not suggest any particular sensitivity towards oxygen or water) 'decomposition' of the product occurred. Although only a slight visible change took place (*i.e.* intesification of the color) the new ^{31}P NMR spectrum displayed two new signals around 0 ppm, while the signal at 205 ppm had disappeared. (Figure 3.3).

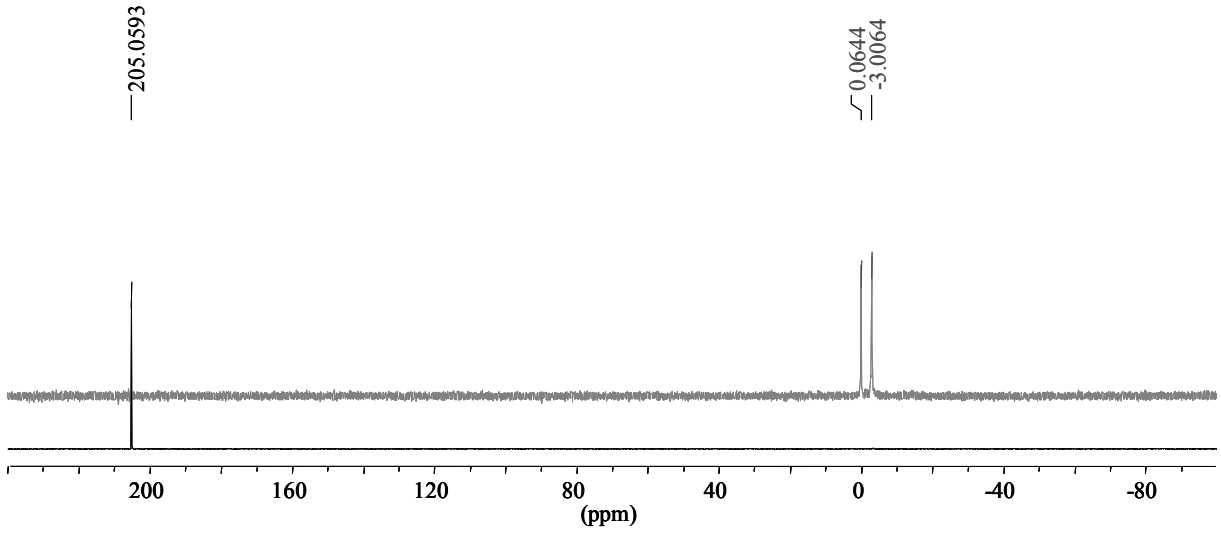
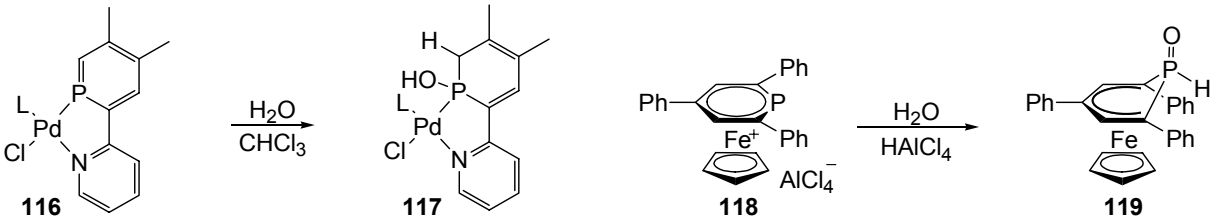


Figure 3.3: ^{31}P{^{1}H} NMR of **105** (bottom) and its 'decomposition' products (top). The spectra are not corrected to the internal standard, and therefore differ from the values given in Experimental.

The ^{1}H NMR spectrum revealed two new species which showed the same sets of signals as **66**, but were somewhat downfield shifted. One set of signals exhibiting a huge coupling (~485

Hz), appeared far downfield at 8.7 ppm. This suggested the addition of a proton, which is directly attached to the phosphorus atom ($^1J_{PH}$ = 110 Hz to 1200 Hz).[132] A broad signal at 9.85 ppm and 9.4 ppm, respectively, suggested an acidic proton. The addition of water from atmospheric moisture seemed to have occured.

The addition of water to phosphinine-complexes was previously observed by Schmid *et al.*[133] and Nief *et al.*.[134] In case of a palladium-complex **116** with P,N-chelating NIPHOS-ligand, addition of water afforded a palladium-coordinated λ^3-1,2-dihydrophosphinine **117** (Scheme 3.11, top). Addition of water to a (η^6-phosphinine)-(η^5-cyclopentadienyl)iron(II) complex **118** resulted in the formation of (η^5-phosphacyclohexadienyl)-(η^5-cyclopentadienyl)iron(II) **119** (Scheme 3.11, bottom).



Scheme 3.11: Reaction of phosphinine-complexes with water

The NIPHOS-adduct ring-moiety (Scheme 3.11, left) can be regarded as phosphinous acid tautomer of a secondary phosphine oxide. Secondary phosphine oxides are known to coordinate either *via* the 'hard' oxygen or in the phosphinous acid tautomeric form *via* the 'soft' phosphorus donor.[135] In the second example (Scheme 3.11, right), formation of a secondary phosphine oxide is observed. Here, one proton is consumed by the aluminate anion and neither the lone-pair at the phosphorus atom nor the electron-pairs at the oxygen atom participate in the coordination at the iron center.

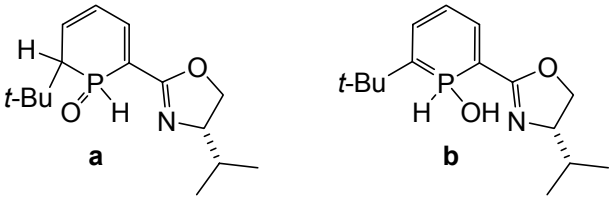


Figure 3.4: Possible water-adducts of phosphineneoxazoline

B. Breit suggested the water-adduct structure **a** (Figure 3.4), which he claimed to have observed after column chromatography. While a direct P-H bond seemed likely, due to the large coupling observed in the ^{1}H NMR spectrum and the non-decoupled ^{31}P NMR, the proton in α-position however was not in accordance with the signal observed at 9.4 or 9.85 respectively. This suggested a somewhat more acidic proton as displayed in **b**. However,

structure **b** suggests that the phosphacycle still had aromatic character.[136] The very high-field shift in the ^{31}P NMR instead suggests that aromaticity is lost.

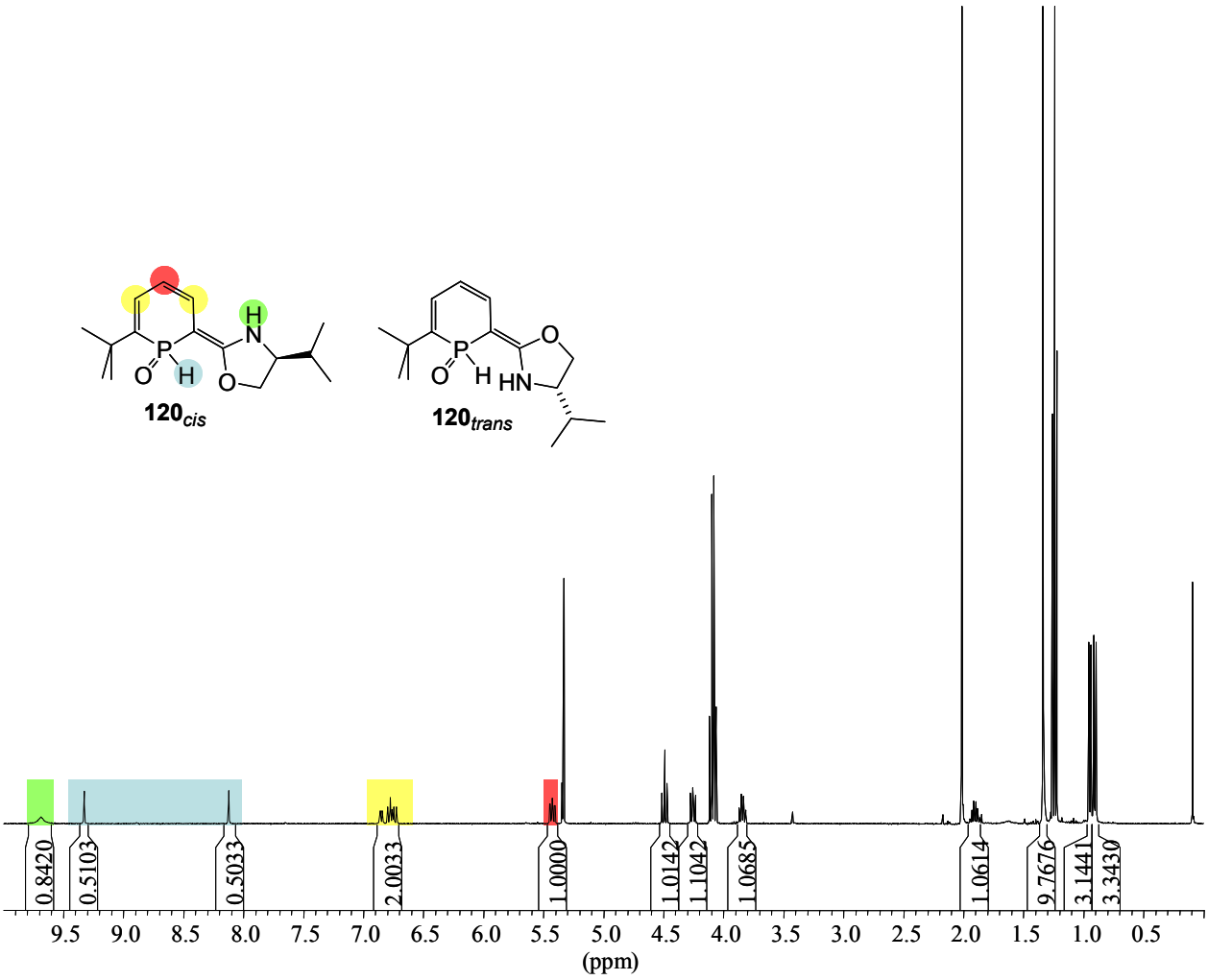


Figure 3.5: ^{1}H NMR Spectrum of **120**$_{cis}$ (spectrum in CD_2Cl_2, contains ethyl acetate peaks)

Reproduction of the synthesis and work-up by column chromatography afforded two isomers of the water-adduct, of which one could be crystallized from ethyl acetate. The structure was solved by x-ray crystallography (compare 3.3.4), and accounted very well for the characteristics observed in NMR spectrometry. The crystal structure matched *cis*-alkene **120**$_{cis}$, which shows a direct P-H bond and an N-H bond which accounts for the broad signal at 9.85. The X-ray crystal structure is discussed in Chapter 3.3.4 and the corresponding ^{1}H NMR spectrum is depicted in Figure 3.5. The conformation of the other isomer *trans*-alkene **120**$_{trans}$ was determined by difference NOESY which displayed the proximity of the phosphorus-bound and the nitrogen-bound proton.

Schmid *et al.* proposed three different mechanisms for the formation of the palladium-NIPHOS water-adduct (*vide supra*). They suggested two different stepwise mechanisms (**I** and **II**) starting either with a nucleophilic attack, or an electrophilic attack. As a third

possibility they envisioned a concerted mechanism (**III**). Without naming the reasons pathway **I** was stated to be the one most likely to occur.

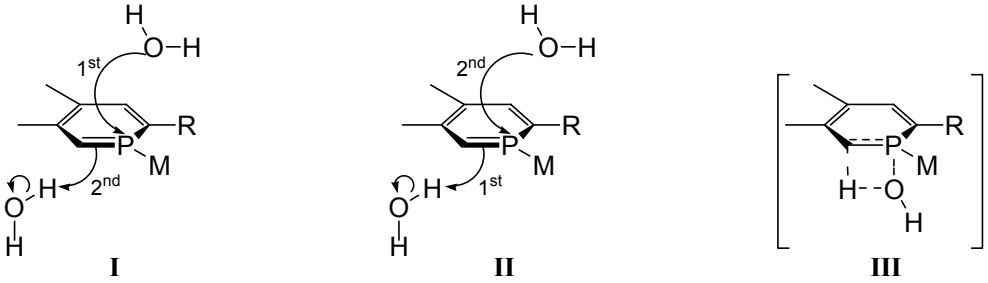
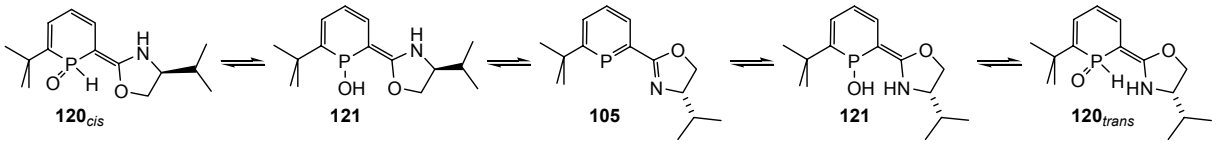


Figure 3.6: Proposed mechanism by Schmid *et al.* for the formation of water adduct

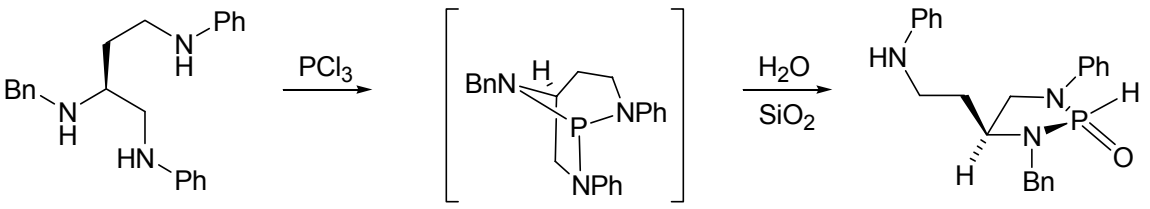
In our case the exact mechanism of water-addition is also unknown. From what is known of the chemistry of λ^3-phosphinines, the attack of a proton can be excluded. Either the mechanism is concerted or occurs by nucleophilic attack of OH^- or water to the phosphorus. Subsequent addition of a proton, leads to a 1,2-dihydrophosphinine or 1,4-dihydrophosphinine (compare 3.1.2) which can possibly tautomerize to the observed water-adducts.



Scheme 3.12: Possible interconversion of the water-adducts

In solution the two isomers **120*cis*** and **120*trans*** slowly interconvert. Thus, one can expect that the water-addition is reversible. Scheme 3.12 depicts a possible equilibrium. In tautomer **121**, the position of the proton, attached to the nitrogen could also be in *ortho*- or *para*-position to the phosphorus atom. Thus, the oxazoline-ring would remain intact. However, in all these isomers the conjugation of double bonds would be interrupted.

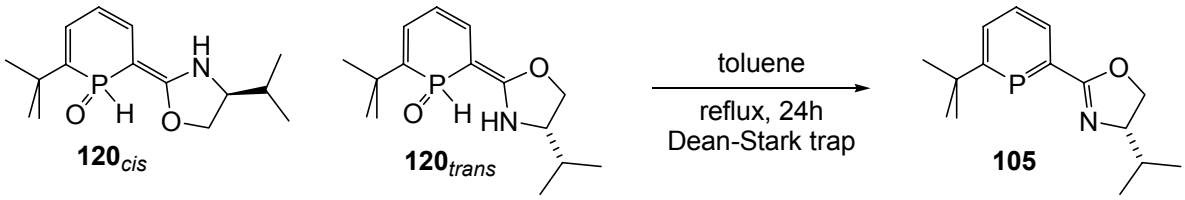
The crystal structure showed that only one diastereomer of **120*cis*** was obtained (compare 3.6). This allows the assumption that nucleophilic attack at the phosphorus is substrate-controlled. This is somewhat surprising, since the stereocenter at the oxazoline ring is relatively remote. Nemoto *et al.* have performed a stereoselective synthesis of a secondary phosphine oxide through substrate control, as depicted in Scheme 3.13.[137]



Scheme 3.13: Substrate-controlled synthesis of a secondary phosphine oxide

3.3.4 (*S*)-2-(6-*tert*-Butylphosphinin-2-yl)-4,5-dihydro-4-isopropyloxazole

The observation of an equilibrium between **120**$_{cis}$ and **120**$_{trans}$ led to the assumption, that shifting the equilibrium back to **105** should be possible. Azeotropic removal of water was achieved by refluxing the water adducts in toluene and use of a Dean-Stark trap. Indeed, ligand **105** could be obtained after 24 hours as a yellow oil. Thus, purification of the [4+2]-cycloaddition crude mixture can be performed by column chromatography and subsequent azeotropic removal of water.



120$_{cis}$ **120**$_{trans}$ **105**

Scheme 3.14: Preparation of **105** from water-adducts

The ^{1}H NMR spectrum of **105** is depicted in Figure 3.7. The ligand was stored in a glove-box at ambient temperature. While the color darkened with time to light brown, the spectrum remained unchanged.

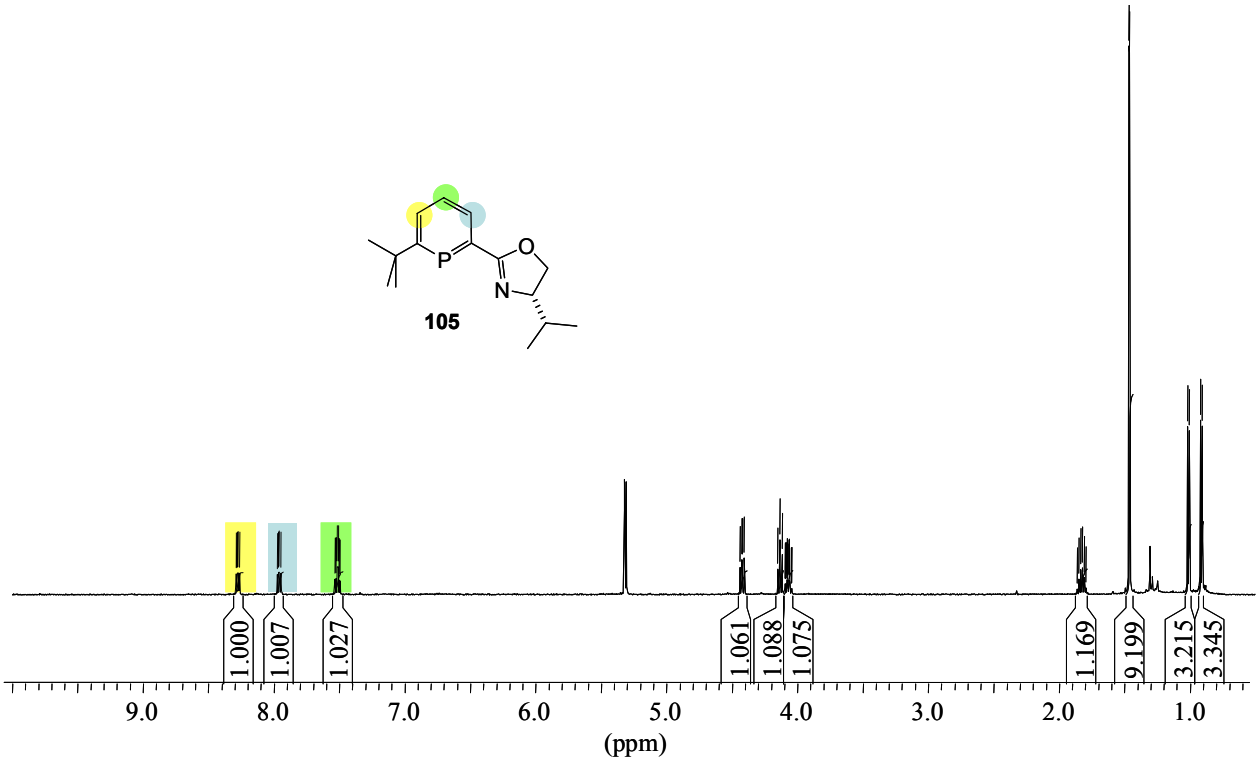
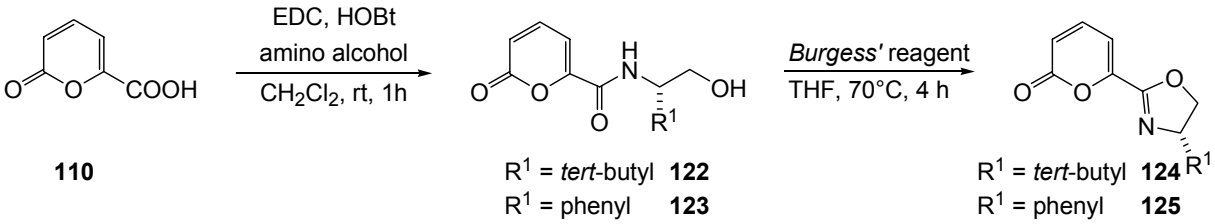


Figure 3.7: ^{1}H NMR Spectrum of **105** (spectrum in CD_2Cl_2)

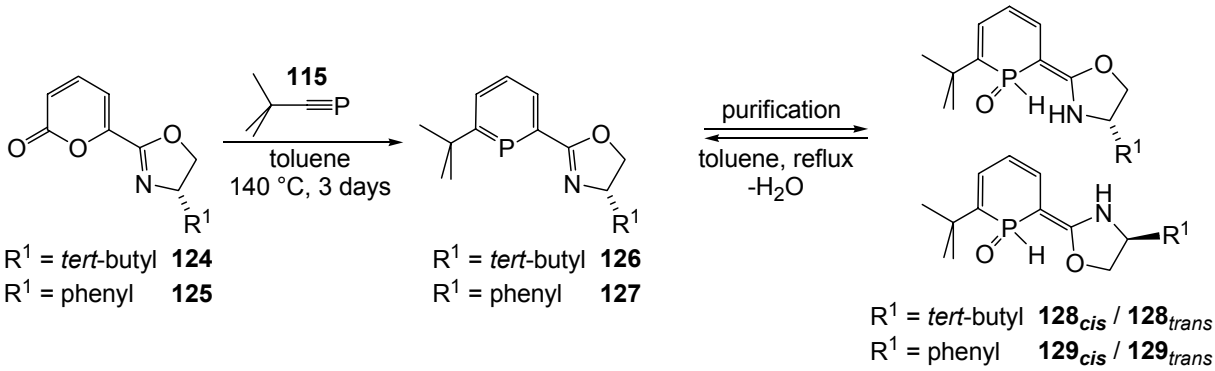
3.3.5 Analogous Phosphininoxazolines

In analogy to **105** two related ligands were prepared. These are bearing different groups in 4-position of the oxazoline ring, namely *tert*-butyl or a phenyl-group. The synthesis followed basically the same route as the preparation of **105**. However, the amide coupling was performed using ethyl-*N,N'*-dimethylamino-propyl-carbodiimide hydrochloride (EDC) and 1-hydroxybenzotriazole (HOBt). This was a faster and also more efficient method for the preparation of the amides **122** (40%) and **123** (52%) than the one employed for **111**.[138] The oxazolines **124** and **125** were obtained in good yields (89% and 55%) using *Burgess'* reagent.



Scheme 3.15: Synthesis of pyronoxazolines **124** and **125**

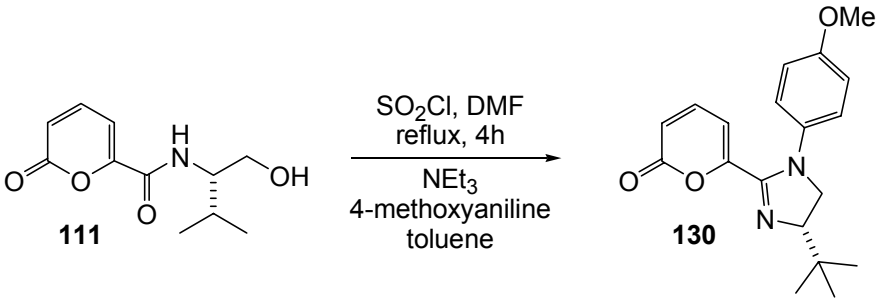
Both pyrones were reacted with phosphaalkyne **115** to give the water-adducts **128** and **129** after purification by column chromatography. The phosphinines **126** (31%) and **127** (28%) were obtained by azeotropic removal of water in toluene with a Dean-Stark trap. The ^{31}P NMR chemical shifts of **126** and **127** are in complete accordance with those observed for other phosphinines, with 208.5 ppm and 210.8 ppm, respectively.[132]



Scheme 3.16: Preparation of phosphininoxazolines **126** and **127**

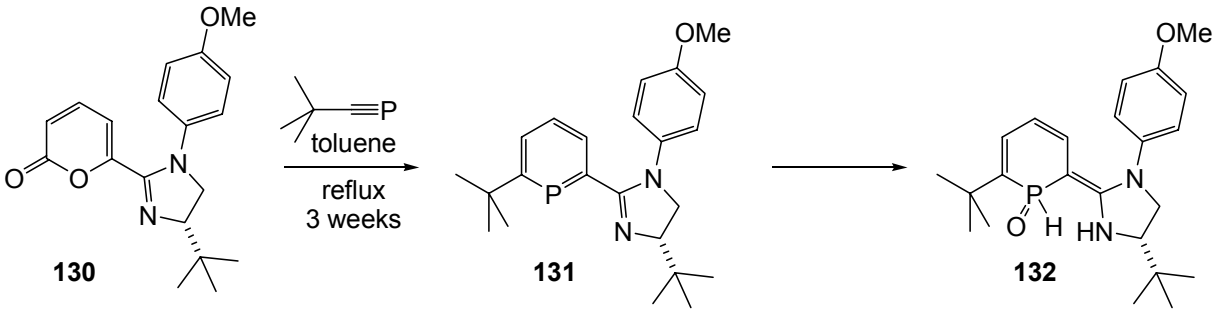
3.3.6 A Related Chiral Chelating Phosphininimidazoline

The imidazoline **130** was obtained *via* a procedure, previously described by Casey and co-workers.[139] Herein, an amide is reacted with thionyl chloride to form an intermediate imidoyl chloride. This then reacts with a primary amine in the presence of triethylamine to the corresponding imidazoline. **130** was obtained in 65% yield.



Scheme 3.17: Reaction of **111** to *N*-(4-methoxy-aninline)-imidazoline **130**

When **130** was reacted under [4+2]-cycloaddition conditions for three weeks, about 8% of a water-adduct could be isolated. It is noteworthy, that while with analogous oxazolines *cis*- and *trans*-somers were obtained, only *trans* isomer **132** was isolated from the reaction of **130**. With these trace amounts of product, formation of the corresponding phosphinine was attempted under the same conditions as for the oxazolines **112**, **124** and **125**. A ^{31}P NMR spectrum revealed formation of, phosphinine-imidazoline **131** showing a chemical shift of 212.4 ppm.

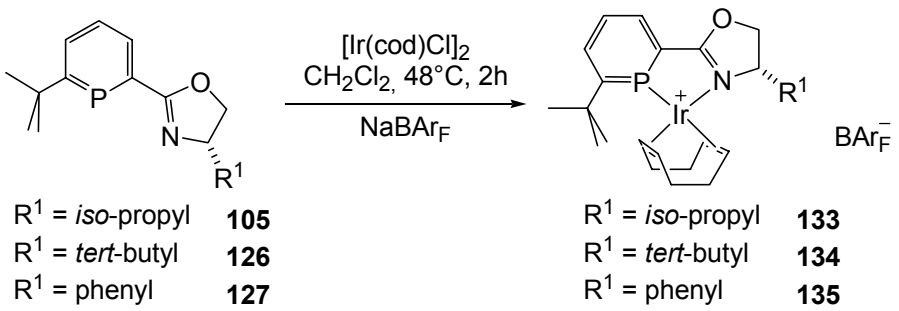


Scheme 3.18: Reaction of **130** giving trace amounts of water-adduct **132** and the corresponding phosphinine **131**

3.4 Synthesis of Phosphinine-Iridium Complexes

3.4.1 Iridium-Complexes with Chelating Phosphinines

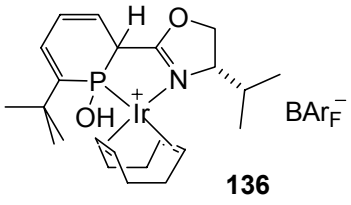
With ligand **105** in hands, the respective cationic iridium complex was prepared using standard procedures. $[Ir(cod)Cl]_2$ was reacted with **105** and stirred for two hours at 48°C. After cooling to room temperature and anion exchange with $NaBAr_F$ complex **133** was obtained.



Scheme 3.19: Preparation of iridium-complex **133, 134** and **135**

In contrast to other PHOX-iridium complexes the addition of $NaBAr_F$ resulted in a drastic color-change from dark-red to almost black. Black needles were obtained when a concentrated solution of **133** in dichloromethane was treated with hexane.

However, when a concentrated solution of **133** in dichloromethane was treated with diethyl ether, an orange solid precipitated. Based on ^{1}H- ^{13}C- and ^{31}P NMR data, structure **136** (Figure 3.8) was suggested.



136

Figure 3.8: Proposed structure of **136**

This structure denotes that a water-adduct was formed, implying that the diethyl ether contained traces of water. As can be seen in Figure 3.9 the protons belonging to the phosphorus heterocycle are shifted the most, *i.e.* about 2.5 ppm upfield. The additional proton α to the phosphorus atom was assigned by COSY since coupling to the vicinal proton was observed. The signal was found at 4.25 ppm, and the corresponding ^{13}C NMR signal at 44.2 ppm with $^{1}J_{CP}$ = 29.3 Hz. This shift is in accordance with reference 121 (compare Scheme

3.11, left), where the proton α to the phosphorus atom has a ^{13}C NMR shift of 36.9 ppm ($^{1}J_{CP}$ = 57.1 Hz). ^{31}P NMR signal is shifted upfield by about 90 ppm from 176.9 ppm to 87.5 ppm.

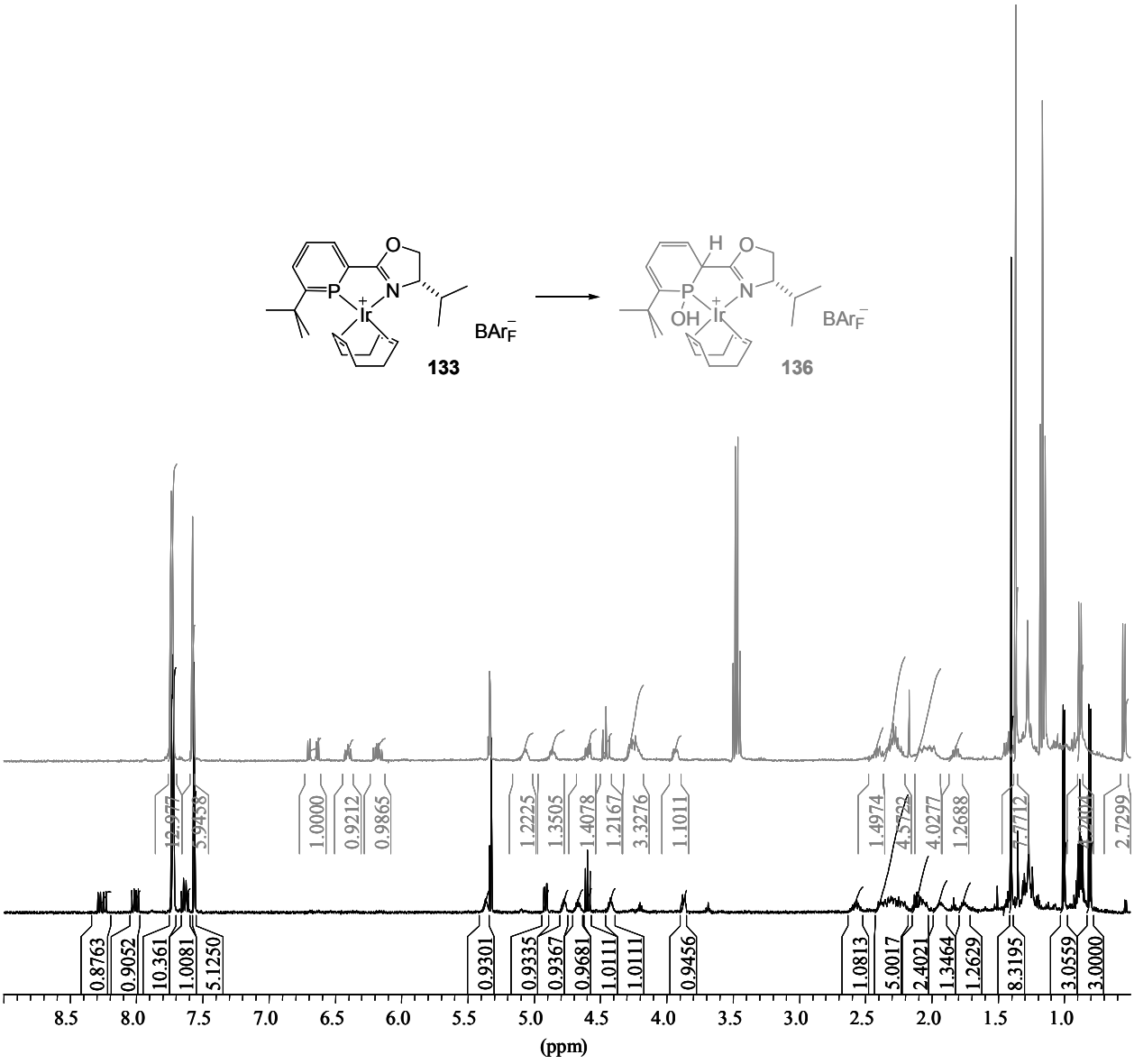


Figure 3.9: ^{1}H NMR spectra of **133** (bottom) and **136** (top, with residual diethyl ether)

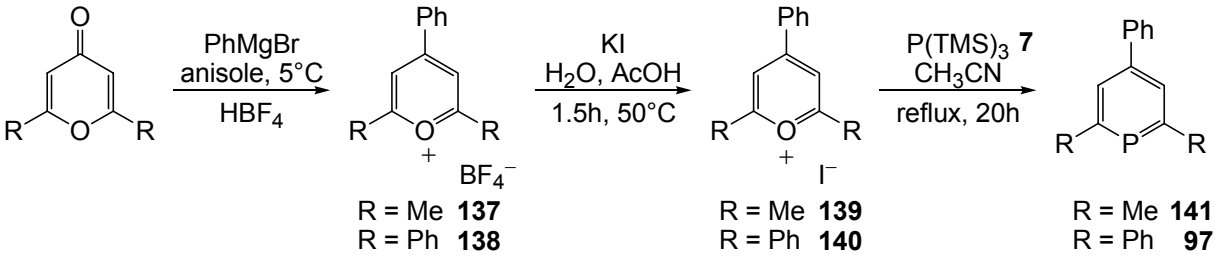
Although **105** containes bulky substituents in 2- and 6-position, formation of a η^6-phosphininoxazoline-iridium complex is unlikely (compare 3.1.3).[120] ^{31}P NMR spectra of η^6-phosphinin-iridium complexes were reported to display a more high-field shift (58 ppm). However, the exact structure of **136** remains unknown.

Iridium-complexes **134** and **135** (**$^{31}P\{^{1}H\}$ NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 179.3 ppm and 176.2 ppm) with ligands **126** and **127** were prepared, accordingly. Unfortunately they contained up to 30% of unidentified side-products with phosphorus signals at 91.3 ppm and 80.8 ppm, and 102.5 ppm and 88.2 ppm, respectively.

3.4.2 Iridium-Complexes with Monodentate Phosphinines

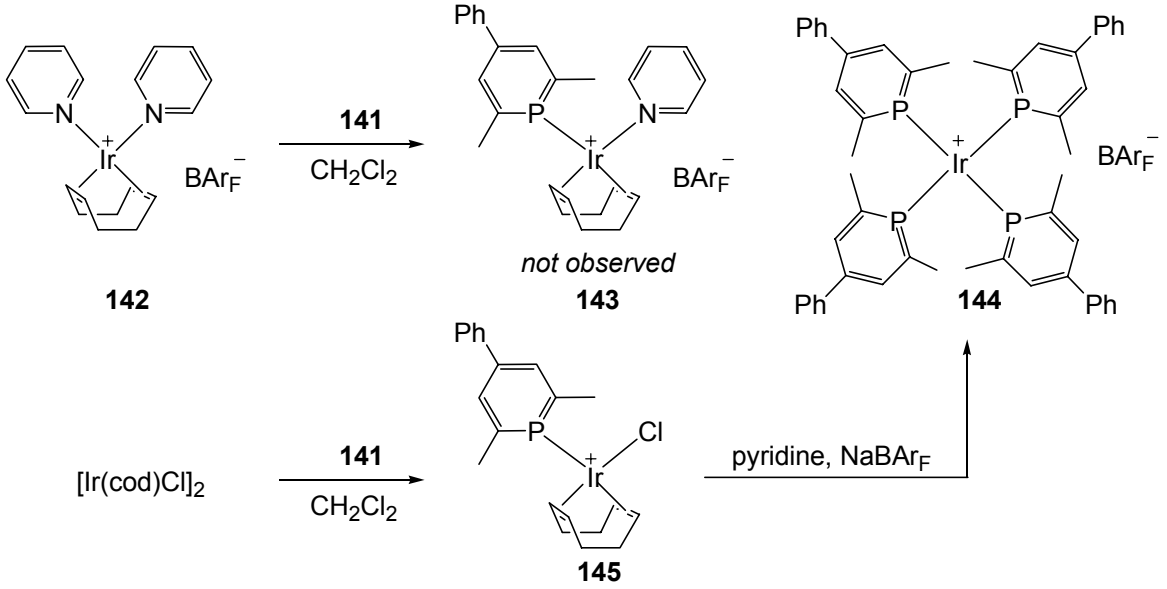
It seemed feasible to synthesize an achiral analogue of **133**, using readily available monodentate phosphinines and pyridine as ligands. With this phosphinine-version of *Crabtree's* catalyst, a better comparison of phosphine and phosphinine ligands (*e.g.* in terms of reactivity in hydrogenation reactions) was envisioned.

2,4,6-Trisubstituted λ^3-phosphinines can be obtained from the corresponding pyrylium salts by the formal exchange of O^+ and P. As phosphorus atom source serves phosphine or a suitable "masked" phosphine, such as $P(TMS)_3$ **113** (see 3.3.2). Two different monodentate λ^3-phosphinines, namely 2,6-dimethyl-4-phenyl-phosphinine **141** and 2,4,6-triphenyl-phosphinine **142** were synthesized.



Scheme 3.20: Synthesis of 2,4,6-trisubstituted phosphinines **95** and **96**

The anion exchange from tetrafluoroborate to iodide was reported to improve the subsequent step, in terms of yield and equivalents of phosphine **113** needed.[122] The phosphinines **141** and **97** were obtained in 52% and 50% yield, respectively (Scheme 3.20).



Scheme 3.21: Attempted synthesis of a phosphinine analogue of *Crabtree's* catalyst

When $[Ir(cod)py_2]BAr_F$ was treated with ligand **141** in dichloromethane-d_2 the ^{31}P NMR signal shifted from 193.6 ppm for the free ligand to 144.9 ppm. When a TLC was run, two spots occured, one bright yellow spot with the same low R_f value as $[Ir(cod)py_2]BAr_F$, and a red spot (R_f = 0.86 in CH_2Cl_2). The red product was isolated by column chromatography. Single crystals were obtained by slow evaporation of the solvent (dichloromethane). Analysis by NMR and X-ray revealed the main product to be the homoleptic tetrakis(2,6-dimethyl-4-phenyl-phosphinine)iridium(I) BAr_F complex **144**.

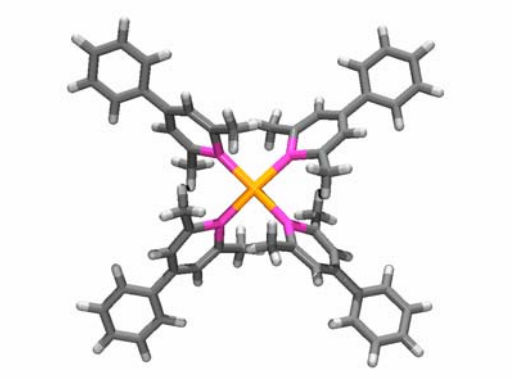


Figure 3.10: X-ray structure of **144**

Starting the synthesis by reaction of $[Ir(cod)Cl]_2$ with **141**, subsequent reaction with pyridine and anion exchange with $NaBAr_F$, also gave the homoleptic complex **144** *via* the intermediate **145**. Since a *Crabtree's* catalyst analogue was not obtained by neither of these routes, the synthesis was abandoned.

3.5 Application in Catalysis

3.5.1 Hydrogenation

Iridium-complex **133** was tested in the hydrogenation of several highly substituted unfunctionalized and functionalized alkenes, as well as *N*-(1-phenylethylidiene)-aniline.

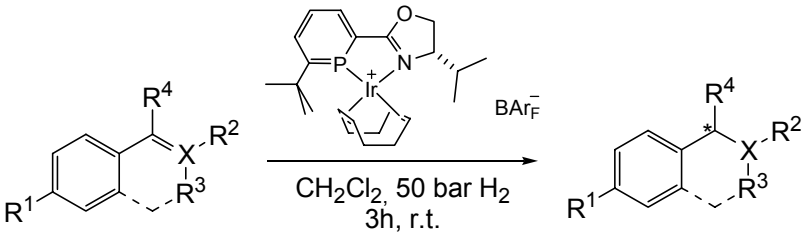


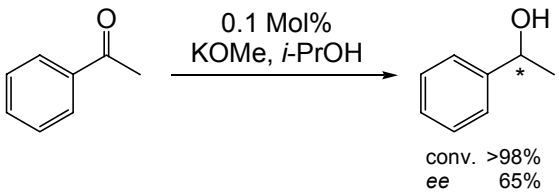
Table 3.1: Hydrogenation with complex **133**

entry	R^1	R^2	R^3	R^4	X	conv.[%][a]	ee [%][a]
1	H	Ph	H	Me	C	67	33 (*R*)
2	OMe	Me	H	Me	C	86	21 (*R*)
3	OMe	H	Me	Me	C	92	rac
4	OMe	Me	Me	Me	C	3	23 (-)
5	OMe	H	$(CH_2)_2$	Me	C	>98	rac
6	H	CO_2Et	H	Me	C	58	29 (*R*)
7	H	CH_2OH	Me	H	C	>98	92 (-)
8	H	Ph	H	Me	N	>98	37 (*R*)

[a]determined by GC, [b]determined by HPLC

Compared to other PHOX-ligands (see chapter 2.5, page 37) complex **133** gave relatively low conversions and enantioselectivities. Only an internal alkene (entry 5), the imine (entry 8) and allylic alcohol (entry 7) were hydrogenated to full conversion. The latter substrate was hydrogenated with high enantioselectivity (92%). Other enantioselectivities were in the range of 21 to 37 %. A *Z*-alkene (entry 3) could be reduced almost to full conversion, but the product was racemic.

Transfer hydrogenation of acetophenone with potassium methoxide in *iso*-propanol gave better results. The reaction was complete within minutes, and showed an enantioselectivity of 65% *ee*.



Scheme 3.22: Transfer Hydrogenation with **130**

3.5.2 Allylic Alkylation

Iridium

Many examples of the iridium-catalyzed asymmetric allylic alkylation with electron-poor catalysts were reported by Helmchen *et al.*. Especially good results were obtained by using rather electron-poor ligands. Since phosphinines show good π-acceptor abilities, it was interesting to see, how they perform in comparison to electron-poor ligands, such as trifluoromethyl-substituted phosphinoxazolines,[140] and phosphoramidites.[141]

Chelating ligand **66** as well as two monodentate phosphinines **141** and **97** were tested in the iridium-catalyzed allylic alkylation of monosubstituted allyl acetates, namely 1-phenylallyl-acetate (**br**) and cinnamylacetate (**lin**). The results are compiled in Table 3.2 and Table 3.3.

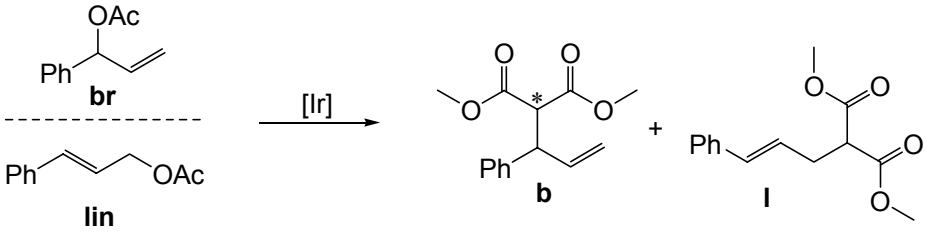


Table 3.2: Iridium-catalyzed allylic alkylation

entry	substrate	anion	additive	T [°C]	conv.[%][a]	ee [%][b]	b/l[a]
1	br	Cl^-	-	20	>98	rac	>98:2
2	lin	Cl^-	-	20	11	*nd*	50:50
3	br	BAr_F^-	-	20	>98	rac	>98:2
4	lin	BAr_F^-	-	20	10	*nd*	50:50
5	lin	Cl^-	-	65	>98	13 (*R*)	63:37
6	lin	Cl^-	$ZnCl_2$	65	>98	21 (*S*)	87:13
7	lin	Cl^-	CuCl	65	16	rac	50:50
8	lin	Cl^-	LiCl	65	61	rac	74:16

[Ir]: 4 mol% **130** or 4 mol% **105** and 2 mol% $[Ir(cod)Cl]_2$, sodium *O,O'*-dimethyl malonate, THF, 24 h
[a]determined by GC, [b]determined by HPLC

The results obtained in iridium-catalyzed allylic alkylation were comparatively disappointing, compared to reported systems.[142] While good branched-to-linear-ratios were obtained using the branched substrate (**br**), no enantioselectivity was observed. Only when the linear substrate (**lin**) was used, some selectivity was obtained, whereas at the same time the branched-to-linear-ratio suffered. In accordance with literature, full conversion for the linear substrate was often only reached at elevated temperature.[140] When $ZnCl_2$ was used as additive, the enantioselectivity could be slightly improved. However, the opposite enantiomer was obtained. Variation of the anion did not show any effect (entries 1-4).

Table 3.3: Iridium-catalyzed allylic alkylation with monodentate phosphinines

entry	ligand	substrate	anion	[M]/L	time [h]	conv.[%][a]	b/l[a]
1	**141**	br	Cl^-	1	24	93	94:6
2	**141**	lin	Cl^-	1	24	4	1:1
3	**141**	br	Cl^-	2	24	>99	87:13
4	**141**	lin	Cl^-	2	24	13	64:32
5	**97**	br	Cl^-	1	24	>99	97:3
6	**97**	lin	Cl^-	1	24	63	83:17
7	**97**	br	Cl^-	2	24	>99	>98:2
8	**97**	lin	Cl^-	2	24	59	80:20
9	PPh_3	br	Cl^-	1	3	15	98:2
10	PPh_3	lin	Cl^-	1	24[c]	58	64:36
11	$P(OPh)_3$	br	Cl^-	1	3	99	98:2
12	$P(OPh)_3$	lin	Cl^-	1	3	98	98:2
13	ohne[b]	br	-	–	3	98	98:2
14	ohne[b]	lin	-	–	24[c]	89	32:68

The reaction was run in THF. 2 mol% $[Ir(cod)Cl]_2$ and 2 equivalents sodium malonate were used.
[a] GC-MS, [b]Helmchen *et al.*, [c] 65°C

Table 3.3 displays that the branched substrate often reacts to full conversion in 24 hours, whereas the linear substrates only reach up to 89% conversion (entry 12). As above (Table 3.2), the branched-to-linear-ratio is higher in those cases where the branched substrate is used. Phosphinine ligand **141** is superior to ligand **97** regarding conversion and branched-to-linear-ratio. The catalyst-to-ligand-ratio shows little influence. Phosphinines **141** and **97** are compared to other monodentate phosphorus ligands, *i.e.* in terms of reactivity (the results are from Helmchen *et al.*, entries 9-14)[142] Apparently the reactivity of the complexes IrCl(cod)L increases in the order L = PPh_3 < **141** < **97** < $P(OPh)_3$.

Palladium and Rhodium

Palladium- and rhodiumprecursor were also tested in the allylic alkylation of monosubstituted allyl acetates with **105**. For the palladium-catalyzed allylic alkylation of the monosubstituted allyl acetates, (η^3-allyl)-chloro-palladium(II)-dimer and for the rhodium-catalyzed allylic alkylation *O*,*O*-acetylacetonato-bis(η^2-ethylene)-rhodium(I)[143] was used. The latter catalyst precursor was prepared for the rhodium-catalyzed allylic alkylation according to Hayashi *et al*.[144] Therefore, a solution of $[Rh(\mu\text{-}Cl)(ethylene)_2]_2$ and acetyl acetone were treated with a solution of potassium hydroxide at -78°C.

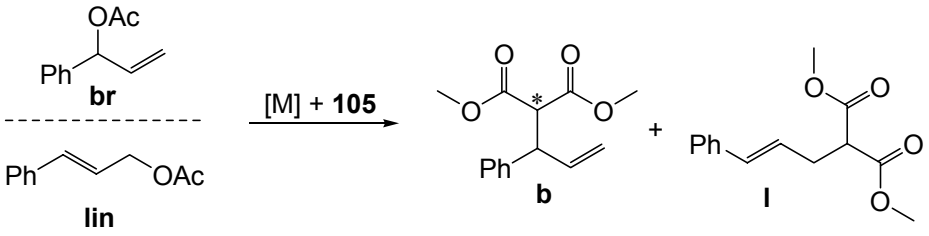


Table 3.4: Allylic alkylation with palladium- and rhodium-catalysts

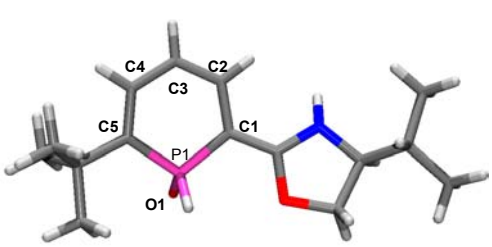
substrate	[M]	anion	additive	T [°C]	conv.[%][a]	ee [%][b]	b/l[a]
br	Pd	Cl^-	-	20	>98	33 (*S*)	33:67
lin	Pd	Cl^-	-	20	>98	47 (*S*)	38:62
br	Rh	acac	-	20	>98	rac	85:15

[Pd]: 4 mol% **105**, 2 mol% $[Pd(allyl)Cl]_2$, 3.1 eq dimethyl malonicester, 3.1 eq BSA, KOAc, CH_2Cl_2, 24h.
[Rh]: 5 mol% **105** and $[Rh(acac)(C_2H_4)_2]$, 3eq sodium malonate, THF, 15h.
[a]determined by GC, [b]determined by HPLC

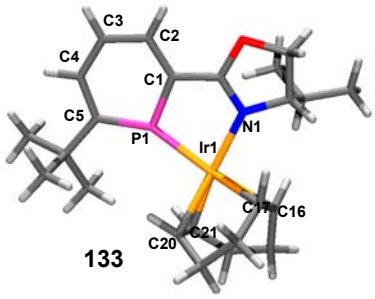
In palladium-catalysis ligand **105** performed better than in iridium-catalysis. Enantioselectivities of 33% and 47% were observed for the branched and the linear substrate, respectively. Unfortunately, here the branched-to-linear-ratio was unfavorable. The rhodium-catalyst gave a better branched-to-linear-ratio, but only racemic product was obtained.

3.6 Discussion of X-Ray Crystal Structures

X-ray structure of **120**$_{cis}$ (see 3.3.3) shows that aromaticity and planarity is lost in the water-adduct. The phosphorus atom is approximately 14° below the plane. Furthermore, the structure displays significant discrimination in bond-length of the localized double bonds (1.353 and 1.359 Å) and the single bonds (1.433 and 1.428 Å) of the phosphorus heterocycle. P-C bond-lengths (1.775 and 1.755 Å) are also slightly longer than in the aromatic coordinated ligand (1.73 Å).



120$_{cis}$



133

Table 3.5: Selected bond lengths and angles of **120**$_{cis}$, **133** and **96**[145]

[Å]/[deg]	**120**$_{cis}$	**133**	**96**[145]
C1-C2	1.428 (2)	1.373 (5)	1.396/1.410
C2-C3	1.359 (2)	1.379 (6)	1.372/1.404
C3-C4	1.433 (3)	1.370 (6)	-
C4-C5	1.353 (3)	1.394 (6)	-
P1-C1	1.756 (2)	1.728 (3)	1.734/1.746
P1-C5	1.774 (2)	1.730 (3)	-
P1-O1	1.502 (2)	-	-
Ir1-P1	-	2.295 (9)	-
Ir1-N1	-	2.084 (3)	-
Ir1-C16	-	2.180 (3)	-
Ir1-C17	-	2.151 (3)	-
Ir1-C20	-	2.167 (3)	-
Ir1-C21	-	2.134 (3)	-
P-Ir-N	-	80.45 (8)	-
C-P-C	103.60 (8)	103.87 (7)	102.9

On the other hand, the X-ray structure of **133** (see 3.4.1) shows that aromaticity is conserved in the iridium complex. C-C bond lengths all lie in a narrower range (1.37 to 1.394 Å) and C-P bonds are considerably shorter (1.728 and 1.730 *versus* 1.756 and 1.774 Å). Furthermore, the phosphorus heterocycle is planar.

Column 3 gives X-ray structural data of 2,6-dimethyl-4-phenyl-λ^3-phosphinine **96**. C-C as well as C-P bond lengths account well for the aromatic structure and lie in the same range as

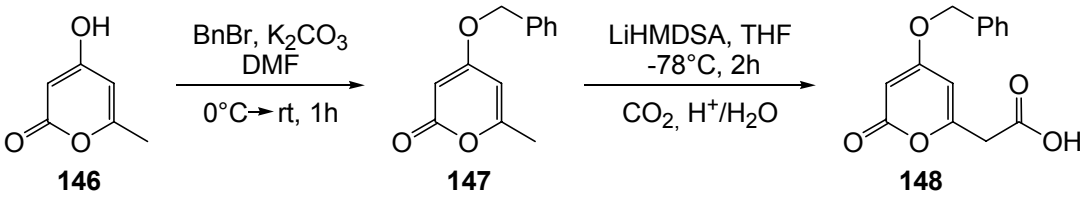
the structural values of **133**. However, the C-P-C angles of both structures **120**$_{cis}$ and **133** are in the same range as observed for monodentate ligand **96** with 103.6° and 103.87°, respectively.

The P-Ir-N angle (80.45°) matches well to those of other five-ring-chelating ligands (78.65 to 82.72°, compare chapter 2.7). The Ir-C bonds trans to the phosphorus are shorter than those of the other discussed complexes. The Ir-P bond is little shorter than those of complexes **80**, **82** and **83**, but still longer than that of complex **88**.

3.7 Towards 6-Ring-Chelating Phosphininoxazolines

The synthesis of related phosphininoxazolines capable of forming six-ring-chelates was tried by preparation of pyronoxazolines containing an additional methylene group between the pyrone- and the oxazoline-ring. Introduction of the phosphorus moiety was intended to be achieved by a [4+2]-cycloaddition reaction, as presented above (see 3.3.3).

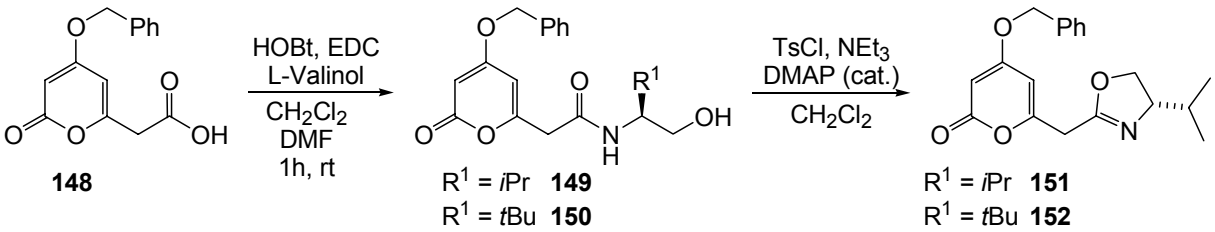
For the preparation of a 6-pyrone acetic acid derivative commercially available 4-hydroxy-methyl-pyrone **146** was chosen. After protection of the hydroxygroup with benzyl bromide, the methyl-group of compound **147** was lithiated. Reaction with gaseous carbon dioxide and acidic work-up afforded acid **148** in 85% yield.[146]



146 **147** **148**

Scheme 3.23: Preparation of acid **148**

Amide coupling was performed as described above (see 3.3.5) using ethyl-*N,N'*-dimethylamino-propyl-carbodiimide hydrochloride (EDC) and 1-hydroxybenzotriazole (HOBt). Amides **149** and **150** were obtained in 75% and 67% yield, respectively. Ring-closure was achieved with tosylchloride, triethylamine and catalytic amounts of 4-dimethylaminopyridine (DMAP). The oxazolines **151** and **152** were obtained in 96% and 84% yield, respectively.



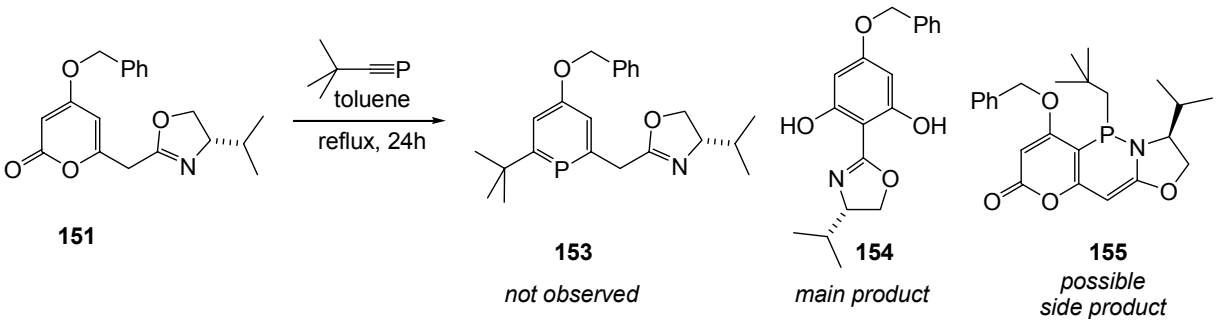
148

R^1 = *i*Pr **149**
R^1 = *t*Bu **150**

R^1 = *i*Pr **151**
R^1 = *t*Bu **152**

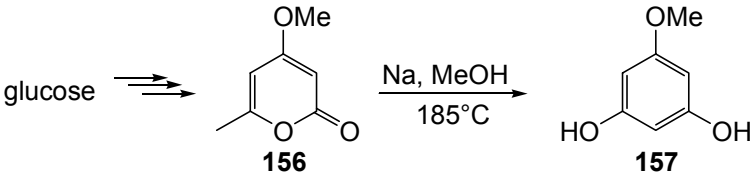
Scheme 3.24: Preparation of pyronoxazolines **151** and **152**

When **151** was subjected to the [4+2]-cycloaddition conditions stated above, *i.e.* reaction with phosphaalkyne **115** in toluene, no traces of the desired product **153** could be observed. A ^{31}P NMR was taken of the crude mixture. The spectrum showed no signals in the characteristic area for phosphinines (~ 190 to 210 ppm). However, one main product **154** was isolated from the reaction mixture. Also a small amount of a bright yellow side product, with the postulated structure of **155**, was obtained.



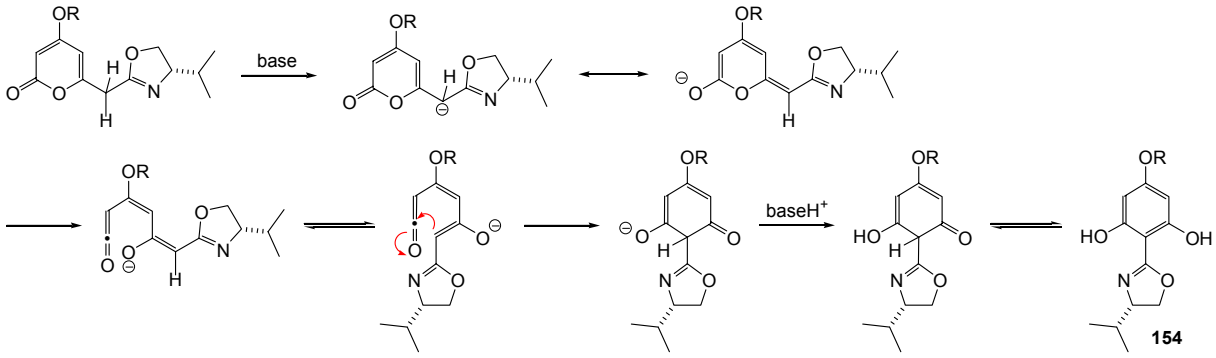
Scheme 3.25: Unwanted reaction of **151** under [4+2]-cycloaddition conditions

It is assumed that **154** was formed *via* a rearrangement previously described by Huber.[147] He observed the formation of a 4,5-disubstituted resorcinol when the corresponding 4,5-disubstituted 6-methyl-2-pyrone was heated with an alkali metal alkoxide. Hansen *et al.* used this method for the preparation of phloroglucinol methyl ether from glucose *via* a 6-methyl-2-pyrone (Scheme 3.26).[148]



Scheme 3.26: Synthesis of phloroglucinol methyl ether from glucose

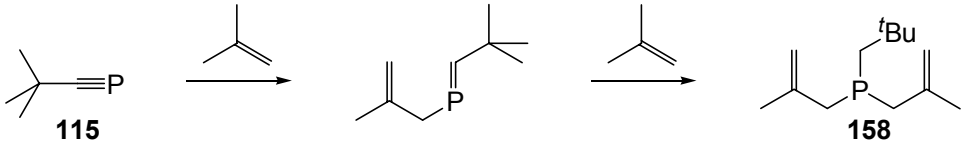
However, the formation of **154** under these relatively mild reaction conditions might be due to the stabilization of an intermediate carbanion by the electron-withdrawing oxazoline ring (compare Scheme 3.27). Only very drastic reaction conditions were reported so far.



Scheme 3.27: Mechanism of the formation of **154**

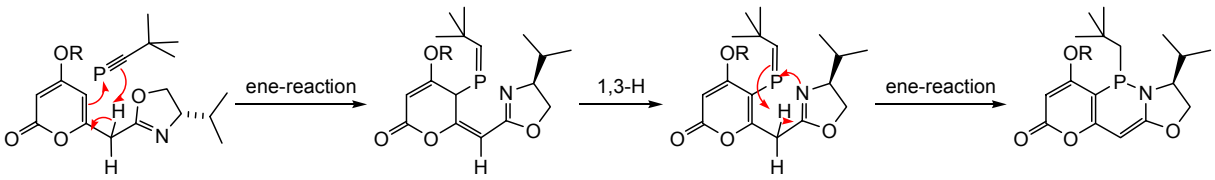
155 was postulated on the basis of ^{1}H- ^{13}C- and ^{31}P NMR. Some substructures, such as the *P*-neopentyl-group were strongly supported. The formation of this group can be achieved through two ene-reactions, which were previously reported for phosphaalkynes. For example, reaction of *tert*-butyl-phosphaalkyne with *iso*-butene gives phosphine **158** (Scheme 3.28).[149]

It is further known that pentamethyl-cyclopentadiene preferentially undergoes ene-reaction rather than Diels-Alder reaction with phosphaalkyne **115**.[150]



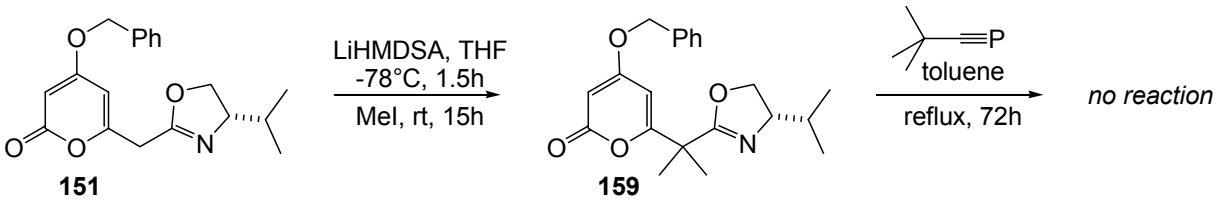
Scheme 3.28: Double ene-reaction with *iso*-butene

A possible mechanism for the formation of **155** is depicted in Scheme 3.29. After a first ene-reaction to the phosphaalkyne, a 1,3 shift reinstalls the 2-pyrone ring. Then a second ene-reaction provides **155**.



Scheme 3.29: Possible mechanism for the formation of **155**

To prevent the rearrangement to substituted dihydroxy-benzene **154** (Scheme 3.29), substitution of the methylene bridge of **151** was envisioned. Therefore, **151** was deprotonated with LiHMDS and quenched with methyl iodide. However, when **159** was subjected to the [4+2]-cycloaddition reaction conditions, no reaction occured.



Scheme 3.30: Envisioned [4+2]-cycloaddition reaction with **159**

Since a six-ring chelating phosphininoxazoline could not be obtained through [4+2]-cycloaddition, one has to think of a different approach. However, no further attempts towards the desired structure were undertaken in the course of this work.

3.8 Conclusion

In summary, three chiral phosphininoxazolines were prepared by dehydration of a water-adduct wherein the phosphorus atom is present as a secondary phosphine oxide. The corresponding cationic iridium-complexes were synthesized.

Ligand **105** showed good conversion and moderate selectivity in the iridium-catalyzed hydrogenation and transfer-hydrogenation. In palladium-catalyzed allylic alkylation it showed moderate enantioselectivities, but a highly unfavorable regioselectivity.

Recently, it was shown by Jiang *et al.* that secondary phosphine oxides are promising ligands in the iridium-catalyzed hydrogenation of imines.[151] The intermediate water-adducts possess a secondary phosphine oxide moiety, and thus could be tested in the hydrogenation of imines.

The synthesis of six-ring chelating phosphininoxazolines was attempted but could not be achieved by [4+2]-cycloaddition of a methyleneoxazoline-substituted 2-pyrone with phosphaalkyne. Instead a rearrangement, and presumably an ene-reaction, were observed.

An alternative approach towards phosphininimidazolines and six-ring chelating phosphininoxazlines could be attempted *via* dihydrostannabenzenes[152] and dihydrozirconabenzenes.[153]

Chapter 4

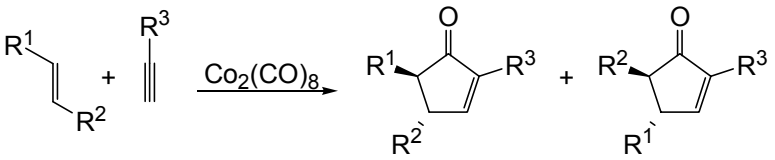
Asymmetric Catalytic Intramolecular Pauson-Khand Reaction

4 Asymmetric Catalytic Intramolecular Pauson-Khand Reaction

Metal-promoted cycloadditions do not only provide a means for the construction of complex cyclic stuctures from readily available starting materials, but are also among the most atom economical methodologies in organic synthesis.[154] One of the most prominent cycloadditions is the Pauson-Khand reaction.

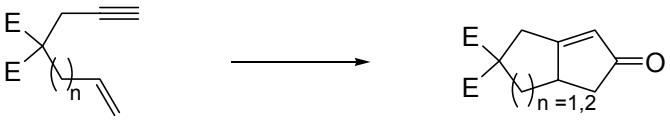
4.1 The Pauson-Khand Reaction

The Pauson-Khand reaction is a formal [2+2+1] cycloaddition of an alkene, an alkyne and carbon monoxide leading to a cyclopentenone. The reaction was first reported in the early seventies,[155] after Khand *et al*. had observed in 1971 that an acetylene-$Co_2(CO)_6$ complex reacted with norbornadiene, acetylene and carbon monoxide to *"hydrocarbon and ketonic products"* (Scheme 4.1).[156] At that time the thermal reaction was performed with stoichiometric amounts of dicobaltoctacarbonyl. The early examples involved only strained reactive alkenes, such as norbornene, since the use of unstrained alkenes usually resulted in low efficiency of the reaction. And the participation of unsymmetrical alkenes led to a mixture of regioisomers. Furthermore, the reaction required relatively harsh reaction conditions, *i.e.* high temperature and long reaction times, which often led to decomposition of substrates or products.



Scheme 4.1: Regioisomeric products in the Pauson-Khand with a monosubstituted alkyne

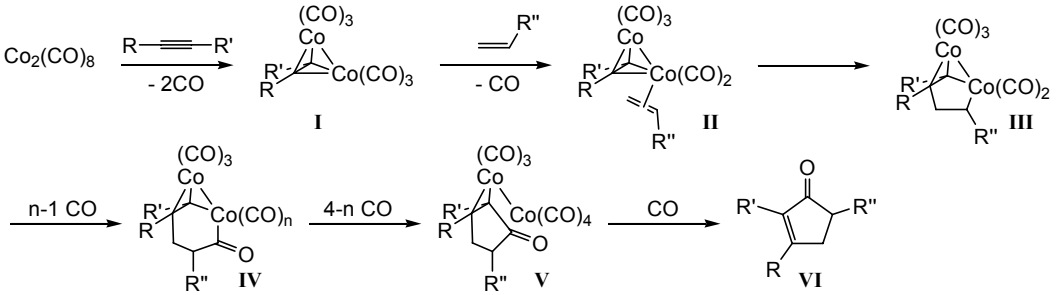
In 1981 Shore introduced the intramolecular version of the Pauson-Khand reaction by connecting the alkene and alkyne moiety.[157] In this reaction strained alkenes were no longer required and only one regioisomer was obtained as 5.5- and 5.6-fused bicycles, respectively.



Scheme 4.2: Intramolecular Pauson-Khand reaction

The now widely accepted mechanism was first suggested 1985 by Magnus *et al*.[158] $Co_2(CO)_8$ reacts with an alkyne under the loss of two CO-ligands to form the stable and fully characterized alkyne-$Co_2(CO)_6$ **I** complex (Scheme 4.3).[159] This step is followed by the π-coordination of an olefin accompanied by the loss of another CO-ligand to form **II**.

Subsequent insertion of the olefine gives cobaltacycle **III** and alkyl migration provides a six-membered acyl complex **IV**. Reductive elimination leads to the η^2-bound cyclopentenone-$Co_2(CO)_6$ complex **V**, which then undergoes elimination to product **VI**.



Scheme 4.3: Mechanism of the dicobaltoctacarbonyl catalyzed Pauson-Khand reaction[158]

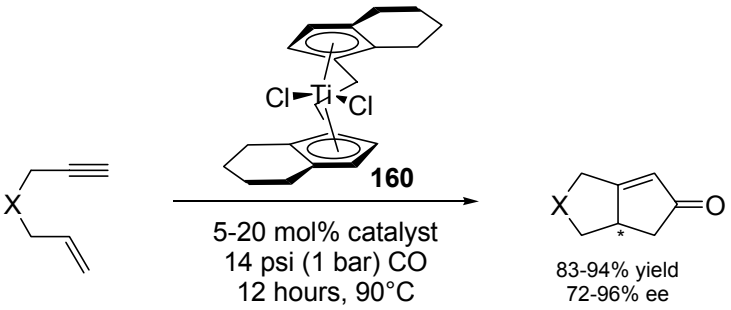
4.2 Catalytic Pauson-Khand Reaction

The first catalytic version of this reaction was reported by Pauson and Khand in 1973.[155a] Later, better catalysts than $Co_2(CO)_8$ were developed, such as (indenyl)Co(cod) or a system derived from $Co(acac)_2$ and $NaBH_4$. Especially the latter was shown to tolerate more functional groups, such as esters and halides.

Kerr and co-workers showed that that the application of an (*R*)-glyphos-substituted (alkyne)pentacarbonyldicobalt-complex resulted in a series of efficient asymmetric intermolecular Pauson-Khand reactions without the use of chiral auxiliaries.[160] Hiroi *et al.* obtained very good enantioselectivities (up to 90%) using chiral chelating diphosphane (*S*)-BINAP. Unfortunately, high catalyst loadings were required for this rather inactive system.

4.3 Pauson-Khand Reaction with other Metals

A number of reviews were published on the recent progress in Pauson-Khand reactions, with respect to catalytic and asymmetric versions, and the use of different transition metals.[155c,161] Catalytic carbonylative alkene-alkyne couplings have not only been reported with Co,[162] but also with Fe[163], Ni[164], Ti[165], Zr[166], Ru[167], Rh[168], and Ir[169]. Furthermore, some trials were made using more physiologically and user friendly procedures that avoid the use of toxic carbon monoxide.[170]



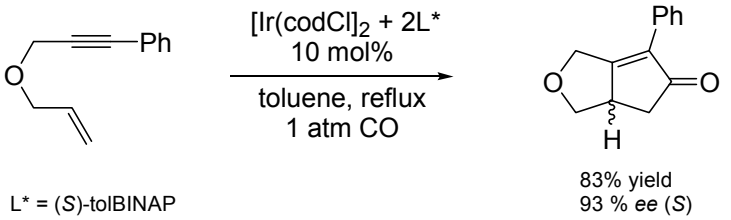
Scheme 4.4: (*S*,*S*)-[(ebthi)Ti(CO)$_2$] **160** catalyzed intramolecular Pauson-Khand reaction

Buchwald and co-workers showed, that titanocene complexes could not only mediate[171] the cyclocarbonylation reaction, but were effective catalysts.[172] In 1996, Hicks, Buchwald *et al.* reported the first example of a titanium-catalyzed asymmetric catalytic Pauson-Khand reaction (ACPKR). They employed a chiral titanocene catalyst,[173] using a reduced form of a Brintzinger-type *ansa*-titanocene (*S*,*S*)-[(ebthi)Ti(CO)$_2$].[ii]

In 1997, Morimoto *et al.* reported that catalytic quantities of [Ru$_3$(CO)$_{12}$] were able to cyclize a range of enynes with an internal alkyne group under 10 atm of carbon monoxide.[167a] Independently, Kondo *et al.* reported the first intramolecular Pauson Khand reaction using the same catalytic system.[167b]

It was shown that a Rh(I) catalyst catalyzed the reaction under 1 atm of CO with only 5 mol% catalyst under optimized conditions. This system was especially efficient for electron-deficient substrates.[168a,174] Following their own work on rhodium(I) catalysts for the Pauson-Khand reaction,[168b] Jeong *et al.* published an asymmetric rhodium(I)BINAP-catalyst, that led to 96% ee with moderate to very good yields under 0.5 to 3 atm of CO.[175]

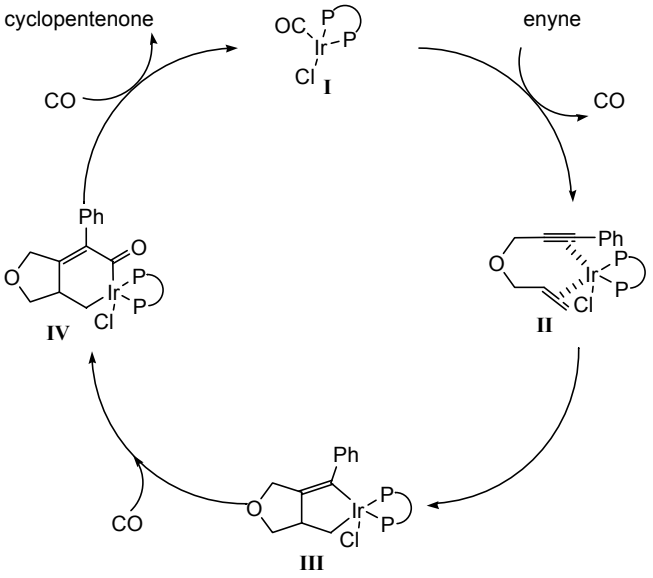
In 2000, Shibata *et al*. described the use of iridium in a Pauson-Khand Type reaction [169] They observed that addition of the triphenylphosphane as coligand improved the reaction yield compared to [Ir(cod)Cl]$_2$. By substituting triphenylphosphane for tolBINAP catalyst they obtained excellent yields and enantiomeric excesses. More recently, they extended the reaction to a wider range of substrates and employed aldehydes as CO source.[176]



Scheme 4.5: Iridium-catalyzed ACPKR[169]

[ii] ebthi = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)

A mechanism for the iridium-catalyzed intramolecular ACPKR was proposed by Shibata *et al.*. The chiral iridium catalyst **I** is formed by reaction of the iridium-complex precursor with CO. According to their mechanism the the enantioselective step is the formation of metallacycle **III** from **II**. Carbon monoxide is inserted between iridium and the sp^2-carbon to provide **IV**. Reductive elimination of iridium gives cyclopentenone and regenerates the chiral iridium catalyst **I**.



Scheme 4.6: Catalytic cycle of the iridium-catalyzed ACPKR

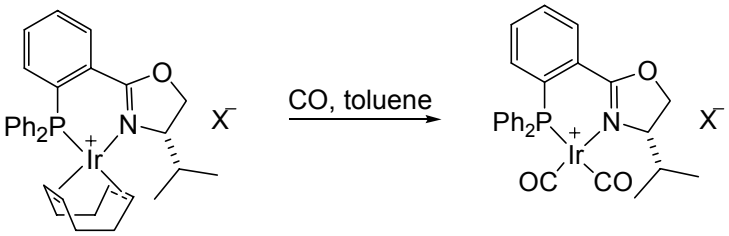
4.4 Objectives of this Chapter

Zhong-Lin Lu in our laboratory obtained very promising results in the iridium catalyzed Pauson-Khand type reaction by using PHOX ligands.[177] In his work, he optimized the system regarding ligand, solvent, catalyst loading, temperature, pressure and time. Furthermore, he observed a distinct influence of the counteranion.

To supplement his studies, the relationship between the catalyst counteranion and the asymmetric induction of the intermolecular catalytic Pauson-Khand reaction was investigated in more detail.

4.5 Catalytic Intramolecular Pauson-Khand Reaction with Iridium-PHOX Catalysts

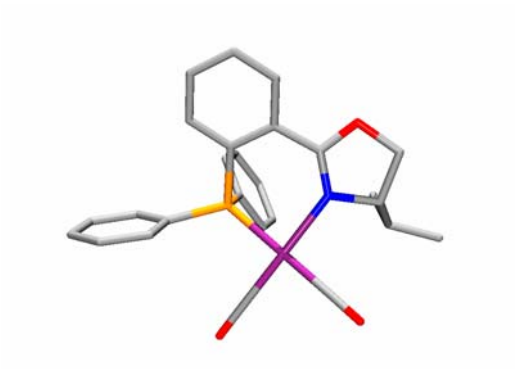
In his postdoctoral research report, Lu described the use of iridium-PHOX catalysts in the ACPKR. The catalytically active species $[Ir(CO)_2PHOX]PF_6$ **162** is formed by treatment of $[Ir(cod)PHOX]PF_6$ **161** with carbon monoxide.



161 **162**

Scheme 4.7: Synthesis of carbonyl-complex **162**

An X-ray crystal structure of the hexafluorophosphate carbonyl complex is depicted in Figure 4.1. As to be expected, the iridium(I) complex exhibits a square-planar structure. The shorter bond length of the C-O bond *trans* to the phosphorus indicates a stronger π-acceptor ability of the phosphorus. Usually carbonyl bands in infrared spectra are consulted for the determination of the "electron donor-acceptor property"[178] of *trans*-standing ligands.[179] In chelating ligands with different coordinating groups (and thus two CO-ligands in different *trans*-positions) however, the assignment of the bands is not possible. Here, the C-O bond lengths in the solid state can give additional information, and help with the assignment of CO-bands in solution.



Ir-P [Å]	2.3166 (7)
Ir-N [Å]	2.086 (2)
Ir-$C_{trans\ to\ P}$ [Å]	1.915 (3)
Ir-$C_{trans\ to\ N}$ [Å]	1.850 (3)
O-$C_{trans\ to\ P}$ [Å]	1.126 (4)
O-$C_{trans\ to\ N}$ [Å]	1.140 (4)

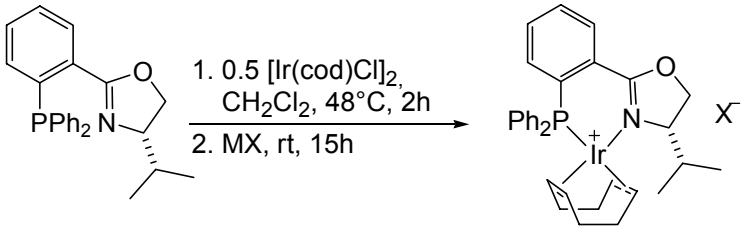
Figure 4.1: Selected bond lengths [Å] of $[Ir(CO)_2PHOX]PF_6$. Anion and hydrogen atoms are omitted for clarity.

Lu also discovered that the best ligands bear phenyl substituents at the phosphorus, and a small substituent at the oxazoline ring. Phosphorus substituents however exerted the biggest influence. Larger steric bulk at the phosphorus (*e.g. o*-tolyl group) resulted in a dramatic drop in yield. Bigger substituents at the oxazoline, namely in the 4-position and to a lesser degree in the 5-position, affected both activity and enantioselectivity. Furthermore, he observed that

among the solvents, THF and DME were the best regarding yield and enantioselectivity. Lu tested a number of enynes (Scheme 4.9) and obtained good results for various substrates using 9 mol% *iso*-propyl substituted diphenylphosphinoxazoline-derived iridium-catalyst at 120°C under 1.1 bar CO pressure with triflate as counteranion.

4.5.1 Complex Synthesis

To test the anion influence of the iridium-PHOX system one can prepare the respective catalysts *in situ* by mixing 1 equivalent of $[Ir(cod)Cl]_2$ with 2 equivalents of ligand and the respective silver salt. The catalyst precursor can also be prepared and characterized prior to the reaction. The latter method was chosen, to obtain well-defined catalyst precursors and therefore reproducible results (Scheme 4.8).



4 **161**

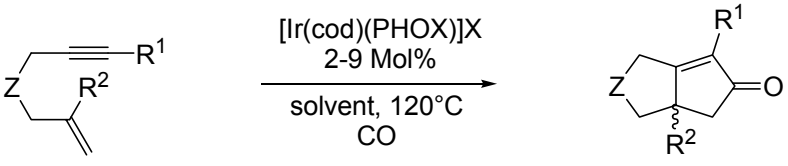
complex	X	M
161a	BAr_F	Na
161b	OTs	Na
161c	OMs	Na
161d	$Al(OC(CF_3)_3)_4$	Li
161e	OTf	Ag
161f	BF_4	Ag
161g	PF_6	Ag
161h	SbF_6	Ag
161i	OAc_F	Ag

Scheme 4.8: Synthesis of iridium-PHOX complexes **161a-i**

The trifluoromethane-sulfonate (OTf^-) **161e**, hexafluorophosphate (PF_6^-) **161g** and tetrafluoroborate (BF_4^-) **161f** were prepared according to standard procedures from $[Ir(cod)Cl]_2$, 2-[2-(diphenylphosphanyl)-phenyl]-4,5-dihydro-4-isopropyl-oxazole and the respective silver or ammonium salts.[56,180] The other iridium salts, namely hexafluoroantimonate (SbF_6^-) **161h**, methylsulfonate (OMs^-) **161c**, toluenesulfonate (OTs^-) **161b**, trifluoroacetate (OAc_F^-) **161i**, and tetrakis(perfluoro-*tert*-butoxy)aluminate ($Al(OC(CF_3)_3)_4^-$)[181] **161d** were prepared accordingly (*i.e.* 1 equivalent of $[Ir(cod)Cl]_2$ and 2 equivalents of ligand were stirred in dichloromethane for two hours at 48°C. Anion exchange over night was followed by filtration over celite and evaporation of the volatiles). The

tetrakis[3,5-bis(trifluoromethyl)phenyl]borate complex **161a** was previously prepared by Esther Hörmann.

4.5.2 Substrate Synthesis

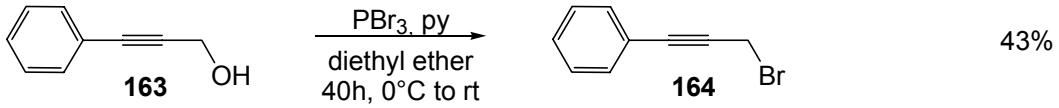


S1-S5 **P1-P5**

	Z	R^1	R^2
S1	O	Ph	H
S2	NTs	Ph	H
S3	$C(COOMe)_2$	Ph	H
S4	O	Me	H
S5	O	Ph	Me

Scheme 4.9: Iridium-PHOX catalyzed AIPKR

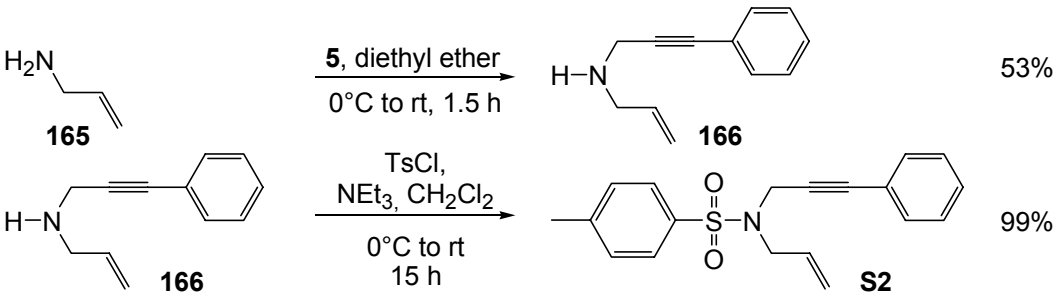
Enynes **S1**, **S4** and **S5** were prepared by Lu. Enynes **S2** and **S3** were prepared according to literature procedures starting from 3-phenyl-propargylic alcohol.[174,177] The alcohol was brominated with phosphorus tribromide and pyridine in diethyl ether to yield (3-bromo-prop-1-ynyl)-benzene **164**.



163 **164**

Scheme 4.10: Synthesis of (3-bromo-prop-1-ynyl)-benzene **164**

Propargyl bromide **164** was reacted with a ten-fold excess of allylamine **165** at 0 °C. The secondary amine **166** was obtained in 53% yield. Tosylation of **166** in dichloromethane and triethylamine afforded enyne **S2** (Scheme 4.11).

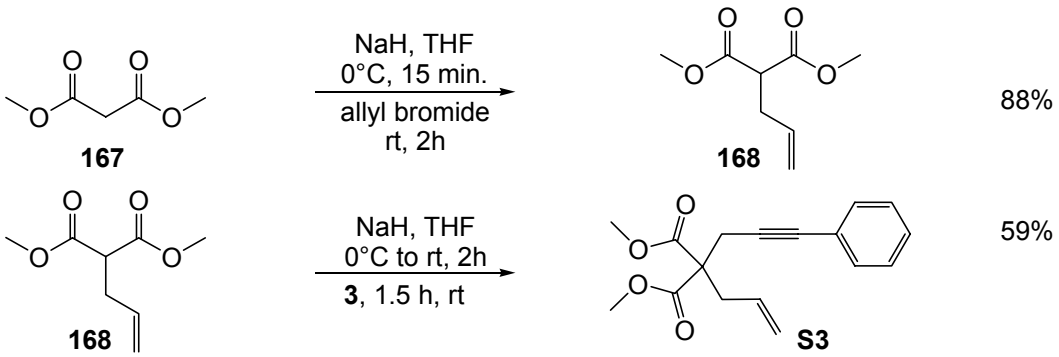


165 **166** **166** **S2**

Scheme 4.11: Synthesis of *N*-allyl-N-(3-phenyl-prop-2-ynyl)-4-methylphenylsulfonamide **S2**[177]

Substrate **S3** was synthesized from dimethylmalonate **167**. Deprotonation with sodium hydride was followed by addition of allyl bromide to afford 2-allyl-dimethylmalonate **168**.

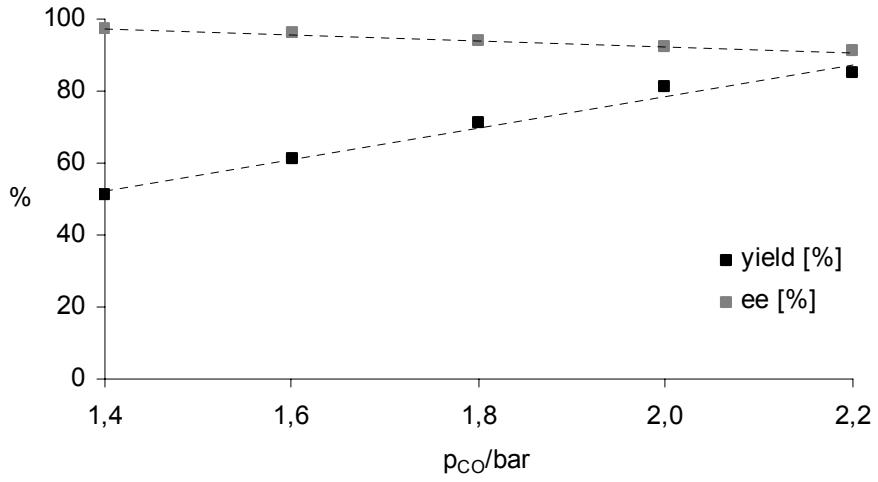
After another deprotonation with sodium hydride, **168** was reacted with (3-bromo-prop-1-ynyl)-benzene **164** to give product **S3** (Scheme 4.12).



Scheme 4.12: Synthesis of 2-acetoxy-2-(3-phenyl-prop-2-ynyl)-pent-4-enoic acid methyl ester **S3**

4.5.3 ACPKR of Allyl-(3-phenyl-prop-2-ynyl) Ether

The results of the standard procedure for ACPKR as evaluated by Lu, (*i.e.* with the iridium-PHOX catalyst at 120°C under 1.1 bar CO pressure) could not be reproduced. In particular, yields were very low under the stated reaction conditions. Changing to higher temperature did not giva a distinct improvement of the reaction. Therefore, the pressure dependence of the ACPKR of **S1** was tested. The reaction was performed at five different pressures between 1.4 and 2.2 bar. A linear dependence of pressure and yield was observed until 2.0 bar (Scheme 4.13).



Scheme 4.13: Correlation of pressure with yield and enantioselectivity on ACPKR of **S1**

Even at 2.2 bar the reported yields were not reached (Table 4.1). In contrast to the conversion, the enantiomeric excess drops to some extent with increasing pressure from 97 % at 1.4 bar to 91 % at 2.2 bar. To obtain a reasonable yield for the ACPKR in the experiments below, a carbon monoxide pressure of 2.2 bar was used.

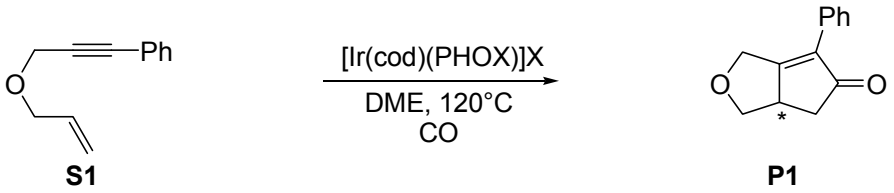


Table 4.1: Influence of CO-pressure on ACPKR of **S1**

entry	X	solvent	p_{CO} (bar)[c]	yield (%)[a]	ee (%)[b]
1	TfO	DME	1.4	51	97 (*R*)
2	TfO	DME	1.6	61	96 (*R*)
3	TfO	DME	1.8	71	94 (*R*)
4	TfO	DME	2.0	81	92 (*R*)
5	TfO	DME	2.2	85	91 (*R*)

Reaction performed with 9 mol% catalyst, reaction time: 24 h.
[a] Isolated yield by silica gel column chromatograpy (*n*-hexane: ethyl acetate, 3:1). [b] determined by HPLC: AD, *n*-heptane: *iso*-propanol 90:10, 20°C, 1.0 ml/min, 220nm/254nm: 11.1 min (*R*), 14.6min (*S*). [c] The CO pressure given in this column is the value at ambient temperature.

The following counteranions were tested in the carbonylative alkene-alkyne coupling of allyl-(3-phenyl-prop-2-ynyl) ether **S1**: BAr_F^-, TfO^-, TsO^-, MsO^-, $F_3CCO_2^-$, $[Al(OCCF_3)]_4^-$, BF_4^-, PF_6^-, and SbF_6^- (Table 4.2). The best results were obtained when catalysts with small, weakly-coordinating counteranions like BF_4^- (**161f**), PF_6^- (**161g**), and SbF_6^- (**161h**) were used. This result is in contrast to Lu's postdoctoral report. Herein, PF_6^- was quoted to be not suitable as a counteranion, since the respective catalyst showed low reactivity.[177]

Larger non-coordinating anions $[Al(OCCF_3)]_4^-$ and BAr_F^- gave somewhat lower yields and enantioselectivities (85%). Triflate **161e** gave approximately the same results as **161f** to **161h,** while the tosylate, mesylate and trifluoracetate did not show any activity.

Table 4.2: Influence of anion on ACPKR of **S1**

entry	X	p_{CO} (bar)	yield (%)[a]	ee (%)[b]
1	BAr_F	2.0	63	85 (*R*)
2	BAr_F	2.2	69	85 (*R*)
3	$Al(OC(CF_3)_3)_4$	2.0	55	85 (*R*)
4	$Al(OC(CF_3)_3)_4$	2.2	78	85 (*R*)
5	TfO	2.0	81	92 (*R*)
6	TfO	2.2	85	91 (*R*)
7	BF_4	2.2	89	91 (*R*)
8	PF_6	2.2	93	91 (*R*)
9	SbF_6	2.2	96	91 (*R*)
10	MsO	2.2	traces	*nd*
11	TsO	2.2	traces	*nd*
12	CF_3COO	2.2	traces	*nd*

Reaction performed with 9 mol% catalyst, reaction time: 24 h.
[a] Isolated yield by silica gel column chromatograpy (*n*-hexane: ethyl acetate, 3:1). [b] determined by HPLC: AD, *n*-heptane: *iso*-propanol 90:10, 20°C, 1.0 ml/min, 220nm/254nm: 11.1 min (*R*), 14.6min (*S*). [c] The CO pressure given in this column is the value at ambient temperature.

The influence of the catalyst loading was tested with **161f** and the results are shown in Table 4.4. This study showed that when using substrate **S1**, the catalyst loading can be reduced to 2 mol% catalyst without significant change of yield and selectivity.

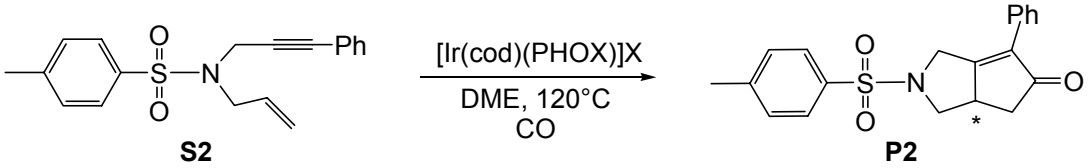
Table 4.3: Influence of catalyst loading on ACPKR of **S1**

entry	X	mol% cat	**yield (%)**[a]	**ee (%)**[b]
1	BF_4	9	89	91 (*R*)
2	BF_4	5	84	91 (*R*)
3	BF_4	2	88	91 (*R*)
4	BF_4	1	59	91 (*R*)

Reaction performed with 9 mol% catalyst, reaction time: 24 h.
[a] Isolated yield by silica gel column chromatograpy (*n*-hexane: ethyl acetate, 3:1). [b] determined by HPLC: AD, *n*-heptane: *iso*-propanol 90:10, 20°C, 1.0 ml/min, 220nm/254nm: 11.1 min (*R*), 14.6min (*S*). [c] The CO pressure given in this column is the value at ambient temperature.

4.5.4 ACPKR of *N*-Allyl-*N*-(3-phenyl-prop-2-ynyl)-4-methylphenylsulfonamide

The results of ACPKR using substrate **S2** are depicted in Table 4.4. Some reactions, particularly those obtained with catalysts **161f** to **161h** were repeated several times to ensure reproducible results. In this reaction, catalysts **161f** (BF_4^-) and **161e** (OTf^-) gave the best results regarding selectivity, whereas the spherical, large and low-coordinating anions BAr_F^- and $[Al(OCCF_3)]_4^-$ showed lower enantioselectivities.



S2 **P2**

Table 4.4: Influence of anion on ACPKR of **S2**

entry	**X**	**yield (%)**[a]	**ee (%)**[b]
1	BAr_F	96	50
2	$Al(OC(CF_3)_3)_4$	96	56
3	OTf	93	81
4	BF_4	98	80-81[c]
5	PF_6	95	77-80[d]
6	SbF_6	95	71-74[d]

Reaction performed with 9 mol% catalyst in DME, reaction time: 24 h.
[a] Isolated yield by silica gel column chromatography (*n*-hexane: ethyl acetate, 2:1). [b] determined by HPLC: AD, *n*-heptane: *iso*-propanol 80:20, 20°C, 0.9 ml/min, 220nm/254nm: 19.7 min (major), 23.4 min (minor).
[c] average of three measurements. [d] average of four measurements.

In contrast to substrate **S1**, catalysts **161f-161h** did not show the same enantioselectivity, which decreased with the size of the anion $BF_4^- > PF_6^- > SbF_6^-$. The enantioselectivites were not reproducible in all cases but varied by about 3%. One possible explanation could be a stronger pressure dependance of the selectivity than in the case of **S1**. Since the pressure can not be adjusted precisely (±0.1 bar), this could lead to somewhat incoherent results.

4.5.5 ACPKR of 2-Allyl-2-(3-phenyl-prop-2-ynyl)-malonic Acid Dimethyl Ester

Dimethylmalonate-derived substrate **S3** was also tested in ACPKR. The solvent influence using catalyst **161a** (BAr_F^-) was investigated (Table 4.5). As can be seen in Table 4.5, the solvent has an influence on the enantioselectivity in the formation of product **P3**. Whereas, entries 1 to 3 all show moderate selectivity, an ee of up to 71% was obtained in THF. However, better yields were obtained with DME and DCE (entries 1 and 2) than with toluene (entry 3) and THF (entry 4). Lu observed yields up to 81% in toluene, but this reaction has been performed presumably under 1.1 bar CO for 40 hours. He observed the best selectivities with [Ir(cod)PHOX]OTf in THF (79 % ee).[177]

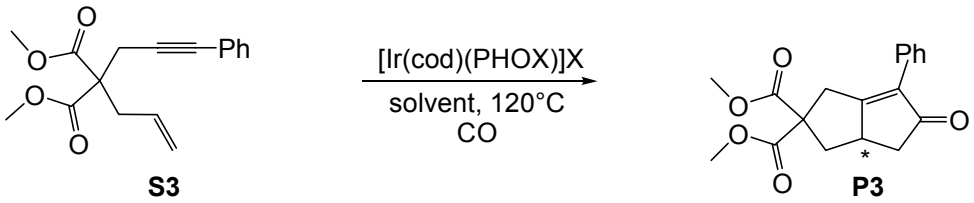


Table 4.5: Influence of solvent on ACPKR of **S3**

entry	solvent	mol% cat	yield (%)[a]	ee (%)[b]
1	DME	9	64	47
2	DCE	9	71	47
3	toluene	9	47	44
4	THF	9	46	71

Reaction performed with 9 mol% **161c**, reaction time: 24 h.
[a] Isolated yield by silica gel column chromatograpy (*n*-hexane: ethyl acetate, 2:1). [b] determined by HPLC: AS, *n*-heptane: *iso*-propanol 90:10, 20°C, 1.0ml/min, 220nm/254nm: 15.1 min (minor), 24.1 min (major).

Table 4.6 comprises the results of ACPKR of **S3** in THF with different reaction times and catalyst loadings. The overall conclusions are similar to those for substrate **S2**. Small anions with medium coordination ability, namely tetrafluoroborate and triflate(and to a lesser degree hexafluorophosphate and hexafluoroantimonate) give better results regarding both yield and enantioselectivity, than large and weakly coordinating anions. The yield is improved with catalyst loading and reaction time. It was observed however that the enantioselectivity slightly drops with both, higher catalyst loading and time. Somewhat contradictory is entry 10, which shows a surprisingly good yield for only 2 mol% catalyst loading, and a strong drop in enantionselectivity: 86% compared to 94% with 5mol%.

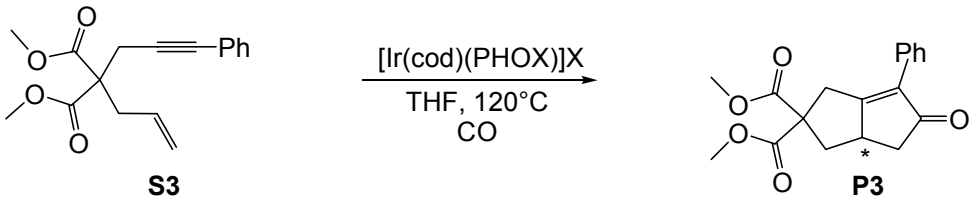


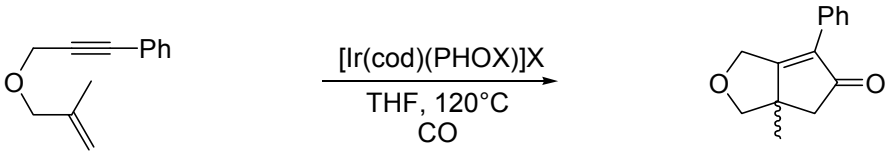
Table 4.6: Influence of anion on ACPKR of **S3**

entry	mol%	time (h)	X	yield (%)[a]	ee (%)[b]
1	9	48	BAr_F	37	72
2	5	24	BAr_F	46	71
3	5	48	$Al(OC(CF_3)_3)_4$	62	72
4	9	24	OTf	57	88
5	9	48	OTf	75	85
6	5	48	OTf	48	94
7	9	24	BF_4	53	93
8	9	48	BF_4	76	91
9	5	48	BF_4	57	94
10	2	48	BF_4	93	86
11	9	24	PF_6	57	92
12	9	48	PF_6	60	92
13	5	48	PF_6	71	91
14	9	24	SbF_6	82	85
15	9	48	SbF_6	80	82
16	5	48	SbF_6	76	86

Reaction performed in THF.
[a] Isolated yield by silica gel column chromatograpy (*n*-hexane: ethyl acetate, 2:1). [b] determined by HPLC: AS, *n*-heptane: *iso*-propanol 90:10, 20°C, 1.0ml/min, 220nm/254nm: 15.1 min (minor), 24.1 min (major).

4.5.6 ACPKR of [3-(2-Methyl-allyloxy)-prop-1-ynyl]-benzene and Allyl-(3-methyl-prop-2-ynyl) Ether

Both substrates **S4** and **S5** show rather poor results in iridium-PHOX-catalyzed ACPKR. The additional methyl-group in substrate **S4** led to a significant drop in yield, as well as enantioselectivity. Only yields up to 28% were achieved for this substrate. With the iridium-tolBINAP system, up to 30% yield and 88% ee in toluene were previously reported.[169]



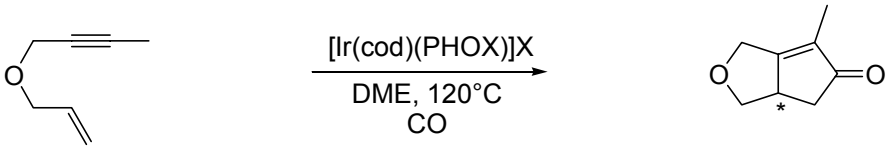
S4 **P4**

Table 4.7: Influence of anion on ACPKR of **S4**

entry	anion	solvent	p_{CO} (bar)	yield (%)[a]	ee (%)[b]
1	TfO^-	DME	2.2	9	58-59 (*R*)
2	BAr_F^-	DME	2.2	traces	*nd*
3	TfO^-	THF	2.2	10	71-73 (*R*)
4	BAr_F^-	THF	2.2	28	64-65 (*R*)
5	$[Al(OC(CF_3)_3]_4^-$	THF	2.2	15	61-63 (*R*)

Reaction performed with 9 mol% catalyst, reaction time: 24 h.
[a] Isolated yield by silica gel column chromatograpy (*n*-hexane: ethyl acetate, 2:1), R_f = 0.4. [b] determined by HPLC: AD, *n*-heptane: *iso*-propanol 90:10, 20°C, 1.0 ml/min, 220nm/254nm: 8.3 min (*R*), 17.7 min (*S*).

Allyl-(3-methyl-prop-2-ynyl) ether **S5** was tested in the ACPKR, but no product was detected. The only difference to **S1** is that the internal alkyne is methyl- instead of phenyl-substituted. It is somewhat surprising that the reactivity should be so strongly influenced by the substituent at the alkyne, especially since Shibata *et al.* observed similarly high activity and enantioselectivity for both substrates using their tolBINAP-iridium catalyst.



S5 **P5**

Scheme 4.14: Pauson-Khand reaction of **S5**

4.5.7 Conclusion

The influence of the counteranion on the enantioselectivity of the iridium-PHOX-catalyzed ACPKR was examined. 3-Phenylsubstituted enynes undergo cycloaddition with good to very good yields and good enantioselectivities. The 3-methylsubstituted enyne **S5** was not converted to the cycloaddition product. Steric hindrance at the alkene moiety leads to a strong drop in yield. Generally, the best counteranions are small weakly-coordinating, such as triflate, tetrafluoroborate, hexafluorophosphate and hexafluoroantimonate. Large, weakly coordinating counteranions, namely BAr_F^- and $[Al(OC(CF_3)_3]_4^-$, showed lower reactivity and selectivity, whereas the better donors tosylate, mesylate and trifluoroacetate were not reactive. A series of pressure experiments shows a strong CO-pressure dependence on the yield, and to a lesser degree, on the enantioselectivity of the iridium-PHOX-catalyzed ACPKR of **S1**.

Chapter 5

Rhodium-Silylene Complexes

5 Rhodium-Silylene Complexes

5.1 Stable Silylenes

Silylenes are divalent highly reactive silicon species, which have been known as reaction intermediates for a long time.[182] During the 1980s several organosilylenes were isolated and studied in argon or hydrocarbon matrices, at temperatures of 77 K or below.[183] While the first stable carbene was discovered in 1991,[30] and stannylenes and germylenes had long been established,[184] silicon was the last of the group 14 elements of which no dicoordinate, stable compound was known. Apart from this only a few divalent, though not dicoordinate compounds, such as decamethylsilicocene **169** (Figure 5.1, a) (π-donor-stabilized)[185] or a σ-donor-stabilized silicon(II) species **170** (Figure 5.1, b),[186] were published.

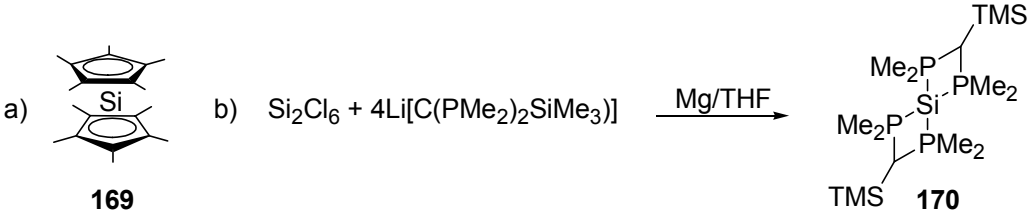


Figure 5.1: Divalent silicon compounds a) decamethylsilicocene **169** b) phoshpinomethanide stabilized silicon(II) **170** [185,186]

The first stable silylene **171**, a silicon analogue of an *N*-heterocyclic carbene (NHC), was reported by Denk *et al*. in 1994.[187] The saturated analogue **172** [188] and some benzo- and pyrido-fused derivatives **173** to **175** were synthesized shortly after.[189,190] All these silylenes are nitrogen-donor stabilized. More recently, Kira *et al.* developed silylene **176** with no such stabilization.[191] Among the mentioned silylenes (Figure 5.2) the saturated and the non-donor stabilized compounds are relatively unstable. An open chain bis(trimethylsilylamide)-stabilized silylene could only be kept in solution for 12h at -20°C.[192]

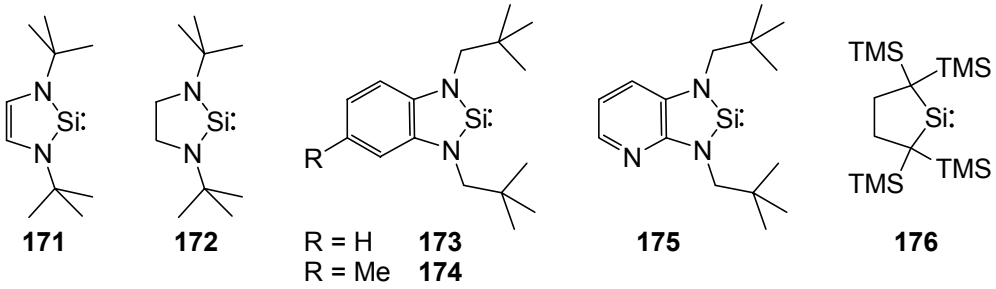


Figure 5.2: Known stable silylenes

The increased stability of the unsaturated silylene, namely 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene, in comparison to the saturated analogue 1,3-di-*tert*-butyl-2,3-

[1,3,2]-diazasilolidine-2-ylidene, has been subject to several investigations. Steric hindrance is insignificant as a stabilizing factor, except for the non-donor-stabilized silylene. Undoubtedly, p-electron donation from the nitrogen lone pair into the empty p-orbital on the silicon is a strong stabilizing factor. Since the nitrogen atoms in the saturated silylene are more basic, which is reflected by shorter silicon-nitrogen bonds in the solid structure, this effect should be somewhat stronger. In the unsaturated, as well as in the benzo- and- pyrido-fused silylenes, on the other hand, additional stabilization can be gained due to aromatic delocalization (Figure 5.3). The extent of aromaticity has been discussed.[193,194,195]

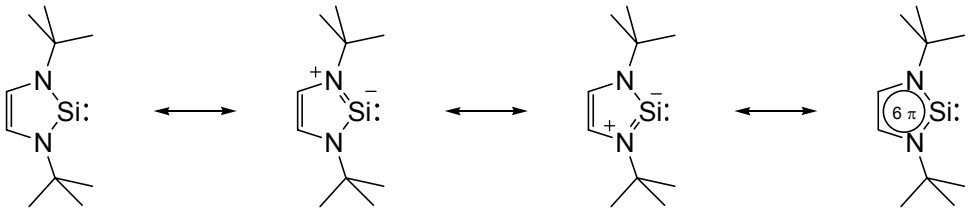
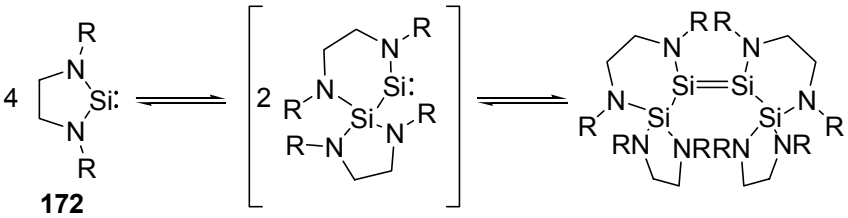


Figure 5.3: Aromatic delocalisation of the silylene 6-π-electron ring

Experimental indications for aromaticity were obtained by Raman and NMR-spectroscopy. The ^{1}H NMR chemical shifts of the ring-protons lie about 0.75 ppm downfield from those in the dichloro-precursor or the dihydro-analogue.[187] This shift is consistent with a moderate ring current, resulting from aromatic delocalization. Nucleus independent chemical shift calculations have also supported aromaticity, though the values are significantly smaller than for benzene (the shielding influence on the ghost atom 2Å above the ring-center is -5.3 for benzene and -2.7 for silylene).[194] Raman data also support the aromatic nature of the unsaturated silylene with its six π-electrons and the pariticipation of the empty silicon p_z-orbital therein.[195]

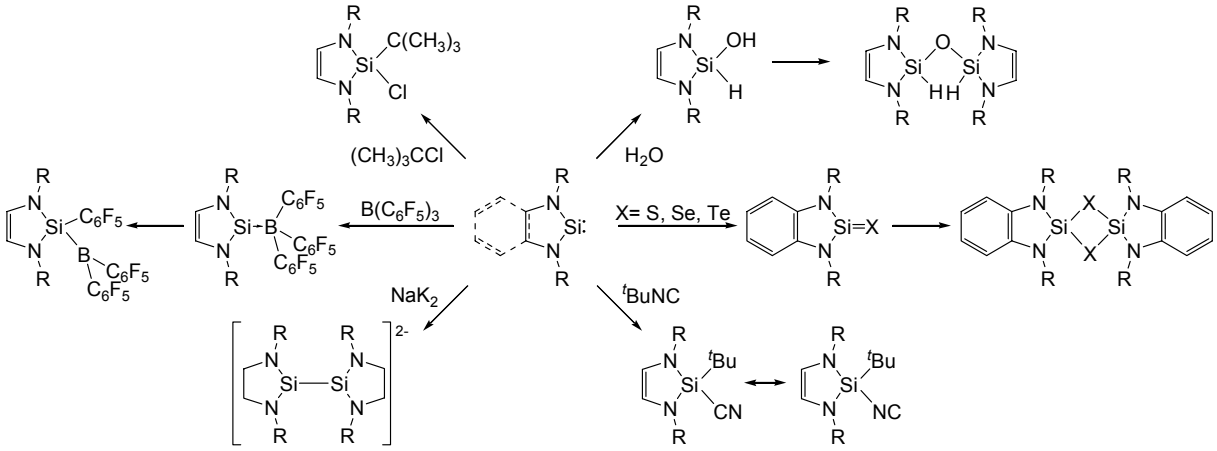
The thermodynamic instability of the saturated silylene in comparison to its saturated analogue is demonstrated by the slow oligomerization that takes place at room temperature. When a solution of the silylene is concentrated, a silicon nitrogen bond is inserted to form (aminosilyl)silylene which then dimerizes to the disilene. The reaction which is accompanied by a change of colour from light-yellow to red is reversible. In solution the monomer is almost exclusively present, whereas the solid state favors the tetramer.[196]



172

Figure 5.4: Oligomerisation of saturated silylene

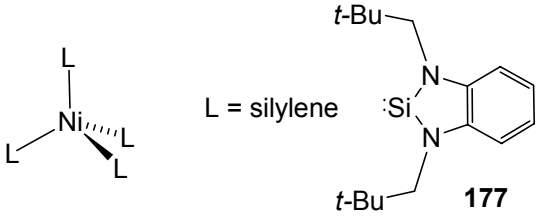
Stable silylenes are an extremely reactive class of compounds: With chalcogenes silylenes form spirocyclic dimers,[197] with Lewis acids they form the respective Lewis acid-base adducts, usually with subsequent insertion to obtain a tetravalent structure.[198] Furthermore, insertion in metal nitrogen bonds[196], carbon-halogen bonds[199], oxygen-hydrogen-bonds[200] and others are reported.[201,202] The amphiphilic character of silylenes has been discussed by Bharatam *et al.*.[203]



Scheme 5.1: Typical reactions of stable *N*-heterocyclic silylenes reported in literature

5.2 Silylene-Complexes

Various transition metal complexes of silylenes[204] have been prepared.[205,206] $Ni(cod)_2$ was shown to form homoleptic tris(silylene) complexes [Ni(**171**)$_3$] and [Ni(**172**)$_3$],[207] whereas a tetravalent (silylene)-nickel complex **177** was obtained starting from a *N,N′*-di-neopentyl-substituted silylene **173** (Figure 5.5).[208,209] The crystal structure of this complex showed a tetrahedral arrangement of the four silylene ligands. Tris- and tetrakis(silylene)-palladium complexes [Pd(**171**)$_3$] and [Pd(**172**)$_4$], as well as dinuclear silylene-bridged compounds, were formed using [$Pd(PPh_3)_3$] or [$Pd(cod)(CH_3)_2$] as precursors.[210,40] However, no crystal structures were reported for the homoleptic complexes.



177

Figure 5.5: Tetrahedral silylene-nickel complex **177**

N-Heterocyclic carbenes (NHC) have emerged as a versatile class of ligands for homogeneous catalysis.[211] Accordingly, a wide variety of NHC-metal complexes have been prepared and

investigated as catalysts. In contrast, analogous silylene metal complexes have received much less attention. The potential of stable silylenes as ligands in catalysis remains to be explored. Recently, Fürstner *et al.* successfully used a mixed dinuclear (silylene)(phosphine)Pd(0) complex, in which a heterocyclic silylene acts as a bridging ligand, to catalyze the Suzuki coupling of aryl boronic acids with bromoarenes.[40] However, the nature of the actual catalytically active species in this reaction is not known. Recently, McGuinness *et al*. have calculated the barrier for methyl migration to the silylene ligand in palladium-silylene complexes.[212] The calculation revealed a low barrier to coupling of an alkyl ligand with the silylene ligand. Consequently, if silylene ligands are applied in homogeneous catalysis, and the catalytic cycle involves a metal-hydrocarbon species, migration is likely to be a significant factor.

5.3 Objectives of this Chapter

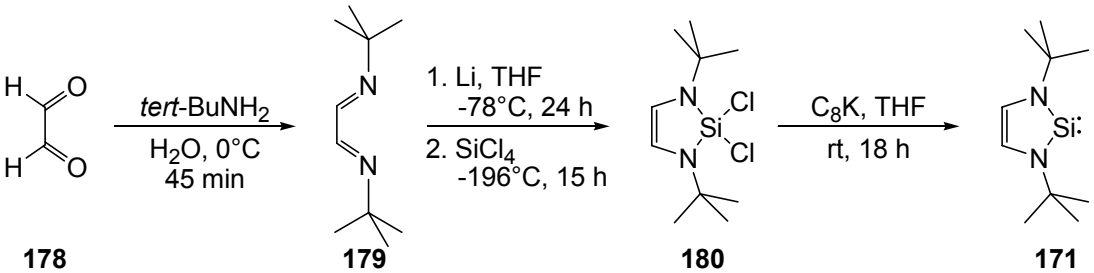
The objective of the research described in this chapter was the synthesis of well-defined iridium-and rhodium silylene complexes, that are potential catalysts for hydrogenation. Our interests were the application and the properties of these strong σ-donor ligands, which have been scarcely investigated to date.

5.4 Ligand and Complex Synthesis

For the investigation unsaturated silyene **171**, first published by Denk *et al.* in 1994[187] and the less stable saturated silylene **172**[188] were synthesized and reacted with different potential metal precursors. Since we were looking for an application in catalysis, we were interested in the presence of a relatively labile group, that can dissociate from the metal centre during the catalytic cycle. In hydrogenation this group is usually a η^4-bound diolefin, such as cyclooctadiene or norbornadiene, which is reduced under hydrogenation conditions. Also phosphines, such as triphenylphosphine in Wilkinson's catalyst,[213] are known to dissociate and provide a free coordination site. The initial goal was the synthesis of cationic iridium complexes, but in the course of the investigation the synthesis of rhodium catalysts proved to be more feasible. Due to the high reactivity of the free stable silylenes the choice of dry and degassed solvents was limited. Chlorinated solvents cannot be used due to the insertion of silylenes into the carbon-halogen bond,[199] and nitriles are at least known to add to the benzo-fused silylene. Alcohols and water also react with silylenes (see Scheme 5.1)

5.4.1 Synthesis of *N*-Heterocyclic Silylenes

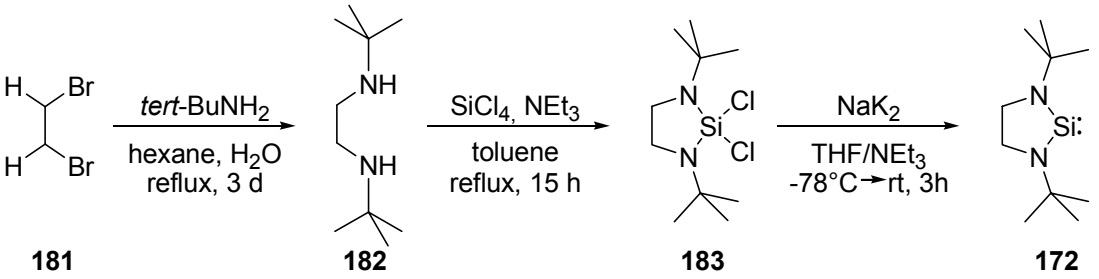
1,3-Di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene **171** was prepared as has been described previously by Haaf *et al.*[200] Glyoxal **178** in aqueous solution was reacted with *tert*-butyl amine to give the diimine **179**. This was lithiated with lithium wire in THF at -78°C. The dark red dianion was then treated with tetrachlorosilane to yield the dichloride **180**. The reduction was performed *via* a slightly different procedure. Instead of sodium-potassium alloy for the reduction of the dichlorosilane, stoichiometric amounts of potassium-graphite were used, according to Fürstner *et al.*[40], to prevent the overreduction and thus decomposition of **171**.



Scheme 5.2: Synthesis of 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene **171**

1,3-Di-*tert*-butyl-2,3-[1,3,2]-diazasilolidine-2-ylidene **172** was prepared according to Haaf *et al.*[204b] Dibromoethane **181** reacted with *tert*-butylamine to the diamine **182**. This was reacted with tetrachlorosilane in the presence of triethylamine in toluene to give the dichloride **183**.

Reduction in THF and triethylamine (15:2) with sodium-potassium alloy gave saturated silylene **172**.

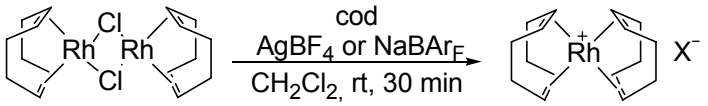


Scheme 5.3: Synthesis of 1,3-di-*tert*-butyl-2,3-[1,3,2]-diazasilolidine-2-ylidene **172**

5.4.2 Rhodium Complex Synthesis

Although rhodium plays an important role in homogeneous catalysis, no complexes of this metal with η^1-bound *N*-heterocyclic silylenes are known. For initial experiments with silylenes we chose rhodium-complex precursors which are all bearing a cyclooctadiene (cod) group. Ligand exchange liberates cod which is inert towards reaction with free silylene ligand. One of the cod groups was meant to not be exchanged, to obtain a catalytically active complex, since cod is expected to be reduced under hydrogenation conditions, whereby a free coordination site at the metal-center is generated.

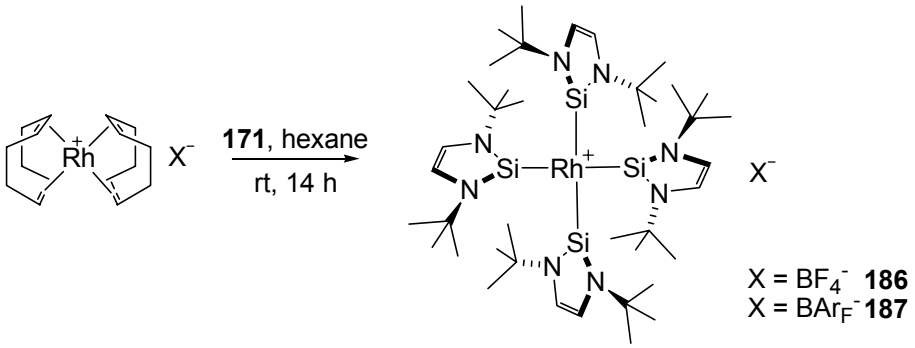
$[Rh(cod)_2]BF_4$ was prepared according to literature procedure, by reaction of $[Rh(cod)Cl]_2$ and cyclooctadiene in dichloromethane, and anion-exchange with silver tetrafluoroborate. $[Rh(cod)_2]BAr_F$ (BAr_F = tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate) was readily prepared, using a modified procedure reported for the preparation of the analogous tetrafluoroborate (Scheme 5.4).[214]



X = BF_4^- **184** 83%
X = BAr_F^- **185** 80%

Scheme 5.4: Synthesis of rhodium-complex precursors **184** and **185**

When a slurry of **184** and **171** was stirred in hexane or benzene, an orange suspension of the cationic tetrakis(silylene) complex **186** was formed. However, it remained unclear, how many ligands were attached to the metal-center. It was assumed that for steric reasons only three ligands were attached to the metal, as it is known from $[Ni(\mathbf{171})_3]$[207] and $[Pd(\mathbf{171})_3]$.[210]



Scheme 5.5: Synthesis of cationic rhodium-silylene complexes **186** and **187**

Therefore, a related complex **187** with a proton containing anion was prepared from **171** *via* the essentially same route as described before. This enables us to identify the number of silylene ligands by integration of the anion moiety in the ^{1}H NMR spectrum.

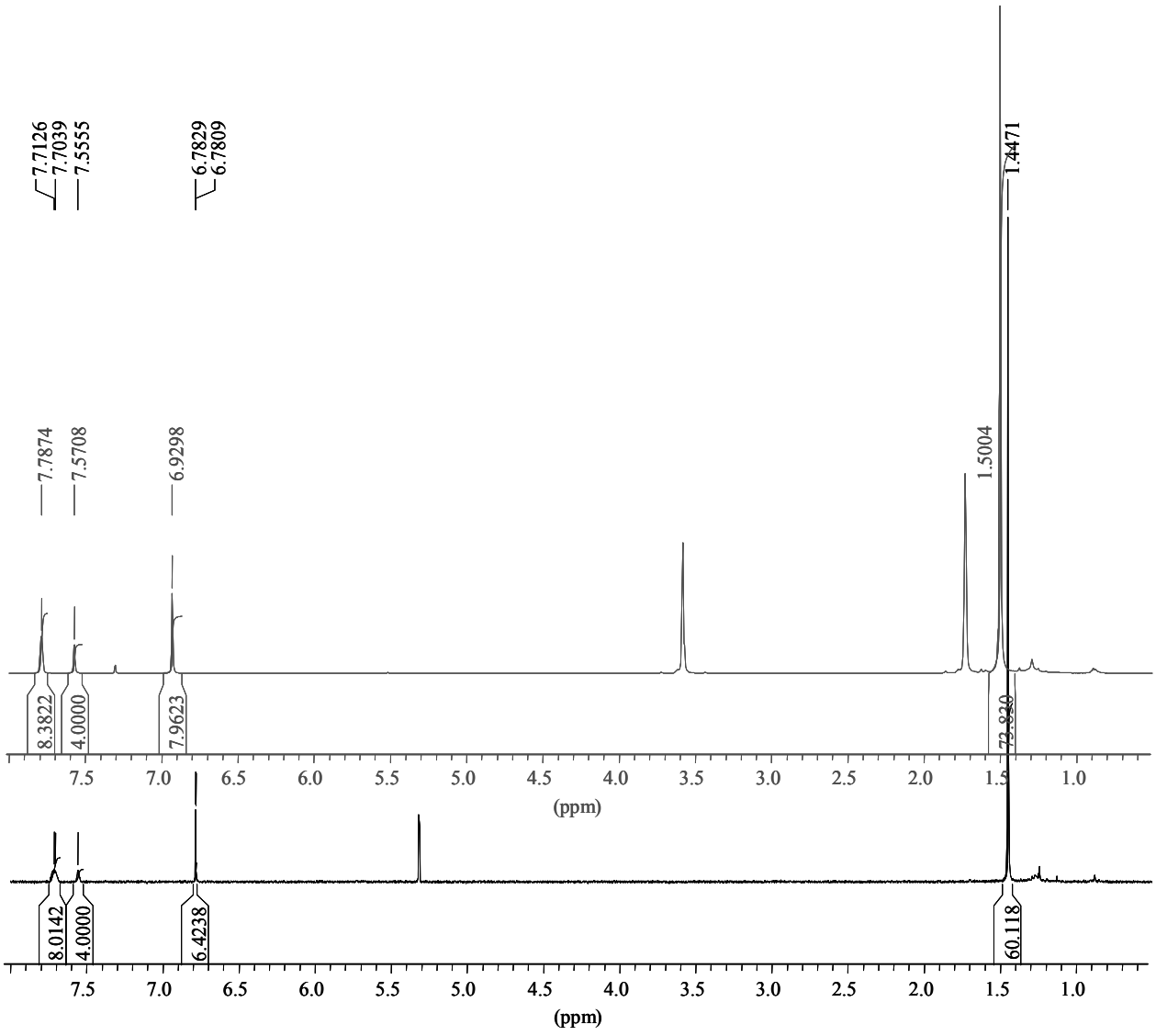
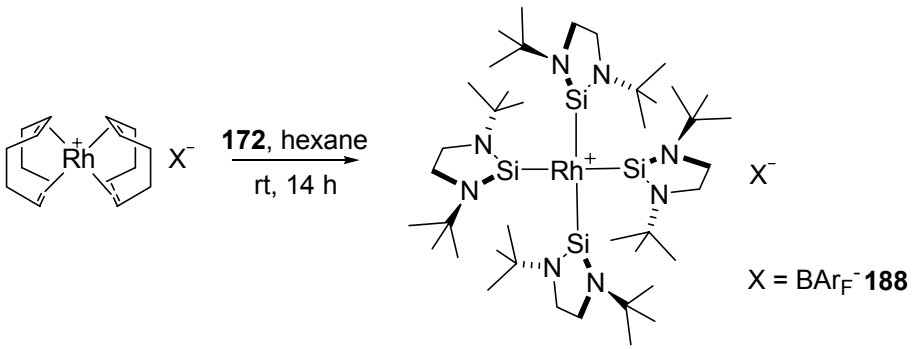


Figure 5.6: ^{1}H NMR of complex **187** in CD_2Cl_2 (bottom) and d_8-THF (top) – with benzene rest signal

Product **187** was obtained after stirring over night at room temperature as an extremely air-sensitive orange solid in quantitative yield and was finally crystallized from dichloromethane-hexane.

The metal/silylene ratio, determined by integration of the silylene and the BAr_F protons, was 1:3 in dichloromethane-d_2 or acetonitrile-d_3. However, x-ray crystal structures revealed, that actually 4 ligands were coordinated to the rhodium center. Solution structures of complex **187**, analyzed by ^{1}H-, ^{13}C-, and ^{29}Si NMR spectroscopy in tetrahydrofuran-d_8 and diethyl ether-d_{10}, were recorded and were consistent with the crystal structure. The reason for this discrepancy remains unclear (Figure 5.6). A dynamic process involving reversible dissociation of one ligand can be excluded, because the free silylenes **171** or **172** are known to decompose in chlorinated solvents,[199] whereas complexes **187** and **188** are stable in dichloromethane (they were recrystallized from this solvent).



Scheme 5.6: Synthesis of cationic rhodium-silylene complex **188**

The analogous cationic rhodium-silylene complex with saturated silylene **172** was obtained in the same way as described for **187**.[204b] Attempts to synthesize mixed bis(silylene)(cod)Rh complexes by replacement of just one 1,5-cyclooctadiene moiety were unsuccesssful. When **185** was diluted in acetonitrile, $[Rh(cod)(CH_3CN)_2]BAr_F$ was formed as a yellow intermediate and the reaction did not proceed as cleanly as in hexane.[215] In both cases exchange of all ligands was observed.

The homoleptic tetrakis(silylene)complexes **187** and **188** were the only products observed, even when less than 4 equivalents of silylene were used. In this respect, the reactivity of the silylenes **171** and **172** differs from that of analogous *N*-heterocyclic carbenes. Only partial ligand exchange leading to Rh(cod)(NHC)X complexes could be achieved, when excess of carbene was reacted with $Rh_2(cod)_2X_2$.[216] Thus, it seems more difficult to form tetrakis(NHC) complexes, probably due to steric strain resulting from the shorter Rh-C compared to Rh-Si bonds.

5.4.3 Characterization of Rhodium-Silylene Complexes

The solution structures of complexes **187** and **188**, analyzed by ^{1}H-, ^{13}C-, and ^{29}Si NMR spectroscopy in tetrahydrofuran-d_8 and diethyl ether-d_{10}, were consistent with the crystal structures. The ^{1}H NMR spectra of the new rhodium-silylene compexes **187** and **188** are easily discussed since only two peaks for each the silylene moities and for the anion are observed. Complexation is accompanied by a downfield shift of the silylene protons of about 0.1 ppm for the *tert*-butyl groups and the ring protons. The metal/silylene ratio, determined by integration of the silylene and the BAr_F protons, was 1:4 (Figure 5.6).

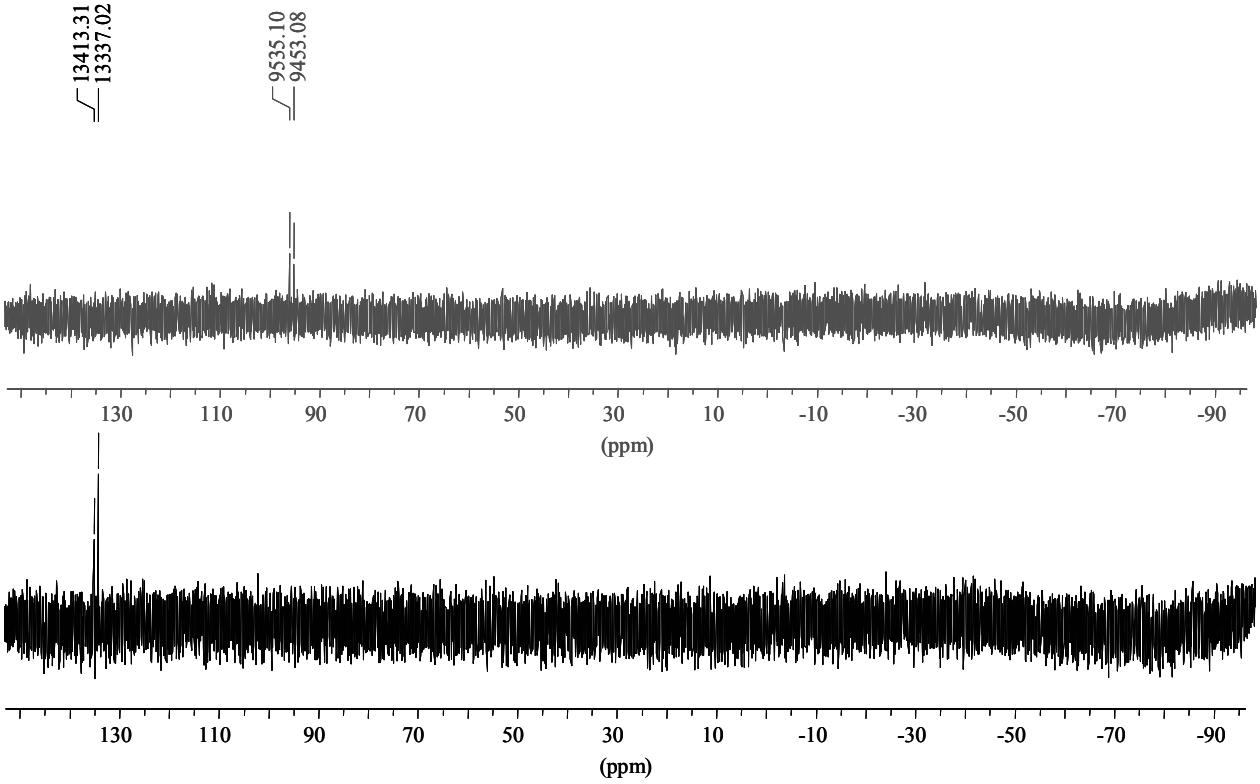


Figure 5.7: ^{29}Si NMR spectra of complexes **187** (top) and **188** (bottom) in d_8-THF

A doublet is observed in the ^{29}Si NMR spectrum of **187** at δ = 95.6 ppm ($^{1}J_{RhSi}$ = 82.5 Hz) and of **188** at δ = 134.4 ppm ($^{1}J_{RhSi}$ = 76.6 Hz). In comparison to the free silylenes **171** (78.0 ppm) and **172** (118.9) this is a considerable downfield shift (Figure 5.7).

5.5 Probing of Catalytic Activity

Preliminary hydrogenation experiments with α-trans-methylstilbene showed some hydrogenation product with up to 78% conversion. Partial conversion also took place when Hg was added to suppress a heterogeneous reaction pathway that could result from decomposition of the complex. Unfortunately, the experiments were not reproducible.

It remained to discover a species that could have led to the observed reactivity, *e.g.* a rhodium-hydride compound. Complexes **187** and **188** were dissolved in a number of different solvents and each purged with hydrogen at 1 bar in a young valve NMR tube, and at 50 bar in an autoclave. After 24 hours still no hydride peaks could be detected by NMR. At 1 bar in diethylether almost no decomposition took place, and the solution also remained unchanged after one week. At 50 bar the complex was destroyed completely, *i.e.* no olefinic ring protons were visible, but a number of different decomposition products with multiplets around 5.6 ppm were detected, which can probably be assigned to tetravalent silylene-addition products. No proof of a dissociative mechanism could was observed.

Reaction of complex **187** under 1 bar carbonmonoxide in tetrahydrofurane led to a brown solution. In the ^{1}H NMR general loss of signal intensity of the ligand protons relative to the solvent residual peaks was observed. Furthermore all peaks derived from the cationic moiety disappeared. No free silylene was observed. No characteristic peaks for rhodium-carbonyl-compounds were detected in the ^{13}C NMR.

5.6 X-ray Crystallographic Studies

Complexes **187** and **188** crystallized from dichloromethane/hexane as orange and yellow plates, respectively, which were subjected to X-ray crystallographic analysis. POV-Ray representations of the crystal structures are depicted in Figure 5.8 and Figure 5.9; crystallographic data are found in the appendix and selected structural parameters are given in Table 5.1.

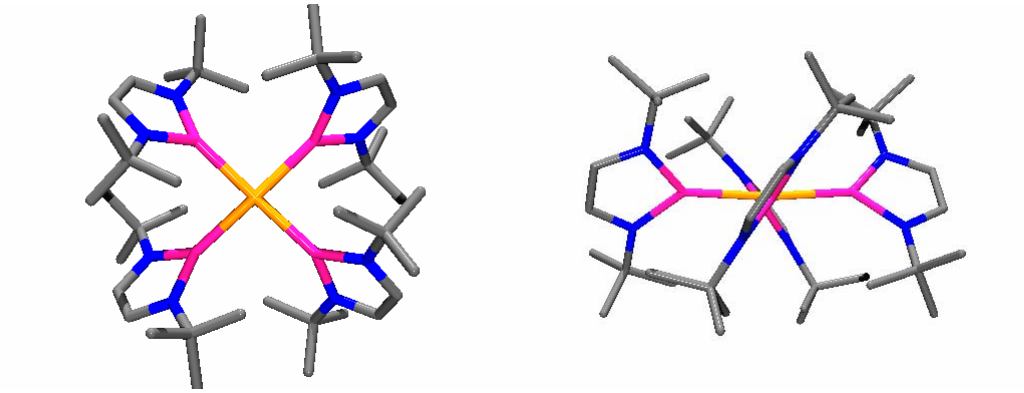


Figure 5.8: Representation of the cation moiety of complex **187** in top view (left) and side view (right).

Both complexes are centrosymmetric and show a windmill-shaped, square-planar arrangement of the four silylene ligands. The three-coordinate silicon atoms adopt an almost perfectly planar geometry, with the sum of bond angles being 360.6° (**187**) and 360.0° (**188**). Rh-Si distances are between 2.29-2.32 Å for both complexes. As expected, the Rh-Si bonds are somewhat shorter than in silyl-Rh complexes (2.32-2.38 Å) or bridged μ-(R_2Si)Rh_2 complexes (2.34-2.36 Å).[217,218]

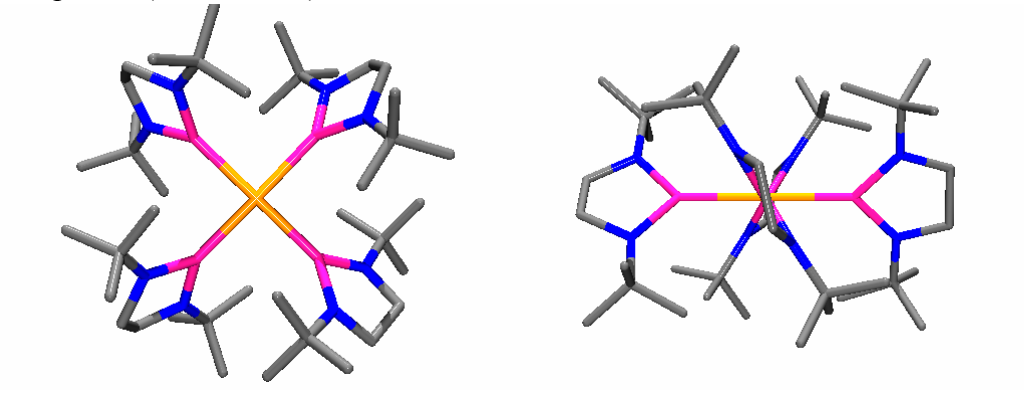


Figure 5.9. Representation of the cation moiety of complex **188** in top view (left) and side view (right).

Si-N Bond distances and N-Si-N angles of the free silylenes change very little upon coordination to Rh (**171**: 1.75 Å, 89.0°; **187**: 1.73-1.74 Å, 91.0-91.3°).[187] No other examples of square-planar tetrakis(silylene) complexes were found in the literature. The only somewhat

related silylene complexes, for which crystal structures were reported, are the above-mentioned tetrahedral [Ni(silylene)$_4$] (Figure 5.5, page 101) and square-planar mixed *trans*-bis(chlorosilyl)-bis(silylene)-Pd(II) and Pt(II) complexes.[207,208]

Table 5.1: Selected Bond Lengths (Å) and Angles (deg) for **187** and **188**

	187	**188**
Rh1-Si1	2.3104(8)	2.2988(8)
Rh1-Si2	2.2922(8)	2.289(2)
Rh1-Si3		2.316(2)
Si1-N1	1.735(2)	1.714(3)
Si1-N2	1.736(2)	1.712(3)
Si2-N3	1.734(2)	1.711(3)
Si2-N4	1.735(2)	
Si1-Rh1-Si1’	94.63(4)	178.83(6)
Si1-Rh1-Si2	173.86(2)	90.59(3)
Si1-Rh1-Si2’	86.72(2)	
Si1’-Rh1-Si2	86.72(2)	90.59(3)
Si1’-Rh1-Si2’	173.86 (2)	
Si2-Rh1-Si2’	92.57(4)	
Si1-Rh1-Si3		89.41(3)
Si1’-Rh1-Si3		89.41(3)
Si2-Rh1-Si3		179.995
N1-Si1-N2	91.0(2)	94.1(2)
N3-Si2-N4	91.3(2)	
N3-Si2-N3’		94.1(2)
N4-Si3-N4’		94.2(2)
Rh1-Si1-N1	131.60(9)	132.2(1)
Rh1-Si1-N2	137.05(8)	133.7(2)
Rh1-Si2-N3	138.32(8)	132.9(2)
Rh1-Si2-N4	129.85(8)	
Rh1-Si3-N4		132.9(1)

Both compounds show C_2-symmetry. While in **188** two of the silicon atoms lie on the C_2-axes, all silicon atoms are in general positions in compound **187**. Therefore, the number of Rh-Si distances, as well as the number of Si-Rh-Si, N-Si-N and Rh-Si-N angles differs in both cases. The symmetry generated atoms are marked with prime’.

5.7 Conclusion

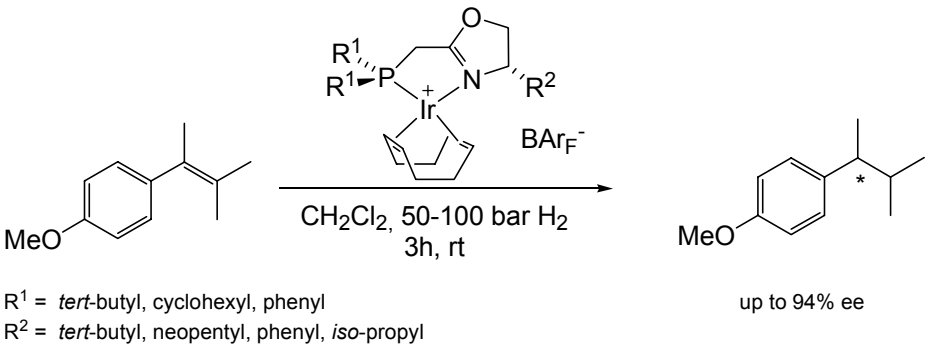
Two cationic rhodium(I)-tetrasilylene **187** and **188** were prepared from $[Rh(cod)_2]BAr_F$ **185** and 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene **171** or its saturated analogue **172**, respectively (Figure 1). The two complexes were characterized by X-ray analysis and NMR spectroscopy. The crystal structures revealed a square-planar coordination geometry for both complexes. Only tetrakis(silylene) complexes were formed, even in the presence of less than 4 equiv. of silylene.

Chapter 6

Synopsis

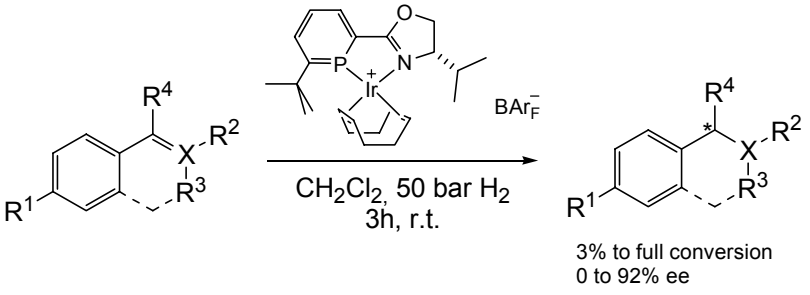
6 Synopsis

We were interested to extend our library of P,N-ligands, and to investigate the influence of a five-memebered ring-chelate, since most of the previously tested ligands form six-membered ring-chelates. In consequence, twelve new phosphinomethyl-oxazolines and their corresponding iridium-complexes were prepared and tested in the enantioselective hydrogenation of unfunctionalized and functionalized olefins. The tetrasubstituted olefin 2-(4'-methoxyphenyl)-3-methyl-2-butene was reduced with higher enantioselectivity than reported for other iridium catalysts.



Scheme 6.1: Hydrogenation of tetrasubstituted alkene with new iridium-catalysts

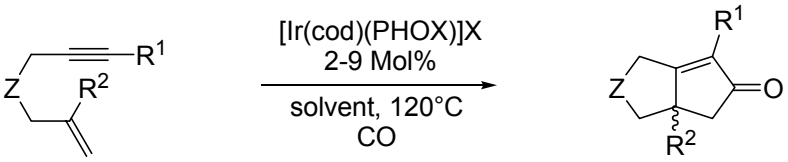
Another objective was to examine the effect of a strong π-accepting and planar phosphorus-moiety. Three chiral phosphininoxazolines were prepared by dehydration of a water-adduct, wherein the phosphorus atom is present as a secondary phosphine oxide. The corresponding cationic iridium-complexes were synthesized. One of these complexes was also tested in the iridium-catalyzed hydrogenation and transfer-hydrogenation showing good conversion, but low to moderate enantioselectivity.



Scheme 6.2: Hydrogenation with phosphininoxazolin-iridium catalyst

We were interested in the scope of iridium-PHOX complexes in other catalytic reactions. Initial studies towards the application of this system in asymmetric catalytic Pauson-Khand reaction were completed regarding pressure influence, reproducability and the influence of the

counteranion on the enantioselectivity of the reaction. 3-Phenylsubstituted enynes undergo cycloaddition with good to very good yields and good enantioselectivities. Steric hindrance at the alkene moiety leads to a strong drop in yield. Among the tested counteranions, small and weakly-coordinating anions, such as triflate, tetrafluoroborate, hexafluorophosphate and hexafluoroantimonate proved to give the highest enantioselectivities.

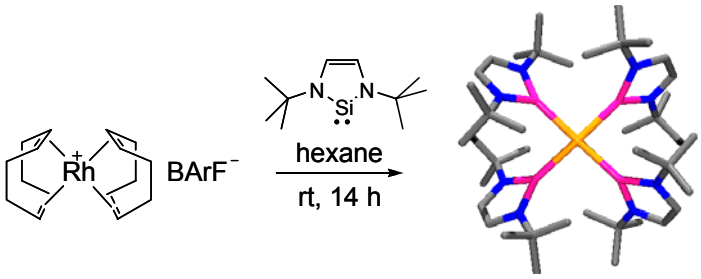


S1-S5 **P1-P5**

	Z	R^1	R^2
S1	O	Ph	H
S2	NTs	Ph	H
S3	$C(COOMe)_2$	Ph	H
S4	O	Me	H
S5	O	Ph	Me

Scheme 6.3: Asymmetric catalytic intramolecular Pauson-Khand reaction with iridium-PHOX catalyst

Inspired by the recent success of NHCs in the iridium catalyzed hydrogenation, we envisioned the synthesis of iridium- and rhodium-complexes containing N-heterocyclic silylenes. Two cationic rhodium(I)-silylene complexes **187** and **188** were prepared from $[Rh(cod)_2]BAr_F$ **185** and 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene **171** and its saturated analogue **172**, respectively (Figure 1). Only catalytically inactive complexes were formed. The corresponding iridium-complexes were not accessible by the same method.



Scheme 6.4: Synthesis of a homoleptic rhodium-silylene complex

Chapter 7

Experimental

7 Experimental

7.1 Analytical Methods

NMR-Spectrometry: NMR spectra were recorded on Bruker Advance 250 (250 MHz), Bruker Advance 400 (400 MHz) and Bruker Advance DRX 500 (500 MHz) NMR spectrometers, equipped with BBO broadband probeheads. The chemical shift δ is given in ppm. References were 7.26 ppm (^{1}H NMR) and 77.16 ppm (^{13}C NMR) for $CHCl_3$, 5.32 ppm (^{1}H NMR) and 53.8 ppm (^{13}C NMR) for CH_2Cl_2, 7.16 ppm (^{1}H NMR) and 128.06 ppm (^{13}C NMR) for C_6H_6, and 3.58 (1.73) ppm (^{1}H NMR) and 67.4 (25.3) ppm (^{13}C NMR) for THF.[219] 85% phosporic acid (0 ppm) was taken as an internal standard in a capillary for ^{31}P NMR (sr(CD_2Cl_2) = 94.2 Hz, sr($CDCl_3$) = 130.69 Hz, sr(C_6D_6) = 127.98 Hz) measured on the 500 MHz NMR spectrometer. For spectra that were measured on the 400 MHz NMR spectrometer, the shifts were corrected (+3.6 ppm for CD_2Cl_2, +3.2 ppm for C_6D_6). The assignment of ^{1}H- and ^{13}C-signals was made by 2D-NMR, namely COSY, HMQC, HMBC and difference NOESY-spectrometry. ^{13}C and ^{31}P, until otherwise noted, were recorded ^{1}H-decoupled. Multiplets were assigned with s (singlet), d (doublet), t (triplet), *ps*t (*pseudo*-triplet), m (multiplet). The index br stands for broad (usually no resolution), the indices eq and ax for equatorial and axial, respectively.

Mass Spectrometry (MS): Mass spectra were recorded by Dr. H. Nadig. Electron ionization (EI) was measured on VG70-250, fast atom bombardment (FAB) was measured on MAR 312, Electron spray ionization (ESI) was measured on Finnigan MAT LCQ by B. Bulic and A. Teichert. FAB was performed with 3-nitrobenzyl alcohol as matrix. The signals are given in mass-to-charge ratio (m/z). The fragment and intensities of the signals are given in brackets.

Infrared Spectrometry (IR): Infrared spectra were measured on a Perkin Elmer 1600 series FTIR spectrometer. Solid samples were prepared as KBr wafers, liquid samples were prepared between NaCl plates. For air and moisture sensitive compounds KBr was thoroughly dried under high vacuum and samples were prepared in the glove box. Absorption bands are given in wave numbers $\tilde{\nu}$ [cm^{-1}]. The peak intesity is assigned with s (strong), m (medium), and w (weak). The index sh stands for shoulder, br for broad.

Melting Point (m.p.): The melting point was measured in a Büchi 535 melting point apparatus. The values are not corrected.

Optical Rotation ($[\alpha]_D^{20}$): α-values were measured in a Perkin Elmer Polarimeter 341 in a cuvette (l = 1 dm) at 20°C at 589 nm (sodium lamp).Concentration c is given in g/100 mL.

Thin Layer Chromatography (TLC): TLC plates were obtained from Macherey-Nagel (Polygram® SIL G/UV_{254}, 0.2 mm silica with fluorescence indicator, 40×80 mm).

Gas Chromatography (GC): The gas chromatographs in use were Carlo Erba HRGC Mega2 Series 800 (HRGC Mega 2). Achiral separations were performed with Macherey-Nagel Optima 5-Amine (30 m × 0.25 mm × 0.50 μm) and Restek Rtx-1701 (30 m × 0.25 mm × 0.25 μm). For chiral separations β- and γ-cyclodextrine columns (30 m × 0.25 mm × 0.25 μm) were used.

High Performance Liquid Chromatography (HPLC): For HPLC analysis Shimadzu systems with SCL-10A System Controller, CTO-10AC column oven, LC10-AD pump system, DGU-14A degasser, and SPD-M10A Diode Array- or UV-vis detector were used. Chiral columns Chiracel OD-H, OB-H, OJ, AS and Chiralpak AD from Daicel Chemical Industries Ltd. were used.

Elemental Analysis (EA): Elemental analyses were carreid out by Mr. W. Kirsch at the Department of Chemistry at the University of Basel, on Leco CHN-900 (C-, H-, N-detection) and Leco RO-478 (O-detection) analysers. The data are indicated in mass percent.

7.2 Working Techniques

Sensitive Compounds: Syntheses of air- and moisture-sensitive compounds were carried out under inert atmosphere in a glove-box (MBRAUN labmaser 130, N_2) or using standard Schlenk techniques (Ar).

Solvents: Dichloromethane, diethyl ether, pentane, tetrahydrofurane, and toluene were dried and degassed by reflux over an adequate drying agent under nitrogen.[220] Other solvents were purchased dry at Fluka or Aldrich in septum sealed bottles, kept under inert atmosphere and over molecular sieves. If necessary, solvents were degassed by three freeze-pump-thaw cycles. Deuterated solvents were degassed and stored over activated molecular sieves (4Å).

Column Chromatography: Silica gel was obtained from CU Chemie Uetikon (C-560 D, 0.040-0.063 mm) or Merck (silica gel 60, 0.040-0.063 mm). Generally, the *flash column chromatography* according to Still[221] was performed.

7.3 New PHOX Ligands for Enantioselective Hydrogenation

Di-*tert*-butylchlorophosphine [13716-10-4], chlorodicyclohexylphosphine [16523-54-9], dicyclohexylphosphine [6476-37-5], diphenylphosphine [829-85-6] and phenylglycinol [56613-80-0] were purchased from Aldrich. $[Ir(cod)Cl]_2$ [12112-67-3] was purchased from Strem, neopentylglycine [88319-43-1] was purchased from Bachem, and L-valinol [473-75-6] and L-*tert*-leucinol [3907-02-6] were bought from Degussa.

Synthesis of Amides **34-44**

general procedure 1: Phosphinoacetic acid-borane adduct (1 eq) and HOBt (1.2 eq) were dissolved in dichloromethane. EDC (1.2 eq) and amino alcohol (1 eq) were added and the mixture was stirred for 15 hours at room temperature. The mixture was then diluted with dichloromethane (20 mL) and water (30 mL) and extracted with 0.5M HCl (20 mL), 2.5% $NaHCO_3$ (20 mL), water (20 mL), and brine (20 mL). Drying over $MgSO_4$ and evaporation of the volatiles gave the crude product. The product was usually used without further purification.

Synthesis of Oxazoline-Borane Adducts **45-47**

general procedure 2: Phosphinoacetamide-borane adduct (1 eq) was dissolvd in THF. *Burgess'* reagent ((methoxycarbonylsulfamoyl)triethylammonium hydroxide, inner salt) (1.2 eq) was added and the mixture stirred for four hours at 70 °C. The reaction mixture was dissolved in water (20 mL) and dichloromethane (20 mL) and the layers were separeted. The water layer was extracted with dichloromethane (3×20 mL). The combined organic layers were then extracted with brine (20 mL) and dried over Na_2SO_4. After evaporation of the volatiles the crude product was purified by column chromatography.

Synthesis of Chloroacetamides **50-53**

general procedure 3: Chloroacetylchloride (1 eq) was slowly added to a solution of amino alcohol (1.01 eq) and triethylamine (1.05 eq) in dichloromethane at -20 °C. The reaction mixture was stirred at room temperature for 20 hours after which time all volatiles were removed and the residue suspended in ethyl acetete. Filtration was followed by evaporation of the solvent and purification by flash column chromatography or Kugelrohr distillation.

Synthesis of Chloromethyloxazolines **54-57**

general procedure 4: To a solution of chloroacetamide (1 eq) in THF was added (methoxycarbonylsulfamoyl)triethyl-ammonium hydroxide, inner salt (1.2 eq).The solution

was heated to reflux for 4 hours after which time all volatiles were removed and the residue diluted in dichloromethane (100 mL). The organic layer was washed with water (100 mL) then brine (50 mL) and dried over $MgSO_4$. After evaporation of the solvent, the crude material was purified by column chromatography.

Synthesis of Oxazoline-Borane Adducts **59-67**

general procedure 5: **method A**: A two-neck flask under argon was charged with NaH (1-2.6 eq) and THF. At 0 °C a mixture of chloro-methyl-4,5-dihydro-oxazoline (0.8-1.3 eq) and a secondary phosphine-borane adduct (1 eq) in THF was added dropwise to the suspension. After the formation of hydrogen had stopped, the mixture was stirred at room temperature until TLC indicated the consumption of starting material. The reaction was then quenched with HCl 1N and diluted with water. After extraction with dichloromethane the combined organic layers were dried over $MgSO_4$. The crude product was purified by flash column chromatography. **method B**: In a schlenk under argon a secondary phosphine-borane adduct (1 eq) in THF was cooled to -78 °C. *n*-BuLi (1.05 eq) was slowly added and the mixture was stirred for 15 minutes at -78 °C and for 2 hours at room temperature. After cooling to -78 °C chloro-methyl-4,5-dihydro-oxazoline (0.8-1.3 eq) in THF was added via cannula, and the cannula was rinsed with THF. The mixture was stirred at room temperature until TLC indicated the consumption of starting material. Then the mixture was poured in saturated $NaHCO_3$ solution and extracted with diethyl ether (3×10 to 20 mL) The combined organic layers were dried over $MgSO_4$ and the crude product was purified by flash column chromatograph on silica eluting with diethyl ether and pentane.

Deprotection of Oxazoline-Borane Adducts to Oxazolines **68-79**

general procedure 6: Borane-protected phosphanyl-methyl-4,5-dihydro-oxazoline was dissolved in diethylamine (1-2 mL) and stirred for 1 to 7 days. The conversion was controlled by ^1H NMR. After completion of the reaction all volatiles were removed under high-vacuum at 60 °C.

Synthesis of Iridium Complexes **80-91**

general procedure 7: Under argon, the corresponding P,N-ligand (1 equiv) was dissolved in dry dichloromethane, and $[Ir(cod)Cl]_2$ (0.5 equiv) was added as a solid. The orange solution was heated for 2 hours to 48 °C in a closed screw-cap schlenk. After cooling to room temperature, $NaBAr_F$ (1.3 equiv) was added. After 15 hours some silica was added and the volatiles were evaporated. Column chromatography with diethyl ether and dichloromethane

(gradient mixtures) afforded the pure complexes of which some could be recrystallized in dichloromethane/hexane.

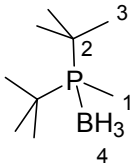
Catalytic Hydrogention at Elevated Pressure

general procedure 8: In a glove box, substrate, iridium complex and dichloromethane were added into little vials (1.5 mL) equipped with a magnetic stir bar. Four vials were added to a 60 mL autoclave (premex AG, Lengnau, Switzerland). The autoclave was pressuriesed with H2 (Carbagas, Switzerland, 99.995%) according to the stated reaction conditions. After reaction, the pressure was released and the solvent was evaporated. The residue was dispersed in hexane/ethyl acetate (9:1) and filtered over a short plug of silica gel eluting with hexane and ethyl acetate (9:1 to 1:1). The filtrate was analyzed by GC, chiral GC, and chiral HPLC to determine the conversion and enantioselectivity. HPLC samples were prepared in heptane and iso-propanol. The analytical procedures were used as previously described in reference 57b.

7.3.1 Phosphinoacetic Acid-Borane Adducts

Di-*tert*-butylmethylphosphine-borane adduct (23)[65]

Di-*tert*-butylchlorophosphine (2 g, 11 mmol) was dissolved in pentane and cooled to -78 °C. Methyllithium (12.2 mmol, 1.6M in diethyl ether) was added dropwise, and the solution was slowly brought to room temperature and stirred for further 12 hours. The resulting suspension was filtered over celite and washed with pentane (2×10 mL). The solution was reduced and added to borane-THF adduct (15 mmol, 1M in THF) at 0 °C. The mixture was stirred at room temperature for 15 hours. Then all volatiles were evaporated and the crude mixture was purified over a short column on silica eluting with pentane and diethyl ether. The product was obtained as a white solid (1.61 g, 84%).

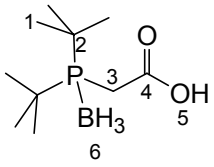


$C_9H_{24}BP$ (174.07)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.5 (m_{br}, 3H, 4)1.18 (d, $^2J_{HP}$ = 9.4 Hz, 3H, 1), 1.26 (d, $^3J_{HP}$ = 12.6 Hz, 18H, 3). **^{31}P{^{1}H} NMR** (202.5 MHz, $CDCl_3$, 300K): δ = 38.5 (m, $^1J_{PB}$ = 62.8 Hz). **TLC** (*n*-pentane/diethyl ether, 10:1) R_f = 0.53

Di-*tert*-butylphosphino acetic acid-borane adduct (24)[65]

Di-*tert*-butylmethylphosphine-borane adduct (450 mg, 2.6 mmol) was dissolved in THF (8 mL) and degassed with three freeze-pump-thaw cycles. At -78 °C 1.9 eq *sec*-butyllithium (1.3 M in cyclohexane) was added, and the yellow solution was stirred for 2 hours at this temperature. The cooling-bath was removed and CO_2 was bubbled through the solution for 45 minutes. The white suspension was diluted with diethylether (8 mL) and extracted with aqueous saturated Na_2CO_3 (4×10 mL). The water-phase was acidified and extracted with diethyl ether (6×20 mL). Drying over Mg_2SO_4 and evaporation of the volatiles afforded di-*tert*-butylphosphine acetic acid-borane adduct **24** as a white solid (463 mg, 82%).

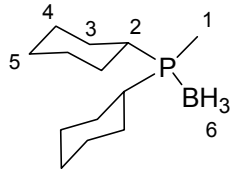


$C_{10}H_{24}BO_2P$ (218.08)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.55 (m, $^{1}J_{HB}$ = 100 Hz, 3H, 6), 1.33 (d, $^{3}J_{HP}$ = 13.4 Hz, 18H, 1), 2.79 (d, $^{2}J_{HP}$ = 11.1 Hz, 2H, 3). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 47.0 (m, $^{1}J_{PB}$ = 69.4 Hz). **MS** (+FAB, 3-NBA) m/z: 217 ($R^1{}_2R^2P(^{11}B)H_2^+$, 81.9), 216 ($R^1{}_2R^2P(^{10}B)H_2^+$, 20.2), 159 (M^+-BH_3,-C_4H_{10}, 15.1), 103 (159-$C_4H_8^+$, 13.1), 57 ($C_4H_9^+$, 100). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 2990.5s, 2967.4s, 2904.3m, 2882.5m, 2671.9w, 2571.4w, 2443.0s, 2586.3s, 2268.0w, 1710.8s, 1481.6m, 1470.9m, 1424.7m, 1394.0m, 1373.9m, 1302.5s, 1224.6w, 1188.3w, 1143.3m, 1076.m6, 1925.3m, 936.0m, 839.9w, 812.0m, 764.1w, 744.9w, 686.8m, 634.6m, 602.1m, 531.4w, 470.6m. **m.p**. 138-140°C. **EA** %found (calcd): C: 55.00 (55.08), H:10.94 (11.09).

Dicyclohexylmethylphosphine-borane adduct (27)

In a flame-dried schlenk, chlorodicyclohexylphosphine (2.13 g, 9.15 mmol) was dissolved in pentane (25 mL). The cloudy solution was cooled to -78 °C and methyllithium (10.1 mmol, 1.6M in diethyl ether) was slowly added. The solution was slowly brought to room temperature and stirred for further 15 hours. The resulting suspension was filtered over celite and washed with pentane (2×10 mL). The filtered solution was reduced and cooled to 0 °C. Borane-THF adduct (12 mmol, 1M in THF) was added and the solution stirred for 6 hours at room temperature. After evaporation of the volatiles the crude product was purified by column chromatography on silica eluting with pentane and diethyl ether. The product was obtained as a white solid (1.95 g, 94 %).



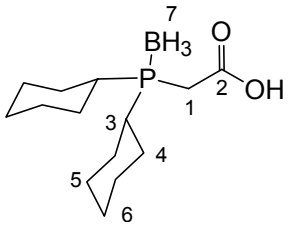
$C_{13}H_{28}BP$ (226.15)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.3 (q, $^{1}J_{BH}$ = ~100Hz, 3H, 6), 1.10 (d, $^{3}J_{HP}$ = 9.5 Hz, 1), 1.25 (m, 10H, Cy_{eq}),1.61 (m, 2H, Cy_{ax}), 1.72 (m, 5H, Cy_{ax}), 1.83 (m, 3H, Cy_{ax}), 1.87 (m, 2H, Cy_{ax}). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$ 300K): δ = 3.7 (d, $^{1}J_{CP}$ = 24.8 Hz, 1), 26.1 (Cy), 26.2 (Cy), 26.6 (5), 26.8 (Cy), 26.9 (Cy), 31.3 (d, $^{1}J_{CP}$ = 34 Hz, 2). **^{31}P{^{1}H} NMR** (202.5 MHz, $CDCl_3$, 300K): δ = 20.3 (m, $^{1}J_{PB}$ = 56 Hz). **MS** (+FAB, 3-NBA) m/z: 223.2 (20.0), 212.2 ($C_{13}H_{25}P^+$, 100), 157.1 (16.6), 130.1 ($C_7H_{15}P$+, 82.3). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3447.7m_{br}, 2916.8s, 2853.9s, 2667.3w, 2371.4s, 2327.5s, 2247.6m, 1447.6s, 1421.3m, 1346.4m, 1295.9m, 1275.3w, 1211.6w, 1180.2w, 1131.4m, 1067.3s, 1048.5m, 1007.6s, 920.7s, 906.6s, 851.8s, 779.0s, 754.4m, 739.5m, 704.1m, 599.m5, 588.9s, 516.4m, 446.9m.

m.p. 78°C. **TLC** (*n*-pentane:diethyl ether; 10:1) R_f = 0.46. **EA** % found (calcd) C 68.96 (69.04), H 12.30 (12.48).

Dicyclohexylphosphino acetic acid-borane adduct (28)

Dicyclohexylmethylphosphine-borane adduct (1.7 g, 7.5 mmol) was dissolved in THF (30 mL) and degassed with three freeze-pump-thaw cycles. At -78 °C 1.8 eq *sec*-butyllithium (1.3 M in cyclohexane) were added, and the yellow solution was stirred for 2 hours at this temperature. The cooling-bath was removed and CO_2 was bubbled through the solution for 45 minutes. The white suspension was diluted with diethylether (40 mL) and extracted with aqueous saturated Na_2CO_3 (4×50 mL). The water-phase was acidified and extracted with diethyl ether (6×100 mL). Drying over Mg_2SO_4 and evaporation of the volatiles afforded the product as a white solid (1.33 g, 66 %).

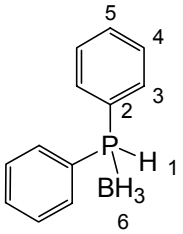


$C_{14}H_{28}BO_2P$ (270.16)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.35 (m_{br}, 3H, 3), 1.25 (m_{br}, 6H, Cy_{eq}), 1.43 (m_{br}, 4H, Cy_{eq}), 1.74 (m_{br}, 2H, Cy_{ax}), 1.84 (m_{br}, 8H, Cy_{ax}), 1.97 (m_{br}, 2H, 4), 2.73 (d, $^2J_{HH}$ = 10.0 Hz, 2H, 1). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 26.0 ($^4J_{CP}$ = 1.2 Hz, 7), 26.5 (6), 26.6 (d, $^1J_{CP}$ = 21 Hz, 4), 26.7 (6), 26.8 ($^2J_{CP}$ = 12 Hz, 5), 26.9 ($^2J_{CP}$ = 10 Hz, 5), 31.5 (d, $^1J_{CP}$ = 30.5 Hz, 1), 172.4 (d, $^2J_{CP}$ = 6.3 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 29.1 (m). **MS** (-ESI), m/z: 270.2 (M^-, 31.0), 269.2 (M^-, 100.0), 268.2 (M^-, 15.3), 225.1 (M^- -CO_2, 7.9). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 2933.5s_{br}, 2855.3s, 2671.5w, 2568.3w, 2383.1s, 2339.3m, 2270.3w, 1700.7s, 1450.0s, 1432.6s, 1391.7m, 1300.8m, 1218.0m, 1140.6m, 1064.0m, 1047.2m, 1002.4m, 950.6m_{br}, 922.8m_{br}, 896.2m, 851.2m, 826.0w, 802.9w, 761.9w, 680.8m, 608.6m, 559.6m, 514.5m, 465.7m_{br}. **m.p.** 149-152°C. **TLC** (*n*-pentane:diethyl ether; 10.1) R_f = 0.46. **EA** %found (calcd): C: 62.19 (62.24), H: 10.22 (10.45).

Diphenylphosphine-borane adduct (30)[66]

To a 1M solution of borane in THF (15 mL, 15 mmol) was added diphenylphosphine (1.9 mL, 11 mmol) at 0 °C. The reaction mixture was stirred room temperature for 15 hours. All volatiles were evaporated and the residue was diluted in diethyl ether and filtered over a plug of silica. After evaporation the product was obtained as a white solid (2.18g, 99%).

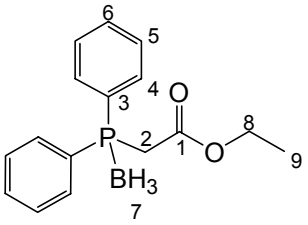


$C_{12}H_{14}BP$ (200.02)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 1.05 (q, $^{1}J_{HB}$ = ~ 80 Hz, 3H, 6), 6.30 (dq, $^{1}J_{HP}$ = 178.7 Hz, $^{3}J_{HP}$ = 7.1 Hz, 1H, 1), 7.43-7.52 (m, 6H, Ph), 7.64-7.69 (m, 4H, Ph). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 126.3 (d, $^{1}J_{CP}$ = 57 Hz, 2), 129.2 (d, $^{2}J_{CP}$ = 10.3 Hz, 3), 131.8 (d, $^{4}J_{CP}$ = 2.3 Hz, 5), 133.1 (d, $^{3}J_{CP}$ = 9.2 Hz, 4). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 2 (q, $^{1}J_{PB}$ ~50 Hz). **MS** (FAB, 3-NBA) m/z: 352 (53.02), 199 ($M\text{-}H^-$, 100), 187 ($Ph_2PH_2^+$, 52.58), 109 (PhP^+, 52.95). **IR** (KCl): $\tilde{\nu}$ [cm^{-1}] = 3418m_{br}, 3052w, 2383s, 1478m, 1431s, 1307w, 1184w, 1134m, 1106m, 1058s, 897s, 742s, 694s, 579m. **m.p.** 49°C, **EA** % found (calcd): C: 71.84 (72.06), H: 7.01 (7.05).

Diphenylphosphino ethyl acetate-borane adduct (32)[66]

NaH (312 mg, 13 mmol) and diphenylphosphine-borane adduct (1 g, 5 mmol) were dissolved in THF (5 mL). At 0 °C chloroethylacetate (0.7 mL, 6.5 mmol) in THF (10 mL) was added *via* a cannula. After stirring at room temperature for 17 hours the suspension was quenched with 1N HCl (4 mL) and extracted with ethyl acetate (3×20 mL). Drying over $MgSO_4$ and evaporation of the solvents afforded a light-yellow oil that was purified by column chromatography on silica eluting with hexane and ethyl acetate. The product was obtained as a colorless oil (1.225g, 86%).



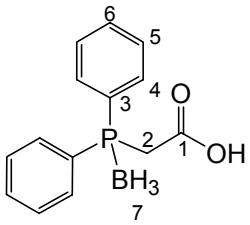
$C_{16}H_{20}BO_2P$ (286.11)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 1.04 (t, 3H, $^{4}J_{HH}$ = 7Hz, 9), 1.05 (q_{br}, 3H, 7), 3.32 (d, 2H, $^{2}J_{HP}$ = 10.9 Hz, 2), 3.97 (q, 2H, $^{3}J_{HH}$ = 7 Hz, 8), 7.44-7.54 (m, 6H, 5-6), 7.71-7.77 (m, 4H, 4). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 13.9 (9), 33.1 (d, $^{1}J_{CP}$ = 28.7 Hz, 2), 61.7 (8), 128.2 (d, $^{1}J_{CP}$ = 56 Hz, 3), 128.9 (d, $^{3}J_{CP}$ = 10.3 Hz, 5), 131.7 (d, $^{4}J_{CP}$ = 2.3 Hz, 6), 132.7 (d, $^{2}J_{CP}$ = 10.0 Hz, 4), 166.9 (1). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 17.2 (m_{br}, $^{1}J_{PB}$ = 60 Hz). **MS** (+FAB, 3-NBA) m/z: 285 ($M\text{-}H^-$, 100), 273 ($MH^{+}\text{-}BH_3$, 16.6), 199

($Ph_2PCH_2^+$, 27.8), 185 (Ph_2P^+, 62.7). **IR** (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3058w, 2984m, 2934w, 2386s, 1733s, 1480w, 1438m, 1400w, 1367w, 1269s, 1189w, 1116s, 1062m-s, 1029m, 884w, 807w, 739m, 695s. **TLC** (*n*-hexane:ethyl acetate, 7:3) R_f = 0.51. **EA** % found (calcd): C: 67.22 (67.17), H: 6.99 (7.05).

Diphenylphosphino ethanoic acid-borane adduct (33)[66]

Potassium hydroxide (216 mg, 3.80 mmol) dissolved in a mixture of water (250 μL) and ethanol (1 mL) were added dropwise at 0 °C to ester **32** (1.00 g, 3.50 mmol). The mixture was stirred for 2 hours at room temperture, and ethanol was evaporated under reduced pressure. The oil obtained was dissolved in water (3 mL), washed with diethyl ether (3×5 mL). The aqueous layer was acidified to pH 1, with 1M hydrochloric acid, saturated with sodium chloride, and extracted with dichloromethane (3×10 mL). The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure affording carboxylic acid as a white powder (808 mg, 89%).



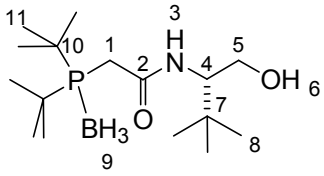
$C_{14}H_{16}BO_2P$ (258.06)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 1.05 (q_{br}, 3H, 7), 3.3 (d, 2H, $^2J_{HP}$ = 11.1 Hz, 2), 7.43-7.55 (m, 6H, 5-6), 7.69-7.74 (m, 4H, 4). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 33.9 (d, $^1J_{CP}$ = 28.4 Hz, 2), 127.7 (d, $^1J_{CP}$ = 56 Hz, 3), 129.1 (d, $^3J_{CP}$ = 10.7 Hz, 5), 132 (d, $^4J_{CP}$ = 2.7 Hz, 6), 132.5 (d, $^2J_{CP}$ = 10.0 Hz, 4), 171.7 (1). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 17.1 (m_{br}, $^1J_{PB}$ = 55.5 Hz). **MS** (-ESI) m/z: 213 (M^--CO_2, 100), 257 (M^-, 27.8), 515 (M_2H^-, 93.3). **IR** (KCl): $\tilde{\nu}$ [cm^{-1}] = 3441br, 3054w, 2957m, 2919m, 2662m, 2566m, 2402s, 2360m, 1972w, 1905w, 1828w, 1702s, 148m, 1432s, 197m, 1301s, 1215w, 1188w, 1137m, 1103m, 1060s, 999w, 952m, 917m, 872m, 815m, 739s, 692s. **m.p.** 135-136°C (lit: 141°C). **EA** %found (calcd): C: 65.05 (65.16), H: 6.28 (6.25).

7.3.2 Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Cyclization

(*S*)-2-(Di-*tert*-butyl-phosphanyl)-*N*-(1-hydroxymethyl-2,2-dimethyl-propyl)-acetamide-borane adduct (34)

According to *general procedure 1*, **24** (229 mg, 1.05 mmol), HOBt (170 mg, 1.26 mmol), EDC (241 mg, 1.26 mmol) and L-*tert*-leucinol (123 mg, 1.05 mmol) were reacted in dichloromethane (10 mL). The crude product was obtained in 93 % yield and was used without further purification.

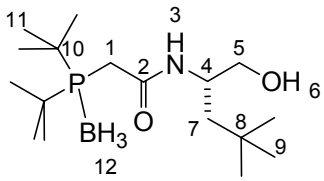


$C_{16}H_{37}BNO_2P$ (317.26)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.6 (m_{br}, 3H, 9), 0.99 (s, 9H, 8), 1.27-1.33 (2×d, $^3J_{HP}$ = 13.1Hz, 18H, 8), 2.75 (m, 2H, 1), 3.60 (m, 1H, 5), 3.78-3.86 (m, 2H, 4/5), 6.86 (d_{br}, $^3J_{HH}$ = 7.3 Hz, 1H, 3). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 41.9 (m).

(*S*)-2-(Di-*tert*-butyl-phosphanyl)-*N*-(1-hydroxymethyl-3,3-dimethyl-butyl)-acetamide borane adduct (35)

According to *general procedure 1*, **24** (504 mg, 2.31 mmol), HOBt (338 mg, 2.5 mmol), EDC (483 mg, 2.5 mmol) and (*S*)-neopentylglycinol **58** (303.5 mg, 2.3 mmol) were reacted in dichloromethane (25 mL). After column chromatography on silica eluting with pentane and diethyl ether the pure product was obtained as a white solid (510 mg, 62%).



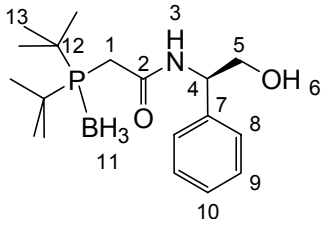
$C_{16}H_{37}BNO_2P$ (317.26)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.64 (m_{br}, 3H, 12), 0.94 (s, 9H, 9), 1.28 (d, 9H, $^3J_{HP}$ = 12.4 Hz, 10), 1.31 (d, 9H, $^3J_{HP}$ = 12.4Hz, 10'), 1.38-1.49 (ddd, 2H, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 4.0 Hz, 7.3 Hz, 7), 2.57 (dd, 1H, $^2J_{HH}$ = 14.7 Hz, $^2J_{HP}$ = 10.9 Hz, 1), 2.74 (dd, 1H, $^2J_{HH}$ = 14.7 Hz, $^2J_{HP}$ = 12.9 Hz, 1'), 3.51 (dd, 1H, $^2J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 6.3 Hz, 5), 3.64 (dd, 1H, $^2J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 4.8 Hz, 5), 4.05 (m, 1H, 4), 6.70 (dbr, 1H, $^3J_{HH}$ = 7.8 Hz, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 27.4 (8), 27.6 (d, $^1J_{CP}$ = 21 Hz, 1), 27.7 (d, $^2J_{CP}$ = 15

Hz, 10'), 29.8 (9), 30.5 (8), 32.7 (d, $^{1}J_{CP}$ = 27 Hz, 11), 33.2 (d, $^{1}J_{CP}$ = 27 Hz, 11'), 45.0 (7), 50.3 (4), 67.8 (5), 167.7 (2). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 42.1 (m, $^{1}J_{PB}$ = 75 Hz). **MS** (+FAB, 3-NBA) m/z: 330 ($M\text{-}H^-$, 63.1), 216 ($C_{10}H_{24}BNOP^+$ 13.2), 57 ($C_4H_9^+$, 100). **IR** (KCl): $\tilde{\nu}$ [cm^{-1}] = 3461s, 3347s, 2960s, 2873s, 2364s, 2301m, 1658s, 1532s, 1471m, 1394m, 1366m, 1320m, 1193w, 1151w, 1083s_{sh}, 962w, 938w_{sh}, 835w, 817w_{sh}, 756w, 650,m, 589m. **m.p.** 94-95°C. $[\alpha]_D^{20}$: -12.5° (c = 0.5, $CHCl_3$). **TLC** (pentane:diethyl ether; 1:4) R_f = 0.17. **EA** % found (calcd): C: 61.85 (61.63), H: 11.80 (11.87), N: 4.29 (4.23).

(*R*)-2-(Di-*tert*-butyl-phosphanyl)-*N*-(1-hydroxymethyl-2-methylpropyl)-acetamide-borane adduct (36)

According to *general procedure 1*, **24** (300 mg, 1.37 mmol), HOBt (223 mg, 1.65 mmol) EDC (315 mg, 1.65 mmol) and (*R*)-phenylglycinol (189 mg, 1.37 mmol) were reacted in dichloromethane (15 mL). The crude product which was used without further purification.

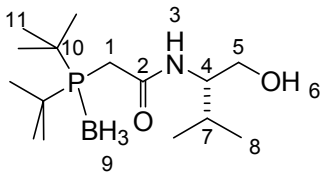


$C_{18}H_{33}BNO_2P$ (337.24)

^{1}H NMR (400.1 MHz, $CDCl_3$ 300K): δ = 0.7 (q, 3H, 11), 1.22-1.35 (dd, 2 × $^{3}J_{HP}$ = 13.2Hz, 2×9H, 13/13'), 1.49 (m, 1H, 4), 2.73 (m, 2H, 1), 3.87 (m, 2H, 5), 5.08 (m, 1H, 3), 7.35-7.38 (m, 5H, Ph). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$ 300K): δ = 42.4 (m). **TLC** (diethyl ether:pentane; 4:1) R_f = 0.12.

(*S*)-2-(Di-*tert*-butyl-phosphanyl)-*N*-(1-hydroxymethyl-2-methylpropyl)-acetamide borane adduct (37)

According to *general procedure 1*, **24** (250 mg, 1.15 mmol), HOBt (187 mg, 1.38 mmol) EDC (264 mg, 1.38 mmol) and L-valinol (119 mg, 1.15 mmol) were reacted in dichloromethane (10 mL). The crude product in 93 % yield. This was used without further purification.

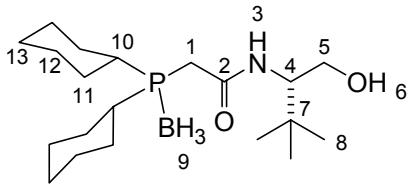


$C_{15}H_{35}BNO_2P$ (303.23)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.6 (m, 3H, 9), 0.98 (d, $^3J_{HH}$ = Hz, 6H, 8), 1.28-1.33 (2×d, $^3J_{HP}$ = 13.1Hz, 18H, 11), 1.42 (m, 1H, 7), 1.93 (m, 1H, 5), 2.73 (m, 2H, 1), 3.63-3.78 (m, 2H, 4/5), 6.8 (d, 1H, 3). **^{31}P{^{1}H} NMR** ($CDCl_3$, 162 MHz, 300K): δ = 42.2 (m, $^1J_{PB}$ = 61.4Hz).

(*S*)-2-Dicyclohexylphosphanyl-*N*-(1-hydroxymethyl-2,2-dimethyl-propyl)-acetamide-borane adduct (38)

According to *general procedure 1*, **28** (158 mg, 0.58 mmol), HOBt (94.6 mg, 0.7 mmol), EDC (133.8 mg, 0.7 mmol) and L-valinol (68.7 mg, 0.58 mmol) were reacted in dichloromethane (10 mL). The crude product (yield: 60 %) was used without further purification.

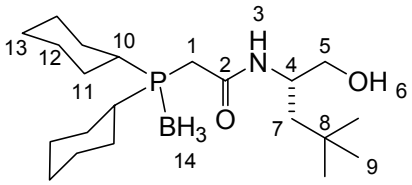


$C_{20}H_{41}BNO_2P$ (369.33)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.5 (m_{br}, 3H, 9), 0.97, (s, 9H, 8), 1.23-1.41 (m, ~10H, Cy_{eq}), 1.73-1.94 (m, 12H, Cy_{ax}), 2.66 (2×dd, 2H, 1), 3.60 (m, 1H, 5), 3.82 (m, 2H, 4/5), 6.30 (d, $^3J_{HH}$ = 9.3 Hz, 1H, 3). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 24.8 (m). **TLC** (*n*-pentane:diethyl ether; 1:2) R_f = 0.15.

(*S*)-2-Dicyclohexylphosphanyl-*N*-(1-hydroxymethyl-3,3-dimethyl-butyl)-acetamide borane adduct (39)

According to *general procedure 1*, **28** (540 mg, 2.0 mmol), HOBt (295 mg, 2.2 mmol), EDC (425 mg, 2.3 mmol) and (*S*)-neopentylglycinol **58** (262 mg, 2.0 mmol) were reacted in dichloromethane (25 mL). The pure product was obtained after column chromatography on silica eluting with pentane and diethyl ether as a white solid (443 mg, 58%).

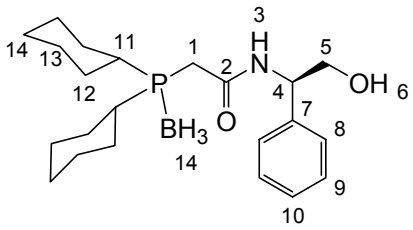


$C_{21}H_{43}BNO_2P$ (383.36)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.94 (s, 9H, 9), 1.2-1.3 (m_{br}, 10H, Cy_{eq}), 1.35-1.45 (m, 2H, 7), 1.69-1.95 (m_{br}, 12H, Cy_{ax}), 2.52 (dd, 1H, $^{2}J_{HP}$ = 10.5 Hz, $^{2}J_{HH}$ = 14.0 Hz, 1), 2.62 (dd, 1H, $^{2}J_{HP}$ 13.1 = Hz, $^{2}J_{HH}$ = 14.0 Hz, 1), 3.48 (dd, 1H, $^{3}J_{HH}$ = 5.8 Hz, $^{2}J_{HH}$ = 11.2 Hz, 5), 3.66 (dd, 1H, $^{3}J_{HH}$ = 3.8 Hz, $^{2}J_{HH}$ = 11.2 Hz, 5), 4.06 (m, 1H, 4), 6.13 (d, 1H, $^{3}J_{HH}$ = 8.2 Hz, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 25.9-27.0 (m, Cy_{11-13}), 29.0 (d, $^{1}J_{CP}$ = 23.5 Hz, 1), 29.8 (9), 30.6 (8), 32.0 (d, $^{1}J_{CP}$ = 30 Hz, 10), 32.0 (d, $^{1}J_{CP}$ = 30 Hz, 10'), 45.2 (7), 49.9 (4), 67.4 (5), 166.9 (2). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 25.1 ($^{1}J_{PB}$ = 71 Hz). **MS** (+FAB, 3-NBA) m/z: 382 (M^{+}-H^{-}, 100), 370 (M^{+}-BH_3, 16.2), 268 (15.5), 129 (20.1), 83 (36.1), 55 ($C_4H_7^{+}$, 76.0). **m.p.** 49 °C. **TLC** (*n*-pentane:diethyl ether; 1:5) R_f = 0.35. $[\alpha]_D^{20}$: -12.6° (c = 0.53, $CHCl_3$). **EA** % found (calcd): C: 65.80 (65.79), H: 11.13 (11.31), N: 3.73 (3.65).

(*R*)-2-Dicyclohexylphosphanyl-*N*-(1-hydroxymethyl-phenyl)-acetamide-borane adduct (40)

According to *general procedure 1*, **28** (400 mg, 1.48 mmol), HOBt (240 mg, 1.78 mmol), EDC (340 mg, 1.78 mmol) and (*R*)-phenylglycinol (203 mg, 1.48 mmol) were reacted in dichloromethane (15 mL). The crude product was obtained in quantitative yield. The product was used without further purification.



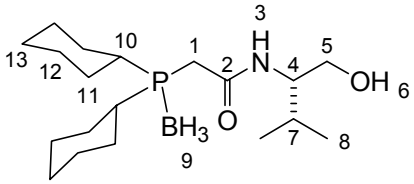
$C_{22}H_{37}BNO_2P$ (389.32)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.5 (q_{br}, 3H, 15), 1.15-1.5 (m, 10H, Cy_{eq}), 1.65-1.95 (m, 12H, Cy_{ax}), 2.65 (m, 2H, 1), 3.89 (d, $^{3}J_{HH}$ = 5.5 Hz, 2H, 5), 5.07 (m, 1H, 4), 6.81 (d_{br}, $^{3}J_{HH}$ = 7.5 Hz, 1H, 3). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 25.2 (m_{br}). **TLC** (*n*-pentane: diethyl ether; 1: 4) R_f = 0.24.

(*S*)-2-(Dicyclohexyl-phosphanyl)-*N*-(1-hydroxymethyl-2-methylpropyl)-acetamide-borane adduct (41)

According to *general procedure 1*, **28** (473 mg, 1.75 mmol), HOBt (284 mg, 2.1 mmol), EDC (401 mg, 2.1 mmol) and L-valinol (181 mg, 1.75 mmol) in dichloromethane (20 mL) gave **41**.

The crude product was purified by column chromatography on silica eluting with pentane and diethyl ether. **41** was obtained as a white solid (407 mg, 65%).

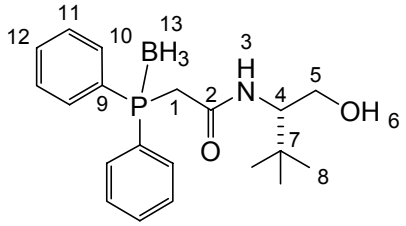


$C_{19}H_{39}BNO_2P$ (355.30)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.48 (m, 3H, 9), 0.98 (2×d, $^3J_{HH}$ = 6.8 Hz, 6H, 8), 1.23-1.4 (m, 10H), 1.73-1.9 (m, 12H), 1.91 (m, 1H, 7), 2.57-2.69 (m, 2H, 1), 3.62-3.74 (m, 3H, 4/5), 6.26 (d, $^3J_{HH}$ = 8.1 Hz 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 18.9 (8), 19.5 (8'), 25.9 (Cy), 26.5 (Cy), 26.7 (Cy), 4×26.8 (Cy), 3×26.9 (Cy), 29.07 (d, $^1J_{CP}$ = 22.5 Hz, 1), 29.14 (7), 32.1 (d, $^1J_{CP}$ = 32Hz, 10), 32.2 (d, $^1J_{CP}$ = 32 Hz, 10'), 58.2 (4), 63.8 (5), 167.7 (2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 25.0 (m, $^1J_{PB}$ = 67.4 Hz). **TLC** (*n*-pentane: diethyl ether; 1: 4) R_f = 0.12.

(*S*)-2-Diphenylphosphanyl-*N*-(1-hydroxymethyl-2,2 dimethyl-propyl)-acetamide-borane adduct (42)

According to *general procedure 1*, **33** (500 mg, 1.94 mmol), HOBt (288 mg, 2.13 mmol), EDC (407 mg, 2.13 mmol) and L-*tert*-leucinol (227 mg, 1.94 mmol) in dichloromethane (25 mL) gave **42**. After column chromatography on silica eluting with pentane and diethyl ether the product was as a white solid (445mg, 64%).



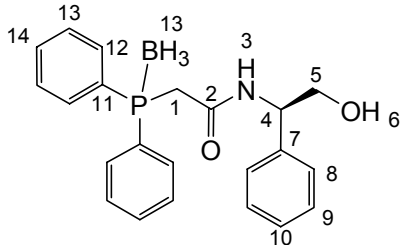
$C_{22}H_{29}BNO_2P$ (357.23)

^{1}H NMR ($CDCl_3$, 400.1 MHz, 300K): δ = 0.84 (s, 9H, 8), 3.29 (dd, $^2J_{HH}$ = 11.4, $^2J_{HP}$ = 14.4 Hz, 1H, 1), 3.42 (dd, $^2J_{HH}$ = 12.9 Hz, $^2J_{HP}$ = 14.7 Hz, 1H, 1), 3.45 (dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 14.4 Hz, 1H, 4), 3.69-3.75 (m, 2H, 5), 6.40 (d, $^3J_{HH}$ = 9.1 Hz, 3), 7.45-7.54 (m, 6H, 10/12), 7.71.7.78 (m, 4H, 11). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125.8 MHz, 300K): δ = 27.0 (8), 33.6 (7), 35.9 (d, $^1J_{CP}$ = 28.7 Hz, 1), 60.8 (4), 63.0 (5), 127.6 (d, $^1J_{CP}$ = 23.4 Hz, 9), 128.1 (d, $^1J_{CP}$ = 23.7 Hz, 9'), 129.2 (d, $^2J_{CP}$ = 10.3 Hz, 10/10'), 132.0 (2×d, $^4J_{CP}$ = 2.7 Hz, 12/12'), 132.3 (2×d, $^3J_{CP}$ = 5.0 Hz, 11/11'), 166.0 (2). **^{31}P{^{1}H} NMR** ($CDCl_3$, 162 MHz, 300K): δ = 13.0 (d_{br}, $^1J_{PB}$ = 63.4

Hz). **MS** (+FAB, 3-NBA) m/z: 356 (M-H$^-$, 100), 344 (M-BH_2^-, 22.85), 256 ($C_{14}H_{16}BNOP^+$, 12.2), 185 (Ph_2P^+, 82.2). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3504s, 3317s, 3061w, 2974m, 2877m, 2379s, 2336m, 1673s, 1547s, 1468w, 1435m, 1367w, 1339m, 1293m, 1221m, 1193w, 1124m, 1054s, 998m, 960w, 910w, 849m, 804w, 734m, 694s. **m.p.** 141-142°C. $[\alpha]_D^{20}$: -21° (c = 0.53, $CHCl_3$). **TLC** (diethyl ether) R_f = 0.11. **EA** % found (calcd): C: 67.09 (67.24), H: 8.04 (8.18), N: 3.93 (3.92).

(*S*)-2-Diphenylphosphanyl-*N*-(2-hydroxy-1-phenyl-ethyl)-acetamide-borane adduct (43)

According to *general procedure 1*, **33** (400 mg, 1.55 mmol), HOBt (230 mg, 1.7 mmol), EDC (325 mg, 1.7 mmol) and (*R*)-phenylglycinol (213 mg, 1.55 mmol) in dichloromethane (20 mL) gave **43**. After column chromatography on silica eluting with pentane and diethyl ether the product was as a white solid (350 mg, 60%).

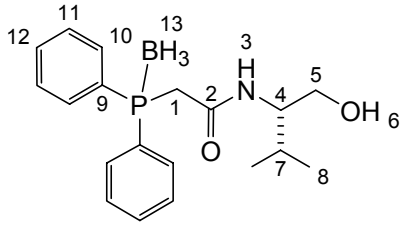


$C_{22}H_{25}BNO_2P$ (377.22)

^{1}H NMR ($CDCl_3$, 400.1 MHz, 300K): δ = 1.2 (m_{br}, 3H, 15), 3.26 (dd, J_{HH} = 11.3, 14.3 Hz, 1H, 1), 3.38 (dd, 12.7, 14.3 Hz, 1H, 1), 3.73 (d, $^3J_{HH}$ = 5.1 Hz, 2H, 5), 4.94 (ddd, $^3J_{HH}$ = 5.1, 12.5 Hz, 1H, 4), 6.82 (d, $^3J_{HH}$ = 7.4 Hz, 1H, 3), 7.15-7.18 (m, 2H, 8), 7.24-7.30 (3H, 9/10), 7.41-7.45 (m, 4H, 12), 7.46-7.54 (m, 2H, 14), 7.67-7.71 (m, 2H, 13), 7.75-7.79 (m, 2H, 13'). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125.8 MHz, 300K): δ = 35.8 (d, $^1J_{CP}$ = 28.5 Hz, 1), 56.6 (4), 66.2 (5), 126.9 (8), 127.8 (dd, $^1J_{CP}$ = 31.5, 57 Hz, 11/11'), 128.0 (10), 128.9 (9), 129.2 (d, $^2J_{CP}$ = 10.5 Hz, 12/12'), 132.0 (d, $^4J_{CP}$ = 2.4 Hz, 14/14'), 132.2 (dd, $^3J_{CP}$ = 2.5 Hz, 10.1 Hz, 13), 132.5 (d, $^3J_{CP}$ = 9.9 Hz, 13'), 138.4 (7), 165.3 (2). **^{31}P{^{1}H} NMR** ($CDCl_3$, 162 MHz, 300K): δ = 13.9 (m_{br}) **MS** (+FAB, 3-NBA) m/z: 376 (M-H$^-$, 100), 364 (M^+-BH_2, 21.3), 256 ($C_{14}H_{16}BNOP^+$, 28.0), 185 (Ph_2P^+, 71.8), 103 (25.6). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3464s, 3313s, 3055m, 2962m, 2866m, 2374s, 2305m, 1974w, 1906w, 1822w, 1675s, 1538s, 1488w, 1458w, 1430m, 1402m, 1345w, 1283m, 1822w, 1110s, 1064s, 1028s, 848m, 806m, 745m, 694s, 657m. **m.p.** 124-126°C. $[\alpha]_D^{20}$ (c = 1.0, $CHCl_3$) = + 42.3°. **TLC** (diethyl ether:pentane; 4:1) R_f = 0.16. **EA** % found (calcd): C: 69.63 (70.05), H: 6.58 (6.68), N: 3.70 (3.71).

(*S*)-2-Diphenylphosphanyl-*N*-(1-hydroxymethyl-2-methyl-propyl)-acetamide-borane adduct (44)

According to *general procedure 1*, **33** (500 mg, 1.94 mmol), HOBt (288 mg, 2.13 mmol), EDC (407 mg, 2.13 mmol) and L-*tert*-leucinol (200 mg, 1.94 mmol) in dichloromethane (25 mL) gave **44**. After column chromatography on silica eluting with pentane and diethyl ether the product was as a white solid (421.6 mg, 63.4%).

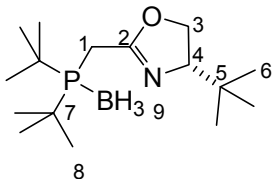


$C_{19}H_{27}BNO_2P$ (343.21)

^{1}H NMR ($CDCl_3$, 400.1 MHz, 300K): δ = 0.82 (d, 3H, $^3J_{HH}$ = 6.8 Hz, 8), 0.84 (d, 3H, $^3J_{HH}$ = 6.8 Hz, 8'), 1.15 (m_{br}, 3H, 13), 1.80 (m, $^3J_{HH}$ = 6.8 Hz 1H, 7), 3.26 (dd, $^2J_{HH}$ = 11.4, $^2J_{HP}$ = 14.4 Hz, 1H, 1), 3.36 (dd, $^2J_{HH}$ = 11.4, $^2J_{HP}$ = 14.4 Hz, 1H, 1), 3.53 (m, 2H, 5), 3.64 (m, 1H, 4), 6.33 (d, $^3J_{HH}$ = 8.1 Hz, 3), 7.45-7.55 (m, 6H, 10/12), 7.70-7.77 (m, 4H, 11). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125.8 MHz, 300K): δ = 18.7 (8), 19.5 (8'), 29.0 (7), 35.9 (d, $^1J_{CP}$ = 28.7 Hz, 1), 58.0 (4), 63.6 (5), 127.6 (d, $^1J_{CP}$ = 20.7 Hz, 9), 128.2 (d, $^1J_{CP}$ = 20.7 Hz, 9'), 129.2 (2×d, $^2J_{CP}$ = 10.3 Hz, 10/10'), 132.0 (2×d, $^4J_{CP}$ = 2 Hz, 12/12'), 132.3 (d, $^3J_{CP}$ = 7.7 Hz, 11), 132.4 (d, $^3J_{CP}$ = 7.7 Hz, 11'), 165.8 (2). **^{31}P{^{1}H} NMR** ($CDCl_3$, 162 MHz, 300K): δ = 13.5 (d_{br}, $^1J_{PB}$ = 63.4 Hz). **MS** (+FAB, 3-NBA) m/z: 342 ($M\text{-}H^-$, 100), 330 ($M\text{-}BH_2^-$, 23.9), 256 ($C_{14}H_{16}BNOP^+$, 12.1), 185 (Ph_2P^+, 75.5). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3494s, 3304s, 3057w, 2965m, 2875m, 2376s, 1977w, 1910w, 1833w, 1670s, 1550s, 1463w, 1435m, 1312m, 1226w, 1194w, 1135m, 1108m, 1054m, 1017m, 850m, 806w, 735m, 693s. **m.p.** 109-110°C. **TLC** (diethyl ether:pentane; 4:1) R_f = 0.09. **EA** % found (calcd): C: 66.26 (66.49), H: 7.72 (7.93), N: 4.09 (4.08).

(*S*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-*tert*-butyl)-4,5-dihydrooxazoline-borane adduct (45)

The product was obtained according to *general procedure 2* from **34** (310.2 mg, 0.98 mmol) and Burgess' reagent (280.84 mg, 1.18 mmol) in THF (10 mL). Purification by column chromatography on silica (*n*-pentane:diethyl ether; 1:1) afforded the product as a colorless oil (163 mg, 56%).

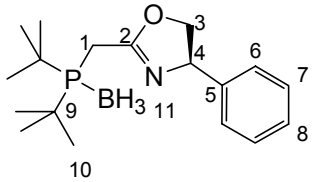


$C_{16}H_{35}BNOP$ (299.24)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.38 (q_{br}, $^{1}J_{HB}$ = 100 Hz, 3H, BH_3, 9), 0.88 (s, 9H, 6), 1.30-1.34 (2×d, $^{3}J_{HP}$ = 13.1 Hz, 18H, 8/8'), 2.75 (m, 2H, CH_2, 1), 3.80 (ddd, $^{3}J_{HH}$ = 10.1, 9.3 Hz, $^{4}J_{HP}$ = 3.3 Hz, 1H, 4), 4.00 (*ps*t, $^{2}J_{HH}$ = 8.8 Hz, $^{3}J_{HH}$ = 8.8 Hz, 1H, 3), 4.17 (dd, $^{2}J_{HH}$ = 8.6 Hz, $^{3}J_{HH}$ = 10.1 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 20.1 (d, $^{1}J_{CP}$ = 24.3Hz, 1), 26.2 (6), 28.1 (d, $^{2}J_{CP}$ = 2.8 Hz, 8), 28.2 (d, $^{2}J_{CP}$ = 2.8 Hz, 8'), 33.0 (d, $^{1}J_{CP}$ = 24.6 Hz, 7), 33.1 (d, $^{1}J_{CP}$ = 24.6 Hz, 7'), 33.7 (5), 69.1 (3), 76.5 (4), 162.4 (d, $^{2}J_{CP}$ = 4.5 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 48.3 (q, $^{1}J_{PB}$ ≈ 50 Hz). **MS** (+FAB, 3-NBA) m/z: 298 ($R^1{}_2R^2P(^{11}B)H_2^+$, 100), 297 ($R^1{}_2R^2P(^{10}B)H_2^+$, 24.4), 286 (M^+-BH_3, 54.8), 228 (286-C_4H_{10}, 13.1), 172 (228-C_4H_8, 12.4), 57 ($C_4H_9^+$, 90.3). **TLC** (*n*-pentane:diethyl ether 1:1) R_f = 0.6.

(*R*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-phenyl)-4,5-dihydrooxazoline-borane (46)

The product was obtained according to *general procedure 2* from **36** (~1.34 mmol) and Burgess' reagent (476 mg, 2 mmol). After column chromatography on silica (*n*-pentane:diethyl ether 1:4) the product was obtained as a colorless oil (182 mg, 43%) over two steps. The other enantiomer was obtained with *general method 5* (vide supra) which yielded 47% ($[\alpha]_D^{20}$: -55° (c = 0.23, $CHCl_3$).



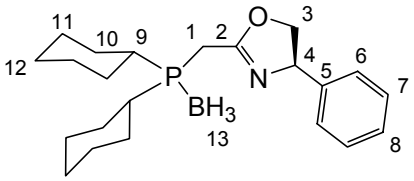
$C_{18}H_{31}BNOP$ (319.23)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.45 (q, $^{1}J_{HB}$ = ~100Hz, 3H, 11), 1.34 (d, $^{3}J_{HP}$ = 13 Hz, 9H, 10), 1.35 (d, $^{3}J_{HP}$ = 13 Hz, 9H, 10'), 2.86 (m, $^{2}J_{HH}$ = 10.9Hz, $^{2}J_{HP}$ = 1Hz, 2H, 1), 4.06 (*ps*t, $^{2}J_{HH}$ = 8.6, 1H, 3), 4.65 (dd, $^{2}J_{HH}$ = 8.4Hz, $^{3}J_{HH}$ = 10.2 Hz, 3), 5.16 (dt, $^{3}J_{HH}$ = 9.6 Hz, 1H, 4), 7.25-737 (m, 5H, 6-8). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 19.8 (d, $^{1}J_{CP}$ = 23.8 Hz, 1), 28.1 (2×d, $^{2}J_{CP}$ = 3 Hz, 10), 33.1 (d, $^{1}J_{CP}$ = 24.6 Hz, 9), 33.2 (d, $^{1}J_{CP}$ = 24.5 Hz, 9), 70.4 (4), 75.1 (3), 127.3 (6), 127.8 (8), 128.9 (7), 142.5 (5), 164.2 ($^{2}J_{CP}$ = 3.8 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 49.0 (m, $^{1}J_{PB}$ = 57.5 Hz). **MS** (+FAB, 3-NBA)

m/z: 320 (MH^+, 41.6), 306 ($M\text{-}BH_2^-$, 27.3), 250 ($C_{14}H_{21}NOP^+$, 9.6), 214 ($C_{10}H_{22}BNOP^+$, 8.3), 147 ($C_8H_{20}P^+$, 10.9), 103 ($C_5H_{12}P^+$, 10.2), 57 (100). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3357.3m_{br}, 2989.1s, 2964.6s, 2901.0m, 2870.4m, 2373.8s, 2349.6s, 2263.0w, 2134.2w, 1959.7w, 1900.5w, 1787.5w, 1735.6w, 1661.8s, 1602.3w, 1466.7m, 1395.4m, 1370.1m, 1353.2m, 1308.7w, 1270.8m,1235.3w, 1208.1w, 1186.3w, 1143.2m, 1072.7m, 1024.2w, 995.6m, 964.4w, 922.1m, 830.7w, 813.6w, 772.3w, 734.7m, 701.8m, 633.0w, 607.6w, 580.4w. **m.p.** 106-107°C. $[\alpha]_D^{20}$: +54.0° (c = 0.45, $CHCl_3$). **TLC:** (diethyl ether:pentane; 4:1) R_f = 0.53. **EA** %found (calcd) C: 67.73 (67.72), H: 9.81 (9.79), N: 4.35 (4.39).

(*R*)-4-Phenyl-2-[(dicyclohexylphosphanyl)-methyl]-4,5-dihydro-oxazoline-borane adduct (47)

The product was obtained according to *general procedure 2* from **40** (604 mg, 1.48 mmol) and Burgess' reagent (423 mg, 1.78 mmol). After purification by column chromatography on silica (*n*-pentane:diethyl ether; 1:4). The product was obtained as a colorless oil (519 mg, 94%) over two steps. The other enantiomer was obtained with *general procedure 5* (vide supra) which yielded 60% ($[\alpha]_D^{20}$:-28° (c = 0.3, $CHCl_3$).



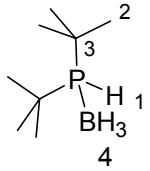
$C_{22}H_{35}BNOP$ (371.30)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.4 (q_{br}, 3H, 13), 1.25 (m, 6H, Cy), 1.43 (m, 4H, Cy), 1.71 (m, 2H, Cy), 1.81 (m, 4H, Cy), 1.89 (m, 4H, Cy), 2.0 (m, 2H, 8), 2.76 (dd, $^2J_{HH}$ = 9.8 Hz, $^1J_{HP}$ = 1 Hz, 2H, 1), 4.07 (*pst*, $^3J_{HH}$ = 8.6 Hz, 1H, 3), 4.65 (dd, $^2J_{HH}$ = 8.5, $^3J_{HH}$ = 10.2 Hz, 1H, 3), 5.19 (m, 1H, 4). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 20.5 (d, $^1J_{CP}$ = 25.9 Hz, 1), 26.3-27.3 (m, Cy), 31.8 (2×d, $^1J_{CP}$ = 30.9 Hz, 9), 70.2 (3), 75.0 (4), 127.0 (6), 127.8 (8), 129.0 (7), 142.5 (5), 163.2 (d, $^2J_{CP}$ = 7.2 Hz , 2). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 28.9 (m_{br}). **MS** (+FAB, 3-NBA) m/z: 370 ($M\text{-}H^-$, 98.5), 358 ($M^+\text{-}BH_3$, 57.8), 266 (14.0), 199 (18.2), 83 (53.8), 55 (100). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3362.3m_{br}, 2932.3s, 2854.3s, 2362.7s, 2249.5w, 1735.8m, 1659.4s, 1491.9w,1446.9s, 1400.0m, 1355.0m, 1318.5m, 1271.7m, 1241.9m, 1174.6w, 1136.6m, 1063.1s, 986.3s, 914.8m, 854.2w, 828.3w, 795.9w, 755.6m, 701.1m, 598.0m. $[\alpha]_D^{20}$: +29.4° (c = 0.5, $CHCl_3$). **TLC** (*n*-pentane: diethyl ether; 1: 4) R_f = 0.57. **EA** %found (calcd) C: 70.95 (71.16), H: 9.40 (9.50), N: 3.91 (3.77).

7.3.3 Secondary Phosphine-Borane Adducts

Di-*tert*-butylmethylphosphine-borane adduct (48)

To di-*tert*-butylphosphine (1 g, 6.84 mmol) in THF (10 ml) at room temperature, was slowly added borane-THF adduct (8 ml, 1M in THF). The reaction mixture was stirred for 2 hours. Then the solvent and other volatiles were removed under reduced pressure. The residue was dissolved in *n*-pentane (8 mL). At 4 °C the white product crystallized from the solution and was removed by filtration (890 mg, 81%).

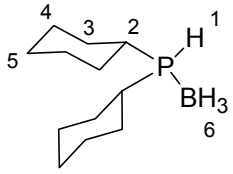


$C_8H_{22}BP$ (160.05)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.49 (m, $^1J_{HB}$ = 100 Hz, 4), 1.32 (d, $^2J_{HP}$ = 13.6 Hz, 2), 4.11 (dq, $^4J_{HH}$ = 6.6 Hz, $^1J_{HP}$ = 351 Hz, 1). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 29.1 (d, $^2J_{CP}$ = 1.5 Hz, 2), 30.6 (d, $^1J_{CP}$ = 17.5 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 48.5 (m, $^1J_{BP}$ = 51.5 Hz). **MS** (+EI), m/z: 159.1 ($M\text{-}H^-$, 5.2), 146.1 ($M^+\text{-}BH_3$, 53.98), 57.1 (tBu$^+$, 100). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 2969s, 2902s$_{sh}$, 2809s, 2383s, 2351s$_{sh}$, 2272m, 2129w, 1809w, 1758w, 1698w, 1467s, 1392w, 1366s, 1196m, 1139m, 2067s, 1023s, 940m, 900s, 754w, 691m, 620m. **m.p.** 62-63°C. **EA** % found (calcd): C: 60.19 (60.04), H: 13.72 (13.86).

Dicyclohexylphosphine-borane adduct (49)[72]

To a solution of dicyclohexylphosphine (1.94 g, 10 mmol) in dry THF (10 mL) at 0 °C under argon was added solid sodium borohydride (574 mg, 15.1 mmol) in one portion followed by a solution of glacial acetic acid (1 mL) in THF (4mL) dropwise over 30 min. Subsequent to the acid addition, the reaction mixture was stirred at room temperature for 18 hours. All volatiles were removed, and the crude product purified by flash column chromatography on silica eluting with hexane and ethyl acetate to afford a white crystalline product (1.78 g, 86%).



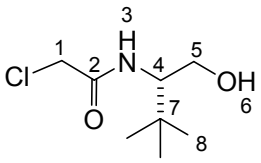
$C_{12}H_{26}BP$ (212.12)

^{1}H NMR (250.1 MHz, $CDCl_3$, 300K): δ = 0.41 (q_{br}, 3H, 6), 1.2-1.5 (m_{br}, 12H, Cy_{eq}), 1.73-1.83 (m_{br}, 10 H, Cy_{ax}), 4.11 (dm, 1H, $^{1}J_{HP}$ = 350 Hz, 1). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 25.9, 26.5, 26.6, 26.7, 26.8, 27.8, 28.9, 29.1, 29.4, 29.5, 31.1. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 18.3 (m_{br}, $^{1}J_{PB}$ = 67 Hz). **MS** (+EI), m/z: 209 ($C_{12}H_{23}BP^+$, 17.6), 198 (Cy_2PH^+, 100), 117 ($CyPH_2^+$, 76.1), 83 (Cy^+, 47.8). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 2930s, 2850s, 2659w, 2377s, 2258s, 2122w, 1644w, 1447s, 1332m, 1298m, 1270m, 1206m, 1176m, 1132m, 1065s, 1003s, 919s, 881s_{sh}, 846m, 755m, 664m, 584m. **m.p.** 78-80°C. **TLC** (hexane:ethyl acetate; 85:15) : R_f = 0.73. **EA** % found (calcd) C: 67.80 (67.95), H: 12.15 (12.35).

7.3.4 Chloromethyloxazolines

(*S*)-2-Chloro-*N*-(1-hydroxymethyl-2-*tert*-butyl)-acetamide (50)

According to *general procedure 3* chloroacetylchloride (1.58 mL, 19.8 mmol), (*S*)-*tert*-leucinol (2.34 g, 20 mmol) and triethylamine (2.9 mL, 20 mmol) were reacted in dichloromethane (50 ml). Kugelrohr distillation (170°C, 0.4 mbar) afforded a colorless oil, that was recrystallized from ethyl acetate (2.81 g, 73%).

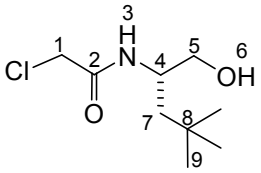


$C_8H_{16}ClNO_2$ (193.67)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.98 (s, 9H, 8), 3.60 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{2}J_{HH}$ = 11.1 Hz, 1H, 5), 3.80-3.90 (m, 2H, 5/4), 4.10 (d_{roof}, $^{2}J_{HH}$ = 15.2 Hz, 2H, 1), 4.14 (d_{roof}, $^{2}J_{HH}$ = 15.2 Hz, 2H, 1), 6.75 (s_{br}, 1H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 27.0 (8), 33.7 (7), 40.1 (5), 60.2 (4), 62.9 (1), 167.2 (2). **MS** (+FAB, 3-NBA) m/z: 194 (MH^+, 100). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3411s, 3280s, 3097w, 2964s, 2892m, 1739w, 1666s, 1566m, 1532m, 1461w, 1410w, 1368m, 1262m, 1169w, 1092w, 1049m, 1002w, 913w, 722m, 701w, 670w, 577m. **m.p.** 62-63°C, $[\alpha]_D^{20}$ (c = 1.04, $CHCl_3$) = -15.3°, **TLC** (ethyl acetate) R_f = 0.28, **EA** % found (calcd): C: 49.48 (49.61), H: 8.32 (8.33), N: 7.27 (7.23).

(*S*)-2-Chloro-*N*-(1-hydroxymethyl-2-neopentyl)-acetamide (51)

According to *general procedure 3* chloroacetylchloride (0.68 mL, 8.61 mmol), (*S*)-neopentylglycinol (1.13 g, 8.61 mmol) and triethylamine (1.3 mL, 9.33 mmol) were reacted in dichloromethane (20 ml). Kugelrohr distillation (150°C, 10^{-1} mbar) afforded a colorless oil (1.32 g, 74%).

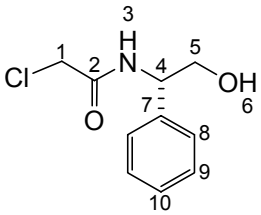


$C_9H_{18}ClNO_2$ (207.70)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.94 (s, 9H, 9), 1.39 (dd, $^2J_{HH}$ = 14.6 Hz, $^3J_{HH}$ = 8.9 Hz, 1H, 7), 1.51 (dd, $^2J_{HH}$ = 14.6 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, 7), 2.06 (s_{br}, 1H, 6), 3.54 (dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, 5), 3.64 (dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 4.2 Hz, 1H, 5), 4.05 (dd, 2×$^2J_{HH}$ = 15.3 Hz, 2H, 1), 4.10 (m, 1H, 4), 6.57 (s_{br}, 1H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 29.9 (9), 30.5 (8), 42.8 (7), 45.1 (5), 49.7 (4), 67.3 (1), 166.3 (2). **MS** (+FAB, 3-NBA) m/z: 210 (MH^+, 11), 209 (MH^+, 31.7), 208 (MH^+, 100), 57 ($C_4H_9^+$, 70.6). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3289s_{br}, 3089w, 2955s, 2872m, 2364w, 1658s, 1548m, 1471w, 1414w, 1367w, 1248w, 1051m, 914w, 778w. $[\alpha]_D^{20}$ (c = 1.02, $CHCl_3$) = -34.5°, **TLC** (ethyl acetate) R_f = 0.28, **EA** % found (calcd): C: 50.74 (52.05), H: 8.72 (8.74), N: 6.71 (6.74).

(*S*)-2-Chloro-*N*-(1-hydroxymethyl-2-phenyl)-acetamide (52)

According to *general procedure 3* chloroacetylchloride (1.65 g, 14.58 mmol), (*S*)-phenylglycinol (2 g, 14.58 mmol) and triethylamine (2.15 ml, 15.4 mmol) were reacted in dichloromethane (50 ml). at -20 °C. The crude product was purified by flash column chromatography on silica eluting with ethyl acetate. The product was obtained as a white solid (2.9 g, 92 %).



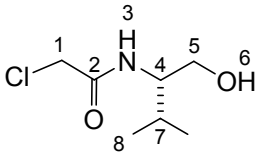
$C_{10}H_{12}ClNO_2$ (213.66)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 2.18 (s_{br}, 1H, 6), 3.91 (m, 2H, 5), 4.07 (d, $^2J_{HH}$ = 15.3 Hz, 1), 4.12 (d, $^2J_{HH}$ = 15.3 Hz, 1), 5.09 (dt, 1H, $^3J_{HH}$ = 8.6, 5.8 Hz, 4), 7.28 (s_{br}, 1H, 3), 7.32 (m, 3H, 8 /10), 7.38 (m, 2H, 9). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 42.8 (1), 55.9 (4), 66.3 (5), 126.7 (8), 128.3 (10), 129.1 (9), 138.3 (7), 166.4 (2). **MS** (+FAB, 3-NBA) m/z: 216 (MH^+, 32.2), 215 (MH^+, 13.2), 214 (MH^+, 100), 182, 121, 94. **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3313s_{br}, 3063w, 2960m, 2923m, 2873m, 2666s, 1539s, 1454m, 1410w, 1230w, 1269w, 1237m, 1095w, 1049m, 908w, 845w, 779w, 701m, 662w, 534m_{br}. **mp.** 105 °C, $[\alpha]_D^{20}$ (c = 0.9,

$CHCl_3$) = + 33.1°, **TLC** (ethyl acetate) R_f = 0.39, **EA** % found (calcd): C: 56.14 (56.21), H: 5.64 (5.66), N: 6.52 (6.56), O: 15.09 (14.98)

(*S*)-2-Chloro-*N*-(1-hydroxymethyl-2-methyl-propyl)-acetamide (53)

According to *general procedure 3* chloroacetylchloride (3.45 g, 29.1 mmol), (*S*)-valinol (3 g, 29.1 mmol) and triethylamine (4.25 ml, 30.5 mmol) were reacted in dichloromethane (50 ml). The crude product was purified by flash column chromatography eluting with ethyl acetate (4.98 g, 95%).

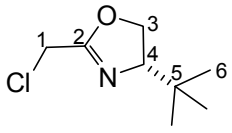


$C_7H_{14}ClNO_2$ (179.64)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.95 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 8), 0.98 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 8'), 1.95 (m, 1H, 7), 3.68-3.80 (m, 3H, 4/5), 4.10 (s, 2H, 1), 6.75 (s_{br}, 1H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 18.8 (8), 19.6 (8'), 29.1 (7), 42.9 (5), 57.6 (4), 63.6 (1), 166.8 (2). **MS** (+FAB, 3-NBA) m/z: 180 (MH^+, 100). **IR** (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3297s_{br}, 3086w, 2963s, 2879, m, 2363w, 1659s, 1546s, 1466w, 1414w, 1370w, 1241m, 1153w, 1075m, 1025w, 979w, 930w, 776w. **m.p.** 43°C. $[\alpha]_D^{20}$ (c = 1.0, $CHCl_3$) = -39.5°. **TLC** (ethyl acetate) R_f = 0.45 , **EA** % found (calcd): C: 46.80 (46.80), H: 7.72 (7.86), N: 7.76 (7.80).

(*S*)-2-Chloromethyl-4-tert-butyl-4,5-dihydro-oxazoline (54)

According to *general procedure 4* amide **50** (2.81 g, 14.5 mmol) and Burgess' reagent (4.1 g, 17.4 mmol) were reacted in THF (70mL). The crude product was purified by column chromatography on silica eluting with ethyl acetate. The product was obtained as a colorless oil (1.65 g, 65%).



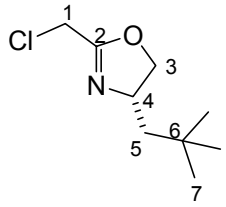
$C_8H_{14}ClNO$ (175.66)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.88 (s, 9H, 6), 3.89 (m, 1H, 4), 4.11 (s, 2H, 1), 4.14 (*pst*, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, 3), 4.26 (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 10.1 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 25.8 (6), 33.9 (5), 37.0 (1), 70.0 (3), 76.4 (4), 162.3 (2). **MS** (+FAB, 3-NBA) m/z: 176 (M^+, 100). **MS** (+EI) m/z: 119 (M^+-C_4H_9, 100),

83 ($C_4H_5NO^+$, 56.2), 57 ($C_4H_9^+$, 61.7). **IR** (NaCl): $\tilde{\nu}$ [cm^{-1}] = 341m_{br}, 2957s, 3000m, 2890m, 1670s, 1481m, 1442w, 1364m, 1309w, 1274m, 1207w, 1166m, 1032w, 983s, 939w, 896m, 855w, 729m, 583m. **TLC** (ethyl acetate) R_f = 0.56. $[\alpha]_D^{20}$ (c = 1.0, $CHCl_3$) = -112.7°. **EA** % found (calcd): C: 54.03 (54.70), H: 7.73 (8.03), N: 8.00 (7.97)

(*S*)-2-Chloromethyl-4-neopentyl-4,5-dihydro-oxazoline (55)

According to *general procedure 4* amide **51** (1.32 g, 6.35 mmol) was reacted with Burgess' reagent (1.97 g, 8.26 mmol) in THF (50 mL). Kugelrohr distillation (100 °C, 10^{-1} mbar) afforded the product as colorless oil (1.07 g, 89%).



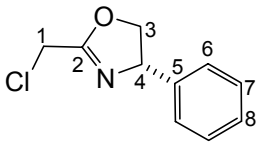
$C_9H_{16}ClNO$ (189.68)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.94 (s, 9H, 7), 1.35 (dd, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, 7) 1.72 (dd, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, 7), 3.86 (*pst*, $^2J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, 3), 4.08 (s, 2H, 1), 4.16 (m, 1H, 3), 4.47 (dd, $^2J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 9.6 Hz, 1H, 3).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300K): δ = 29.9 (7), 30.4 (6), 37.1 (1), 50.5 (5), 64.4 (4), 75.6 (3), 161.8 (2).

(*S*)-2-Chloromethyl-4-phenyl-4,5-dihydro-oxazoline (56)

According to *general procedure 4* amide **52** (2.12 g, 9.92 mmol) was reacted with Burgess' reagent (2.6 g, 10.9 mmol) in THF (50 mL). Distillation (100°C, 10^{-1}bar) afforded the product as a colorless oil (1.5g, 77 %).



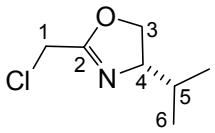
$C_{10}H_{10}ClNO$ (195.65)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 4.19 (t, $^2J_{HH}$ = 8.6 Hz, 1H, 3), 4.23 (s, 2H, 1), 4.72 (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 10.4 Hz, 1H, 3), 5.24 (*pst*, $^3J_{HH}$ = 9.4/9.1 Hz, 1H, 4), 7.25 (m, 2H, 6), 7.30 (m, 1H, 8), 7.35 (m, 2H, 7). **^{13}C{^{1}H} NMR** (100.6 MHz, CD_2Cl_2, 300K): δ = 36.8 (1), 69.6 (3), 75.4 (5), 126.3 (6), 127.4 (8), 128.5 (7), 141.5 (5), 163.3 (2). **MS** (+EI), m/z: 195

(M^+, 35.9), 160 (M-Cl^-, 53.7), 130 (100), 103 (65.4). **IR** (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3030m, 2930m, 2903m, 2368w, 233w, 1665s, 1494w, 1453w, 1429w, 1361m, 1307w, 1241m, 1155m, 1112w, 1080w, 981s, 926w, 890w, 758s, 701s. TLC (pentane:diethyl ether; 1:1) R_f = 0.2. **EA** %found (calcd): C: 61.39 (60.20), H: 5.13 (5.15), N: 7.01 (7.16).

(*S*)-2-Chloromethyl-4-isopropyl-4,5-dihydro-oxazoline (57)

According to *general procedure 4* amide **53** (4.75 g, 26.4 mmol) was reacted with Burgess' reagent (7.69 g, 32.3 mmol) in THF (50 mL). Distillation (40°C, 10^{-1} mbar) afforded the product as a colorless oil (2.6g, 61%).

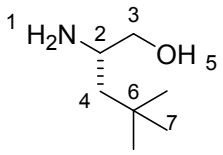


$C_7H_{12}ClNO$ (161.63)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.89 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 6), 0.97 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 6'), 1.78 (m, 1H, 5), 3.96 (m, 1H, 4), 4.07 (t, $^3J_{HH}$ = 8.3 Hz, 3), 4.11 (s, 2H, 1), 4.35 (dd, $^3J_{HH}$ = 8.3 Hz, $^2J_{HH}$ = 9.6 Hz, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 18.2 (6), 18.8 (6'), 32.6 (5), 36.6 (1), 71.3 (3), 72.6 (4), 162.5 (2). **MS** (+FAB, 3-NBA) m/z: 180 (MH_3O^+,100). **MS** (+EI) m/z: 118 (M^+-C_3H_7, 100), 90 (30.8), 83 ($C_4H_5NO^+$, 16.3), 43 ($C_3H_7^+$, 17.6). **IR** (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3319m_{br}, 2962s, 2906m, 2364w, 1670s, 1526w, 1469m, 1431w, 1361m, 1306w, 1245m, 1158m, 1113w, 981s, 890w, 751m, 722m. **EA** %found (calcd): C: 51.72 (52.02), H: 7.45 (7.48), N: 8.59 (8.67).

(*S*)-Neopentylglycinol (58)[73]

To a suspension of $LiAlH_4$ (0.531 g, 14 mmol) in THF (35 mL) was added (*S*)-2-amino-4,4-dimethylpentanoic acid (1.02 g, 7 mmol) portionwise at 0 ºC. The mixture was stirred under reflux for 4 hours after which time the reaction was successively quenched with water (0.6 mL), 15% NaOH (0.6 mL), and water (1.8 mL) at 0 ºC. Filtration and concentration was followed by Kugelrohr distillation (bp 150°C, 37 mbar) to afford a colorless oil, that gave colorless crystals after drying in the desiccator (745 mg, 82%).



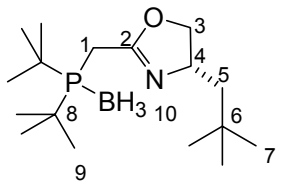
$C_7H_{17}NO$ (131.22)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.95 (s, 9H, 7), 1.10-1.16 (m, 1H, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 6.8 Hz, 4), 1.29-1.33 (m, $^3J_{HH}$ = 3.5 Hz, $^2J_{HH}$ = 14.4 Hz, 4), 2.17 (s_{br}, 3H, 1/5), 2.89-2.95 (m, 1H, 2), 3.15-3.20 (dd, $^3J_{HH}$ = 8.6 Hz, $^2J_{HH}$ = 10.3 Hz, 3), 3.48-3.51 (m, $^3J_{HH}$ = 4.3 Hz, $^2J_{HH}$ = 10.4 Hz, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 30.2 (7), 30.6 (6), 49.2 (4), 50.0 (3), 68.1 (2). **MS** (+FAB, 3-NBA) m/z: 132 (MH^+,100), 100 ($C_6H_{14}N^+$, 11.3), 57 ($C_4H_9^+$, 24.6). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3368m, 3306m, 3172m, 2954s, 2123w, 1612s, 1544s, 1479s, 1370s, 1218m, 1286w, 1245w, 1205w, 1138w, 1056s, 974m, 907w, 818w, 886w, 843w, 567w. **m.p.** 39°C. $[\alpha]_D^{20}$ (c = 1.0, $CHCl_3$) = +5.2°. **EA** % found (calcd): C: 63.16 (64.07), H: 12.24 (13.06), N: 10.47 (10.67).

7.3.5 Phosphanyl-methyl-4,5-dihydro-oxazoline-Borane Adducts by Coupling

(*S*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-neopentyl)-4,5-dihydrooxazole-borane (59)

The product was prepared according to *general procedure 5* method A from **48** (161.2 mg, 1.0 mmol), chloromethyloxazoline **55** (247.6 mg, 1.3 mmol), and NaH (72 mg, 3 mmol) in THF (15 mL). After column chromatography on silica eluting with pentane and diethyl ether the product was obtained as a colorless oil that solidified in the freezer (164 mg, 57%).

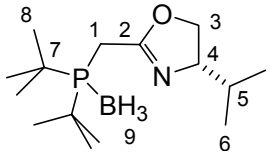


$C_{17}H_{37}BNOP$ (313.27)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.37 (q_{br}, 3H, 10), 0.93 (s, 9H, 7), 1.31 (d, $^3J_{HP}$ = 12.9 Hz, 9H, 9), 1.32 (d, $^3J_{HP}$ = 12.9 Hz, 9H, 9'), 1.33 (dd, 1H, 5), 1.69 (dd, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 5.1 Hz, 1H, 5), 2.73 (m, 2H, 1), 3.76 (*pst*, $^2J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, 3), 4.0 (m_{br}, 1H, 4), 4.37 (dd, $^2J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 9.4 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 20.1 (d, $^1J_{CP}$ = 23.8 Hz, 1), 28.2 (d, $^2J_{CP}$ = 1.5 Hz, 9'), 28.2 (d, $^2J_{CP}$ = 1.5 Hz, 9'), 30.0 (7), 30.4 (6), 33.1 (d, $^1J_{CP}$ = 24.5 Hz, 8), 33.2 (d, $^1J_{CP}$ = 24.2 Hz, 8'), 50.44 (5), 64.2 (3), 74.6 (4), 161.9 (d, $^2J_{CP}$ = 5.0 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 48.3 (m_{br}). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3448m_{br}, 2955s, 2905s, 2383s, 2267w, 1664s, 1472m, 1396w, 1365m, 1281w, 1252w, 1192w, 1147w, 1073m, 986m, 948w, 817w, 632w. $[\alpha]_D^{20}$: -43° (c = 0.25, $CHCl_3$).**TLC** (diethyl ether:pentane; 1:1) R_f = 0.54.

(*S*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-isopropyl)-4,5-dihydrooxazoline-borane (60)

Synthesis according according to *general procedure 5* method B, using **48** (200 mg, 1.25 mmol), *n*-BuLi (1.05 eq), chloromethyloxazoline **57** (152.2 mg, 0.94 mmol) in THF (10 ml). After column chromatography on silica eluting with pentane and diethyl ether the product was obtained as a colorless oil (231.3 mg, 86%).

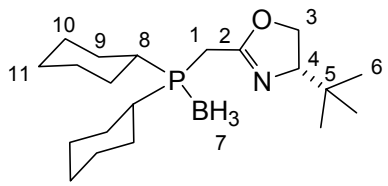


$C_{15}H_{33}BNOP$ (285.21)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.38 (q_{br}, $^1J_{HB}$ = 100 Hz, 3H, 9), 0.85 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 6), 0.96 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 6'), 1.31 (dd, $^3J_{HP}$ = 13.1 Hz, 18H, 8/8'), 1.68 (m, 1H, 5), 2.74 (d, $^2J_{HP}$ = 10.8 Hz, 2H, 1), 3.77 (m, 1H, 4), 3.93 (*ps*t, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, 3), 4.26 (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 9.6 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, CD_2Cl_2, 300K): δ = 18.0 (6), 18.7 (6'), 19.4 (d, $^1J_{CP}$ = 24.1 Hz, 1), 27.4 (*ps*t, $^2J_{CP}$ = 2 Hz, 8/8'), 32.3 (d, $^1J_{CP}$ = 6.9 Hz, 7), 32.5 (d, $^1J_{CP}$ = 6.9 Hz, 7'), 32.6 (5), 70.3 (3), 72.4 (4), 161.7 (d, $^2J_{CP}$ = 5 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 48.4 (q, $^1J_{PB}$ = 55.5 Hz). **MS** (+FAB, 3-NBA) m/z: 284 ($R^1{}_2R^2P(^{11}B)H_2^+$, 71.2), 283 ($R^1{}_2R^2P(^{10}B)H_2^+$, 17.4), 272 (M^+-BH_3, 39.9), 214 (272-C_4H_{10}, 18.8), 158 (214-C_4H_8, 14.2), 57 ($C_4H_9^+$, 100). **IR** (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2960s, 2903ssh, 2379s, 2269w, 1663s, 1472m, 1395w, 1367m, 1302w, 1254w, 1188w, 1146m, 1073m, 1023w, 987m, 938m, 817w, 771w. **TLC** (*n*-pentane:diethyl ether; 1:1) R_f = 0.38.

(*S*)-4-*tert*-Butyl-2-[(dicyclohexylphosphanyl)-methyl]-4,5-dihydro-oxazoline-borane adduct (61)

Synthesis according to *general procedure 5* method B, using **49** (198 mg, 0.93 mmol), *n*-BuLi (1 mmol), chloromethyloxazoline **54** (169.1 mg, 0.96 mmol) in THF (10 ml). After column chromatography on silica eluting with pentane and diethyl ether the product was obtained as a white solid (293 mg, 89%).

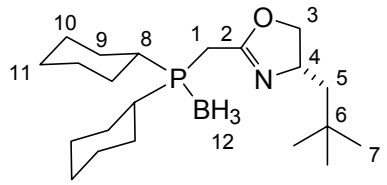


$C_{20}H_{39}BNOP$ (351.31)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.26 (q_{br}, 3H, 7), 0.89 (s, 9H, 6), 1.25 (m, 6H, Cy_{eq}), 1.41 (m, 4H, Cy_{eq}), 1.71 (m, 2H, Cy_{ax}), 1.81 (m, 8H, Cy_{ax}), 1.86 (m, 2H, Cy_{ax}), 2.00 (m, 2H, 8), 2.63 (d, $^{3}J_{HH}$ = 9.6 Hz, 2H, 1), 3.83 (m, 1H, 4), 3.98 (*ps*t, $^{2}J_{HH}$ = 8.9 Hz, $^{3}J_{HH}$ = 8.9 Hz, 1H, 3), 4.19 (dd, $^{2}J_{HH}$ = 8.6 Hz, $^{3}J_{HH}$ = 10.1 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 20.5 (d, $^{1}J_{CP}$ = 26.8 Hz, 1), 26.1 (6), 26.3-27.3 (m, Cy), 31.7 (2×d, $1J_{CP}$ = 31.2 Hz, 8), 33.7 (5), 69.0 (3), 76.6 (4), 161.4 (2). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 28.3 (m). **MS** (+FAB, 3-NBA) m/z: 350 (MH^+, 100), 338 (MH^+-BH_3, 56.6), 83 (Cy^+, 36.2), 55 (63.0). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3448m_{br}, 2937s, 2852s, 2661w, 2372s, 2342m, 2248w, 2115w, 1660s, 1474w, 1446m, 1408w, 1359m, 1333m, 1299w, 1258m, 1178w, 1134m, 1064m, 1004sh, 980m, 933m, 891w, 855w, 829w, 793w, 756w, 705w, 606m. **m.p.** 53 °C. $[\alpha]_D^{20}$ (c = 1.06, $CHCl_3$): -41.1°. **TLC** (*n*-pentane:diethyl ether; 1:2) R_f = 0.76. **EA** %found (calcd) C: 68.37 (68.38), H: 10.93 (11.19), N: 4.09 (3.99).

(*S*)-2-[(Dicyclohexylphosphanyl)methyl]-4-neopentyl-4,5-dihydro-oxazole-borane (35)

The product was obtained according to *general procedure 5* method B from **49** (214.8 mmol), chloromethyloxazoline **55** (211.6 mg, 1.11 mmol), and *n*-BuLi (0.7 mL of 1.6M solution in hexane, 1.1 mmol) in THF (15 mL). After column chromatography on silica (pentane and diethyl ether) the product was obtained as a white solid (306 mg, 83%).



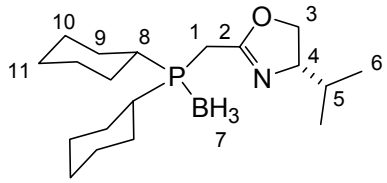
$C_{21}H_{41}BNOP$ (365.34)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.25 (q_{br}, 3H, 12), 0.96 (s, 9H, 7), 1.26 (m_{br}, H, Cy), 1.32 (dd, $^{2}J_{HH}$ = 13.9 Hz, $^{3}J_{HH}$ = 6.8 Hz, 5), 1.40 (m_{br}, H, Cy), 1.65 (dd, $^{2}J_{HH}$ = 13.9 Hz, $^{3}J_{HH}$ = 6.1 Hz, 5), 1.71 (m_{br}, 2H, Cy), 1.83 (m_{br}, 8H, Cy), 1.97 (m_{br}, 2H, Cy), 2.61 (m, 2H, 1), 3.74 (*ps*t, $^{2}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 8.3 Hz, 3), 4.09 (m, 1H, 4), 4.37 (dd, $^{2}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 9.6 Hz, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 20.4 (d, $^{1}J_{CP}$ = 26.1 Hz, 1), 26.3 (Cy), 26.8 (Cy), 27.0 (Cy), 27.1 (Cy), 27.2 (Cy), 30.0 (7), 30.5 (6), 31.5 (d, $^{1}J_{CP}$ = 31.1Hz, 8), 31.6 (d, $^{1}J_{CP}$ = 31.1 Hz, 8'), 50.7 (5), 64.3 (4), 74.6 (3), 160.9 (d, $^{2}J_{CP}$ = 7.7 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 28.1 (d, $^{1}J_{PB}$ = 69.4 Hz). **MS** (+FAB, 3-NBA) m/z: 364 ($M\text{-}H^-$, 100), 352 (MH^+-BH_3, 60.1), 57 ($C_4H_9^+$, 56.6), 55 ($C_4H_7^+$, 62.2). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3436m_{br}, 2932s, 2857s, 2374s, 2343m, 2247w, 1658s, 1448m, 1405w, 1357m, 1302w,

1277w, 1202w, 1138w, 1064m, 1006w, 980m, 951w, 911w, 891w, 855w, 796w, 756w, 607w. **m.p.** 65-67°C. $[\alpha]_D^{20}$**:** -47° (c = 0.37, $CHCl_3$). **TLC** (*n*-pentane: diethyl ether; 1:1) R_f = 0.43. **EA** % found (calcd): C: 69.07 (69.04), H: 11.09 (11.31), N: 3.95 (3.83).

(*S*)-2-[(Dicyclohexylphosphanyl)-methyl]-4-isopropyl-4,5-dihydro-oxazoline-borane adduct (63)

Synthesis according to *general procedure 5* method B, using **49** (299 mg, 1.4 mmol), *n*-BuLi (1 eq), chloromethyloxazoline **57** (217.5 mg, 1.35 mmol) in THF (20 ml). After column chromatography on silica eluting with pentane and diethyl ether the product was obtained as a white solid (370 mg, 82%).

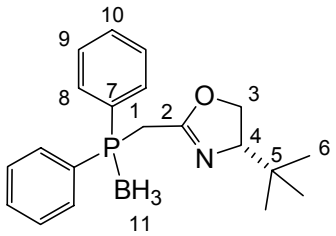


$C_{19}H_{37}BNOP$ (337.29)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.88 (d, $^3J_{HH}$ = 6.7 Hz, 6), 0.98 (d, $^3J_{HH}$ = 6.7 Hz, 6'), 1.25 (m, 6H, 10_{eq}, 11_{eq}), 1.41 (m, 4H, 9_{eq}), 1.65 (m, 1H, 5), 1.71 (m, 2H, 11_{ax}), 1.79-1.87 (m, 8H, 9_{ax}, 10_{ax}), 1.96 (m, 2H, 8), 2.58-2.68 (m, 2H, 1), 3.79 (m, 1H, 4), 3.91 (*pst*, $^2J_{HH}$ = 8.5 Hz, 1H, 3), 4.25 (dd, $^2J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 9.7 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 18.8 (6), 19.3 (6'), 20.5 (d, $^1J_{CP}$ = 26.3 Hz, 1), 26.3 (dd, 11), 26.8 (dd, 9), 27.0-27.2 (m, 9/10), 31.6 (*pst*, $^1J_{CP}$ = 61.8 Hz, 8), 33.5 (5), 71.0 (3), 73.2 (4), 161.4 (d, $^2J_{CP}$ = 7.8 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 28.1 (m, $^1J_{PB}$ = 69.4 Hz). **MS** (+FAB, 3-NBA) m/z: 336 ($M\text{-}H^-$, 100), 324 (MH^+-BH_3, 52.9). **IR** (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2930s, 2856s, 2664w, 2372s, 2255w, 1663s, 1450m, 1404w, 1351m, 1201w, 1274w, 1252w, 1214w, 1176w, 1139m, 1065m, 983m, 936m, 891w, 855w, 758w. **TLC** (*n*-pentane:diethyl ether; 4:1) R_f = 0.53. **EA** % found (calcd): C: 67.43 (67.66), H: 10.81 (11.06), N: 4.23 (4.15).

(*S*)-4-tert-Butyl-2-[(diphenylphosphanyl)-methyl]-4,5-dihydro-oxazoline-borane adduct (64)

Synthesis according to *general procedure 5* method A, using **30** (400 mg, 2 mmol), chloromethyloxazoline **54** (457 mg, 2.6 mmol) and NaH (125 mg, 5.2 mmol) in THF (15 ml). After column chromatography on silica eluting with pentane and diethyl ether the product was obtained as a white solid (452.6 mg, 67%).

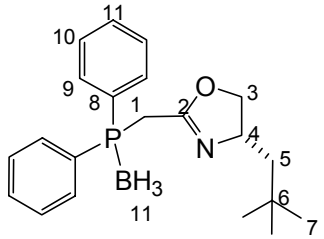


$C_{20}H_{27}BNOP$ (339.22)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.72 (m_{br}, 3H, 11), 3.28 (ddd, $^{2}J_{HH}$ = 14.4 Hz, $^{2}J_{HP}$ = 10.6 Hz, 1H, 1), 3.43 (dd, $^{2}J_{HH}$ = 14.4 Hz, $^{2}J_{HP}$ = 11.6 Hz, 1H, 1), 3.73 (dt, $^{3}J_{HH}$ = 9.7 Hz, $^{4}J_{HH}$ = 3.0 Hz, 1H, 4), 3.85 (t, $^{2}J_{HH}$ = 8.6 Hz, 1H, 3), 4.04 (dd, $^{2}J_{HH}$ = 8.6, $^{3}J_{HH}$ = 10.1 Hz, Hz, 1H, 3), 7.43-7.52 (m, 6H, 8/10), 7.72-7.80 (m, 4H, 9). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 25.9 (6), 27.4 (d, $^{1}J_{CP}$ = 32.2 Hz, 1), 33.4 (5), 69.2 (3), 76.1 (4), 128.2 (d, $^{1}J_{CP}$ = 55.6 Hz, 7), 128.7 (d, $^{1}J_{CP}$ = 55.6 Hz, 7'), 128.8 (d, $^{2}J_{CP}$ = 10.3 Hz, 8), 128.9 (d, $^{2}J_{CP}$ = 10.0 Hz, 8'), 131.6 (2×d, $^{4}J_{CP}$ = 2.7 Hz, 10/10'), 132.6 (d, $^{3}J_{CP}$ = 9.6 Hz, 9), 132.9 (d, $^{3}J_{CP}$ = 10.0, 9'), 160.7 (2). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 17.6 (d, $^{1}J_{PB}$ = 65.4 Hz). **MS** (+FAB, 3-NBA) m/z: 340 (MH^+, 52.5), 339 (M^+, 29.3), 338 ($M\text{-}H^-$, 74.5), 326 (M^+-BH_3, 100), 185 (PPh_2^+, 54.7). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 2959s, 2888m, 2387s, 2349m, 1668s, 1477m, 1437m, 1400w, 1357m, 1333w, 1295w, 1252m, 1207m, 1134m, 1105m, 1060m, 1022w, 991m, 932m, 745m, 695s, 580m. **mp.** 71 °C. $[\alpha]_D^{20}$: -35.0° (c = 1.01, $CHCl_3$). **TLC** (diethyl ether:pentane ethanol; 4:1): R_f = 0.43. **EA** % found (calcd): C: 70.94 (70.81), H: 7.96 (8.02), N: 4.10 (4.13).

(*S*)-4-Neopentyl-2-[(diphenylphosphanyl)-methyl]-4,5-dihydro-oxazole borane (65)

The product was obtained according to *general procedure 5* method B from **30** (206.7 mg, 1.03 mmol), chloromethyloxazoline **55** (146 mg, 0.77 mmol), and *n*-BuLi (0.7 mL of 1.6M solution in hexane, 1.1 mmol) in THF (15 mL). After column chromatography on silica eluting with pentane and diethyl ether the product was obtained as a white solid (95 mg, 35 %).

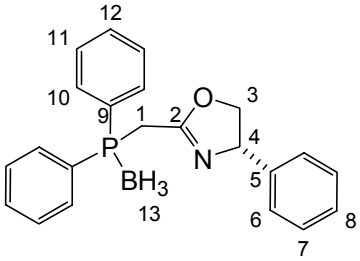


$C_{21}H_{29}BNOP$ (353.25)

^{1}H NMR ($CDCl_3$, 400.1 MHz, 300K): δ = 0.87 (s, 9H, 7), 1.11 (q_{br}, 3H, 11), 1.11 (dd, $^{3}J_{HH}$ = 7.1 Hz, $^{2}J_{HH}$ 13.9 Hz, 1H, 5), 1.44 (dd, $^{3}J_{HH}$ = 5.6 Hz, $^{2}J_{HH}$ 13.9 Hz, 1H, 5), 3.25 (dd, $^{2}J_{HH}$ = 14.4 Hz, $^{2}J_{HP}$ = 10.6 Hz, 1H, 1), 3.32 (dd, $^{2}J_{HH}$ = 14.4 Hz, $^{2}J_{HP}$ = 11.1 Hz, 1H, 1), 3.51 (*pst*, $^{2}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 8.3 Hz, 1H, 3), 3.96 (m, 1H, 4), 4.18 (dd, $^{2}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 9.6 Hz, 3), 7.45-7.53 (m, 6H, 9/11), 7.71-7.78 (m, 4H, 10). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz, 300K): δ = 27.3 (d, $^{1}J_{CP}$ = 32 Hz, 1), 29.9 (7), 30.4 (6), 50.5 (5), 64.1 (4), 74.7 (3),128.7 (d, $^{1}J_{CP}$ = 55.6 Hz, 8), 128.9 (d, $^{1}J_{CP}$ = 55.6 Hz, 8'), 129.0 (d, $^{2}J_{CP}$ = 10.3 Hz, 9), 129.1 (d, $^{2}J_{CP}$ = 10.0 Hz, 9'), 131.8 (d, $^{4}J_{CP}$ = 2.4 Hz, 11/11'), 132.9 (d, $^{3}J_{CP}$ = 9.7 Hz, 10), 133.0 (d, $^{3}J_{CP}$ = 9.7, 10'), 159.9 (d, $^{2}J_{CP}$ = 6.3 Hz, 2). **^{31}P{^{1}H} NMR** ($CDCl_3$, 162 MHz, 300K): δ = 17.6 (m, $^{1}J_{PB}$ = 69 Hz). **TLC** (diethyl ether:pentane ethanol, 4:1): R_f = 0.46.

(*S*)-2-[(Diphenylphosphanyl)-methyl]-4-phenyl-4,5-dihydro-oxazole-borane adduct (66)

The product was obtained according to *general procedure 5* method A from **30** (278.7 mg, 1.39 mmol), chloromethyloxazoline **56** (257.2 mg, 1.31 mmol), and NaH (33.3 mg, 1.39 mmol) in THF (15 mL). After column chromatography on silica eluting with pentane and diethyl ether the product was obtained as a white solid (209 mg, 44%).



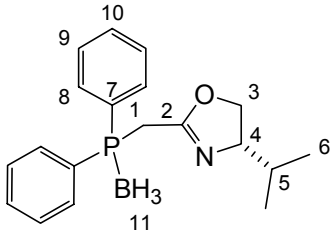
$C_{22}H_{23}BNOP$ (359.21)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 3.38-3.5 (m, 2H, 1), 3.84 (t, $^{3}J_{HH}$ = 8.6 Hz, 3), 4.46 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{2}J_{HH}$ = 9.4 Hz, 3), 5.05 (ddd, 1H, 4), 7.01 (m, 2H, 6), 7.25-7.29 (m, 3H, 7/8), 7.46-7.50 (m, 4H, 10/10'), 7.53-7.54 (m, 2H, 12/12'), 7.75-7.81 (m, 4H, 11/11'). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 27.4 (d, $^{1}J_{CP}$ = 32 Hz, 1), 70.2 (3), 75.3 (4), 126.9 (6), 127.7 (8), 128.6 (d, $^{1}J_{CP}$ = 55.5 Hz, 9), 128.8 (7), 128.8 (d, $^{1}J_{CP}$ = 55.5 Hz, 9'), 129.1 (d, $^{2}J_{CP}$ = 10.3 Hz, 10), 129.2 (d, $^{2}J_{CP}$ = 10.3 Hz, 10'), 131.9 (2×d, $^{4}J_{CP}$ = 2.8 Hz, 12/12'), 132.9 (d, $^{3}J_{CP}$ = 9.7 Hz, 11), 133.1 (d, $^{3}J_{CP}$ = 9.7 Hz, 11'), 142.3 (5), 162.1 (d, $^{2}J_{CP}$ = 5.5 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 17.8 (d, $^{1}J_{PB}$ = 61.5 Hz). **MS** (+FAB, 3-NBA) m/z: 360 (MH^+, 15.3), 346 (MH^+-BH_3, 26.2), 185 ($Ph2P^+$, 14.7). **IR** (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3059m, 2969m, 2901m, 2386s, 2259w, 1964w, 1895w, 1815w, 1660s, 1487m,

1437m, 1400m, 1355m, 1308m, 1274m, 1247m, 1139m-s, 1109m-s, 1062s, 985s, 920m, 846w, 745s, 689s. **TLC** (diethyl ether:pentane ethanol, 4:1): $R_f = 0.3$.

(*S*)-2-[Diphenylphosphanyl-methyl]-4-isopropyl-4,5-dihydro-oxazoline-borane adduct (67)

Synthesis according to *general procedure 5* method A, using diphenylphosphine-borane adduct (400 mg, 2 mmol), chloromethyloxazoline **57** (420 mg, 2.6 mmol) and NaH (125 mg, 5.2 mmol) in THF (15 ml). After column chromatography on silica eluting with pentane and diethyl ether the product was obtained as a white solid (529 mg, 91%).



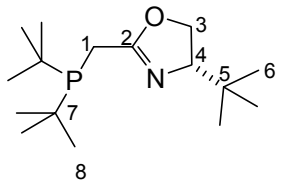
$C_{19}H_{25}BNOP$ (325.19)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.74 (d, 3H, $^3J_{HH}$ = 6.8 Hz, 6), 0.81 (d, 3H, $^3J_{HH}$ = 6.8 Hz, 6'), 1.47 (m, 1H, 5), 3.27 (dd, $^2J_{HH}$ = 14.5 Hz, $^2J_{HP}$ = 11.2 Hz, 1H, 1), 3.34 (dd, $^2J_{HH}$ = 14.5 Hz, $^2J_{HP}$ = 11.2 Hz, 1H, 1), 3.69 (m, 1H, 4), 3.72 (m, 1H, 3), 4.06 (dd, 1H, 3), 7.44-7.553 (m, 6H, 8/10), 7.72-7.76 (m, 4H, 9). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 18.2 (6), 18.6 (6'), 27.0 (d, $^1J_{CP}$ = Hz, 1), 32.8 (5), 70.7 (3), 72.6 (4),128.6 (2×d, $^1J_{CP}$ = 2×55.5 Hz, 7/7'), 128.6 (d, $^2J_{CP}$ = 10.3 Hz, 8), 128.7 (d, $^2J_{CP}$ = 10.3 Hz, 8'), 131.4 (dd, $^4J_{CP}$ = 2.5 Hz, 10/10'), 132.5 (d, $^3J_{CP}$ = 9.6 Hz, 9), 132.6 (d, $^3J_{CP}$ = 9.6, 9'), 159.9 (d, $^1J_{CP}$ = 6.1 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 17.8 (d, $^1J_{PB}$ = 65.4 Hz). **MS** (+FAB, 3-NBA) m/z: 324 ($M\text{-}H^-$, 81.3), 312 ($MH^+\text{-}BH_3$, 100), 185 (Ph_2P^+, 55.2). **IR** (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3057w, 2961s, 2900sh, 2382s, 2259w, 1664s, 1476w, 1437m, 1399w, 1354m, 1304w, 1250w, 1139m, 1109m,1061m, 983m, 935m, 843w, 743m, 696s. **TLC** (diethyl ether:pentane ethanol; 4:1): $R_f = 0.34$.

7.3.6 Deprotection and Complex Synthesis

(*S*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-*tert*-butyl)-4,5-dihydrooxazoline (68)

The product was obtained according to *general procedure 6* from protected ligand **45** (71 mg, 237 μmol) in diethylamine (1 mL) in 3 days. To separate the diethylamine-borane adduct the brown oil was purified over a short argon column. The product was obtained as a colorless oil (45 mg, 66%).

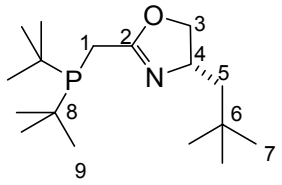


$C_{16}H_{32}BNOP$ (285.41)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.85 (s, 9H, 6), 1.4-1.18 (2×d, $^3J_{HP}$ = 11.1 Hz, 18H, 8/8'), 2.39 (s_{br}, 2H, 1), 3.76 (*ps*t, $^3J_{HH}$ = 9.6 Hz, 1H, 4), 3.97 (*ps*t, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, 3), 4.13 (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 9.8 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 21.5 (d, $^1J_{CP}$ = 28 Hz, 1), 26.1 (6), 29.4 (d, $^2J_{CP}$ = 14 Hz, 8), 29.5 (d, $^2J_{CP}$ = 14 Hz, 8), 33.9 (5), 68.9 (3), 76.4 (4) quarternary carbons missing. **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 27.3. **TLC:** (*n*-pentane:diethylether; 1:2) R_f = 0.46.

(*S*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-neopentyl)-4,5-dihydrooxazole (69)

The product was obtained according to *general procedure 6* from protected ligand **59** (139 mg, 440 μmol) in diethylamine (2 mL) in 7 days. Evaporation of the volatiles afforded the product as a colorless oil. The ligand was used without further purification.

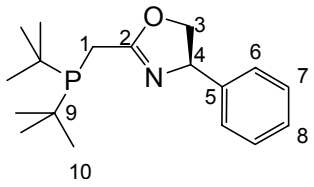


$C_{17}H_{34}NOP$ (299.43)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.92 (s, 9H, 7), 1.13 (d, $^3J_{HP}$ = 11.1 Hz, 9H, 9), 1.14 (d, $^3J_{HP}$ = 11.1 Hz, 9H, 9'), 1.28 (dd, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, 5), 1.66 (dd, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, 5), 2.39 (ddq, $^2J_{HP}$ = 25.4 Hz, $^2J_{HH}$ = 14.3 Hz, $^5J_{HH}$ = 1.5 Hz, 2H, 1), 3.73 (*ps*t, $^2J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, 3), 4.03 (m_{br}, 1H, 4), 4.33 (dd, $^2J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 9.4 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 21.5 (d, $^1J_{CP}$ = 28.4 Hz, 1), 29.4 (d, $^2J_{CP}$ = 8.4 Hz, 9), 29.5 (d, $^2J_{CP}$ = 8.4 Hz, 9'), 30.0 (7), 30.4 (6), 31.8 (d, $^1J_{CP}$ = 23.1 Hz, 8), 31.8 (d, $^1J_{CP}$ = 23.3 Hz, 8), 50.8 (5), 64.1 (3), 74.6 (4), 166.5 (d, $^2J_{CP}$ = 11.8 Hz, 2). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 27.3.

(*R*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-phenyl)-4,5-dihydrooxazole (70)

The product was obtained according to *general procedure 6* from protected ligand **46** (110 mg, 345 μmol) in diethylamine (2 mL) in 7 days. Evaporation of the volatiles afforded the product as a colorless oil. The ligand was used without further purification.

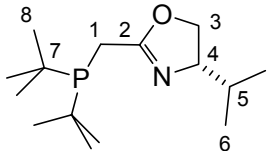


$C_{18}H_{28}NOP$ (305.39)

^{1}H NMR (CD_2Cl_2, 500.1 MHz, 300K): δ = 1.17 (d, $^{3}J_{HP}$ = 11.1 Hz, 9H, 10), 1.18 (d, $^{3}J_{HP}$ = 11.1 Hz, 9H, 10'), 2.52 (m, 2H, 1), 4.01 (*pst*, $^{2}J_{HH}$ = 8.5, 1H, 3), 4.59 (dd, $^{2}J_{HH}$ = 8.5 Hz, $^{3}J_{HH}$ = 10.1 Hz, 3), 5.12 (*pst*, $^{3}J_{HH}$ = 10 Hz, 1H, 4), 7.22-7.28 (m, 3H, 6/8), 7.31-7.35 (m, 2H, 7). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125.8 MHz, 300K): δ = 21.5 (d, $^{1}J_{CP}$ = 28.7 Hz, 1), 2×29.5 (dd, 2×$^{2}J_{CP}$ = 14 Hz, 10), 31.9 (d, $^{1}J_{CP}$ = 23.0 Hz, 9), 70.2 (4), 75.1 (3), 127.0 (6), 127.6 (8), 128.9 (7), 143.3 5), 168.9 ($^{2}J_{CP}$ = 12.6 Hz, 2). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 162.0 MHz, 300K): δ = 28.8.

(*S*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-*tert*-butyl)-4,5-dihydrooxazoline (71)

The product was obtained according to *general procedure 6* from protected ligand **60** (220 mg, 677 μmol) in diethylamine (1.5 mL) in 1 day. Evaporation of the volatiles afforded the product as a colorless oil. The ligand was used without further purification.

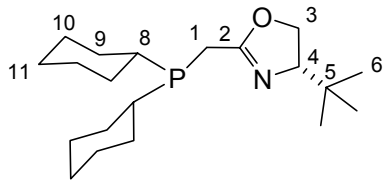


$C_{15}H_{30}NOP$ (271.38)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.84 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, 6), 0.93 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, 6'), 1.30 (d, $^{3}J_{HP}$ = 11.1 Hz, 9H, 8), 1.14 (d, $^{3}J_{HP}$ = 11.1 Hz, 9H, 8'), 1.65 (m, 1H, 5), 2.40 (2H, 1), 3.78 (m, 1H, 4), 3.89 (*pst*, $^{3}J_{HH}$ = 8.1 Hz, $^{2}J_{HH}$ = 8.1 Hz, 1H, 3), 4.19 (dd, $^{3}J_{HH}$ = 11.6 Hz, $^{2}J_{HH}$ = 8.3 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 18.5 (6), 19.1 (6'), 21.5 (d, $^{1}J_{CP}$ = 28.3 Hz, 1), 29.5 (d, $^{2}J_{CP}$ = 14.2 Hz, 8), 29.6 (d, $^{2}J_{CP}$ = 1.24 Hz, 8), 31.8 (d, $^{1}J_{CP}$ = 23 Hz, 7), 31.9 (d, $^{1}J_{CP}$ = 23 Hz, 7), 33.2 (5), 70.6 (3), 72.9 (4). 167.1 (2). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 27.2.

(*S*)-4-*tert*-Butyl-2-[(dicyclohexylphosphanyl)-methyl]-4,5-dihydro-oxazole (72)

The product was obtained according to *general procedure 6* from protected ligand **61** (155.5 mg, 443 μmol) in diethylamine (2 mL) in 5 days. Evaporation of the volatiles afforded the product as a colorless oil. The ligand was used without further purification.

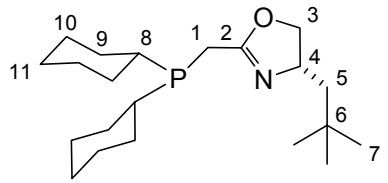


$C_{20}H_{306}NOP$ (337.48)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.86 (s, 9H, 6),1.24 (m, 8H, Cy_{eq}), 1.56 (m_{br}, 1H, Cy), 1.59 (m_{br}, 2H, Cy), 1.68 (m_{br}, 2H, Cy_{ax}), 1.78 (m_{br}, 9H, Cy_{ax}), 2.34 (m, 2H, 1), 3.77 (ddd, 1H, 4), 3.96 (t, $^{2}J_{HH}$ = 8.6 Hz, 1H, 3), 4.12 (dd, $^{2}J_{HH}$ = 8.6 Hz, $^{3}J_{HH}$ = 10.1 Hz, 1H, 3). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = -2.7.

(*S*)-2-[(Dicyclohexylphosphanyl)methyl]-4-neopentyl-4,5-dihydro-oxazole (73)

The product was obtained according to *general procedure 6* from protected ligand **62** (181 mg, 195 μmol) in diethylamine (2 mL) in 4 days. Evaporation of the volatiles afforded the product as a colorless oil. The ligand was used without further purification.

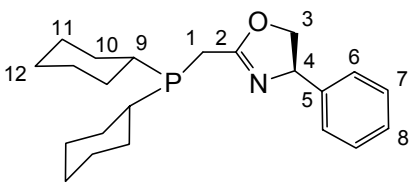


$C_{21}H_{38}NOP$ (351.51)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.93 (s, 9H, 7), 1.23 (m, 10H, Cy_{eq}), 1.28 (dd, $^{2}J_{HH}$ = 13.9 Hz, $^{3}J_{HH}$ = 7.6 Hz, 1H, 5), 1.64 (m, 2H, Cy_{ax}), 1.66 (dd, $^{2}J_{HH}$ = 13.9 Hz, $^{3}J_{HH}$ = 4.8 Hz, 1H, 5), 1.75 (m_{br}, 10H, Cy_{ax}), 2.34 (dd, $^{2}J_{HP}$ = 22.5 Hz, $^{2}J_{HH}$ = 13.9 Hz, 2H, 1), 3.71 (*pst*, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 8.3 Hz, 1H, 3), 4.03 (m, 1H, 4), 4.31 ($^{2}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 9.3 Hz, 1H, 3). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = -3.1

(*R*)-4-Phenyl-2-[(dicyclohexylphosphanyl)-methyl]-4,5-dihydro-oxazoline (74)

The product was obtained according to *general procedure 6* from protected ligand **47** (180 mg, 485 μmol) in diethylamine (1.5 mL) in 7 days. The crude product was purified over a short argon column. The product was obtained as a colorless oil (181 mg, 87%).

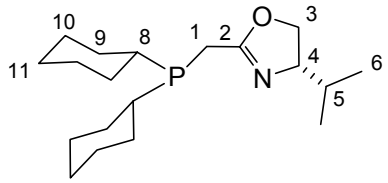


$C_{22}H_{32}NOP$ (357.47)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 1.25 (m_{br}, 6H, Cy_{eq}), 1.43 (m_{br}, 4H, Cy_{eq}), 1.71 (m_{br}, 2H, Cy_{ax}), 1.81 (m_{br}, 4H, Cy_{ax}), 1.89 (m_{br}, 4H, Cy_{ax}), 2.0 (m, 2H, 8), 2.48 (s, 2 H, 1), 4.03 (*pst*, $^{2}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 8.3 Hz, 1H, 3), 4.58 (dd, $^{2}J_{HH}$ = 8.6, $^{3}J_{HH}$ = 9.9 Hz, 1H, 3), 5.12 (m, $^{3}J_{HH}$ = 9.6 Hz, 1H, 4). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = -1.9

(*S*)-2-[(Dicyclohexylphosphanyl)-methyl]-4-isopropyl-4,5-dihydro-oxazoline-borane adduct (75)

The product was obtained according to *general procedure 6* from protected ligand **63** (179 mg, 530 μmol) in diethylamine (1.5 mL) in 1 day. Purification by column chromatography on silica with diethyl ether and pentane under argon afforded the product as a colorless oil (124 mg, 72%).

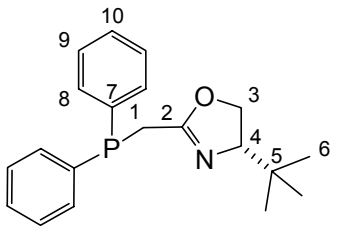


$C_{19}H_{34}NOP$ (323.45)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.85 (d, $^{3}J_{HH}$ = 6.8 Hz, 6), 0.94 (d, $^{3}J_{HH}$ = 6.8 Hz, 6'), 1.1-13 (m, 6H, 9_{eq}, 10_{eq}, 11_{eq}), 1.56-1.62 (m, 2H, 8_{ax}), 1.66-1.68 (m, 3H, 5, 11_{ax}), 1.75-1.77 (m, 8H, 9_{ax}, 10_{ax}), 2.36 (m, $^{2}J_{HH}$ = 13.9 Hz, $^{2}J_{HP}$ = 7 Hz, 1), 3.77 (m, 1H, 4), 3.88 (*pst*, $^{2}J_{HH}$ = 8.3 Hz, 1H, 3), 4.18 (*pst*, ^{2} J_{HH} = 8.6 Hz, $^{3}J_{HH}$ = 9.1 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 18.5 (6), 19.1 (6'), 21.6 (d, $^{1}J_{CP}$ = 25.4 Hz, 1), 26.8 (11),27.5 (m, 10), 27.6 (m, 10'), 27.6 (m, 11'), 29.1 (dd, 9), 30.2 (*pst*, 9'), 32.3 (5), 33.9 (dd, $^{1}J_{CP}$ = 2×15 Hz, 8), 72.9 (3), 73.2 (4), 166.2 (d, $^{2}J_{CP}$ = 7 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = -2.9. **TLC:** (*n*-pentane:diethylether; 1:4) R_f = 0.53.

(*S*)-4-*tert*-Butyl-2-[(diphenylphosphanyl)-methyl]-4,5-dihydro-oxazoline (76)

The product was obtained according to *general procedure 6* from protected ligand **64** (108 mg, 0.32 mmol) in diethylamine (2 mL) in 1 day. Evaporation of the volatiles afforded the product as a colorless oil.

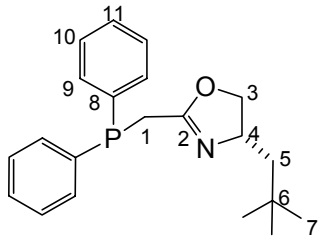


$C_{20}H_{24}NOP$ (325.38)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.74 (s, 9H, 6), 2.00 (dd, $^{2}J_{HH}$ = 14.4 Hz,$^{2}J_{HP}$ = 34 Hz, 1H, 1), 3.09 (dd, $^{2}J_{HH}$ = 14.4 Hz, $^{2}J_{HP}$ = 1 Hz, 1H, 1), 3.74 (m, 1H, 4), 3.93 (t, $^{2}J_{HH}$ = 8.3 Hz, 1H, 3), 4.08 (dd, $^{2}J_{HH}$ = 8.6, $^{3}J_{HH}$ = 10.0 Hz, 1H, 3), 7.33(m, 6H, 8/10), 7.47 (m, 4H, 9). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 25.8 (6), 28.4 (d, $^{1}J_{CP}$ = 18.3 Hz, 1), 33.7 (5), 69.1 (3), 76.4 (4), 128.8 (d, $^{2}J_{CP}$ = 6.7 Hz, 8/8'), 129.2 (d, $^{2}J_{CP}$ = 4.9 Hz, 10/10'), 133.0 (d, $^{3}J_{CP}$ = 14.1 Hz, 9), 133.1 (d, $^{3}J_{CP}$ = 14.1 Hz, 9'), 138.4 (d, $^{1}J_{CP}$ = 34.4, 7), 138.5 (d, $^{1}J_{CP}$ = 34.4, 7'), 163.9 (d, $^{2}J_{CP}$ = 8.3 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = -17.3.

(*S*)-4-Neopentyl-2-[(diphenylphosphanyl)-methyl]-4,5-dihydro-oxazole (77)

The product was obtained according to *general procedure 6* from protected ligand **65** (95 mg, 269 μmol) in diethylamine (2 mL) in 2 days. Evaporation of the volatiles afforded the product as a colorless oil. The ligand was used without further purification.

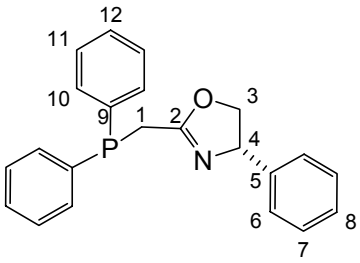


$C_{21}H_{26}NOP$ (339.41)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K) δ = 0.88 (s, 9H, 7), 1.17 (dd, $^{2}J_{HH}$ = 13.9 Hz, $^{3}J_{HH}$ = 7.6 Hz, 1H, 5), 1.52 (dd, $^{2}J_{HH}$ = 13.9 Hz, $^{3}J_{HH}$ = 5.1 Hz, 1H, 5), 3.01 (ddd, $^{2}J_{HH}$ = 14.2 Hz, $^{4}J_{HH}$ = 1.3 Hz, $^{2}J_{HP}$ = 20.2 Hz, 2H, 1), 3.65 (*ps*t, $^{2}J_{HH}$ = 8.2 Hz, $^{3}J_{HH}$ = 8.2 Hz, 1H, 3), 3.99 (m, 1H, 4), 4.27 (dd, $^{2}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 9.3 Hz, 1H, 3), 7.33-7.35 (m, 6H, 9/11), 7.42-7.46 (m, 4H, 10). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K) δ = 28.2 (d, $^{1}J_{CP}$ = 18.7 Hz, 1), 30.0 (7), 30.4 (6), 50.8 (5), 64.1 (4), 74.7 (3),128.7 (d, $^{4}J_{CP}$ = 6.8 Hz, 11), 128.9 (d, $^{2}J_{CP}$ = 54.8 Hz, 9), 129.0 (d, $^{2}J_{CP}$ = 54.9 Hz, 9'), 132.9 (d, $^{3}J_{CP}$ = 19.5 Hz, 10), 133.1 (d, $^{1}J_{CP}$ = 19.5 Hz, 10'), 138.4 (d, $^{1}J_{CP}$ = 14.3 Hz, 8/8'), 163.3. **^{31}P{^{1}H} NMR** (202.5 MHz, $CDCl_3$, 300K) δ = -17.0.

(*S*)-2-[(Diphenylphosphanyl)-methyl]-4-phenyl-4,5-dihydro-oxazole (78)

The product was obtained according to *general procedure 6* from protected ligand **66** (180 mg, 501 μmol) in diethylamine (1 mL) in 1 day. Evaporation of the volatiles afforded the product as a colorless oil. The ligand was used without further purification.

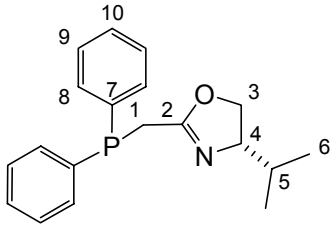


$C_{22}H_{20}NOP$ (345.37)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 3.19 (2×dd, $^{2}J_{HH}$ = 14.4 Hz, $^{2}J_{HP}$ = 1.1 Hz, 2H, 1), 3.91 (*ps*t, $^{2}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 8.3 Hz, 1H, 3), 4.53 (dd, $^{2}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 10.2 Hz,1H, 3), 5.08 (t_{br}, 1H, 4), 6.96 (m, 2H, 6), 7.23-7.25 (m, 3H, 7/8), 7.36-7.38 (m, 6H, 10/12), 7.47-7.54 (m, 4H, 11). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 28.3 (d, $^{1}J_{CP}$ = 19 Hz, 1), 70.2 (3), 75.4 (4), 126.9 (6), 127.6 (8), 128.8 (7), 128.8 (d, $^{2}J_{CP}$ = 3.1 Hz, 10), 128.9 (d, $^{2}J_{CP}$ = 3.6 Hz, 10'), 129.3 (d, $^{4}J_{CP}$ = 24.1, 12/12'), 132.9 (d, $^{3}J_{CP}$ = 19.5 Hz, 11), 133.3 (d, $^{3}J_{CP}$ = 20.0 Hz, 11'), 138.0 (d, $^{1}J_{CP}$ = 30 Hz, 9), 143.0 (5), 165.6 (d, $^{2}J_{CP}$ = 7.5 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = -17.1.

(*S*)-2-[Diphenylphosphanyl-methyl]-4-isopropyl-4,5-dihydro-oxazole (79)

The product was obtained according to *general procedure 6* from protected ligand **67** (317 mg, 975 μmol) in diethylamine (3 mL) in 1 day. Evaporation of the volatiles afforded the product as a colorless oil. The ligand was used without further purification.

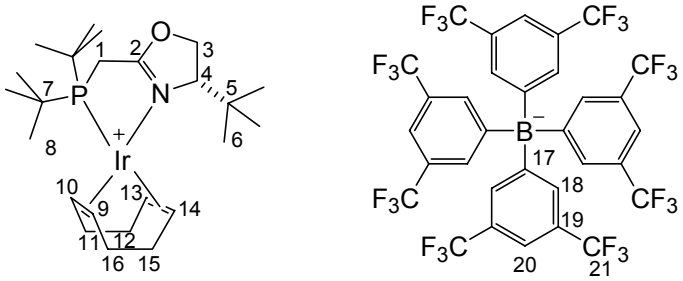


$C_{19}H_{22}NOP$ (311.36)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.75 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, 6), 0.81 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, 6'), 1.54 (m, $^{3}J_{HH}$ = 6.8 Hz, 1H, 5), 3.03 (dd, $^{2}J_{HH}$ = 14.1 Hz, $^{2}J_{HP}$ = 22.5 Hz, 2H, 1), 3.76 (m, 1H, 4), 3.83 (*ps*t, $^{3}J_{HH}$ = 8.1 Hz, $^{2}J_{HH}$ = 8.8 Hz, 1H, 3), 4.13 (dd, $^{3}J_{HH}$ = 9.3 Hz, $^{2}J_{HH}$ = 8.1 Hz, 1H, 3), 7.33-7.34 (m, 6H, 8, 10), 7.42-7.48 (m , 4H, 9). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 18.3 (6), 18.8 (6'), 18.4 (d, $^{1}J_{CP}$ = 18.5 Hz, 1), 33.0 (5), 70.6 (3), 72.8 (4), 128.7 (d, $^{2}J_{CP}$ = 6.8 Hz, 8/8'), 129.1 (d, $^{4}J_{CP}$ = 7.7 Hz, 10/10'), 132.9 (d, $^{3}J_{CP}$ = 19.3 Hz, 9), 133.2 (d, $^{3}J_{CP}$ = 19.4 Hz, 9'), 138.3 (d, $^{1}J_{CP}$ = 14.6 Hz, 7), 138.5 (d, $^{1}J_{CP}$ = 15.0 Hz, 7'), 163.9 (d, $^{2}J_{CP}$ = 7.9 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = -20.7.

(*S*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-*tert*-butyl)-4,5-dihydrooxazoline-η^4-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (80)

The reaction was performed according to *general procedure 7* from ligand **68** (40 mg, 140 µmol), $[Ir(cod)Cl]_2$ (44 mg, 65 µmol) and $NaBAr_F$ (149 mg, 168 µmol) in dichloromethane (3 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (188 mg, 80%). Single crystals could be obtained from dichloromethane /hexane.

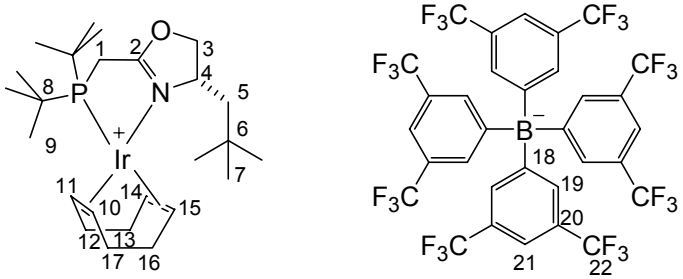


$C_{56}H_{56}BF_{24}IrNOP$ (1449.01)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 1.00 (s, 9H, 1), 1.31 (d, $^3J_{HP}$ = 14.5 Hz, 9H, 8), 1.43 (d, $^3J_{HP}$ = 14.3 Hz, 9H, 8'), 1.45 (m, 2×1H, cod, 15/12), 1.93 (m, 1H, cod, 15), 2.00 (m, 1H, cod, 11), 2.11 (m, 1H, cod, 12), 2.22 (m, 1H, cod, 11), 2.41 (m, 2H, cod, 16), 2.58 (ddd, $^2J_{HH}$ = 19.5 Hz, $^2J_{HP}$ = 5.5 Hz, 1.5 Hz, 1H, 6), 3.36 (dd, $^2J_{HH}$ = 19.5 Hz, $^2J_{HP}$ = 8.5 Hz, 1H, 6), 3.67 (dt, $^3J_{HH}$ = 8.2 Hz, 1.8 Hz, 1H, 3), 3.97 (m, 1H, cod, 14), 4.30 (m, 1H, cod, 9), 4.47 (dd, $^2J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, 4), 4.82 (dd, $^2J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 2.1 Hz, 1H, 4), 4.82 (m, 1H, cod, 13), 4.99 (tbr, 1H, cod, 10), 7.56 (s, 4H, 20), 7.72 (t, 8H, 22). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 22.5 (d, $^2J_{CP}$ = 25.0 Hz, 6), 24.7 (15), 25.8 (1), 29.1 (12), 29.7 (d, $^2J_{CP}$ = 3.5 Hz, 8), 30.1 (d, $^2J_{CP}$ = 5.0 Hz, 8), 33.8 (11), 35.4 (d, $^1J_{CP}$ = 21.2 Hz, 7), 35.6 (2), 37.6 (16), 37.9 (d, $^1J_{CP}$ = 15.3 Hz, 7), 57.8 (14), 68.9 (13), 70.2 (3), 75.5 (4), 80.4 (d, $^2J_{CP}$ = 16.6 Hz, 9), 91.6 (d, $^2J_{CP}$ = 6.1 Hz, 10), 117.8 (q, $^3J_{CF}$ = 4 Hz, 20), 125.0 (q, $^1J_{CF}$ = 270 Hz, 21), 129.2 (q, $^2J_{CF}$ = 25.7 Hz 19), 135.1 (s, 18), 162.1 (q, $^1J_{CB}$ = 50 Hz, 17), 184.7 (d, $^2J_{CP}$ = 16.4Hz, 5). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 42.8. **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3446.3m_{br}, 2968.1m, 2889.5w, 1602.2m, 1474.5w, 1355.1s, 1277.4s, 1161.4s, 1124.7s, 997.5w, 938.1w, 928.1w, 899.8w, 887.3m, 838.3w, 745.1w, 716.0m, 682.2m, 668.8m, 581.0w, 453.4w. **MS** (+ESI) m/z: 587.3 (M^+, 23.2), 586.3 (M^+, 100), 584.3 (M^+, 60.2). **m.p.** 228-230°C. $[\alpha]_D^{20}$: +82° (c = 0.1, $CHCl_3$). **EA** %found (calcd): C: 46.32 (46.42), H: 3.90 (3.73), N: 0.97 (1.08), O: 1.10 (1.32).

(*S*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-*neo*-pentyl)-4,5-dihydrooxazole-η^4-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (81)

The reaction was performed according to *general procedure 7* from ligand **69** (118 mg, 394 µmol), $[Ir(cod)Cl]_2$ (127 mg, 190 µmol) and $NaBAr_F$ (452 mg, 510 µmol) in dichloromethane (5 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (458 mg, 83%).



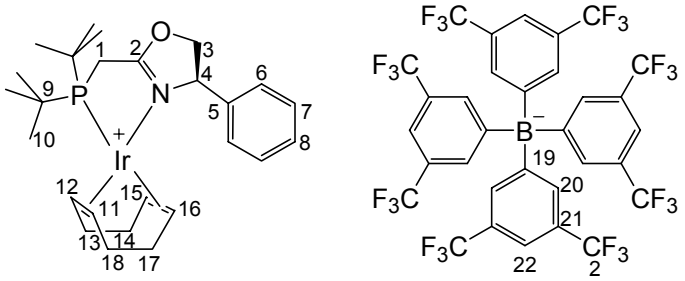
$C_{57}H_{58}BF_{24}IrNOP$ (1463.04)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K) δ: 0.96 (s, 9H, 7), 1.31 (d, $^3J_{HP}$ = 14.5 Hz, 9H, 9), 1.35 (d , $^3J_{HP}$ = 14.5 Hz, 9H, 9'), 1.49 (dd, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 11.3 Hz, 1H, 5), 1.52-1.59 (m, 2H, 13/16), 1.59 (d, $^2J_{HH}$ = 14.1 Hz, 1H, 5), 2.00 (m, 1H, 16), 2.13 (m, 2H, 12/13), 2.71 (m, 1H, 12), 2.42 (m, 2H, 17), 2.57 (ddd, $^2J_{HH}$ = 18.9 Hz, $^2J_{HP}$ = 5.3 Hz, 1.8 Hz, 1), 3.16 (dd, $^2J_{HH}$ = 18.9 Hz, $^2J_{HP}$ = 11.3 Hz, 1H, 1), 3.99 (m, 2H, 14/4), 4.59 (t, $^{2/3}J_{HH}$ = 9.2 Hz, 1H, 3), 4.59 (m, 2H, 10/15), 4.65 (dd, $^2J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, 3), 4.86 (m, 1H, 11), 7.56 (s, 4H, 20), 7.72 (t, 8H, 22). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K) δ: 22.6 (d, $^1J_{CP}$ = 24.8 Hz, 1), 26.3 (d, $^3J_{CP}$ = 2. 0 Hz, 16), 29.3 (d, $^2J_{CP}$ = 3.7 Hz, 9'), 29.9 (d, $^3J_{CP}$ = 1.6 Hz, 13), 30.0 (7), 30.1 (d, $^2J_{CP}$ = 3.2 Hz, 9), 30.9 (6), 32.2 (d, $^3J_{CP}$ = 1.4 Hz, 12), 35.2 (d, $^1J_{CP}$ = 20.3 Hz, 8'), 36.0 (d, $^3J_{CP}$ = 3.9 Hz, 17), 39.6 (d, $^1J_{CP}$ = 16.3 Hz, 8), 49.1 (5), 60.8 (14), 62.5 (4), 65.4 (15), 78.8 (3), 84.2 (d, $^2J_{CP}$ = 13.0 Hz, 10), 91.3 (d, $^2J_{CP}$ = 11.4 Hz, 11), 117.8 (q, $^3J_{CF}$ = 4 Hz, 21), 125.0 (q, $^1J_{CF}$ = 270 Hz, 22), 129.2 (q, $^2J_{CF}$ = 25.7 Hz 20), 135.1 (s, 19), 162.1 (q, $^1J_{CB}$ = 50 Hz, 18), 185.3 (d, $^2J_{CP}$ = 15.3 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K) δ: 49.7. **MS** (+ESI) m/z : 601.4 (M^+, 25.1), 600.4 (M^+, 100), 599.5 (M^+, 14.1), 598.5 (M^+, 59.3).

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3421m_{br}, 2968m, 1611m, 1476w, 1423w, 1357s, 1279s, 1129s, 1004w, 950w, 889m, 839w, 745w, 714m, 675m. **m.p.** 128-129°C. $[\alpha]_D^{20}$: +45° (c = 0.13, $CHCl_3$). **EA** %found (calcd) C: 46.89 (46.80), H: 3.99 (4.00), N: 1.20 (0.96).

(*R*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-phenyl)-4,5-dihydrooxazoline -η^4-(1,5-cyclo-octadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (82)

The reaction was performed according to *general procedure 7* from ligand **70** (68 mg, 222 μmol), $[Ir(cod)Cl]_2$ (74.3 mg, 110 μmol) and $NaBAr_F$ (252 mg, 290 μmol) in dichloromethane (3 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (256 mg, 79%). Single crystals could be obtained from dichloromethane /hexane.

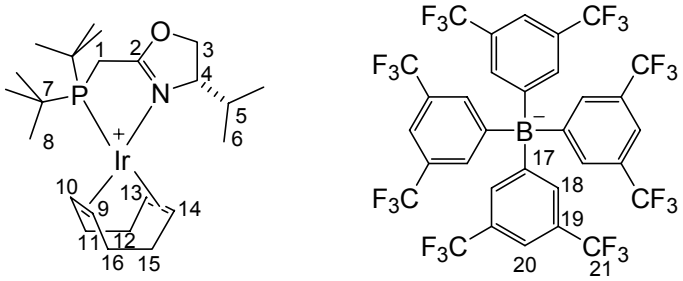


$C_{58}H_{52}BF_{24}IrNOP$ (1469.01)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 1.37 (d, $^3J_{HP}$ = 14.4 Hz, 9H, 10), 1.41 (d, $^3J_{HP}$ = 14.3 Hz, 9H, 10'), 1.6 (m, 2×1H, cod), 1.67 (m, 1H, cod), 1.9 (m, 1H, cod), 2.02 (m, 1H, cod), 2.09 (m, 1H, 18), 2.14 (m, 1H, cod), 2.2 (m, 1H, cod), 2.82 (ddd, $^2J_{HH}$ = 19.0 Hz, $^2J_{HP}$ = 7 Hz, 2 Hz, 1H, 1), 3.18 (dd, $^2J_{HH}$ = 18.9 Hz, $^2J_{HP}$ = 8.5 Hz, 1H, 1), 3.97 (m, 1H, 11), 4.21 (m, 1H, 15), 4.30 (m, 1H, 16), 4.57 (dd, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, 3), 4.78 (m, 1H, 12), 5.03 (*pst*, $^2J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 10.1 Hz, 1H, 3), 5.26 (ddd, 1H, 4), 7.15 (m, 2H, 6), 7.44 (m, 3H, 7/8), 7.56 (s, 4H, 22), 7.72 (t, 8H, 20). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 22.8 (d, $^2J_{CP}$ = 24.1 Hz, 1), 28.5 (17), 29.6 (14), 30.1 (d, $^2J_{CP}$ = 3.8 Hz, 10), 30.4 (d, $^2J_{CP}$ = 3.8 Hz, 10), 31.4 (cod 13), 33.7 (18), 37.1 (d, $^1J_{CP}$ = 19.2 Hz, 9'), 38.4 (d, $^1J_{CP}$ = 18.4 Hz, 9), 62.9 (15), 63.1 (16), 68.5 (4), 81.1 (3), 88.8 (d, $^2J_{CP}$ = 11 Hz, 11), 89.7 (d, $^2J_{CP}$ = 11 Hz, 12), 117.8 (d, $^4J_{CB}$ = 3.8 Hz, 22), 125.0 (q, $^1J_{CF}$ = 273 Hz, 23), 126.6 (6), 129.2 (d, $^2J_{CF}$ = 32 Hz, 21) 130.0 (8), 130.1 (7), 135.1 (20), 138.5 (5), 162.1 (q, $^1J_{CB}$ = 49.5 Hz, 19), 188.3 (2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 44.7. **MS** (+ESI) m/z: 607.35 (M^+, 26.5), 606.18 (M^+, 100), 604.25 (M^+, 59.8). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3426.6m_{br}, 2973.5m, 2361.1w, 1605.3m, 1475.5w, 1421.7w, 1356.6s, 1278.0s, 1130.0s, 1004.1w, 941.6w, 888.8m, 836.7w, 765.4w, 743.5w, 711.0m, 673.7m. **m.p.** 150°C. $[\alpha]_D^{20}$: -54° (c = 0.1, $CHCl_3$). **EA** %found (calcd): C: 47.28 (47.42), H: 3.38 (3.57), N: 1.05 (0.95).

(*S*)-2-[(Di-*tert*-butyl-phosphanyl)-methyl]-4-*iso*-propyl)-4,5-dihydrooxazole-η^4-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (83)

The reaction was performed according to *general procedure 7* from ligand **71** (181 mg, 608 µmol), $[Ir(cod)Cl]_2$ (201 mg, 300 µmol) and $NaBAr_F$ (700 mg, 790 µmol) in dichloromethane (8 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (827 mg, 96%). Single crystals could be obtained from dichloromethane /hexane.

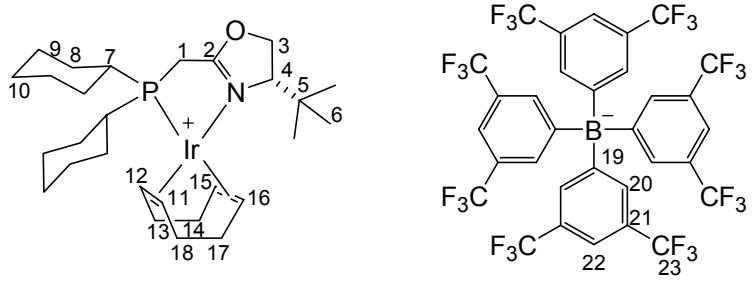


$C_{55}H_{54}BF_{24}IrNOP$ (1434.99)

^{1}H NMR (400.1 MHz, CD_2C_2, 300K) δ = 0.78 (d, $^3J_{HH}$ = 6.6 Hz, 3H, 1), 0.96 (d, $^3J_{HH}$ = 7.1 Hz, 3H, 1'), 1.33 (d, $^3J_{HP}$ = 14.4 Hz, 3H, 8), 1.37 (d, $^3J_{HP}$ = 14.4 Hz, 3H, 8'), 1.60 (m, 2H, 16/11), 2.01 (m, 3H, 2/15/16), 2.1-2.3 (m, 3H, 15/11/12), 2.3-2.45 (m, 1H, 12), 2.64 (ddd, $^2J_{HH}$ = 19.2 Hz, $^2J_{HP}$ = 1.8 Hz , 6.3 Hz, 6), 3.10 (dd, $^2J_{HH}$ = 19.2 Hz, $^2J_{HP}$ = 8.6 Hz, 6), 3.92 (m, 1H, 3), 4.12 (m, 1H, 14), 4.49 (*ps*t, $^2J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 9.3 Hz, 4), 4.50 (m, 1H, 9), 4.60 (m, 1H, 13), 4.71 (dd, $^2J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 3.5 Hz, 4), 4.86 (m, 1H, 10), 7.56 (s, 4H, 20), 7.72 (*ps*t, 8H, 18). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2C_2, 300K) δ = 14.6 (1), 19.4 (1'), 22.5 (d, $^1J_{CP}$ = 24.7 Hz, 6), 26.9 (*ps*d, 16/16'), 29.6 (d, $^2J_{CP}$ = 3.8 Hz, 8), 30.0 (d, $^2J_{CP}$ = 4.5 Hz, 8'), 30.3 (*ps*d, 11/11'), 31.9 (2), 32.2 (*ps*d, 15/15'), 35.8 (*ps*d, 12/12'), 36.4 (d, $^1J_{CP}$ = 19.9 Hz, 7), 38.4 (d, $^1J_{CP}$ = 16.8 Hz, 7'), 61.5 (14), 66.2 (13), 68.3 (3), 73.5 (4), 82.1 (d, $^2J_{CP}$ = 13.5 Hz, 9), 91.1 (d, $^2J_{CP}$ = 9.1 Hz, 10), 117.8 (q, $^3J_{CF}$ = 4 Hz, 20), 125.0 (q, $^1J_{CF}$ = 270 Hz, 21), 129.2 (q, $^2J_{CF}$ = 25.7 Hz 19), 135.1 (s, 18), 162.1 (q, $^1J_{CB}$ = 50 Hz, 17), nd. **^{31}P{^{1}H} NMR** (162 MHz, CD_2C_2, 300K) δ = 45.3. **+ESI, m/e :** 573.4 (M^+, 21.8), 572.4 (M^+, 100), 571.4 (M^+, 14.7), 570.4 (M^+, 59.8). **IR (KBr):** $\tilde{\nu}$ [cm^{-1}] = 3426m_{br}, 2969m, 1611m, 1476w, 1423w, 1358s, 1281s, 1164s, 1128s, 1004w, 938w, 889m, 837w, 746w, 714w, 675m. **m.p.** 188-190°C. $[\alpha]_D^{20}$: +49° (c = 0.2 in $CHCl_3$). **EA** %found (calcd): C: 45.91 (46.04), H: 3.74 (3.79), N: 1.16 (0.98)

(*S*)-2-[(Di-cyclohexyl-phosphanyl)-methyl]-4-*tert*-butyl)-4,5-dihydrooxazole-η^4-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (84)

The reaction was performed according to *general procedure 7* from ligand **72** (140 mg, 398 µmol), $[Ir(cod)Cl]_2$ (121 mg, 180 µmol) and $NaBAr_F$ (445 mg, 500 µmol) in dichloromethane (5 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (428 mg, 78%).

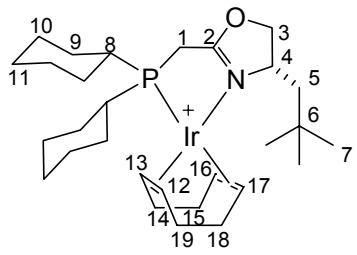


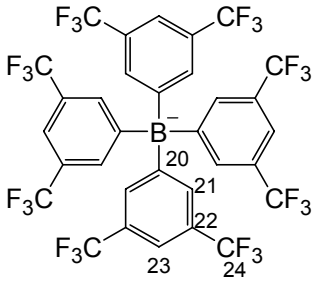
$C_{60}H_{60}BF_{24}IrNOP$ (1501.09)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K) δ = 0.98 (s, 9H, 6), 1.25-1.39 (m, 10H, Cy_{eq}), 1.50-1.59 (m, 2H, $cod_{a,b}$), 1.64 (m_{br}, 1H, Cy_{eq}), 1.77-1.95 (m, 9H, Cy_{ax}), 1.96-2.11 (m, 3H, $cod_{a,c,b}$), 2.11-2.18 (m, 2H, 7), 2.19 (m, 1H, cod_c), 2.34 (m_{br}, 1H, Cy_{ax}), 2.40 (m, 2H, cod_d), 2.67 (ddd, $^2J_{HP}$ = 6.0 Hz, $^2J_{HH}$ = 19.6 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, 1), 3.12 (dd, $^2J_{HP}$ = 9.2 Hz, $^2J_{HH}$ = 19.5 Hz, 1H, 1) 3.44 (m, 1H, 15), 3.64 (d, = 8.1 Hz, 1H, 4), 4.36 (m, 1H, 11), 4.46 (dd, $^3J_{HH}$ = 8.3, $^2J_{HH}$ = 9.8 Hz, 1H, 3), 4.61 (m, 1H, 16), 4.80, (dd, $^3J_{HH}$ = 2.1, $^2J_{HH}$ = 9.8 Hz, 1H, 3), 5.10 (m_{br}, 1H, 12), 7.56 (s, 4H, 22), 7.72 (s, 8H, 20). **^{13}C{^{1}H} NMR** (100.8 MHz, CD_2Cl_2, 300K) δ = 21.3 ($^1J_{CP}$ = 28.2 Hz, 1), 24.9 (d, cod_a), 25.6 (6), 25.9 (Cy), 26.2 (Cy), 26.5-26.7 (dd, 2×CH_2), 26.9 (Cy), 27.0 (d, Cy), 27.4 (d, Cy), 28.1 (Cy), 28.4 (Cy), 29.4 (cod_b), 30.8 (d, $^1J_{CP}$ = 29.4 Hz, 7), 30.9 (Cy), 33.6 (cod_c), 35.2 (5), 35.6 (d $^1J_{CP}$ = 24.5 Hz, 7'), 37.6 (d, $^3J_{CP}$ = 4.2 Hz, cod_d), 58.0 (15), 66.1 (16), 70.8 (4), 75.3 (3), 84.2 (d, $^2J_{CP}$ = 15.5 Hz, 11), 94.7 (d, $^2J_{CP}$ = 7.7 Hz, 12), 117.8 (t, $^3J_{CF}$ = 4 Hz, 22), 124.9 (q, $^1J_{CF}$ = 270 Hz, 23), 129.2 (qq, $^2J_{CF}$ = 28.8 Hz, $^3J_{BC}$ = 3 Hz, 21), 135.2 (20), 162.1 (q, $^1J_{BC}$ = 50 Hz, 19), 186.2 (d, $^2J_{CP}$ = 17.2 Hz, 2). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K) δ = 25.3. **MS** (+ESI) m/z: 639.4 (M^+, 28.2), 638.4 (M^+, 100), 637.4 (M^+, 22.5), 636.4 (M^+, 51.1). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3426br, 2940m, 2863w, 1590m, 1451w, 1356s, 1277s, 1130s, 997w, 930w, 889m, 837w, 745w, 713w, 675m. **m.p.** 94°C. $[\alpha]_D^{20}$: +54° (c = 0.18, $CHCl_3$).

(*S*)-2-[(Di-cyclohexyl-phosphanyl)-methyl]-4-neopentyl)-4,5-dihydrooxazole-η^4-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (85)

The reaction was performed according to *general procedure 7* from ligand **73** (155 mg, 441 µmol), $[Ir(cod)Cl]_2$ (142 mg, 210 µmol) and $NaBAr_F$ (501 mg, 570 µmol) in dichloromethane (5 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (452 mg, 67%).



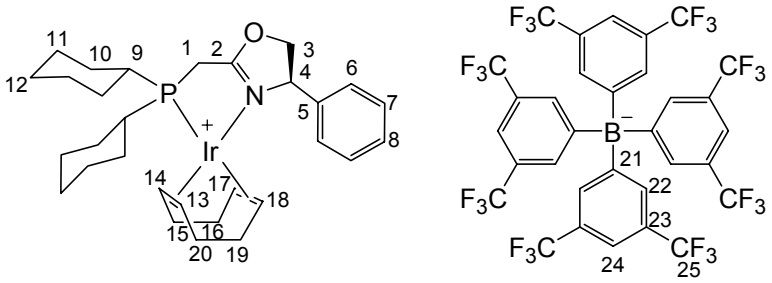


$C_{61}H_{62}BF_{24}IrNOP$ (1515.11)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.96 (s, 9H, 7), 1.29 (m, 1H, cod_a/9H, Cy), 1.52 (m, 1H, cod_a/2H, 5), 1.65 (m, 2H, cod_b/Cy), 1.78 (m, 3H, Cy), 1.88 (m, 5H, Cy), 2.11-2.18 (m, 2H, $cod_{b,c}$/1H, 8/2H, Cy), 2.19-2.3 (m, 2H, cod_c/8), 2.37 (m, 2H, cod_d), 2.69 (ddd, $^2J_{HH}$ = 19.0 Hz, $^2J_{HP}$ = 16.6 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, 1), 2.95 (dd, $^2J_{HH}$ = 19.0 Hz, $^2J_{HP}$ = 9.6 Hz, 1H, 1), 3.65 (m, 1H, 16), 3.97 (m, 1H, 4), 4.31 (m, 1H, 17), 4.60 (*pst*, $^2J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, 3), 4.62-4.68 (m, 2H, 3/12), 4.99 (m, 1H, 13), 7.57 (s, 4H, 23), 7.72 (*pst*, $^3J_{HB}$ = 2 Hz, 8H, 21). **^{13}C{^{1}H} NMR** (100.8 MHz, CD_2Cl_2, 300K): δ = 21.7 (d, $^1J_{CP}$ = 27.6 Hz, 1), 26.1 (Cy), 26.2 (Cy), 26.7-27.0 (Cy), 27.7 (Cy), 28.5 (Cy), 29.1 (Cy), 29.7 (cod_a), 30.0 (7), 30.2 (cod_b), 30.9 (Cy), 31.4 (d, $^1J_{CP}$ = 28.0 Hz, 8), 32.1 (cod_c), 36.0 (cod_d), 36.9 (d, $^1J_{CP}$ = 25.7 Hz, 8'), 49.4 (5), 60.5 (16), 61.4 (4), 63.4 (17), 79.0 (3), 87.4 (d, $^2J_{CP}$ = 13.0 Hz, 12), 94.4 (d, $^2J_{CP}$ = 9.6 Hz, 13), 117.8 (t, $^3J_{CF}$ = 4 Hz, 23), 125.0 (q, $^1J_{CF}$ = 270 Hz, 24), 129.2 (qq, $^2J_{CF}$ = 28.8 Hz, $^3J_{BC}$ = 3 Hz, 22), 135.2 (21), 162.1 (q, $^1J_{BC}$ = 50 Hz, 20), 185.5 (d, $^2J_{CP}$ = 16.9 Hz, 2). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 28.9. **MS** (+ESI) m/z: 653.5 (M^+, 28.8), 652.5 (M^+, 100), 651.6 (M^+, 15.2), 650.7 (M^+, 58.2). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3426m_{br}, 2942m, 2863w, 1604m, 1476w, 1451w, 1424w, 1357s, 1279s, 1126s, 1004w, 950w, 889m, 839w, 744w, 713m, 676m. **m.p.** 72°C. $[\alpha]_D^{20}$: +50° (c = 0.13, $CHCl_3$). **EA** % found (calcd): C: 48.31 (48.36), H: 4.10 (4.12), N: 1.14 (0.92).

(*R*)-2-[(Di-cyclohexyl-phosphanyl)-methyl]-4-phenyl)-4,5-dihydrooxazoline-η^4-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (86)

The reaction was performed according to *general procedure 7* from ligand **74** (70 mg, 196 µmol), $[Ir(cod)Cl]_2$ (64 mg,95 µmol) and $NaBAr_F$ (226 mg,255 µmol) in dichloromethane (4 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (232 mg, 80%).

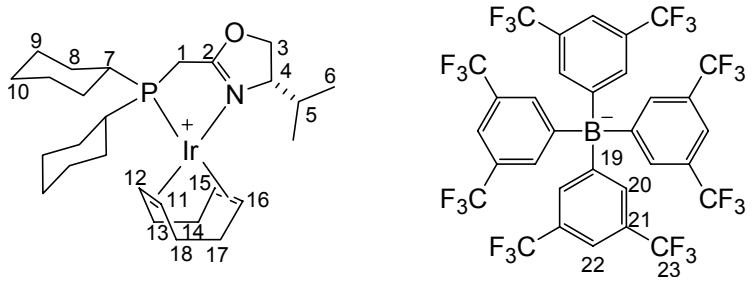


$C_{62}H_{56}BF_{24}IrNOP$ (1521.08)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 1.14-1.48 (m, 11H, Cy/15), 1.56 (m, 1H, 15), 1.67 (m, 1H, 16), 1.71-1.85 (m, 5H, Cy), 1.86-1.99 (m, 6H, Cy/20), 2.04-2.1 (m, 3H, 16/16'/19), 2.16-2.25 (m, 4H, 9/9'/19'/20), 2.82 (dd, $^2J_{HP}$ = 7.6 Hz $^2J_{HH}$ = 19.7 Hz, 1H, 1), 3.06 (dd, $^2J_{HP}$ = 8.6 Hz, $^2J_{HH}$ = 19.2 Hz, 1H, 1), 3.83 (m, 1H, 18), 3.93 (m, 1H, 14), 4.0 (m, 1H, 17), 4.55 (dd, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 7.1, 1H, 3), 4.88 (m, 1H, 13), 5.02, (*pst*, $^2J_{HH}$ = 9.4, $^3J_{HH}$ = 10.1 Hz, 1H, 3), 5.23 (m, 1H, 4), 7.14 (s, 2H, Ph), 7.43 (m, 3H, Ph), 7.56 (s, 4H, 24), 7.72 (*pst*, 8H, 22). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 21.6 ($^1J_{CP}$ = 27.3 Hz, 1), 26.0-28.2 (Cy), 28.4 (15), 29.1 (Cy), 30.7 (20), 31.2 (d, $^3J_{CP}$ = 2.4 Hz, 16), 33.1 (d, $^1J_{CP}$ = 27.7 Hz, 9), 34.5 (d, $^3J_{CP}$ = 3.5 Hz, 19), 35.5 (d, $^1J_{CP}$ = 27 Hz, 9'), 60.8 (18), 61.4 (17), 68.2 (4), 81.1 (3), 92.2 (d, $^2J_{CP}$ = 11.4 Hz, 14), 93.6 (d, $^2J_{CP}$ = 10.7 Hz, 13), 117.8 (d, $^4J_{CB}$ = 3.8 Hz, 24), 124.9 (q, $^1J_{CF}$ = 273 Hz, 25), 126.3 (6), 129.1 (q, $^2J_{CF}$ = 32 Hz, 23) 130.0 (7/8), 135.2 (22), 138.7 (5), 162.1 (q, $^1J_{CB}$ = 49.5 Hz, 21), 188.1 (d, $^2J_{CP}$ = 17.3 Hz, 2). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 26.2. **MS** (+ESI) m/z: 659.3 (M^+, 29.2), 658.3 (M^+, 100), 657.3 (M^+, 19.8), 656.3 (M^+, 62.4). **m.p.** 116-118°C. $[\alpha]_D^{20}$: -37° (c = 0.102, $CHCl_3$).

(*S*)-2-[(Di-cyclohexyl-phosphanyl)-methyl]-4-isopropyl)-4,5-dihydrooxazoline-η4-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (87)

The reaction was performed according to *general procedure 7* from ligand **75** (116 mg, 359 µmol), $[Ir(cod)Cl]_2$ (117 mg, 175 µmol) and $NaBAr_F$ (404 mg, 467 µmol) in dichloromethane (10 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (410mg, 78%).

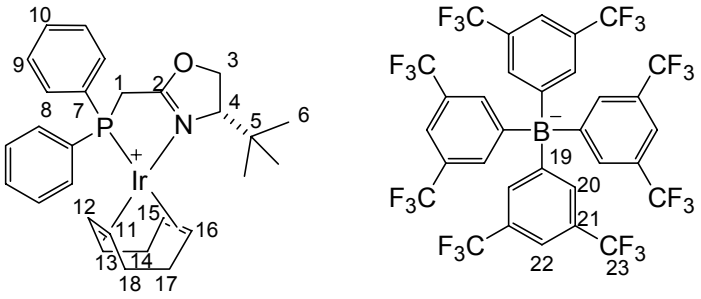


$C_{59}H_{58}BF_{24}IrNOP$ (1487.06)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.77 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, 6), 0.95 (d, $^{3}J_{HH}$ = 7.1 Hz, 3H, 6), 1.2-1.41 (m, 1H, cod_b/11H, Cy), 1.59-1.69 (m, 1H, cod_b/ 2H, Cy), 1.72-1.82 (m, 3H, Cy), 1.84-1.97 (m, 3H, Cy, 1H cod_a), 2.01 (m, 1H, 5), 1.97-2.12 (m, 1H, cod_c/2H, Cy), 2.12 -2.3 (m, 3H, $cod_{a,c,d}$ /1H, 7), 2.31-2.42 (m, 2H, cod_d/7'), 2.67 (ddd, $^{2}J_{HH}$ = 19.3 Hz, $^{2}J_{HP}$ = 17.5 Hz, $^{5}J_{HH}$ = 1.8 Hz, 1H, 1), 2.95 (dd, $^{2}J_{HH}$ = 19.3 Hz, $^{2}J_{HP}$ = 9.1 Hz, 1H, 1), 3.69 (m, 1H, 15), 3.94 (m, 1H, 4), 4.33 (m, 1H, 16), 4.48 (*pst*, $^{2}J_{HH}$ = 9.4 Hz, $^{3}J_{HH}$ = 9.4 Hz, 1H, 3), 4.60 (m, 1H, 11), 4.68 (dd, $^{2}J_{HH}$ = 9.6 Hz, $^{3}J_{HH}$ = 3.7 Hz, 1H, 3), 5.00 (m, 1H, 12), 7.56 (s, 4H, 22), 7.72 (*pst*, $^{3}J_{HB}$ = 2 Hz, 8H, 20). **^{13}C{^{1}H} NMR** (100.8 MHz, CD_2Cl_2, 300K): δ = 14.2 (6), 19.0 (6), 21.3 (d, $^{1}J_{CP}$ = 27.9 Hz, 1), 26.1 (Cy), 26.5-27 (Cy), 27.8 (Cy), 28.5 (cod_a), 28.7 (Cy), 29.6 (cod_b), 30.3 (d, Cy), 32.0 (5), 32.2 (cod_c), 32.3 (d, $^{1}J_{CP}$ = 28.3 Hz, 7), 36.1 (d, $^{1}J_{CP}$ = 26 Hz, 7'), 36.1 (d, $^{3}J_{CP}$ = 3.7 Hz, cod_d), 60.1 (15), 63.9 (16), 68.6 (4), 73.4 (3), 86.9 (d, $^{2}J_{CP}$ = 13.5 Hz, 11), 94.7 (d, $^{2}J_{CP}$ = 9.4 Hz, 12), 117.8 (t, $^{3}J_{CF}$ = 4 Hz, 22), 125 (q, $^{1}J_{CF}$ = 270 Hz, 23), 129.2 (qq, $^{2}J_{CF}$ = 28.8 Hz, $^{3}J_{BC}$ = 3 Hz, 21), 135.2 (20), 162.1 (q, $^{1}J_{BC}$ = 50 Hz, 19), 186.2 (d, $^{2}J_{CP}$ = 17.6 Hz, 2). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 162 MHz, 300K): δ = 26.5. **MS** (+ESI) m/z: 625.3 (M^+, 27.6), 624.3 (M^+, 100), 623.3 (M^+, 15.8), 622.3 (M^+, 58.6). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3448m_{br}, 2941m, 2862w, 1600m, 1452w, 1421w, 1356s, 1278s, 1129s, 1004w, 939w, 889m, 838w, 743w, 713m, 674m. **m.p.** 128-129°C. $[\alpha]_D^{20}$: +45° (c = 0.1, $CHCl_3$).

(*S*)-2-[(Diphenyl-phosphanyl)-methyl]-4-*tert*-butyl)-4,5-dihydrooxazole-η^4-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (88)

The reaction was performed according to *general procedure 7* from ligand **76** (96 mg, 294 μmol), $[Ir(cod)Cl]_2$ (97 mg, 145 μmol) and $NaBAr_F$ (335 mg, 382 μmol) in dichloromethane (5 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (278 mg, 77%). Single crystals could be obtained from dichloro-methane/hexane.

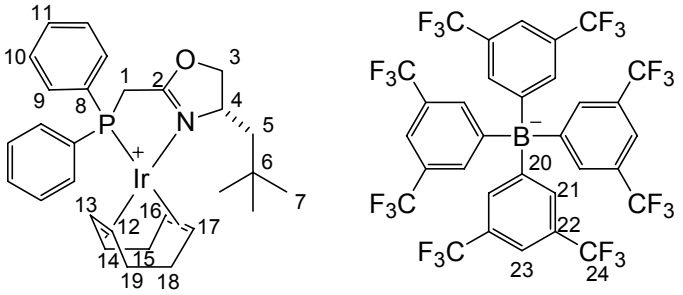


$C_{60}H_{48}BF_{24}IrNOP$ (1488.99)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.73 (s, 9H, 1), 1.53 (m, 1H, 17), 1.73 (m, 1H, 13), 1.96 (m, 1H, 17), 2.11 (m, 1H, 13), 2.25 (m, 1H, 18), 2.35 (m, 1H, 18), 2.47 (m, 1H, 14), 2.55 (m, 1H, 14), 2.92 (m, 1H, 16), 3.57 (ddd, $^2J_{HH}$ = 18.7 Hz, $^2J_{HP}$ = 1.7 Hz , 5.0 Hz, 1H, 6), 3.73 (d, $^3J_{HH}$ = 7.6 Hz, 1H, 3), 3.96 (dd, $^2J_{HH}$ = 18.7 Hz, $^2J_{HP}$ = 11.6 Hz , 1H, 6), 4.21 (m, 1H, 15), 4.51 (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 9.8 Hz, 1H, 4), 4.76 (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 1.5 Hz, 1H, 4), 4.87 (m, 1H, 12), 5.23 (m, 1H, 11), 7.31-7.36 (m, 2H, 8_a), 7.51-7.57 (m, 2H, 8_b / 1H, 10_c), 7.56 (s, 4H, 22), 7.59-7.62 (m, 2H, 9_d), 7.64-7.67 (m, 1H, 10_e), 7.72 (pst, 8H, 20), 7.79-7.84 (m, 2H, 9_f). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 25.1 (1), 26.2 (d, $^3J_{CP}$ = 2.6 Hz, 13), 29.3 (d, $^4J_{CP}$ = 2.0 Hz, 17), 31.5 (d, $^1J_{CP}$ = 34.2 Hz, 6), 33.1 (18), 34.9 (2), 36.6 (d, $^4J_{CP}$ = 4.7 Hz, 14), 63.2 (15), 64.1 (16), 71.7 (3), 75.1 (4), 89.3 (d, $^2J_{CP}$ = 15.2 Hz, 12), 97.4 (d, $^2J_{CP}$ = 9.3 Hz, 11), 117.8 (q, $^3J_{CF}$ = 4 Hz, 22), 125.0 (d, $^1J_{CP}$ = 56.4 Hz, 7), 125.0 (q, $^1J_{CF}$ = 270 Hz, 23), 129.0 (d, $^1J_{CP}$ = 56.4 Hz, 7'), 129.2 (q, $^2J_{CF}$ = 25.7 Hz 21), 130.0 (d, $^2J_{CP}$ = 11.1 Hz, 8_b), 130.2 (d, $^3J_{CP}$ =11.2 Hz, 9_d), 131.6 (d, $^2J_{CP}$ = 10.9 Hz, 8_a), 132.6 (d, $^4J_{CP}$ = 2.6 Hz, 10_c), 133.8 (d, $^4J_{CP}$ = 2.3 Hz, 10_e), 135.2 (s, 20), 135.8 (d, $^3J_{CP}$ = 24 Hz, 9_f), 162.1 (q, $^1J_{CB}$ = 50 Hz, 19), 180.3 (5). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 28.5. **MS** (+ESI) m/z: 626.3 (100.0), 624.5 (77.8), 627.3 (28.3), 625.4 (24.0), 628.4 (4.5). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3427m_{br}, 2969w, 2891sh, 240w, 2366w, 1601m, 1481w, 1434w, 1357s, 1279s, 1132s, 997w, 930w, 890m, 837m, 747w, 713m, 675m. **m.p.** 150-151°C. $[\alpha]_D^{20}$: +16° (c = 0.22, $CHCl_3$). **EA** % found (calcd): C: 48.24 (48.40), H: 3.14 (3.25), N: 1.15 (0.94).

(*S*)-2-[(Diphenyl-phosphanyl)-methyl]-4-neopentyl)-4,5-dihydrooxazole-η^4-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (89)

The reaction was performed according to *general procedure 7* from ligand **77** (80 mg, 240 μmol), $[Ir(cod)Cl]_2$ (75 mg, 111 μmol) and $NaBAr_F$ (266 mg, 300 μmol) in dichloromethane (3 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (216 mg, 65%).

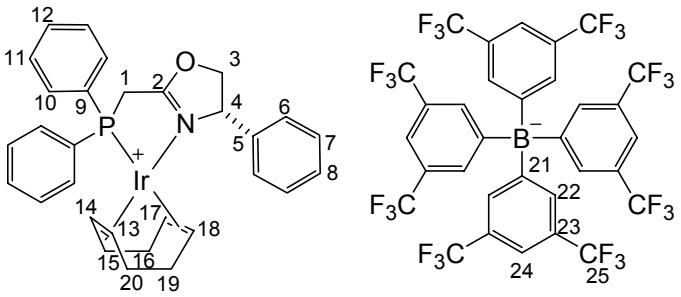


$C_{61}H_{50}BF_{24}IrNOP$ (1503.02)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.96 (s, 9H, 1), 1.42 (dd, $^{2}J_{HH}$ = 14.2 Hz, $^{3}J_{HH}$ = 11.3 Hz, 1H, 3), 1.57 (m, 1H, 15), 1.64 (d, $^{2}J_{HH}$ = 14.1 Hz, 1H, 3), 1.78 (m, 1H, 19), 1.96 (m, 1H, 15), 2.20 (m, 1H, 19), 2.30 (m, 1H, 14), 2.35 (m, 1H, 14), 2.41 (m, 1H, 18), 2.49 (m, 1H, 18), 3.00 (m, 1H, 16), 3.48 (ddd, $^{2}J_{HP}$ = 18.4 Hz, $^{2}J_{HH}$ = 7.0 Hz, $^{4}J_{HH}$ = 2.0 Hz, 1H, 7), 3.68 (dd, $^{2}J_{HP}$ = 18.4 Hz, $^{2}J_{HH}$ = 11.3 Hz, 1H, 7), 3.93 (m, 1H, 17), 4.11 (m, 1H, 4), 4.56 (dd, $^{2}J_{HH}$ = 9.3 Hz, $^{3}J_{HH}$ = 4.1 Hz, 1H, 5), 4.69 (*pst*, $^{2}J_{HH}$ = 9.1 Hz, $^{3}J_{HH}$ = 9.0 Hz, 1H, 5), 5.12 (m, 1H, 12), 5.19 (m, 1H, 13), 7.37-7.41 (m, 2H, 9_a), 7.52-7.55 (m, 3H, 9_b/10_d), 7.56 (s, 4H, 23), 7.57 (m, 2H, 11_c), 7.65 (m, 1H, 11_e), 7.72 (s, 8H, 21), 7.76-7.80 (m, 2H, 10_f). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 27.7 (d, $^{3}J_{CP}$ = 2.2 Hz, 19), 29.6 (15), 29.9 (1), 30.8 (2), 31.5 (d, $^{1}J_{CP}$ = 32.8 Hz, 7), 32.3 (14), 35.5 (d, $^{3}J_{CP}$ = 4.4 Hz, 18), 50.1 (3), 61.8 (4), 62.5 (17), 64.6 (16), 79.3 (5), 91.8 (d, $^{2}J_{CP}$ = 13.6 Hz, 12), 97.0 (d, $^{2}J_{CP}$ = 10.4 Hz, 13), 117.8 (q, $^{3}J_{CF}$ = 4 Hz, 23), 125.0 (q, $^{1}J_{CF}$ = 270 Hz, 24), 125.1 (d, $^{1}J_{CP}$ = 51.6 Hz, 8), 129.1 (d, $^{1}J_{CP}$ = 51.6 Hz, 8'), 129.2 (q, $^{2}J_{CF}$ = 25.7 Hz 22), 130.0 (d, $^{2}J_{CP}$ = 11.0 Hz, 9_b), 130.2 (d, $^{3}J_{CP}$ =11.3 Hz, 10_d), 131.8 (d, $^{2}J_{CP}$ = 11.0 Hz, 9_a), 132.6 (d, $^{4}J_{CP}$ = 2.5 Hz, 11_c), 133.5 (d, $^{4}J_{CP}$ = 2.4 Hz, 11_e), 135.2 (s, 21), 135.3 (d, $^{3}J_{CP}$ = 13.3 Hz, 10_f), 162.1 (q, $^{1}J_{CB}$ = 50 Hz, 20), 183.3 (d, $^{2}J_{CP}$ = 19.0 Hz, 6). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 24.1. **MS** (+ESI) m/z: 641.5 (M^+, 29.5), 640.5 (M^+, 100), 639. 4 (M^+, 18.1), 638.6 (M^+, 60.0). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3426m_{br}, 2964m, 1602m, 1477w, 1424w, 1357s, 1279s, 1127s, 1004w, 948w, 889m, 837w, 743w, 712m, 677m, 529w, 487w, 449w. **m.p.** 70°C. $[\alpha]_D^{20}$: +8° (c = 0.11, $CHCl_3$). **EA** % found (calcd): C 48.56 (48.75), H 3.44 (3.35), N 1.14 (0.93).

(*S*)-2-[(Diphenyl-phosphanyl)-methyl]-4-phenyl)-4,5-dihydrooxazole-η^{4}-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (90)

The reaction was performed according to *general procedure 7* from ligand **78** (120 mg, 346 μmol), $[Ir(cod)Cl]_2$ (113 mg, 168 μmol) and $NaBAr_F$ (399 mg, 450 μmol) in dichloromethane (8 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (148 mg, 29%).



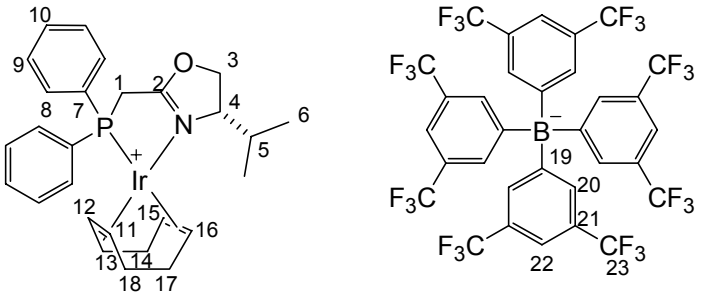
$C_{62}H_{44}BF_{24}IrNOP$ (1508.98)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 1.59 (m, 2H, 19/15), 1.71 (m, 1H, 15), 1.99 (m, 1H, 19), 2.15 (m, 3H, 16/20), 2.30 (m, 1H, 20), 3.12 (m, 1H, 18), 3.63 (m, 1H, 17), 3.63 (ddd, $^2J_{HH}$ = 18.3 Hz, $^2J_{HP}$ = 8.0 Hz, 2.3 Hz, 1H, 1), 3.82 (dd, $^2J_{HH}$ = 18.3 Hz, $^2J_{HP}$ = 11.0 Hz, 1H, 1), 4.28 (m, 1H, 13), 4.50 (dd, $^3J_{HH}$ = 6.7 Hz, $^2J_{HH}$ = 9.4 Hz, 1H, 3), 5.06 (dd, $^3J_{HH}$ = 10.3 Hz, $^2J_{HH}$ = 9.4 Hz, 1H, 3), 5.12 (m, 1H, 14), 5.32 (m, 1H, 4), 7.05 (dd, 2H, 6), 7.38-7.41 (m, 3H, 7/8), 7.44-7.48 (m, 2H, 10), 7.54-7.57 8 (m, 5H, 10-12), 7.56 (s, 4H, 24), 7.64 (m, 1H, 12), 7.72 (*ps*t, 8H, 22), 7.84 (m, 2H, 11). **C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 28.6 (d, $^4J_{CP}$ = 1.8 Hz, 15), 30.4 (d, $^4J_{CP}$ = 2.6 Hz, 19), 31.2 (d, $^4J_{CP}$ = 1.8 Hz, 20), 31.8 (d, $^1J_{CP}$ = 32.0 Hz, 1), 34.2 (d, $^4J_{CP}$ = 4.1 Hz, 16), 61.7 (17), 64.6 (18), 68.3 (4), 81.1 (3), 95.6 (d, $^2J_{CP}$ = 12.2 Hz, 13), 96.2 (d, $^2J_{CP}$ = 11.3 Hz, 14), 117.8 (q, $^3J_{CF}$ = 4 Hz, 24), 125.6 (d, $^1J_{CP}$ = Hz,), 125.0 (q, $^1J_{CF}$ = 270 Hz, 25), 126.5 (6), nd (9'), 129.2 (q, $^2J_{CF}$ = 25.7 Hz, 23), 130.0 (7), 130.0 (d, $^2J_{CP}$ = 11.0 Hz, 10), 130.1 (8), 130.2 (d, $^3J_{CP}$ =11.3 Hz, 11), 130.4 (5), 132.1 (d, $^2J_{CP}$ = 11.2 Hz, 10), 132.7 (d, $^4J_{CP}$ = 3.6 Hz, 12), 133.6 (d, $^4J_{CP}$ = 2.5 Hz, 12), 135.1 (s, 22), 135.3 (d, $^3J_{CP}$ =13.1 Hz, 11), 138.5 (), 162.1 (q, $^1J_{CB}$ = 50 Hz, 21), nd (2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 22.8. **MS** (+ESI) m/z: 647.4 (M^+, 30.8), 646.4 (M^+, 100), 645. 5 (M^+, 19.2), 644.5 (M^+, 60.4).

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3426m_{br}, 2890w, 1600m, 1478w, 1422w, 1357s, 1279s, 1126s, 968w, 935w, 889m, 637w, 743w, 710m, 678m, 527w, 487w. **m.p.** 64°C. $[\alpha]_D^{20}$: +8° (c = 0.09, $CHCl_3$).

(*S*)-2-[(Diphenyl-phosphanyl)-methyl]-4-*iso*-propyl)-4,5-dihydrooxazole-η^4-(1,5-cyclooctadiene) iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (91)

The reaction was performed according to *general procedure 7* from ligand **79** (111 mg, 356 μmol), $[Ir(cod)Cl]_2$ (117 mg, 175 μmol) and $NaBAr_F$ (404 mg, 456 μmol) in dichloromethane (5 mL). Column chromatography with diethyl ether and dichloromethane (gradient mixture) afforded the product (336 mg, 65%).



$C_{60}H_{48}BF_{24}IrNOP$ (1474.97)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.40 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, 6), 0.90 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, 6'), 1.59 (m, 1H, 17), 1.78 (m, 1H, 13), 1.96-2.01 (m, 1H, 17 & 1H, 5), 2.17-2.20 (m, 1H, 13), 2.26-2.31 (m, 1H, 18), 2.34-2.40 (m, 1H, 18), 2.40-2.45 (m, 1H, 14), 2.51 (m, 1H, 14), 3.02 (m, 1H, 16), 3.50 (ddd, $^{2}J_{HH}$ = 18.3 Hz, $^{2}J_{HP}$ = 6.8 Hz, 1.7 Hz, 1H, 6), 3.75 (dd, $^{2}J_{HH}$ = 18.5 Hz, $^{2}J_{HP}$ = 11.3 Hz, 1H, 6), 3.99 (m, 1H, 15), 4.06 (m, 1H, 4), 4.54 (pst, $^{3}J_{HH}$ = 9.5 Hz, $^{2}J_{HH}$ = 9.6 Hz, 1H, 3), 4.64 (dd, $^{3}J_{HH}$ = 3.8 Hz, $^{2}J_{HH}$ = 9.9 Hz, 1H, 3), 5.01 (m, 1H, 12), 5.19 (m, 1H, 11), 7.36-7.40 (m, 2H, 8), 7.51-7.60 (m, 5H, 8-10), 7.56 (s, 4H, 22), 7.64-7.66 (m, 1H, 10), 7.72 (pst, 8H, 20), 7.80-7.84 (dd, 2H, 9). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 13.6 (6), 18.5 (6'), 27.6 (d, $^{3}J_{CP}$ = 2.2 Hz, 13), 29.6 (d, $^{4}J_{CP}$ = 2.2 Hz, 17), 31.4 (d, $^{1}J_{CP}$ = 33 Hz, 1), 32.3 (18), 32.4 (5), 35.7 (d, $^{4}J_{CP}$ = 4.4 Hz, 14), 62.8 (15), 64.9 (16), 68.5 (4), 73.5 (3), 91.2 (d, $^{2}J_{CP}$ = 13.7 Hz, 12), 97.3 (d, $^{2}J_{CP}$ = 10.3 Hz,11), 117.8 (q, $^{3}J_{CF}$ = 4 Hz, 22), 125.2 (d, $^{1}J_{CP}$ = 53.6 Hz, 7), 125.0 (q, $^{1}J_{CF}$ = 270 Hz, 23), 129.1 (d, $^{1}J_{CP}$ = 51.6 Hz, 7'), 129.2 (q, $^{2}J_{CF}$ = 25.7 Hz 21), 130.0 (d, $^{2}J_{CP}$ = 11.0 Hz, 8_b), 130.2 (d, $^{3}J_{CP}$ =11.2 Hz, 9_d), 131.7 (d, $^{2}J_{CP}$ = 11.0 Hz, 8_a), 132.6 (d, $^{4}J_{CP}$ = 2.6 Hz, 10_c), 133.6 (d, $^{4}J_{CP}$ = 2.4 Hz, 10_e), 135.2 (s, 20), 135.5 (d, $^{3}J_{CP}$ = 13.4 Hz, 9_f), 162.1 (q, $^{1}J_{CB}$ = 50 Hz, 19), 182.9 (d, $^{2}J_{CP}$ = 19.1 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 25.2. **MS** (+ESI) m/z: 612.4 (100.0), 610.4 (79.7), 613.3 (37.7), 611.4 (30.3), 614.4 (5.1). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3426m_{br}, 2970w, 2842w, 1603m, 1483w, 1431m, 1357s, 1278s, 1128s, 1005w, 938w, 889m, 637w, 742w, 712m, 675m. **m.p.** 75-76°C. $[\alpha]_D^{20}$: +3 (c = 0.14, CH_2Cl_2).

7.4 Phosphinines as Ligands in Catalysis

Crotonoyl chloride [10487-71-5], 2,4,6-triphenylpyrylium tetrafluoroborate **27** [448-61-3] were purchased from Fluka. 4-Hydroxy-methyl-pyrone **35** [675-10-5] and Dimethyl-gamma-pyrone [1004-36-0] were purchased from Aldrich.

Synthesis of 6-oxo-6*H*-pyran-2-carboxylic acid amides **111, 122, 123**

general procedure 9: 6-Oxo-6H-pyran-carboxylic acid (1 eq) and HOBt (1.2-1.6 eq) were dissolved in dichloromethane. EDC (1.2-1.6 eq) and amino alcohol (1 eq) were added and the mixture was stirred for 1 hour at room temperature. The mixture was then diluted with dichloromethane (20 mL) and water (30 mL) and extracted with 0.5M HCl (20 mL), 2.5% $NaHCO_3$ (20 mL), water (20 mL), and brine (20 mL). Drying over Na_2SO_4 and evaporation of the volatiles gave the crude product. The products were purified by column chromatography.

Synthesis of 6-oxo-6*H*-pyran-2-acid oxazolines **112, 124, 125** and [(4,5-dihydro-oxazol-2-yl)methyl]-*2H*-pyran-2-ones **151, 152**

general procedure 10: To a 0.5 M solution of amide in THF was added of *Burgess'* reagent (1.2 eq). The mixture was stirred for four hours at under reflux. After cooling to room temperature the solution was extracted with water (50 mL) and dichloromethane (50 mL). The layers were separated and the aqueous phase was washed with dichloromethane (3×50 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The crude product was purified by column chromatography.

Synthesis of *2E*- and *2Z*-2-(6-*tert*-butylphosphininoxide-2(*1H*)-ylidene)-oxazolinines **120, 128, 129**

general procedure 11: 6-Oxo-6*H*-pyran-2-acid oxazoline (1 eq) and (2,2-dimethylpropylidyne)phosphin (3 eq) were dissolved in toluene and heated to 140°C for 4 to 8 days. After cooling to room temperature a small amount of silica was added and all volatiles were removed. Column chromatography on silica afforded both isomers of the respective water-adducts.

Synthesis of 2-(6-*tert*-butylphosphinin-2-yl)-oxazolines **105, 126, 127**

general procedure 12: Wateradduct was dissolved in toluene (12-15 mL), and heated to reflux under argon. Water was removed by means of a Dean-Stark-trap. The product had to be handled under dry and inert atmosphere.

Synthesis of 6-Oxo-6*H*-pyran-2-carboxylic acetamides **149** and **150**

general procedure 13: Acid (1 eq) and HOBt (1.3 eq) were dissolved in dichloromethane and DMF. EDC (1.3 eq) and amino alcohol (1 eq) were added and the mixture was stirred overnight. Addition of 0.5 M HCl (20 mL) was followed by phase separation. The organic layer was then subsequently extracted with 2.5% $NaHCO_3$ (20 mL), water (20 mL), and brine (20 mL) and dried over Na_2SO_4. Filtration and evaporation of the volatiles was followed by column chromatography on silica.

Synthesis of Iridium-Complexes **133**, **134** and **135**

general procedure 14: Phosphinineoxazoline (2eq) was dissolved in dichloromethane. Solid $[Ir(cod)Cl]_2$ (1eq) added. The reaction mixture was heated to 48-50°C for two hours. In the glove-box water-free $NaAr_F$ (2.6 eq) was added which resulted in a colorchange from deep-red to almost black. The solution was stirred over night. The mixture was filtered over celite and dried under high-vacuum. Excess $NaAr_F$ could only be removed by recrystallization. About 10 to 20% of side product were observed each time.

Catalytic Hydrogenation at Elevated Pressure

Hydrogenation with dihydrogen was performed according to *general procedure 8*.[57b]

Transfer Hydrogenation

The iridum catalyst (0.7 mg, 0.5 μmol) was dissolved in 2-propanol (10 mL) in a 25 mL Young- tube under argon. Then acetophenone (0.4 mmol) was added and the solution was degassed by three freeze-pump-thaw cycles before the flask was inserted into an oil-bath and stirred at 80°C. After 5 minutes the reaction was started by addition of a degassed solution of potassium methylate in dry 2-propanol (0.1 mL of 0.05 M). The reaction was finished after 15 minutes. The analytical procedures were used as previously described.[61]

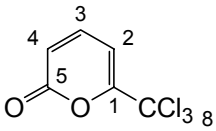
Allylic Alkylation

Allyic Alkylation with palladium[222], iridium[142] and rhodium[144] was performed as previously described.

7.4.1 Synthesis of Diene-Moiety

6-(Trichlormethyl)-*2H*-pyran-2-one (109)[126]

Crotonoyl chloride (1.18 g, 11.27 mmol) and trichloroacetic acid chloride (3.94 g, 21.7 mmol) were dissolved in dichloromethane (10 mL). At 0°C triethylamine (3.4 mL) in dichloromethane (10 mL) was slowly added. The darkbrown solution was left to stand for 20 hours. Volatiles were removed under reduced pressure and the residue was diluted with diethyl ether (10 mL). After filtration and evaporation of the volatiles, the crude product was purified by Kugelrohr destillation (10^{-1} mbar, 200 °C) to yield a white solid (1.46 g, 61%).

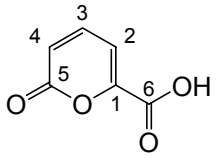


$C_6H_3Cl_3O_2$ (213.45)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = (400 MHz, $CDCl_3$): 6.43 (dd, $^4J_{HH}$ = 1 Hz, $^3J_{HH}$ = 9.6 Hz, 1H, 2), 6.86 (dd, $^4J_{HH}$ = 1 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, 4), 7.41 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 9.6 Hz, 1H,3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 102.3 (2), 118.4 (4), 142.5(3), 158.0 (1), 159.6 (5), 188.4 (8). **MS** (+FAB, 3-NBA), m/z: 211.9 (M^+, 9.8), 177 (M^+-Cl, 25.4), 148.9 (M^+-CO, 7.0), 95 (M^+-CCl_3, 100). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3118w, 1749s, 1632s, 1550s, 1340m, 1331w, 1207m 1093s, 992s, 909s, 812s, 762s, 617s, 551m. **m.p.** 60°C (Lit 63-64°C). **EA** %found (calcd): C:33.76 (33.76), H: 1.39 (1.42), O: 15.12 (14.99).

6-Oxo-6*H*-pyran-carboxylic acid (110)[126]

6-(Trichlormethyl)-*2H*-pyran-2-one **109** (1g, 4.68 mmol) was dissolved in concentrated sulfuric acid (4 mL) and heated to 80°C for 4 hours. After cooling to room temperature the reaction mixture was carefully poured onto ice. The suspension was allowed to stand over night. The product was obtained by filtration. Extraction of the filtrate with ethyl acetate (3×40 mL) afforded the second crop. The product was obtained as an off-white solid (542 mg, 83%).

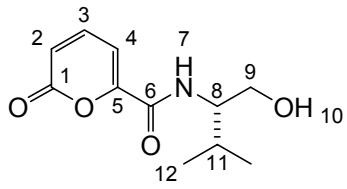


$C_6H_4O_4$ (140.09)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = (400 MHz, $CDCl_3$): 6.59 (dd, $^4J_{HH}$= 1 Hz, $^3J_{HH}$ = 9.36 Hz, 1H, 2), 7.12 (dd, $^4J_{HH}$= 1 Hz, $^3J_{HH}$ = 6.56 Hz, 1H, 4), 7.63 (dd, $^3J_{HH}$ = 6.56 Hz, $^3J_{HH}$ = 9.32 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 110.8 (2), 120.8 (4), 144.3 (3), 160.8 (1), 161.2 (5) quarternary carbon 6 missing. **EA** %found (calcd): C: 51.19 (51.44), H: 3:00 (2.88).

(*S*)-6-Oxo-6H-pyran-2-carboxylic-acid-(1-hydroxymethyl-2-methyl-propyl)-amide (111)[124]

6-Oxo-6*H*-pyran-carboxylic acid **110** (240 mg, 1.71 mmol) was dissolved in benzene (4 mL) and DMF (2 drops). After the addition of thionyl chloride (0.5 mL, 6.86 mmol) the mixture was heated to reflux for 4 hours. All volatiles were removed, and the residue was dissolved in dichloromethane (4 mL). At 0°C a solution of L-valinol (176.6 mg, 1.71 mmol) in triethylamine (0.3 mL) and dichloromethane (5 mL) was added. After stirring at room temperature for 1 hour, the mixture was diluted with dichloromethane (40 mL) and washed with saturated NH_4Cl solution (40 mL). After reextraction of the aqueous layer with dichloromethane (3×30 mL), the combined organic layers were washed with 1M HCl (40 mL) and saturated $NaHCO_3$ (40 mL) solution and dried over Na_2SO_4. Evaporation of the volatiles afforded the crude product that was purified by column chromatography on silica eluting with ethyl acetate (2% ethanol). The product was obtained as a white solid (270 mg, 70%).

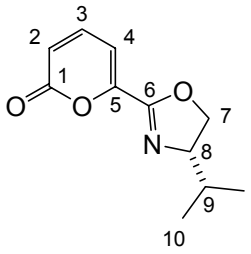


$C_{11}H_{15}NO_4$ (225.24)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.98 (d, $^3J_{HH}$ = 6.84 Hz, 3H, 12), 1.01 (d, $^3J_{HH}$ = 6.84 Hz, 3H, 12'), 1.98 (m, 1H, 11), 3.77 (m, 2H, 9), 3.89 (m, 1H, 8), 6.48 (dd, $^4J_{HH}$ = 1 Hz, $^3J_{HH}$ = 9.32 Hz, 1H, 2), 7.00 (d, $^3J_{HH}$ = 8.08 Hz, 1H, 7), 7.13 (dd, $^4J_{HH}$ = 1 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, 4), 7.46 (dd, $^3J_{HH}$ = 6.56 Hz, $^3J_{HH}$ = 9.32 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 19.1 (12), 19.6 (12'), 29.2 (11), 57.7 (9), 63.3 (8), 107.2 (4), 119.3 (2), 143.2 (3), 152.5 (5), 158.9 (6), 160.0 (1). **MS** (+FAB, 3-NBA), m/z: 226 (MH^+, 100), 140 (17.3), 95 ($C_5H_3O_2^+$, 33.4), 39 ($C_3H_3^+$, 11.1). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3439s, 3294s, 3084m, 2955s, 2872m, 2368w, 1722s, 1654s, 1567s, 1541s, 1472m, 1412m, 1355m, 1340s, 1316m, 1295m, 1231m, 1098s, 1067m, 1023m, 980w, 942w, 903w, 887m, 854m, 820s, 708m, 650m, 596m, 558m. **TLC** (ethyl acetate, 2% ethanol) R_f = 0.28.

6-[(*S*)-4,5-dihydro-4-Isopropyloxazol-2-yl]-*2H*-pyran2-one (112)

6-Oxo-6H-pyran-2-carboxylic acid amide **111** (400 mg, 1.8 mmol) in THF (50 mL) was reacted with *Burgess'* reagent (476 mg, 2 mmol) according to *general procedure 10*. The crude product was purified by column chromatography on silica eluting with diethyl ether and pentane (4:1) to yield of a light yellow solid (285 mg, 77%).



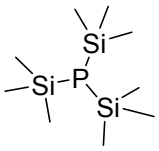
$C_{11}H_{13}NO_3$ (207.23)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.92 (d, $^3J_{HH}$ = 6.82 Hz, 3H, 10), 1.02 (d, $^3J_{HH}$ = 6.82 Hz, 3H, 10'), 1.85 (m, 1H, 9), 4.13 (m, 2H, 7), 4.43 (m, 1H, 8), 6.45 (dd, $^4J_{HH}$ = 0.76, $^3J_{HH}$ = 9.6 Hz, 1H, 4), 6.89 (d, $^3J_{HH}$ = 6.56 Hz, 1H, 2), 7.36 (dd, $^3J_{HH}$ = 6.56 Hz, $^3J_{HH}$ = 9.6 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 18.3 (10), 19.0 (10'), 32.8 (9), 71.0 (7), 73.3 (8), 107.5 (4), 119.2 (2), 142.2 (3), 149.4 (5), 156.7 (6), 160.0 (1). $[\alpha]_D^{20}$: - 70.4° (c = 1.00, $CHCl_3$). **MS** (+EI), m/z: 207.1 (M^+, 9.7), 164 (M^+-*i*Pr, 65.3), 95 ($C_5H_3O_2^+$,100). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3115w, 3059w, 2966m, 2903w, 2871w, 1726s, 1633m, 1549m, 1471m, 1411w, 1265m, 1316m, 1265m, 1123w, 1085m, 1029m, 980m, 949m, 911m, 828m, 725w, 660w. **m.p.** 103-104 °C. **TLC** (TBME:hexane, 4:1) R_f = 0.25. **EA** %found (calcd): C: 63.47 (63.76), H: 6.29 (6.32), N: 6.73 (6.76).

7.4.2 Synthesis of Phosphaalkyne

Tris(trimethylsilyl)phosphan (113)[129]

In a flame-dried three-necked flask equipped with reflux-condenser, sodium (857 mg, 37.3 mmol) and potassium (1.09 g, 27.7 mmol) were stirred in DME (50 mL) until the alloy formed. Then the suspension was heated to reflux for 2 hours. After cooling to room temperature, red phosphorus (670 mg, 21.6 mmol) was added, and the suspension was heated to reflux for 24 hours. After cooling to room temperature, freshly destilled TMSCl (9 ml, 70.9 mmol) in DME (20 mL) was slowly added. When the addition was finished, the solvent was distilled from the suspension. Then the product was distilled under reduced pressure (0.1 mbar, ~50°C), to yield a colorless air-sensitive liquid that solidifies at 4°C (2.5 g, 58%).

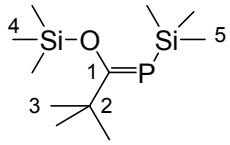


$C_9H_{27}PSi_3$ (250.54)

^{1}H NMR (500.1 MHz, C_6D_6, 300K): δ = 0.31 (d, $^3J_{HP}$ = 4.4 Hz, 27H). **^{13}C{^{1}H} NMR** (125.8 MHz, C_6D_6, 300K) δ = 4.5 ($^2J_{CP}$ = 11.2 Hz) **^{31}P{^{1}H} NMR** (202.5.0 MHz, C_6D_6, 300K) δ = -252.2.

[2,2-Dimethyl-1-(trimethylsiloxy)propyliden]-trimethylsilylphosphane (114)[223]

To a solution of pivaloyl chloride (24 mL, 195 mmol) in pentane (250 mL) $P(TMS)_3$ **113** (43.34 g, 173 mmol) is added *via* cannula. The solution is stirred for one week. Pentane is removed by distillation, and the yellow product is then distilled at reduced pressure using a vigreux column (40 g, 88%).



$C_{11}H_{27}OPSi_2$ (262.48)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.32 (s, 9H, 4), 0.43 (d, $^3J_{HH}$ = 4 Hz, 9H, 5), 1.35 (d, $^4J_{HH}$ = 1.5 Hz, 9H, 3). **^{31}P{^{1}H} NMR** (162.0 MHz, $CDCl_3$, 300K) δ = 131.9.

(2,2-Dimethylpropylidyne)phosphane (115)[131]

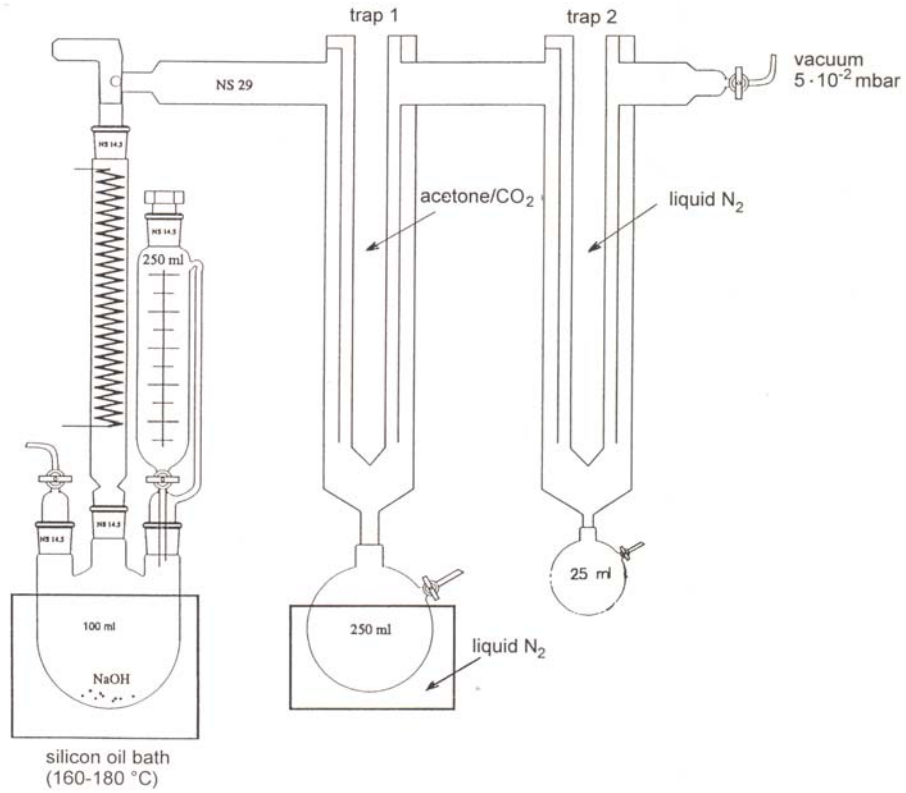
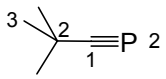


Figure 7.1: Apparatus for the preparation of (2,2-dimethylpropylidyne)phosphane

[2,2-Dimethyl-1-(trimethylsiloxy)propyliden]-trimethylsilyl-phosphane **114** (51 g, 193 mmol) was reacted with NaOH (22g, 550 mmol) under vacuum (~10^{-3} mbar) at 180°C. The side-product TMS_2O was trapped at -78°C, the product was trapped at -193°C. The product was obtained as a solution in TMS_2O (25 g, 3.79 M in TMS_2O, 61.4%) The colorless solution was stored at -20°C. It slowly turnes yellow upon standing, but without ma*J*or changes of the ^{1}H NMR spectrum.



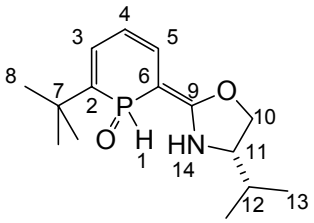
C_5H_9P (100.1)

^{1}H NMR (400.1 MHz, C_6D_6, 300K): δ = 1.16 (d, $^4J_{HP}$ = 0.76 Hz). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 300K): δ = 31.4 (d, $^3J_{CP}$ = 6.13 Hz, 3), 36.5 (d, $^2J_{CP}$ = 18.4 Hz, 2), 185 (d, $^1J_{CP}$ = 38.34 Hz, 1). **^{31}P{^{1}H} NMR** (162.0 MHz, C_6D_6, 300K) δ = -68.4.

7.4.3 [4+2] Cycloaddition of α-Pyrone and *tert*-Butylphosphaalkyne

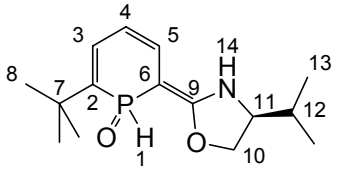
(*S,2E*)-2-(6-*tert*-Butylphosphininoxide-2(1H)-ylidene)-4-isopropyloxazolidine (120$_{trans}$)
(*S,2Z*)-2-(6-*tert*-Butylphosphininoxide-2(*1H*)-ylidene)-4-isopropyloxazolidine (120$_{cis}$)

According to *general procedure 11* 6-oxo-6*H*-pyran-2-acid oxazoline **112** (947 mg, 4.57 mmol), (2,2-dimethylpropylidyne)phosphin **115** (2.1 mL, 3.79 M in TMS_2O, 8 mmol) were reacted in chlorobenzene (6 mL) and toluene (2 mL) for 4 days. The brown crude was purified by column chromatography eluting with ethyl acetate and methanol (both isomers:500 mg, 39%).



$C_{15}H_{24}NO_2P$ (281.33)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 260K): δ = 0.89 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 13), 0.94 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 13'), 1.32 (s, 9H, 8), 1.89 (m, 1H, 12), 3.82 (m, 1H, 10), 4.25 (dd, 1H, 11), 4.49 (dd, 1H, 11), 5.40 (ddd, $^3J_{HH}$ = 9.3Hz, 7.1, $^4J_{HP}$ = 2.8 Hz, 1H, 4), 6.74 (dd, $^3J_{HH}$ = 9.3 Hz, 1H, 3), 6.87 (dd, $^3J_{HH}$ = 7.3, 1H, 5), 8.70 (d, $^1J_{PH}$ = 482 Hz, 1H, 1). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 260K): δ = 16.6 (13), 18.3 (13'), 31.0 (d, $^2J_{CP}$ = 5 Hz, 8), 31.2 (12), 35.6 (d, $^2J_{CP}$ = 8.6 Hz, 7), 61.9 (11), 70.3 (10), 106.6 (d, $^3J_{CP}$ = 16.8 Hz, 4), 127.2 (5), 130.5 (d, $^1J_{CP}$ = 100 Hz, 2), 134.2 (d, $^2J_{CP}$ = 5.2 Hz, 3), 168.5 (9), quarternary carbon 6 missing. **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 300K): δ = -1.0 (d, $^1J_{PH}$ = 485 Hz). **TLC** (ethyl acetate:methanol 18:1) R_f = 0.16.



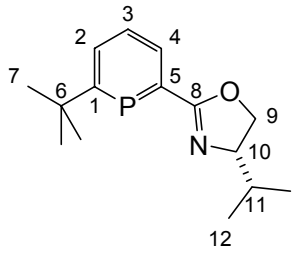
$C_{15}H_{24}NO_2P$ (281.33)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.89 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 13), 0.93 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 13'), 1.33 (s, 9H, 8), 1.90 (m, 1H, 12), 3.85 (m, 1H, 10), 4.24 (m, 1H, 11), 4.47 (m, 1H, 11), 5.43 (m, 1H, 4), 6.78 (m, 1H, 3), 6.80 (m, 1H, 5), 8.7 (d, $^1J_{PH}$ = 485 Hz, 1H, 1). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 17.3 (13), 18.5 (13'), 30.9 (d, J_{CP} = 5 Hz, 8), 31.2 (12), 36.2 (7), 62.3 (11), 71.2 (10), 107.6 (d, $^3J_{CP}$ = 15.7 Hz, 4), 127.5 (d, $^2J_{CP}$ = 6Hz, 5),

134.7 (d, $^{2}J_{CP}$ = 6.1 Hz, 3), quarternary carbons 2, 6 and 9 are missing. **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 300K): δ = -3.2 (d, $^{1}J_{PH}$ = 485 Hz). **TLC** (ethyl acetate:methanol 18:1) R_f = 0.11.

(*S*)-2-(6-*tert*-Butylphosphinin-2-yl)-4,5-dihydro-4-isopropyloxazole (105)

According to general *general procedure 12* the product was obtained after evaporation of the toluene as an orange-yellow sticky solid, which becomes brown upon storage at room-temperature. However, the NMR remains unchanged.



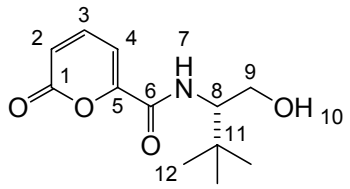
$C_{15}H_{22}NOP$ (263.32)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.91 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, 12), 1.01 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, 12'), 1.46 (d, $^{4}J_{PH}$ = 1.52 Hz, 9H, 7), 1.83 (m, $^{3}J_{HH}$ = 7.4 Hz, 1H, 11), 4.07 (m, 1H, 10), 4.13 (m, $^{2}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 8.2 Hz, 1H, 9), 4.42 (m, $^{2}J_{HH}$ = 8.1 Hz, $^{3}J_{HH}$ = 9.35 Hz, 1H, 9), 7.51 (d*ps*t, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{HP}$ = 4.05 Hz, 1H, 3), 7.96 (dd, $^{3}J_{HH}$ = 8.6 Hz, $^{3}J_{HP}$ = 6.65 Hz, 1H, 2), 8.28 (m, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HP}$ = 4.5 Hz, 1H, 4). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 18.4 (12), 19.1 (12'), 32.9 (d, $^{3}J_{CP}$ = 1.5 Hz, 7), 33.4 (11), 39.1 (d, $^{2}J_{CP}$ = 12.6 Hz, 6), 70.8 (9), 73.3 (10), 129.6 (d, $^{3}J_{CP}$ = 14.4 Hz, 3), 132.7 (d, $^{2}J_{CP}$ = 13.1 Hz, 4), 133.0 (d, $^{2}J_{CP}$ = 11 Hz, 2), 153.4 (d, $^{1}J_{CP}$ = 50.6 Hz, 5), 165.1 (d, $^{2}J_{CP}$ = 25 Hz, 8), 185.3 (d, $^{1}J_{CP}$ = 58.4 Hz, 1). **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 300K): δ = 208.7. **MS** (+FAB, 3-NBA), m/z: 264 (MH^+, 100), 179 (11.2).

7.4.4 Analogous Phosphininoxazolines

(*S*)-6-Oxo-6*H*-pyran-2-carboxylic-acid-(1-hydroxymethyl-2,2-dimethyl-propyl)-amide (122)

6-Oxo-6*H*-pyran-carboxylic acid (6 g, 42.8 mmol), HOBt (9.5 g, 70.6 mmol), EDC (13.5 g, 70.6 mmol) and (S)-*tert*-leucinol (5.02 g, 42.8 mmol) were reacted in dichloromethane (300 mL) and DMF (20 mL) according to *general procedure 9*. Column chromatography on silica eluting with ethyl acetate and ethanol yielded the product as an off-white solid (4.1 g, 40%).

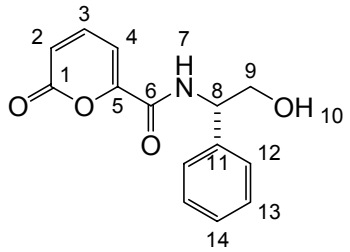


$C_{12}H_{17}NO_4$ (239.27)

^{1}H NMR (400.1 MHz, $CDCl_3$ 300K): δ = 0.97 (s, 9H, 12), 3.63 (m, 1H, 9), 3.91 (m, 1H, 9), 3.98 (m, 1H, 8), 6.45 (m, 1H, 2) 7.08 (m, 2H, 7/4), 7.44 (m, 1H, pyron 3). **^{13}C{^{1}H} NMR** (100.6 $CDCl_3$ 300K): δ = 27.0 (12), 34.1 (11), 60.1 (8), 62.2 (9), 107.2 (3), 119.2 (4), 143.2 (2), 152.4 (5), 159.3 (6), 159.9 (1). **MS** (+FAB, 3-NBA) m/z: 240 (MH^+, 100), 140 (21.1), 95 (pyron, 28.5). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3464.2s, 3361.8s, 3093.8w, 2962.9m, 2870.8m, 2361.9w, 1975.5w, 1723.6s, 1674.0s, 1557.9m, 1517.2s, 1474.1m, 1405.3, 1371.1m, 1331.0m, 1266.1s, 1229.5m, 1098.1s, 1047.5s, 1001.4m, 942.1w, 880.8s, 817.0s, 645.0s, 589.7m, 558.0m, 533.9m. **m.p.** 109°C. $[\alpha]_D^{20}$ = +9.5° (c = 1.02, $CHCl_3$). **TLC** (ethyl acetate:ethanol; 98:2) R_f = 0.38. **EA** %found (calcd): C: 60.21 (60.24), H: 7.10 (7.16) N: 5.82 (5.85) O: 26.99 (26.75).

(*S*)-6-Oxo-6*H*-pyran-2-carboxylic acid (2-hydroxy-1-phenyl-ethyl)-amid (123)

6-Oxo-6*H*-pyran-carboxylic acid (1.18 g, 8.42 mmol), HOBt (1.25 g, 9.26 mmol), EDC (1.77 g, 9.26 mmol) and (S)-phenylglycinol (1.16 g, 8.42 mmol) were reacted in dichloromethane (70 mL) according to *general procedure 9*. Column chromatography on silica eluting with ethyl acetate (2% ethanol) yielded the product as a white solid (1.127 g, 52%).



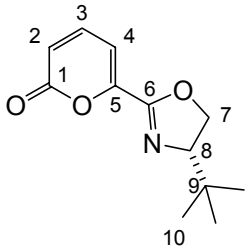
$C_{14}H_{13}NO_4$ (259.26)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 3.98 (m, 1H, 9), 5.20 (m, 1H, 8), 6.49 (d, $^3J_{HH}$ = 9.3 Hz, 1H, 4) 7.11 (d, $^3J_{HH}$ = 6.8 Hz, 1H, 2) 7.26-7.40 (m, 5H, Ph), 7.46 (dd, d, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, 3), 7.60 (d, 1H, 7). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 56.2 (8), 65.9 (9), 107.3 (4), 119.6 (2), 127.0 (12), 128.4 (14), 129.1 (13), 138.1(11), 143.1 (3), 152.3 (5), 158.5 (6), 159.8 (1). **MS** (+FAB, 3-NBA), m/z: 260 (MH^+, 96.25%), 228 (MH^+ - CH_3OH, 21.16%), 140 ($C_6H_6NO_3^+$, 100), 121 (36.6), 95 ($C_5H_3O_2^+$, 88.0), 77 (Ph^+, 19.9). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3460.8m_{br} (ν_{NH}), 3239.3s ($\nu_{arom.}$), 3082.4m ($\nu_{aliph.}$), 2940.8w($\nu_{aliph.}$), 1711.6s

($\nu_{CO\text{-}Lacton}$), 1654.9s ($\nu_{CO\text{-}Amid}$), 1536.3m($\nu_{C=C}$), 1406.6w, 1354.4w, 1307.9w, 1230.6w, 1096.2s, 1064.9w, 895.8w, 857.6w, 817.6m, 739.9m($\nu_{C\text{-}OH}$), 692.1m ($\delta_{arom.}$), 629.0w($\delta_{arom.}$), 585.2w, 551.6w, 483.5w. **mp.** 136°C. $[\alpha]_D^{20}$ = -39.2° (c = 1.0, $CHCl_3$). **TLC** (ethyl acetate:ethanol;98:2) R_f = 0.37. **EA** %found (calcd): C: 64.73 (64.86), H: 5.10 (5.05), N: 5.30 (5.40).

6-[(*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2yl)-*2H*-pyran-2-one (124)

6-Oxo-6H-pyran-2-carboxylic acid amide **122** (609 mg, 2.54 mmol) in THF (30 mL) was reacted with *Burgess'* reagent (7.26 mg, 3.05 mmol) according to *general procedure 10*. The crude product was purified by column chromatography on silica eluting with ethyl acetate and ethanol to yield **124** (502 mg, 89%).



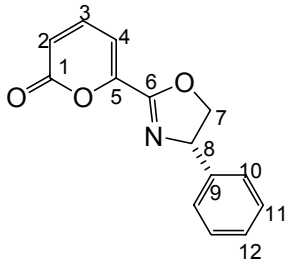
$C_{12}H_{15}NO_3$ (221.25)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.93 (s, 9H, 10), 4.08 (m, $^3J_{HH}$ = 8.3, 10.1 Hz, 1H, 8), 4.22 (*pst*, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, 7), 4.35 (m, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 10.1 Hz, 1H, 7), 6.44 (dd, $^3J_{HH}$ = 6.6 Hz, 9.4 Hz, 1H, 4), 6.87 (dd, $^4J_{HH}$ = 0.7 Hz, $^3J_{HH}$ = 6.6Hz, 1H, 2), 7.36 (dd, $^4J_{HH}$ = 1.0 Hz, $^3J_{HH}$ = 9.4 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 26.0 (10), 34.2 (9), 69.5 (8), 76.8 (7), 107.5 (4), 119.1 (2), 142.2 (3), 149.5 (5), 156.6 (6), 160.1 (1). **MS** (+FAB, 3-NBA), m/z: 222 (MH^+, 100), 95 ($C_5H_3O_2^+$, 6.1). **IR** (KBr) $\tilde{\nu}$ [cm^{-1}] = 3460.7s_{br}, 3110.4w, 3059.6w, 2962.8s, 2888.3m, 1739.0s_{br}, 1667.4m, 1612.7m, 1547.5m, 1481.3m, 1384.0m, 1325.2m, 1298.7m, 1255.7m, 1211.9w, 1126.2m, 1093.0s, 1034.8m, 976.6m, 952.0m, 903.6m, 812.0s, 741.5m, 661.4m, 568.3m. **m.p.** 90°C. $[\alpha]_D^{20}$: -94.5° (c = 1.05, $CHCl_3$). **TLC** (ethyl acetate:ethanol; 98:2) R_f = 0.72. **EA** %found (calcd): C: 65.05 (65.14), H: 6.81 (6.83), N: 6.29 (6.33), O: 21 .79 (21.69).

(*R*)-6-[4-Phenyl-4,5-dihydrooxazol-2yl)-*2H*-pyran-2-one (125 S)

6-Oxo-6H-pyran-2-carboxylic acid amide **123** (1.08 mg, 4.16 mmol) in THF (60 mL) was reacted with *Burgess'* reagent (1.19 mg, 5 mmol) according to *general procedure 10*. The

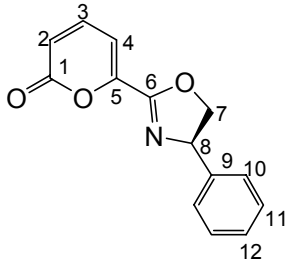
crude product was purified by column chromatography on silica eluting with diethyl ether and pentane to yield **125** (550 mg, 55%).



$C_{14}H_{11}NO_3$ (241.24)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 4.29 (*pst*, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, 7), 4.82 (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 10.4 Hz, 1H, 7), 5.43 (*pst*, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 9.8 Hz, 1H, 8), 6.45 (d, $^3J_{HH}$ = 9.6 Hz, 1H, 4), 6.95 (d, $^3J_{HH}$ = 6.6 Hz, 1H, 2), 7.40 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 9.4 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 70.4 (8), 75.4 (7), 108.0 (4), 119.5 (2), 126.8 (10), 128.0 (12), 128.9 (11), 141.0 (9), 142.1 (3), 149.1 (5), 157.9 (6), 169.8 (1). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3448.2m$_{br}$, 2996.9w ($\nu_{arom.}$), 2952.8m ($\nu_{aliph.}$), 2895.2m ($\nu_{aliph.}$), 1734.2s ($\nu_{C=OLacton}$), 1661.0m ($\nu_{C=N}$), 1608.9m ($\nu_{C=C}$), 1549.3m ($\nu_{C=C}$), 1491.2w, 1450.1m, 1375.6m, 1300.1m, 1253.0m, 1195.6w, 1089.1s (ν_{C-O}), 1034.1m, 973.2m, 888.8m, 805.4s, 757.2m ($\delta_{arom.}$), 698.4m ($\delta_{arom.}$). **m.p.** 119 °C. $[\alpha]_D^{20}$: -39.2° (c = 1.0, $CHCl_3$). **TLC** (*n*-pentane: diethyl ether; 1: 20) R_f = 0.21. **EA** %found (calcd): C: 69.35 (69.70), H: 4.67 (4.60), N: 5.86 (5.81), O: 20.14 (19.90).

(*R*)-6-[4-Phenyl-4,5-dihydrooxazol-2yl)-*2H*-pyran-2-one (125$_R$)



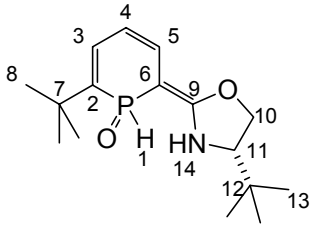
$C_{14}H_{11}NO_3$ (241.24)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 4.29 (*pst*, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, 7), 4.82 (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 10.4 Hz, 1H, 7), 5.43 (*pst*, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 9.8 Hz, 1H, 8), 6.45 (d, $^3J_{HH}$ = 9.6 Hz, 1H, 4), 6.95 (d, $^3J_{HH}$ = 6.6 Hz, 1H, 2), 7.40 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 9.4 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 70.7 (8), 75.6 (7), 108.3 (4), 119.5 (2), 127.0 (10), 128.2 (12), 129.1 (11), 141.7 (9), 142.6 (3), 149.3 (5), 158.1 (6), 160.2 (1). **MS** (+FAB, 3-NBA), m/z: 483 (M_2H^+, 5.1), 242 (MH^+, 100), 95 ($C_5H_3O_2^+$, 34.81).

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3447.7m$_{br}$, 2996.9w, 2952.8m, 2895.1m, 1733.9s, 1660.6m, 1608.8m, 1549.0m, 1490.0w, 1450.3m, 1375.4m, 1299.9m, 1252.9m, 1195.3w, 1117.8w, 1089.0s, 1033.9m, 972.7m, 888.9m, 805.1s, 757.0m, 698.3m. **m.p.** 122-123°C. $[\alpha]_D^{20}$: +41.5° (c = 1.0, $CHCl_3$). **TLC** (*n*-pentane: diethyl ether; 1: 20) R_f = 0.22. **EA** %found (calcd): C: 69.53 (69.70), H: 4.58 (4.60), N: 5.85 (5.81).

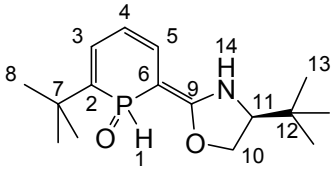
(*S,2E*)-2-(6-*tert*-Butylphosphininoxide-2(*1H*)-ylidene)-4-*tert.*-butyloxazolidine (128$_{trans}$)
(*S,2Z*)-2-(6-*tert*-Butylphosphininoxide-2(*1H*)-ylidene)-4-*tert.*-butyloxazolidine (128$_{cis}$)

According to *general procedure 11* 6-oxo-6*H*-pyran-2-acid oxazoline **124** (400 mg, 1.81 mmol), (2,2-dimethylpropylidyne)phosphine **115** (1.5 mL, 3.79 M in TMS_2O, 5.69 mmol) were reacted in toluene (3 mL) for 5.5 days. The brown crude was purified by column chromatography eluting with ethyl acetate and methanol (*E*-isomer:118 mg, 22%; *Z*-isomer: 30 mg, 5.6%; mixed 20 mg, 3.7%).



$C_{15}H_{24}NO_2P$ (295.36)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.91 (s, 9H, 13), 1.34 (s, 9H, 8), 3.79 (dd, 1H, 10), 4.35 (dd, 1H, 11), 4.46 (*ps*t, 1H, 11), 5.44 (ddd, $^4J_{PH}$ = 2.8 Hz, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, 4), 6.73 (ddd, $^3J_{PH}$ = 21.8 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, 5), 6.80 (ddd, $^3J_{PH}$ = 34.1 Hz, $^3J_{HH}$ = 7.1 Hz, 1H, 3), 8.64 (d, $^1J_{PH}$ = 483.8 Hz, 1H, 1). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 25.2 (13), 31.1 (d, $^3J_{CP}$ = 5.2 Hz, 8), 32.9 34.2 (12), 36.1 (d, $^2J_{CP}$ = 8.0 Hz, 7), 65.1 (11), 70.4 (10), 76.5 (d, $^1J_{CP}$ = 110.4 Hz, 6), 108.1 (d, $^3J_{CP}$ = 17.0 Hz, 4), 127.2 (5), 131.9 (d, $^1J_{CP}$ = 97.9 Hz, 2), 134.8 (d, $^2J_{CP}$ = 5.6 Hz, 3), 169.3 (d, $^2J_{CP}$ = 16.0 Hz, 9). **^{31}P NMR** (162.0 MHz, $CDCl_3$, 300K): δ = -1.2 (d, $^1J_{PH}$ = 485 Hz). **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 300K): δ = -6.0. **MS** (+FAB, 3-NBA), m/z: 296 (MH^+, 100), 278 (M^+-H_2O, 10.5), 220 (278-C_4H_{10}, 9.5), 57 ($C_4H_9^+$, 14.1). $[\alpha]_D^{20}$: +295.5° (c = 1.0, $CHCl_3$). **TLC** (ethyl acetate:methanol 10:1) R_f = 0.21. **EA** %found (calcd): C 64.84 (65.05), H 8.65 (8.87), N 4.59 (4.74), O 10.73 (10.83).

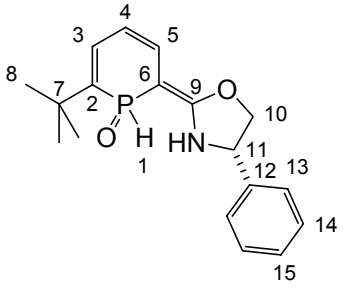


$C_{15}H_{24}NO_2P$ (295.36)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 0.95 (s, 9H, 13), 1.34 (s, 9H, 8), 3.75 (dd, 1H, 10), 4.37 (dd, 1H, 11), 4.47 (*ps*t, 1H, 11), 5.37 (ddd, $^4J_{PH}$ = 2.8 Hz, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, 4), 6.70 (d, $^3J_{PH}$ = 21.8 Hz, $^3J_{HH}$ = 9.3 Hz, 1H, 5), 6.74 (d, $^3J_{PH}$ = 35.9 Hz, $^3J_{HH}$ = 7.1 Hz, 1H, 3), 8.75 (d, $^1J_{PH}$ = 481.2 Hz, 1H, 1). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 25.2 (13), 30.2 (d, $^3J_{CP}$ = 5.2 Hz, 8), 33.9 (12), 65.2 (11), 70.0 (10), 108.1 (d, $^3J_{CP}$ = 17.4 Hz, 4), 127.1 (5), 135.1 (d, $^2J_{CP}$ = 6.5 Hz, 3), quarternary carbons 2, 6, 7, and 9 are missing.**^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 300K): δ = 1.8 (d, $^1J_{PH}$ = 485 Hz). **MS** (+FAB, 3-NBA), m/z: 296 (MH^+, 100), 278 (M^+-H_2O, 10.5), 220 (278-C_4H_{10}, 9.5), 57 ($C_4H_9^+$, 14.1). **m.p.** 171-172 °C. $[\alpha]_D^{20}$: +73.4° (c = 1.0, $CHCl_3$). **TLC** (ethyl acetate: methanol 10:1) R_f = 0.08.

(*S,2E*)-2-(6-*tert*-Butylphosphininoxide-2(*1H*)-ylidene)-4-phenyloxazolidine (129$_{trans}$)
(*S,2Z*)-2-(6-*tert*-Butylphosphininoxide-2(*1H*)-ylidene)- 4-phenyloxazolidine (129$_{cis}$)

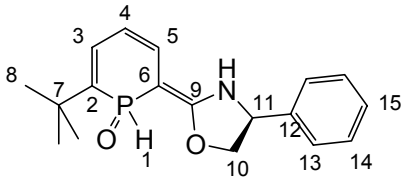
According to *general procedure 11* 6-oxo-6*H*-pyran-2-acid oxazoline **125** (480.5 mg, 1.99 mmol), (2,2-dimethylpropylidyne)phosphin (1.6 mL, 3.79 M in TMS_2O, 5.97 mmol) were reacted in toluene (5 mL) for 8 days. The brown crude was purified by column chromatography eluting with ethyl acetate and methanol (*E*-isomer:110 mg, 16%; *Z*-isomer: 77 mg, 12.2%).



$C_{18}H_{22}NO_2P$ (315.35)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 1.07 (s, 9H, 13), 4.34 (dd, $^3J_{HH}$ = 4.5 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, 11), 4.81 (*ps*t, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, 11), 5.16 (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 4.5 Hz 1H, 10), 5.54 (ddd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 9.3 Hz, $^4J_{HP}$ = 3 Hz, 1H, 4), 6.85 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 20 Hz, 1H, 3), 6.89 (dd, $^3J_{HH}$ = 9.3 Hz, $^3J_{HP}$ = 30 Hz, 1H, 5), 7.22-7.24 (m, 2H, 13/13'), 7.26-7.34 (m, 3H, 14/14'/15), 8.59 (d, $^1J_{HP}$ = 483 Hz, 1), 11.2 (s_{br}, 1H, NH). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 31.2 (d, $^3J_{CP}$ = 5.3 Hz, 8), 35.7 (d, $^2J_{CP}$ = 8.2 Hz, 7), 59.6 (11), 76.4 (10), 77.6 (d, $^1J_{CP}$ = 112.2 Hz, 6), 108.0 (d, $^3J_{CP}$ = 16.8 Hz, 4), 126.4 (13/13'), 127.3 (5), 128.6 (15), 129.3 (14/14'), 131.8 (d, $^1J_{CP}$ = 99.3 Hz, 2), 135.2 (d, $^2J_{CP}$ = 5.7 Hz, 3), 140.8 (12), 169.3 (d, $^2J_{CP}$ = 16.8 Hz, 9). **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2,

300K): δ = -6.5 (ddd, $^{1}J_{PH}$ = 483 Hz, $^{3}J_{PH}$ = 20 Hz, $^{3}J_{PH}$ = 30 Hz). **TLC** (ethyl acetate:methanol; 9:1) R_f = 0.37.

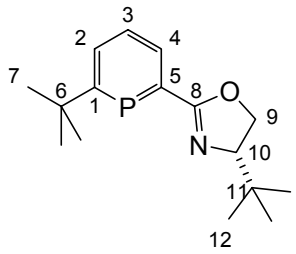


$C_{18}H_{22}NO_2P$ (315.35)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 1.33 (s, 9H, 13), 4.30 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, 10), 4.84 (t, $^{2}J_{HH}$ = 8.6 Hz, $^{3}J_{HH}$ = 8.6 Hz 1H, 11), 5.13 (dd, $^{2}J_{HH}$ = 8.6 Hz, $^{3}J_{HH}$ = 7.6 Hz 1H, 11), 5.47 (ddd, $^{3}J_{HH}$ = 7.3, 9.3 Hz, $^{4}J_{HP}$ = 3 Hz, 1H, 4), 6.79 (dd, $^{3}J_{HH}$ = 9.3 Hz, $^{3}J_{HP}$ = 20 Hz, 1H, 3), 6.82 (dd, $^{3}J_{HH}$ = 7.3 Hz, $^{3}J_{HP}$ = 33.1 Hz, 1H, 5), 7.31 (m, 5H, 13/13'/14/14'/15), 8.74 (d, $^{1}J_{HP}$ = 487 Hz, 1), 10.6 (s_{br}, 1H, NH). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 31.1 (8), 36.1 (7), 60.1 (11), 75.4 (10), 108.3 (d, $^{3}J_{CP}$ = 16.8 Hz, 4), 126.7 (13/13'), 127.2 (5), 128.7 (15), 129.1 (14/14'), 131.6 (d, $^{1}J_{CP}$ = 98 Hz, 2), 134.7 (d, $^{2}J_{CP}$ = 5.2 Hz, 3), 138.9 (12), 168.9 (d, $^{2}J_{CP}$ = 16. Hz, 9), quarternary carbon 6 missing. **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 300K): δ = -5.3 (d, $^{1}J_{PH}$ = 487 Hz). **TLC** (ethyl acetate:methanol; 9:1) R_f = 0.22.

(*S*)-2-(6-*tert*-Butylphosphinin-2-yl)-4,5-dihydro-4-*tert*-butyloxazol (126)

According to *general procedure 12* the product was obtained after evaporation of the toluene as a yellow solid.



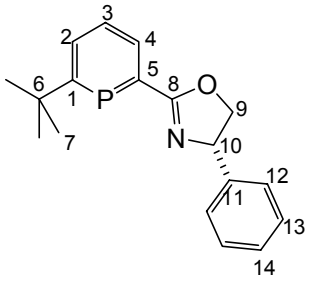
$C_{16}H_{24}NOP$ (277.34)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.95 (s, 9H, 12), 1.48 (d, $^{4}J_{PH}$ = 1.55 Hz, 9H, 7), 4.05 (dd, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HH}$ = 10.1 Hz, 1H, 10), 4.25 (*pst*, $^{3}J_{HH}$ = 8.1 Hz, $^{2}J_{HH}$ = 8.6 Hz, 1H, 9), 4.37 (dd, $^{2}J_{HH}$ = 8.6 Hz, $^{3}J_{HH}$ = 10.1 Hz, 1H, 9), 7.53 (m, $^{3}J_{HH}$ = 8.4, $^{4}J_{HP}$ = 6.4 Hz, 1H, 3), 7.97 (dd, $^{1}J_{HH}$ = 8.6 Hz, $^{3}J_{HP}$ = 4.7 Hz, 1H, 2), 8.30 (m, $^{1}J_{HH}$ = 8.1 Hz, $^{3}J_{HP}$ = 4.1 Hz, 1H, 4). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 26.0 (12), 32.9 (d, $^{3}J_{PC}$ = 12.5 Hz, 7), 34.4 (11), 39.2 (d, $^{2}J_{CP}$ = 21.8 Hz, 6), 69.3 (10), 76.7 (9), 129.6 (d, $^{3}J_{CP}$ = 14.3 Hz, 3), 132.8 (d,

$^{2}J_{CP}$ = 13.1 Hz, 2), 133.0 (d, $^{2}J_{CP}$ = 10.9 Hz, 4), 153.7 (d, $^{1}J_{CP}$ = 58.6 Hz, 1), 177.2 (8), 185.5 (d, $^{1}J_{CP}$ = 51 Hz, 5). **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 300K): δ = 208.5.

(*S*)-2-(6-*tert*-Butylphosphinin-2-yl)-4,5-dihydro-4-phenyloxazol (127)

According to *general procedure 12* the product was obtained after evaporation of the toluene as a yellow solid (104 mg, 89%).



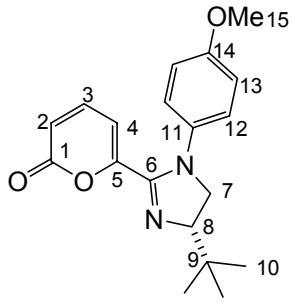
$C_{18}H_{20}NOP$ (297.33)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 1.49 (d, $^{4}J_{PH}$ = 1.8 Hz, 9H, 7), 4.29 (*ps*t, $^{2}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 8.3 Hz, 1H, 9), 4.83 (dd, $^{3}J_{HH}$ = 10.1 Hz, $^{2}J_{HH}$ = 8.3 Hz, 1H, 9), 5.40 (*ps*t, $^{3}J_{HH}$ = 8.4 Hz, $^{3}J_{HH}$ = 9.9 Hz, 1H, 10), 7.29-7.38 (m, 5H, Ph), 7.57 (dt, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HP}$ = 4.3 Hz, 1H, 3), 8.02 (dd, $^{3}J_{HH}$ = 8.6 Hz, $^{3}J_{HP}$ = 6.3 Hz, 1H, 2), 8.30 (dd, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HP}$ = 4.6 Hz, 1H, 4). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 32.9 (d, $^{3}J_{CP}$ = 12.5 Hz, 7), 39.3 (d, $^{2}J_{CP}$ = 21.9 Hz, 6), 70.5 (10), 75.3 (9), 127.1 (12), 127.8 (14), 129.0 (13), 129.8 (d, $^{3}J_{CP}$ = 14.2 Hz, 3), 133.1 (d, $^{2}J_{CP}$ = 13.2 Hz, 4), 133.3 (d, $^{2}J_{CP}$ = 10.7 Hz, 2), 143.1 (11), 152.9 (1), ~175 (8), 185.7 (d, $^{1}J_{CP}$ = 58.7 Hz, 5). **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 300K): δ = 210.8.

7.4.5 A Related Chiral Chelating Phosphininimidazoline

6-[(*S*)-4-*tert*-Butyl-4,5-dihydro-1-(4-methoxyphenyl)-1*H*-imidazol-2yl]-2*H*-pyran-2-one (130)[139]

Compound **122** (430 mg, 2.07 mmol) was dissolved in thionyl chloride (3 mL) and DMF (4 drops) and stirred for 4 h at reflux. Excess thionyl chloride was removed by and the chloroimidoylchloride was dissolved in dry toluene (5 mL). Dry triethylamine (0.9 mL, 6.3 mmol), and 4-methoxyaniline (565 mg, 5.28 mmol) were added and the reaction mixture was stirred for 15 h under reflux. The solution was washed with 10% NaOH (20 mL) and the aqueous layer was reextracted with dichloromethane (2 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over $MgSO_4$. Column chromatography on silica eluting with ethyl acetate and hexane afforded light yellow crystals (440 mg, 65%).

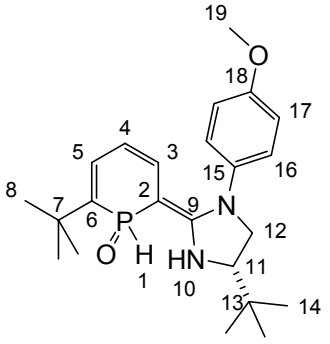


$C_{19}H_{22}N_2O_3$ (326.39)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.96 (s, 9H, 10), 3.56 (*ps*t, 1H, 7), 3.77 (s, 3H, 15), 3.97 (m, 2H, 7/8), 6.26 (dd, $^3J_{HH}$ = 9.4 Hz, $^4J_{HH}$ = 1 Hz, 1H, 4), 6.62 (dd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1Hz, 1H, 2), 6.81 (d, $^3J_{HH}$ = 9.0 Hz, 1H, 18), 6.91 (d, $^3J_{HH}$ = 9.0 Hz, 1H, 19), 7.26 (dd, $^3J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 26.0 (10), 34.4 (9), 55.6 (15), 56.2 (7), 75.0 (8), 107.1 (4), 114.7 (12), 117.5 (2), 124.9 (13), 135.7 (11), 142.6 (3), 153.3 (5), 155.3 (6), 157.3 (14), 160.3 (1). **TLC** (hexane: ethyl acetyte; 1:10) R_f = 0.14-0.32. **EA** %found (calcd): C: 67.61 (69.92), H: 6.77 (6.79), N: 8.30 (8.58).

(*S,2E*)-2-(6-*tert*-Butylphosphininoxide-2(*1H*)-ylidene)-4-*tert*-butyl-4,5-dihydro-1-(4-methoxyphenyl)-1*H*-imidazolidine (132)

According to *general procedure 11* 6-oxo-6*H*-pyran-2-acid imidazoline **130** (365 mg, 1.1 mmol), (2,2-dimethylpropylidyne)phosphine **115** (0.87 mL, 3.79 M in TMS_2O, 3.3 mmol) were reacted in toluene (3 mL) for 3 weeks. Since the heater was out of order for some time, the actual reaction time is shorter. The brown crude was purified by column chromatography (ethyl acetate: ethanol, 9:1) to yield a yellow to brown oil (36.6 mg, 8.3%). 82% of the 6-oxo-6*H*-pyran-2-acid imidazoline could be reisolated.



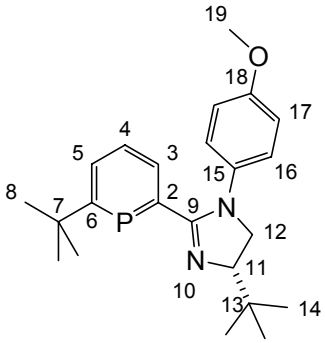
$C_{23}H_{33}N_2O_2P$ (400.49)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.92 (s, 9H, 14), 1.35 (s, 9H, 8), 3.46 (dd, $^3J_{HH}$ = 5.8, $^2J_{HH}$ = 10.1Hz, 1H, 12), 3.72 (m, 1H, 11), 3.79 (s, 3H, 19), 4.28 (*ps*t, $^2J_{HH}$ = 10.1 Hz, 1H, 12), 5.06 (ddd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 9.3 Hz, $^4J_{PH}$ = 3.1 Hz 1H, 4), 6.01 (dd, $^3J_{HH}$ = 9.3 Hz,

$^{3}J_{PH}$ = 23.2 Hz, 1H, 5), 6.78 (dd, $^{3}J_{HH}$ = 7.3 Hz, $^{3}J_{PH}$ = 34 Hz, 1H, 3), 6.86 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, 17), 7.09 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, 18), 8.75 (d, $^{1}J_{PH}$ = 484.4 Hz, 1H, 1). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 25.1 (14), 31.0 (d, $^{3}J_{CP}$ = 5.2 Hz, 8), 33.9 (13), 36.1 (d, $^{2}J_{CP}$ =7.7 Hz, 7), 55.6 (19), 56.1 (12), 62.3 (11), 105.3 (d, $^{3}J_{CP}$ = 17.8 Hz, 4), 115.0 (16), 115.3 (d, $^{1}J_{CP}$ = 70.4 Hz, 1), 126.0 (17), 128.5 (d, $^{2}J_{CP}$ = 0 Hz, 5), 129.4 (d, $^{1}J_{CP}$ = 95.1 Hz, 6), 135.0 (d, $^{2}J_{CP}$ = 23.0 Hz, 3), 135.0 (15), 157.8 (18), 162.6 (d, $^{2}J_{CP}$ = 10.7 Hz, 9). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 1.7. **TLC** (ethyl acetate:ethanol; 98:2): R_f = 0.18.

(*S*)-2-(6-*tert*-Butylphosphinin-2-yl)-4-*tert*-butyl-4,5-dihydro-1-(4-methoxyphenyl)-1*H*-imidazol (131)

According to *general procedure 12* the crude product was obtained after evaporation of toluene.



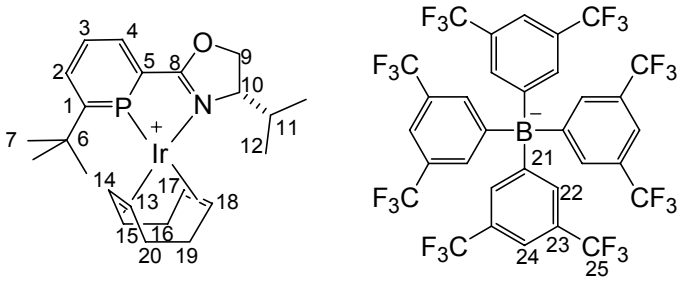
$C_{23}H_{31}N_2OP$ (382.48)

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2 , 300K): δ = 212.4.

7.4.6 Synthesis of Phosphinine-Iridium Complexes

(*S*)-2-(6-*tert*-Butylphosphinin-2-yl)-4,5-dihydro-4-isopropyloxazol-η^{4}-(1,5-cycloocta-diene)-iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (133)

According to *general procedure 14* **105** (40 mg, 152 μmol),$[Ir(cod)Cl]_2$ (51 mg, 76 μmol) and $NaBAr_F$ (175 mg, 197 μmol) were reacted in dichloromethane (3.5 mL). The product was obtained as a black foam that could be recrystallized from dichloromethane/hexane in black needles.

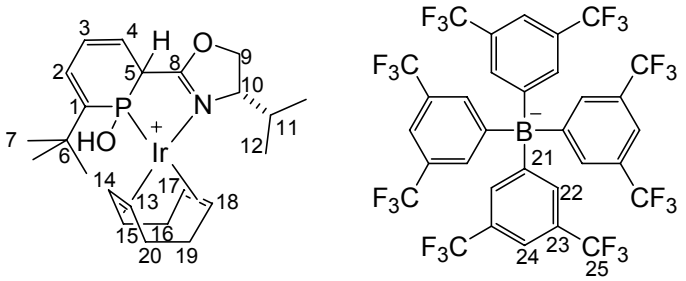


$C_{55}H_{46}BF_{24}IrNOP$ (1426.92)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.81 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, 12), 1.0 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H, 12'), 1.4 (s, 9H, 7), 1.76 (m, 1H, cod_a), 1.93 (m, 1H, cod_b), 2.07 (m, 1H, cod_c), 2.11 (m, 1H, 11), 2.20-2.4 (m, 4H, cod_{a-d}), 2.56 (m, 1H, cod_d), 3.87 (m, 1H, 10), 4.42 (m, 1H, cod, 18), 4.59 (t, 1H, 9), 4.67 (m, 1H, cod, 14), 4.77 (m, 1H, cod, 17), 4.91 (m, 1H, 9), 5.36 (m, 1H, cod, 13), 7.56 (s, 4H, 24), 7.63 (m, 1H, 3), 7.72 (s, 8H, 22), 8.01 (ddd, 1H, 4), 8.25 (ddd, 1H, 2). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 14.6 (12), 18.4 (12), 28.6 (cod_a), 30.1 (cod_b), 30.5 (cod_c), 32.2 (d, $^{3}J_{CP}$ = 8.5 Hz, 7), 34.5 (cod_d), 39.1 (d, $^{1}J^{CP}$ 3.8 Hz, 6),39.2 (11), 68.8 (18), 72.8 (9), 74.0 (17), 86.6 (d, $^{2}J_{CP}$ = 17.5 Hz, 14), 92.9 (d, $^{2}J_{CP}$ = 7.8 Hz, 13), 117.8 (q, $^{3}J_{CF}$ = 3.8 Hz, 24), 125.0 (q, $^{1}J_{CF}$ = 272.5 Hz, 25), 129.2 (qq, 23), 130.3 (d, $^{3}J_{CP}$ = 26.4 Hz, 3), 135.2 (s, 22), 136.4 (d, $^{2}J_{CP}$ = 13.9 Hz, 2), 140.8 (d, $^{2}J_{CP}$ = 12.8 Hz, 4), 162.1 (q, $^{1}J_{BC}$ = 50 Hz, 21), 171.0 (8). **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 300K) δ = 176.9. **MS** (+ESI) m/z: 564.4 (M^+(^{193}Ir), 90.4), 562.4 (M^+(^{191}Ir), 90.4), 413.4 ($C_{12}H_5IrNOP^+$, 39.0).

(*S*)-2-(6-*tert*-Butylphosphinin-2-yl)-4,5-dihydro-4-isopropyloxazol-η^4-(1,5-cycloocta-diene)-iridium(I) Tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (136)

An attempt to recrystallize **133** in dichloromethane/diethyl ether (which probably contained traced of water) led to compound **136** an orange powder.

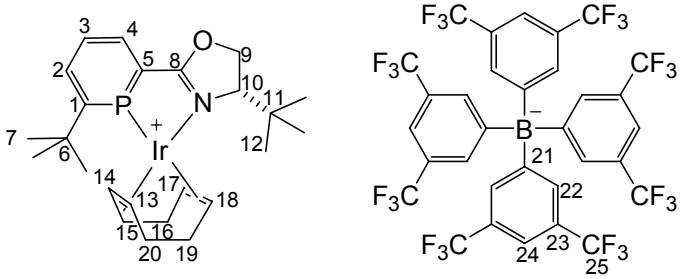


^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 0.54 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, 12), 0.87 (d, $^{3}J_{HH}$ 7.1 Hz, 3H, 12'), 1.35 (s, 9H, 7), 1.80 (m, 1H, 11), 2.0 (m, 3H, cod), 2.28 (m, 4H, cod), 2.39 (m, 1H, cod), 3.92 (m, 1H, 10), 4.21 (m, 1H, 13), 4.25 (m, 2H, 5/14), 4.44 (t, 1H, 9), 4.58 (ddd, 1H, 9), 4.84 (m, 1H, 18), 5.04 (m, 1H, 17), 6.16 (dt, 1H, 4), 6.38 (m, 1H, 3), 6.65 (dd, 1H, 2),

7.56 (s, 4H, 24), 7.72 (s, 8H, 22). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 14.1 (12), 18.4 (12'), 28.4 (d, $^{4}J_{CP}$ = 3.4 Hz, cod), 31.0 (d, $^{4}J_{CP}$ = 4.4 Hz, cod), 31.1 (d, $^{3}J_{CP}$ = 5.3 Hz, 7), 31.7 (d, $^{4}J_{CP}$ = 2.9 Hz, cod), 33.9 (d, $^{4}J_{CP}$ = 4.8 Hz, cod), 36.7 (d, $^{2}J_{CP}$ = 14.4 Hz, 6), 44.2 (d, $^{1}J_{CP}$ = 29.3 Hz, 5), 64.5 (14), 66.9 (13), 67.6 (10), 72.7 (9), 89.5 (d, $^{3}J_{CP}$ = 15.8 Hz, 18), 96.6 (d, $^{3}J_{CP}$ = 12.5 Hz, 17), 117.8 (q, $^{3}J_{CF}$ = 3.8 Hz, 24), 120.4 (d, $^{2}J_{CP}$ = 8.6 Hz, 4), 125.0 (q, $^{1}J_{CF}$ = 272.5 Hz, 25), 128.3 (d, $^{2}J_{CP}$ = 14.4 Hz, 3), 129.2 (qq, 23), 129.4 (d, $^{3}J_{CP}$ = 5.8 Hz, 2) 130.3 (d, $^{3}J_{CP}$ = 26.4 Hz, 3), 135.2 (s, 22), 144.3 (d, $^{1}J_{CP}$ = Hz, 1), 162.1 (q, $^{1}J_{BC}$ = 50 Hz, 21), 172.8 (8). **^{31}P{^{1}H} NMR** (162.0 MHz, CD_2Cl_2, 300K) δ = 87.5.

(*S*)-2-(6-*tert*-Butylphosphinin-2-yl)-4,5-dihydro-4-*tert*-butyloxazol-η^{4}-(1,5-cyclooctadiene)-iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (134)

According to *general procedure 14* **126** (35 mg, 136 μmol),$[Ir(cod)Cl]_2$ (38.6 mg, 57.4 μmol) and $NABAr_F$ (145 mg, 164 μmol) were reacted in dichloromethane (3 mL). The product was obtained as a black foam. The product could not be recrystallized from either dichloromethane/hexane, dichloromethane/diethyl ether or diethyl ether/hexane.

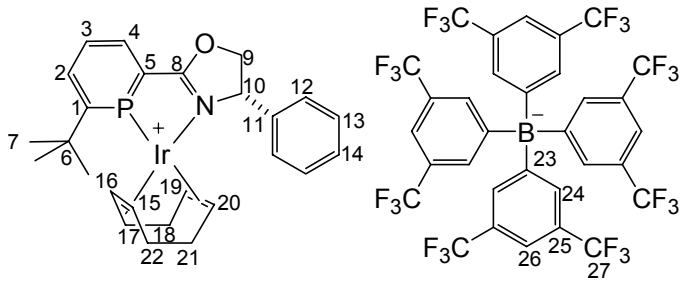


$C_{56}H_{48}BF_{24}IrNOP$ (1440.95)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 1.03 (s, 9H, 12), 1.40 (s, 9H, 7), 1.65 (m, 1H, cod), 1.93 (m, 1H, cod), 2.05 (m, 1H, cod), 2.13-2.30 (m, 3H, cod), 2.43 (m, 1H, cod), 2.54 (m, 1H, cod), 3.72 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, 10), 4.29 (m, 1H, 14), 4.57 (t, 1H, 9), 4.65 (m, 1H, 18), 4.80 (m_{br}, 1H, 13), 5.04 (dd, $^{3}J_{HH}$ = 2.5, 10.0 Hz, 1H, 9), 5.40 (m br, 1H, 17), 7.56 (s, 4H, 24), 7.62 (dd, $^{3}J_{HH}$ = 7.5, $^{3}J_{PH}$ = 16.5, 21.5 Hz, 1H, 3), 7.72 (s, 8H, 22), 8.02 (dd, $^{3}J_{HH}$ = 8.0, $^{3}J_{PH}$ = 14.5 Hz, 1H, 4), 8.26 (dd, $^{3}J_{HH}$ = 8.5, $^{3}J_{PH}$ = 20.5 Hz, 1H, 2). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 25.9 (12), 27.3 (d, $^{2}J_{CP}$ = 4Hz, cod), 29.6 (11), 30.8 (d, $^{2}J_{CP}$ = 17.4 Hz, cod), 31.9 (d, $^{3}J_{CP}$ = 8.9 Hz, 7) 35.6 (cod), 36.0 (d, $^{2}J_{CP}$ = 6.4 Hz, 6), 67.5 (14), 70.3 (10), 74.1 (9), 74.4 (13), 87.1 (d, $^{2}J_{CP}$ = 19.8 Hz, 18), 92.8 (d, $^{2}J_{CP}$ = 19.8 Hz, 17), 117.8 (q, $^{3}J_{CF}$ = 4Hz, 24), 125.0 (q, $^{1}J_{CF}$ = 270 Hz, 25), 129.3 (q, $^{2}J_{CF}$ = 25.7 Hz 23), 129.4 (d, $^{3}J_{CP}$ = 16.25 Hz, 3), 135.2 (s, 22), 136.2 (d, $^{2}J_{CP}$ = 13.3 Hz, 4), 140.9 (d, $^{2}J_{CP}$ = 11.4 Hz, 2), 162.0 (q, $^{1}J_{CB}$ = 50 Hz, 21). **^{31}P{^{1}H} NMR** (202.5 MHz, CD_2Cl_2, 300K): δ = 179.3.

(*S*)-2-(6-*tert*-Butylphosphinin-2-yl)-4,5-dihydro-4-phenyloxazol-η^4-(1,5-cyclooctadiene)-iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (135)

According to *general procedure 14* **127** (30 mg, 101 µmol),$[Ir(cod)Cl]_2$ (33.7 mg, 50.2 µmol) and $NABAr_F$ (115.2 mg, 130 µmol) were reacted in dichloromethane (5 mL). The product was obtained as an orange foam and contained about 20% impurities.

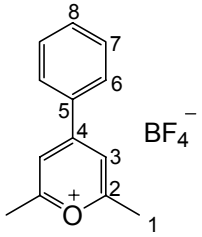


^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 1.41 (s, 9H, 7), 1.75 (m, 1H, cod), 1.86 (m, 2H, cod), 1.99 (m, 1H, cod), 2.10 (m, 1H, cod), 2.16-2.32 (m, 3H, cod), 4.51 (m, 1H, cod), 4.60 (m, 2H, cod), 4.77 (dd, $^2J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 5.3 Hz, 1H, 9), 5.11 (dd, $^2J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 9.8 Hz, 1H, 9), 5.22 (ddd, 1H, cod), 5.38 (m, 1H, 10), 7.25 (m, 2H, 12), 7.45 (m, 3H, 13/14), 7.56 (s, 4H, 26), 7.69 (dd, $^3J_{HH}$ = 8.9 Hz, 1H, 3), 7.72 (s, 8H, 24), 8.12 (ddd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.0 Hz, $^3J_{PH}$ = 15.2 Hz, 1H, 4), 8.30 (ddd, $^3J_{HH}$ = 9.1, $^4J_{HH}$ = 1.0 Hz, $^3J_{PH}$ = 21.7 Hz, 1H, 2).
^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 300K): δ = 176.2.

7.4.7 Iridium-Complexes with Monodentate Phosphinines

2,6-Methyl-4-phenyl-pyrylium tetrafluoroborate (137)[119]

2,6-Dimethyl-4-pyrone (5.0 g, 40 mmol) was dissolved in anisole (40 mL) with gentle heating. The solution was cooled to 5 °C and PhMgBr (1M in diethyl ether, 40 mmol) was added slowly *via* cannula. The purple solution was then warmed to room temperature and poured over HBF_4 (54% in diethyl ether, 6.7 mL 48 mmol). The pale pink precipitate was isolated by filtration and washed with diehtyl ether. The pink-orange powder was recrystallized from hot water to give thin yellow-orange crystalls (26%-44%).

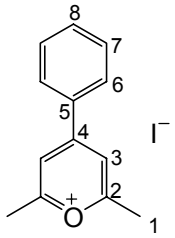


$C_{13}H_{13}BF_4O$ (272.05)

^{1}H NMR (400.1 MHz, DMSO, 300K): δ = 2.04 (s, 6H, 1), 6.72 (dd, $^{3}J_{HH}$ = 7.3 Hz, 2H, 6), 6.83 (*pst*, $^{3}J_{HH}$ = 7.3 Hz, 1H, 8), 7.22 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H, 7), 7.47 (s, 2H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, DMSO, 300K): δ = 21.1 (1), 118.0 (3), 129.3 (7), 129.8 (6), 131.1 (8), 135.3 (5), 166.0 (4), 177.7 (2). **MS** (+FAB, 3-NBA), m/z: 185 (M^+, 100). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3368m$_{br}$, 3096m, 2929w, 1639s, 1590s, 1534m, 1453m, 1335m, 1288w, 1218m, 1065s$_{br}$, 941m, 881m, 786m, 685m, 559w, 519m. **m.p.** 205°C. **EA** %found (calcd): C: 57.47 (57.40), H: 4.84 (4.82), O: 5.99 (5.88).

2,6-Methyl-4-phenyl-pyrylium iodide (139)[122]

To a warm slurry of 2,6-dimethyl-4-phenyltetrafluoroborate (2.85 g, 10.48 mmol) in water (50 mL) and acetic acid (2 drops) was added KI (1.64 g, 10.48 mmol). The solution was stirred at 50°C for 1.5 hours, until red, and cooled to room temperature. The iodide was collected by filtration, washed several times with diethyl ether and dried under high-vacuum. The product was obtained as a red crystalline solid (3.25 g, 100%).

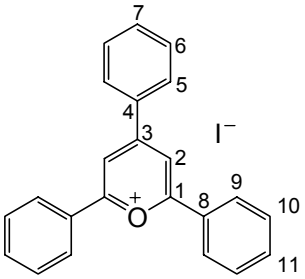


$C_{13}H_{13}IO$ (312.15)

^{1}H NMR (400.1 MHz, DMSO, 300K): δ = 2.00 (s, 6H, 1), 6.68 (*pst*, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HH}$ = 7.3 Hz, 2H, 6), 6.80 (*pst*, $^{3}J_{HH}$ = 7.3 Hz, 1H, 8), 7.24 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H, 7), 7.58 (s, 2H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, DMSO, 300K): δ = 21.4 (1), 118.2 (3), 129.5 (7), 129.8 (6), 131.2 (8), 135.3 (5), 165.6 (4), 177.6 (2). **MS** (+FAB, 3-NBA), m/z: 185 (M^+, 100). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3019m, 2929w, 2365w, 1636s, 1589m, 1533s, 1450m, 1331m, 1218m, 1190w, 1155w, 1078m, 1032m, 941m, 896w, 868w, 787m, 683m. **m.p.** 213-214°C.

2,4,6-Triphenyl-pyrylium iodide (140)

To a warm slurry of 2,4,6-triphenylpyrylium tetrafluoroborate (1.505 g, 3.8 mmol) in water (20 mL) and acetic acid (2 drops) was added KI (0.59 g, 3.8 mmol). The solution was stirred for 1.5 hours, until red, and cooled to room temperature. The iodide was collected by filtration, washed several times with diethyl ether and dried under high-vacuum. The product was obtained as a red crystalline solid (1.65 g, 100%).

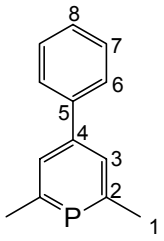


$C_{23}H_{17}IO$ (436.28)

^{1}H NMR (400.1 MHz, MeOD, 300K): δ = 7.75-7.88 (m, 9H), 8.44 (d, 2H), 8.52 (m, 4H), 9.00 (d, 2H). **MS** (+FAB, 3-NBA), m/z: 309 (MH^+, 100), 77 (Ph^+, 18.1). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 1621.1s, 1577.6s, 1528.6m, 1496.2222s, 1467.8s, 1419.4m, 1345.1w, 1273.4m, 1248.7s, 1195.1w, 1158.7w, 1056.7w, 996.1s, 953.9m, 883.6w, 772.3s, 716.0m, 679.5s, 602.7s. **m.p.** 246°C.

2,6-Methyl-4-phenyl-λ^3-phosphinin (141)

To a solution of 2,6-dimethyl-4-phenylpyrylium iodide (717 mg, 2.3 mmol) in dry acetonitrile (13 mL) under argon is added tris(trimethylsilyl)phosphine (0.75 mL, 2.6 mmol). The mixture is heated to reflux and stirred at this temperature for 20 hours. Then silica is added and the volatiles are carefully evaporated through a frit. The mixture is purified by column chromatography on silica eluting with hexane (2% ethyl acetate). The product is obtained as a light-yellow solid (240 mg, 52%). Kugelrohrdistillation (10^{-1} mbar, 150°C) affords a white solid.



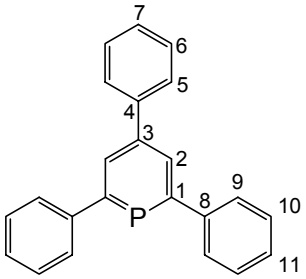
$C_{13}H_{13}P$ (200.22)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 2.72 (d, $^3J_{HP}$ = 14.9 Hz, 6H, 1), 7.36 (*pst*, $^3J_{HH}$ = 7.3 Hz, 1H, 8), 7.45 (m, 2H, 6), 7.58 (m, 2H, 7), 7.73 (d, $^3J_{HP}$ = 6.8, Hz, 2H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 24.8 (d, $^2J_{CP}$ = 36.0 Hz, 1), 127.7 (8), 127.8 (d, $^5J_{CP}$ = 1.5 Hz, 6), 129.0 (7), 132.3 (d, $^2J_{CP}$ = 13.4 Hz, 3), 142.5 (5), 143.5 (4), 168.6 (d, $^1J_{CP}$ = 50.2 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 193.6. **MS** (+EI) m/z**:** 200.1 (M^+, 100), 185.1 (M^+-CH_3, 38.6). **IR (KBr):** $\tilde{\nu}$ [cm^{-1}] = 3448br, 2994m, 2946m, 2904m, 2847m, 1953w, 1891w, 1814w, 1766w, 1596w, 1565m, 1439s, 1377s, 1180w, 1102m, 1075m, 877s, 736s,

898s. **m.p.** 56-57**°C. TLC** (hexane:ethyl acetate; 98:2) R_f = 0.4. **EA** %found (calcd) C: 78.11 (77.99), H: 6.60 (6.54).

2,4,6-Triphenyl-λ^3-phosphinine (97)

2,4,6-Triphenylpyrylium iodide (1.1 g, 2.5 mmol) was dissolved in acetonitrile (15 mL). $P(TMS)_3$ (0.7g, 2.8mmol) was added *via* syringe and the mixture was heated to reflux for 24 hours. After evaporation of the volatiles the mixture was purified by column chromatography on silica (hexane:ethyl acetate, 10:1). The product is obtained as a light-yellow solid (405 mg, 50%).

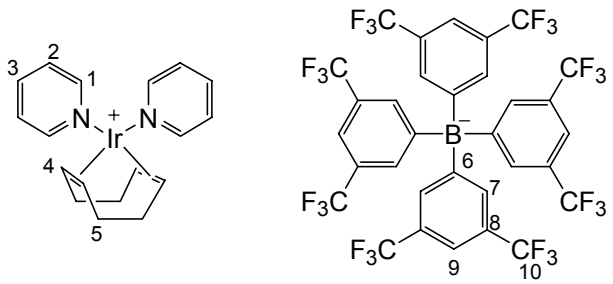


$C_{23}H_{17}P$ (324.25)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 7.43 (m, 3H, 8/11), 7.50 (m, 6H, 5/9), 7.70 (d, $^3J_{HH}$ = 7.3 Hz, 2H, 7), 7.75 (d, $^3J_{HH}$ = 8.3 Hz, 4H, 9), 8.18-8.2 (d, $^3J_{HP}$ = 5.8 Hz, 2H, 2). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 127.8 (7), 127.9 (5), 128.0 (d, $^3J_{CP}$ = 15.3 Hz, 9), 128.1 (6), 129.1 (10), 129.2 (11), 131.9 (d, $^2J_{CP}$ = 12.3 Hz, 2), 142.3 (d, $^4J_{CP}$ = 3.0 Hz, 4), 143.5 (d, $^2J_{CP}$ = 24.2 Hz, 8), 144.2 (d, $^3J_{CP}$ = 13.8 Hz, 3), 171.9 (d, $^1J_{CP}$ = 51.8 Hz, 1). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 184.1. **MS** (+EI) m/z: 324 (M^+, 100), 246 (15.08), 233 (11.77), 191 (14.17). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3447br, 3018w, 1569m, 1489m, 1442m, 1379m, 1348m, 1075m, 1026m, 887m, 754s, 693s, 587m, 484m. **m.p.** 167°C. **TLC** (hexane:ethyl acetate 10:1) R_f = 0.56. **EA** %found (calcd) C 84.83 (85.17), H 5.36 (5.28).

η^4-(1,5-Cyclooctadiene)bis(pyridine)iridium(I) Tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate (142)[224]

[Ir(cod)Cl]2 (420 mg, 620 μmol) was dissolved in dichloromethane (20 mL). Pyridine (0.7 mL, 8.62 mmol) were added, which resulted in a colorchange from orange to yellow. After stirring for 15 minutes at room temperature, $NaBAr_F$ (1.2 g, 1.35 mmol) was added and the solution was stirred for 7 hours at room temperature. Filtration and evaporation of the volatiles afforded **142** as a yellow powder that was recrystallized from dichloromethane/hexane (1.64 g, 95%).

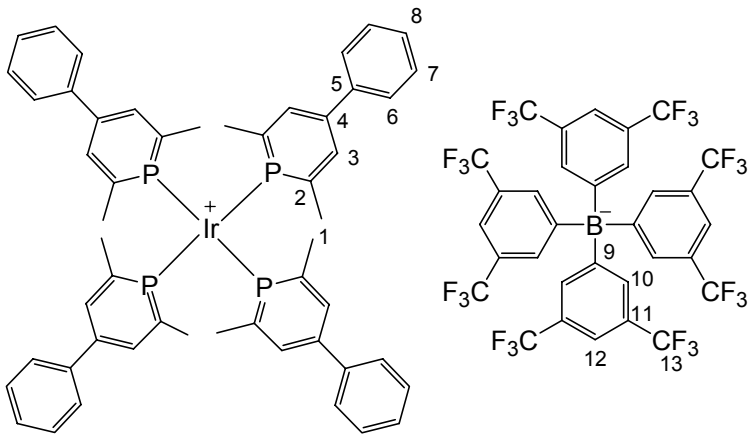


$C_{50}H_{34}BF_{24}IrN_2$ (1321.81)

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 1.86 (q, 4H, 5), 2.39 (m, 4H, 5), 3.81 (d, 4H, 4), 7.27 (m, 4H, 1), 7.5 (s, 4H, 7), 7.63 (m, 2H, 3), 7.7 (s, 8H, 9), 8.6 (d, 4H, 2). **^{13}C{^{1}H} NMR** (100.6 MHz, CD_2Cl_2, 300K): δ = 31.4 (5), 71.7 (4), 117.6 (9), 124.6 (q, $^1J_{CF}$ = 272 Hz, 10), 127.1 (2), 129.1(q, $^2J_{CF}$ = 28.7 Hz, 8), 134.9 (7), 139.4 (3), 149.2 (1). **MS** (+ESI) m/z: 460.0 (M^+, 19.3), 458.9 (M^+, 100), 457.0 (M^+, 59.5). **EA** %found (calcd): C 45.35 (35.43); H 2.60 (2.59); N 2.30 (2.12).

Tetrakis(2,4-methyl-6-phenyl-phosphinine)-iridium(I) tetrakis-[3,5-bis(trifluoromethyl) phenyl]borate (144)

To a solution of bis(pyridine)-η^4-(1,5-cyclooctadiene)-iridium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (132.2 mg, 0.1 mmol) in dichloromethane (1 mL) was added 2,6-dimethyl-4-phenylphosphinine (20 mg, 0.1 mmol). The yellow solution turned instantaniously red. Column chromatography of the mixture afforded a violet-red product and starting material.



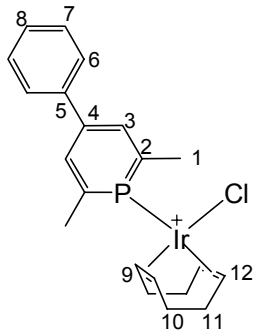
$C_{84}H_{64}BF_{24}IrP_4$ (1856.29)

^{1}H NMR (500.1 MHz, CD_2Cl_2, 300K): δ = 2.62 (t, 24H, 1), 7.42 (m, 12H, 6/8), 7.54 (m, 12H, 7/12), 7.7 (s, 8H, 10), 7.98 (m, 8H, 3). **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 300K): δ = 23.7 (m, 1), 117.8 (q, $^3J_{CF}$ = 3.8 Hz, 12), 125.0 (q, $^1J_{CF}$ = 272.5 Hz, 13), 128.7 (3), 129.2 (q, $^2J_{CF}$ =

31.1 Hz, 11), 129.5 (7), 135.2 (s, 10), 137.6 (6/8), 141.2 (5), 142.0 (4), 154.7 (m, 2), 162.1 (q, $^{1}J_{BC}$ = 50 Hz, 9). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 144.9. **MS** (+FAB, 3-NBA), m/z: 993 (M^+, 100), 793 (M^+-L, 53.6), 793 (M^+-2L, 81.7). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 2923.8, 1609.7, 1457.0, 1355.5, 1277.9, 1124.3, 885.6, 836.9, 725.5, 674.9. **TLC** (dichloromethane) R_f = 0.86.

Chloro-η^4-(1,5-cyclooctadiene)-(2,4-methyl-6-phenyl-phosphinine)-iridium(I) (145)

To a solution of bis-chloro-η^4-(1,5-cyclooctadiene) iridium (I) dimer (50 mg, 74 μmol) in dichloromethane (1 mL), was added ,6-dimethyl-4-phenylphosphinine (30 mg, 150 μmol). The solution was stirred for 1 hour at room temperature. Then the solvent was evaporated and the crude was washed with pentane (3×1 mL). Drying under high-vacuum yielded an orange solid (78.5 mg, 99%).



$C_{21}H_{25}ClIrP$ (536.07)

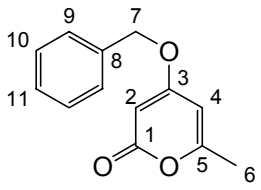
^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 1.91 (s_{br}, 4H, 10/11), 2.34 (s_{br}, 4H, 10/11), 2.80 (d, $^{3}J_{HP}$ = 14.9 Hz, 6H, 1), 3.53 (s_{br}, 2H, 9), 5.36 (s_{br}, 2H, 12), 7.38 (m, 1H, 8), 7.44 (m, 2H, 7), 7.50 (m, 2H, 6), 7.84 (d, $^{3}J_{HP}$ = 19.7 Hz, 2H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 23.1 (d, $^{2}J_{CP}$ = 19.55 Hz, 1), 29.8 (10), 34.4 (11), 54.3 (9), 97.5 (d, $^{3}J_{CP}$ = 11.8 Hz, 12), 127.5 (d, $^{4}J_{CP}$ = 3.2 Hz, 6), 127.9 (8), 129.1 (7), 136.5 (d, $^{2}J_{CP}$ = 12.1 Hz, 3), 140.5 (d, $^{3}J_{CP}$ = 26.0 Hz, 4), 141.8 (d, $^{4}J_{CP}$ = 5.6 Hz, 5), 154.3 (d, $^{2}J_{CP}$ = 24.5 Hz, 2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 300K): δ = 178.1.

7.4.8 Towards 6-Ring-Chelating Phosphininoxazolines

4-(Benzyloxy)-6-methyl-2*H*-pyran-2-one (147)[146]

4-Hydroxy-6-methyl-2-pyrone (3 g, 23.79 mmol) and K_2CO_3 (9.85 g, 71.34 mmol) were dissolved in DMF (100 mL). At 0°C benzyl bromide was added dropwise to the solution. After stirring at room temperature for 1 hour the solution was quenched with water (100 mL).

Extraction with ethyl acetate (3×100 mL) was followed by column chromatography (hexane:ethyl acetate, 7:3) to afford a white crystalline solid (1.42 g, 28 %).

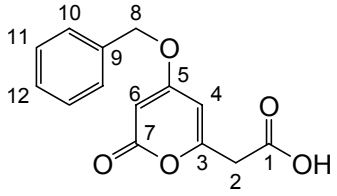


$C_{13}H_{12}O_3$ (216.23)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 2.20 (s, 3H, 6), 5.00 (s, 2H, 7), 5.49 (d, $^4J_{HH}$ = 2.0 Hz, 1H, 2), 5.83 (dd, $^4J_{HH}$ = 1.0 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, 4), 7.38 (m, 5H, 9-11). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 20.0 (6), 70.8 (7), 88.6 (2), 100.7 (4), 127.9 (9), 128.9 (11), 128.9 (10), 134.5 (8), 162.3 (5), 165.0 (3), 170.4 (1). **MS** (+EI) m/z: 216.1 (M^+, 2.8), 132 (9.9), 91, (Bn^+, 100), 65 (7.7). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3076w, 3035w, 1736s, 1648s, 1569s, 1497m, 1451s, 1380s, 1318m 1259s, 1181m, 1145s, 1014s, 949m, 909m, 859m, 819s, 737s, 692s, 594m. **m.p.** 89-90°C. **TLC** (hexane:ethyl acetate; 7:3) R_f = 0.28. **EA** %found (calcd): C: 72.18 (72.21), H: 5.59 (5.59).

2-(4-(Benzyloxy)-6-oxo-6*H*-pyran-2-yl)acetic acid (148)

To a solution of 4-benzyloxy-6-methyl-2-pyron (108 mg, 0.5 mmol) in dry THF (10 mL) at -78° LHMDS (1M in hexane, 0.8 mmol) are added over 10 minutes. The solution is stirred for 1 hour at -78°C. Then the dry-ice bath is removed and CO_2 is bubbled through the solution. The white dispersion is allowed to warm to room temperature. After extraction with diethyl ether (10 mL) and water (10 mL) the layers were separated. The organic layer was discarded. The aqueous layer was acidified to pH ≈1, and then extracted diethyl ether (3×10 mL). the combined organic phases were dried over Na_2SO_4. Filtration and evaporation of the volatiles gave a light-yellow oil which solidified upon standing to give an off-white solid (110 mg, 85%).



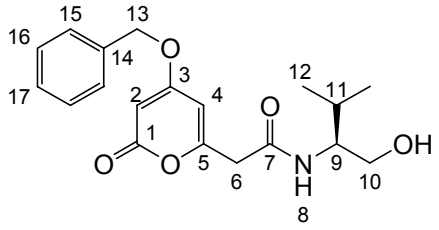
$C_{14}H_{12}O_5$ (260.24)

^{1}H NMR (400.1 MHz, DMSO, 300K): δ = 3.55 (s, 2H, 2), 5.15 (s, 2H, 8), 5.71 (d, $^3J_{HH}$ = 2.3 Hz, 1H, 4), 6.24 (d, $^3J_{HH}$ = 2.28 Hz, 1H, 6), 7.39 (m, 5H, 10-12). **^{13}C{^{1}H} NMR** (125.8 MHz,

DMSO, 300K): δ = 38.7 (2), 70.4 (8), 88.9 (4), 102.2 (6), 128.2 (11), 128.4 (12), 128.6 (10), 135.0 (9), 158.7 (3), 163.3 (5), 169.4 (1), 169.6 (7). **MS** (+FAB, 3-NBA), m/z: 261 (MH^+, 48.1), 149 (32.9), 91 ($PhCH_2^+$, 100). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 2941w_{br}, 2517 w_{br}, 1749m, 1720m, 1670s, 1636m, 1614s, 1549s, 1501m, 1456m, 1431m, 1367m ,1344s, 1313m, 1252s, 1236s, 1202m, 1190m, 1138m, 1080w, 1013m, 1003m_{sh}, 962s, 903w, 885m, 835m, 821m. **m.p.** 112-114°C. **EA** %found (calcd): C: 64.39 (64.61), H: 4.79 (4.65), O: 30.70 (30.74).

(*S*)-2-[4-(Benzyloxy)-6-oxo-6*H*-pyran-2-yl]-*N*-[(*S*)-1-hydroxy-3-methylbutan-2-yl]-acetamide (149)

According to *general procedure 13*, (5'-benzyloxy-3'-pyron)-acetic acid **148** (130 mg, 0.5 mmol), HOBt (91 mg, 0.67 mmol), EDC (128.4 mg, 0.67 mmol) and L-valinol (52 mg, 0.5 mmol) were reacted in dichloromethane (5 mL) and DMF (1 mL) to yield **149** (130 mg, 75%).



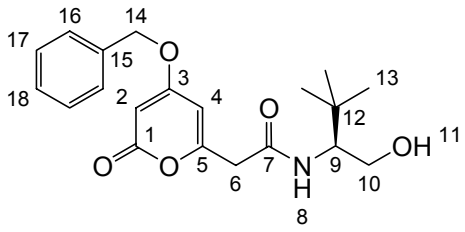
$C_{19}H_{23}NO_5$ (345.39)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.94 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 12), 0.90 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 12'), 1.89 (m, 1H, 11), 3.43 (2×d, $^2J_{HH}$ = 15.0 Hz, 2H, 6), 3.71 (m, 3H, 9/10), 5.02 (s, 2H, 13), 5.54 (d, $^3J_{HH}$ = 2.3 Hz, 1H, 4), 6.09 (d, $^3J_{HH}$ = 2.0 Hz, 1H, 2), 7.36 (m, 5H, Ph). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 18.9 (12), 19.5 (12), 28.9 (11), 41.8 (6), 57.6 (10), 63.3 (9), 71.0 (13), 89.4 (4), 102.9 (2), 127.9 (Ph), 128.8 (Ph), 128.9 (Ph), 134.1 (14), 158.5 (5), 164.4 (3), 166.9 (7), 170.2 (1). **MS** (+FAB, 3-NBA), m/z: 346 (MH^+, 29.6), 91 (Bn^+, 100). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3300w, 3072w, 2961w, 1726s, 11643s, 1545s, 1499w, 1456w, 1435m, 1373w, 1331w,1244m, 1167w, 1140m, 1078w, 1018m, 1003m_{sh}, 943w, 914w, 866w, 810m. **m.p.** 154°C. $[\alpha]_D^{20}$: -23.1° (c = 1.01, $CHCl_3$). **TLC** (ethyl acetate:ethanol; 98:2): R_f = 0.33. **EA** %found (calcd): C: 65.91 (66.07), H: 6.63 (6.71), N: 3.95 (4.06), O: 23.22 (23.16).

(*S*)-2-[4-(Benzyloxy)-6-oxo-6*H*-pyran-2-yl]-*N*-[(S)-1-hydroxy-3,3-dimethylbutan-2-yl]acetamid (150)

According to *general procedure 13* **148** (1g, 3.85 mmol), HOBt (1.04 g, 7.7 mmol), EDC (1.47 mg, 7.7 mmol), and L-*tert*-leucinol (450 mg, 3.85 mmol) were reacted in DMF (4 mL)

and dichloromethane (40 mL). After column chromatography on silica eluting with ethyl acetate and ethanol **150** was obtained as an off-white solid (935 mg, 67%).

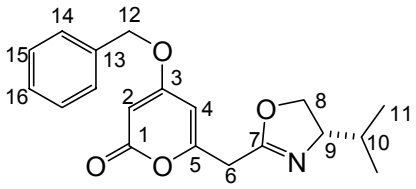


$C_{20}H_{25}NO_5$ (359.42)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.95 (s, 9H, 13), 3.01 (s_{br}, 1H, 11), 3.48 (m, 2H, 6), 3.56 (m, 1H, 10), 3.81 (m, 2H, 9/10), 5.0 (s, 2H, 14), 5.52 (d, 1H, 2), 6.1 (d, 1H, 4), 6.75 (d, 1H, 8), 7.36 (m, 5H, 16-18). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 27.0 (13), 33.9 (12), 41.7 (6), 60.1 (9), 62.4 (10), 71.1 (14), 89.4 (2), 103.0 (4), 127.9 (16/18), 129.0 (17), 134.3 (15), 159.1 (5), 164.8 (1), 167.5 (7), 170.5 (3). **TLC** (ethyl acetate:ethanol; 98:2) R_f = 0.2

(*S*)-4-Benzyloxy-6-[(4,5-dihydro-4-isopropyloxazol-2-yl)methyl]-*2H*-pyran-2-one (151)

Amide **149** (750 mg, 2.18 mmol) and DMAP (27 mg, 10 mol%) were dissolved in dichloromethane (5 mL). Triethylamine (0.73 mL, 5.5 mmol) and tosyl chloride (415 mg, 2.18 mmol) in dichloromethane (6 mL) were added successively. The mixture was allowed to stir for 24 hours at room temperature. Extraction with saturated ammoniumchloride (15 mL), $NaHCO_3$ solution (15 mL) and brine (15 mL) was followed by drying over Na_2SO_4. After filtration the volatiles were evaporated. After column chromatography on silica with eluting with diethyl ether and triethylamine, product **151** was obtained as a light yellow solid (681 mg, 96 %).



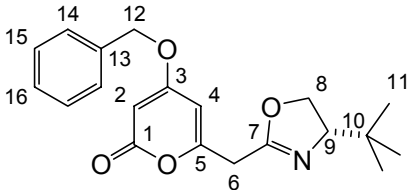
$C_{19}H_{21}NO_4$ (327.37)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.84 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 11), 0.92 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 11'), 1.70 (m, 1H, 10), 3.42 (s, 2H, 6), 3.89 (m, 1H, 9), 3.95 (m, 1H, 8), 4.24 (m, 1H, 8), 4.99 (s, 2H, 12), 5.48 (d, $^3J_{HH}$ = 2.28 Hz, 1H, 4), 6.02 (d, $^3J_{HH}$ = 2.28 Hz, 1H, 2), 7.37 (m, 5H, 14-16). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 17.9 (11), 18.5 (11'), 32.6 (10),

32.9 (6), 70.6 (8), 70.8 (12), 72.5 (9), 89.1 (4), 101.6 (2), 127.9 (Ph), 128.7 (Ph), 134.6 (13), 158.9 (5), 161.0 (7), 163.6 (3), 169.8 (1). **MS** (+FAB, 3-NBA), m/z: 328 (MH^+, 85.4), 91 (Bn^+, 100). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = . **m.p.** 90°C. $[\alpha]_D^{20}$ = - 41.8° (c = 1.00, $CHCl_3$). **TLC** (dietyhl ether:triethylamine; 4:1): R_f = 0.47. **EA** %found (calcd): C: 69.69 (69.71), H: 6.5 (6.47), N: 4.15 (4.28).

(*S*)-4-Benzyloxy-6-[(4-*tert*-butyl-4,5-dihydrooxazol-2-yl)methyl]-*2H*-pyran-2-one (152)

Amid **150** (900 mg, 2.5 mmol) and DMAP (30.5 mg, 10 mol%) were dissolved in dichloromethane (12 mL). Triethylamine (0.9 ml, 6.3 mmol) and tosyl chloride (477 mg, 2.5 mmol) in dichloromethane (3 mL) were added successively. After evaporation of the volatiles the residue was directly sub*J*ected to column chromatography on silica eluting with diethyl ether and triethylamine to give **152** (717 mg, 84 %).

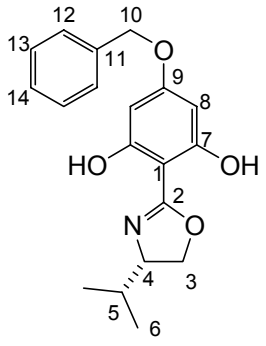


$C_{20}H_{23}NO_4$ (341.4)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 0.9 (s, 9H, 11), 3.49 (s, 2H, 6), 3.89 (m, 1H, 9), 4.09 (*ps*t, 1H, 8), 4.21 (*ps*t, 1H, 8), 5.0 (s, 2H, 12), 5.53 (d, 1H, $^4J_{HH}$ = 2 Hz, 2), 6.05 (d, 1H, $^4J_{HH}$ = 2.2 Hz, 4), 7.39 (m, 5H, 14-16). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = ($CDCl_3$, 500 MHz) 25.9 (11), 33.1 (6), 46.3 (10), 69.3 (9), 71.0 (8), 76.1 (12), 89.6 (2), 101.9 (4), 128.0 (14), 129.0 (15/16), 134.4 (13), 159.0 (5), 161.3 (1), 164.2 (7), 170.0 (3). TLC (diethyl ether:triethylamine; 4:1) R_f = 0.6.

(*S*)-5-Benzyloxy-2-[4,5-dihydro-4-isopropyloxazol-2-yl]benzene-1,3-diol (154)

According to *general procedure 11* **151** (162 mg, 514 μmol) was reacted with phosphaalkyne **115** (1 mmol) in toluene (1 mL) and chlorobenzene (1 mL) to yield after the crude reaction mixture was sub*J*ected to column chromatography on silica gel eluting with ethyl acetate and hexane (95 mg, 56%).

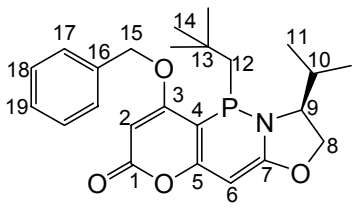


$C_{19}H_{21}NO_4$ (327.37)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.95 (d, $^3J_{HH}$ = 6.8Hz, 3H, 6), 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 6'), 1.13 (m, 1H, 5), 4.07 (ddd, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, 4), 4.17 (*pst*, $^2J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, 3), 4.89 (dd, $^2J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 9.4 Hz, 1H, 3), 5.04 (s, 2H, 10), 6.14 (s, 2H, 8), 7.38 (m, 5H, 12-14). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 18.5 (6), 18.6 (6'), 32.8 (5), 69.7 (4), 69.9 (10), 70.3 (3), 92.3 (1), 94.7 (8), 127.0 (12), 127.5 (14), 128.6 (13), 136.3 (11), 163.5 (2), 163.7 (9). **MS** (+EI) m/z: 327.1 (M^+, 62.9), 284.1 (49.8), 242.1 (6.7), 208.1 (12.0), 110.1 (14.8), 91.1 (Bn^+, 100). **TLC** (ethyl acetate:hexane; 1:2) R_f = 0.56. $[\alpha]_D^{20}$ = -23.7° (c = 1.00, $CHCl_3$). **EA** %found (calcd) C: 69.25 (69.71), H: 6.49 (6.47), N: 4.27 (4.28).

(*S*)-5-Benzyloxy-4-(2,2-dimethyl-propyl)-3-isopropyl-2,3-dihydro-*4H*-1,8-dioxa-*3a*-aza-4-phospha-cyclopenta[b]naphthalen-7-one (155)

Was afforded as a side product of the reaction **154** when pyrone **151** (316mg, 0.97 mmol) and phosphaalyne (1.9 mmo) in chlorobenzene (0.5 mL) were used (75mg, 18%).



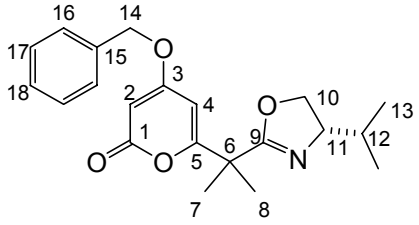
$C_{24}H_{30}NO_4P$ (427.47)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.80 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 11), 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 3H, 11'), 0.93 (s, 9H, 14), 1.30 (dd, $^2J_{HH}$ = 14.5 Hz, $^2J_{HP}$ = 2.6 Hz, 1H, 12), 2.09 (m, 2H, 10/12), 3.79 (m, 1H, 9), 4.27 (m, 2H, 8), 4.86 (s,1H, 6), 5.03 (s, 2H, 15), 5.22 (d, $^4J_{HP}$ = 4.9 Hz, 1H, 2), 7.38 (m, 5H, 17-19). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 15.6 (d, $^4J_{CP}$ = 1.5 Hz, 11), 17.8 (11'), 29.4 (d, $^2J_{CP}$ = 12.5 Hz, 13), 30.6 (d, $^3J_{CP}$ = 8.1 Hz, 14), 31.0 (d, $^3J_{CP}$ = 1 Hz, 10), 45.9 (d, $^1J_{CP}$ = 30 Hz, 12), 64.5 (d, $^2J_{CP}$ = 18.8 Hz, 9), 69.7 (d, $^3J_{CP}$ = 3 Hz, 8),

70.3 (15), 72.0 (6), 82.8 (d, $^{3}J_{CP}$ = 2.7 Hz, 2), 86.5 (d, $^{1}J_{CP}$ = 1 Hz, 4), 127.5 (17), 128.3 (19), 128.5 (18), 135.3 (16), 164.1 (1), 165.1 (d, $^{2}J_{CP}$ = 12.9 Hz, 7), 165.8 (d, $^{2}J_{CP}$ = 4.1 Hz, 5), 170.2 (d, $^{2}J_{CP}$ = 20.7 Hz, 3). **^{31}P{^{1}H} NMR** (162.0 MHz, $CDCl_3$, 300K): δ = 18.2. **MS** (+FAB, 3-NBA), m/z: 428 (MH^+, 93.8), 356 (M^+-Np, 100), 266 (M^+-Np-OBn, 24.4), 91 (Bn^+, 93.2). **TLC** (ethyl acetate:hexane; 1:2) R_f = 0.28.

(*S*)-4-Benzyloxy-6-[2-(4,5-dihydro-4-isopropyloxazol-2-yl)propan-2-yl]-*2H*-pyran-2-one (159)

LiHMDSA (1M in hexane, 4.3 mmol) was dissolved in THF (15 mL). At -78°C a solution of pyrone **151** (469 mg, 1.43 mmol) in THF (10 mL) was added *via* cannula. The cannula was then rinsed with THF (5 mL). The orange to yellow solution was stirred at -78°C for 1.5 hours. After quenching with methyl iodide (0.3 mL, 4.78 mmol) the solution was allowed to warm to room temperature over night. The orange-brown suspension was reduced and then diluted dichloromethane (20 mL). Extraction with 1M NH_4Cl solution (20 mL) was followed by reextraction of the aqueous layer with dichloromethane (3×20 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Column chromatography on silica eluting with diethyl ether and hexan afforded **159** (206 mg, 40%).



$C_{21}H_{25}NO_4$ (355.43)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 0.86 (d, $^{3}J_{HH}$ = 7 Hz, 3H, 13), 0.93 (d, $^{3}J_{HH}$ = 7 Hz, 3H, 13'), 1.54 (2×s, 6H, 7-8,), 1.81 (m, 1H, 12), 3.97 (m, 2H, 10-11), 4.21 (m, 1H, 10), 4.99 (s, 2H, 14), 5.52 (d, 1H, 4), 5.97 (d, 1H, 2), 7.38 (m, 5H, 16-18). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 17.7 (13), 18.8 (13'), 24.6 (7/8), 32.4 (12), 41.8 (6), 70.3 (10), 71.0 (14), 71.8 (11), 89.4 (2), 99.0 (4), 128.1 (16), 129.0 (17-18), 134.5 (15), 164.3 (5), 167.3 (9), 168.4 (1), 170 (3).

7.5 Asymmetric Catalytic Intramolecular Pauson-Khand Reaction

3-Phenylprop-2-yn-1-ol [1504-58-1] was purchased from Lancaster. Iridium complexes (*S*)-[Ir(cod)PHOX]OTf **161e**, (*S*)-[Ir(cod)PHOX]PF_6 **161g**, (*S*)-[Ir(cod)PHOX]BF_4 **161f** were prepared according to literature procedures.[180,56] (*S*)-[Ir(cod)PHOX]OAc_F **161i**, and (*S*)-[Ir(cod)PHOX]SbF_6 **161h** were prepared from the corresponding chloro-complexes by ion exchange with silver salts. (*S*)-[Ir(cod)PHOX]OTs **161b** and (*S*)-[Ir(cod)PHOX]OMs **161c** were prepared from the respective sodium salts. (*S*)-[Ir(cod)PHOX] BAr_F **161a** was prepared by Esther Hörmann. (*S*)-[Ir(cod)PHOX][$Al(OC(CF_3)_3)_4$] **161d** was prepared with lithium tetrakis(perfluoro-*tert*-butoxy)aluminate (from Ingo Krossing[181]) according to the procedure of **161a**. Allyl-(3-phenyl-prop-2-ynyl) ether **S1**, allyl-(3-methyl-prop-2-ynyl) ether **S5** and [3-(2-methyl-allyloxy)-prop-1-ynyl]-benzene **S4** were prepared by Zhong-Lin Lu.

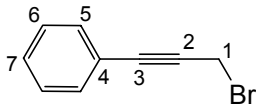
Synthesis of Pauson-Khand Products **P1** to **P4**

general procedure 15: In the glove-box a flame-dried young-tube was charged with substrate **S1** to **S5** (0.22 mmol), catalyst (2.2 - 20 μmol) and solvent (5 mL). The mixture was degassed with three freeze-pump cycles, and charged with CO. After reaction at 140 °C (24 to 48 h) the reaction mixture was concentrated and purified by column chromatography on silica gel.

7.5.1 Substrate Synthesis

3-Phenyl-prop-2-ynyl-bromide (164)[177]

At 0°C PBr_3 (7.4 g, 38 mmol) in diethyl ether (5 mL) was added to 3-phenylprop-2-yn-1-ol **163** (5.0 g, 37.8 mmol) in diethyl ether (30 mL) and pyridine (5 mL). After stirring for 40 h, the mixture was poured into water (150 mL), and extracted with diethyl ether (3×100 mL). The combined organic layers were washed with brine (100 mL) and dried over $MgSO_4$. After removal of solvent, the crude product was purified by column chromatography on silica eluting with hexane. The product was obtained as a colourless liquid that turns yellow upon standing (3.2 g, 43%).

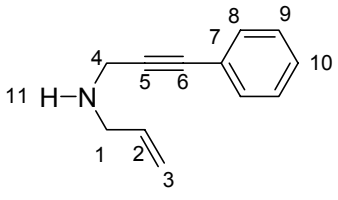


C_9H_7Br (195.06)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 4.17 (s, 2H, 1), 7.29-7.35 (m, 3H, 5/7) 7.43-7.46 (m, 2H, 6). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 15.5 (1), 84.3 (2), 86.9 (3), 122.2 (4), 128.5 (5), 129.0 (7), 132.0 (6). **MS** (+EI) m/z: 194 (M^+, 5.3), 196 (M^+, 5.1), 115.2 (M-Br^-, 100). **IR** (KBr): $\tilde{\nu}$ = 3057w, 2955w, 2926w, 2861w, 2364w, 2338w, 2219m, 2597w, 1490m, 1442m, 1272m, 1203s, 1069w, 1029w, 985w, 756s, 689s.**TLC** (*n*-hexane) R_f = 0.36

***N*-Allyl-*N*-(3-phenyl-prop-2-ynyl) amine (166)**[174]

In a dry flask under argon, a diethyl ether solution (5 mL) of allylamine **165** (2.4 mL, 31.4 mmol) was added to a diethyl ether solution (5 mL) of 3-phenyl-prop-2-ynyl-bromide **164** (613 mg, 3.14 mmol) at 0°C. The reaction mixture was stirred for 50 min at 0°C and then for 45 min at ambient temperature. The reaction was quenched with water (15 mL) and extracted three times with ethyl acetate (3×15 mL). The combined organic layers were washed with brine (15 mL) and dried over magnesium sulfate. The solvent was removed *in vacuo* and purification by flash column chromatography (*n*-hexane: ethyl acetate 2:1 to 1:1) afforded *N*-allyl-*N*-(3-phenyl-prop-2-ynyl)-amine (475 mg, 88 %).

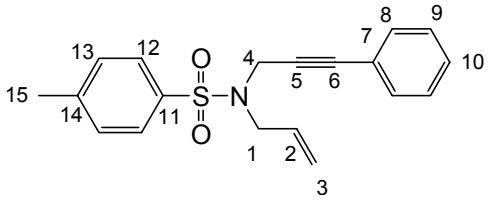


$C_{12}H_{13}N$ (171.24)

^{1}H NMR (500.1 MHz, $CDCl_3$, 300K): δ = 1.9 (br, 1H, 11), 3.43 (dt, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, 1), 3.67 (s, 2H, 4), 5.16 (d, 1H, $^3J_{HHcis}$ = 10.2 Hz, 3), 5.27 (d, 1H, $^3J_{HHtrans}$ = 17.2 Hz, 3), 5.94 (ddt, 1H, 2), 7.29-7.31 (m, 3H, 8/10), 7.41-7.44 (m, 2H, 9). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 38.3 (4), 51.1 (1), 84.0 (5), 87.1 (6), 117.2 (3), 123.2 (2), 128.3 (10), 128.4 (8), 131.8 (9), 135.8 (7). **MS** (+EI) m/z: 170.2 (M^+-H, 68.0), 142.1 ($C_{10}H_8N$, 41.8), 115 (C_9H_7, 100). **IR** (NaCl): $\tilde{\nu}$ = 3324m, 3076m, 2979w, 2913m, 2825m, 2362s, 2338s_{sh}, 1738w, 1644m, 1598m, 1490m, 1446s, 1327m, 1249m, 1105s, 1030w, 995m, 920s, 756s, 691s. **TLC** (*n*-hexane: ethyl acetate, 2:1) R_f = 0.14

N-Allyl-*N*-(3-phenyl-prop-2-ynyl)-4-methylphenylsulfonamide (S2)[177]

To a mixture of *N*-allyl-*N*-(3-phenyl-2-propynyl) amine **166** (713 mg, 4.16 mmol), triethylamine (0.9 mL) and dichloromethane (5 mL) was added a solution of *p*-toluenesulfonyl chloride (953 mg, 5 mmol) in dichloromethane (5 mL) at 0°C. The mixture was allowed to reach room temperature over night. The reaction was quenched after 14 hours with phosphate buffer (pH 7) and extracted with chloroform (3×10 mL). The combined extracts were washed with brine and dried over anhydrous $MgSO_4$. Evaporation and flash column chromatography on silica (*n*-hexane: ethyl acetate, 1:1) were followed by recrystallization in ethyl acetate. The title compound was obtained as colorless crystals (1.2 g, 89 %).



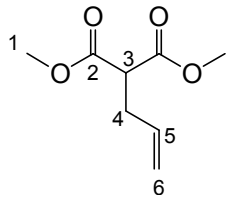
$C_{19}H_{19}NO_2S$ (325.42)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 2.33 (s, 3H, 15), 3.88 (d, $^3J_{HH}$ = 6.4 Hz, 2H, 1), 4.3 (s, 2H, 4), 5.27 (dd, 1H, $^3J_{HHcis}$ = 10.1 Hz, 3), 5.33 (dd, 1H, $^3J_{HHtrans}$ = 19.9 Hz, 3), 5.75-5.85 (ddt, 1H, 2), 7.04-7.07 (m, 2H, 12), 7.23-7.27 (m, 5H, 8-10), 7.76-7.79 (m, 2H, 13). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 21.6 (15), 36.9 (4), 49.4 (1), 81.8 (5), 85.8 (6), 120.1 (3), 122.4 (14), 128.0 (13), 128.3 (8), 128.5 (10), 129.7 (9), 131.6 (12), 132.2 (2), 136.1 (7), 143.7 (11). **MS** (+FAB, 3-NBA) m/z: 326 (MH^+, 58.7), 224 ($C_{11}H_{14}NO_2S^+$, 83.8), 170 (M^+-Ts, 25.9), 155 (Ts^+, 25.7), 115 ($C_9H_7^+$, 100), 91 ($C_7H_7^+$, 48.8). **IR** (KBr): $\tilde{\nu}$ = 3424m_{br}, 3085w, 3059w, 3012w, 2962w, 2909w, 2859w, 1922w, 1891w, 1648w, 1594w-m 1488w,

1442m, 1348s, 1322s, 1255w, 1160s, 1091m, 1060m, 996w, 942m, 902s, 814m, 762s, 694m, 661s, 583s, 536s. **TLC** (*n*-hexane: ethyl acetate, 1:1) $R_f = 0.47$

2-Allyl-malonic acid dimethyl ester (168)[177]

To a suspension of NaH (1.01 g, 42 mmol) in THF (50 mL) was added dimethyl malonate **167** (5.34 g, 40.4 mmol) at 0°C. After stirring for additional 15 min at 0°C, allyl bromide (9.7 g, 80 mmol) was added dropwise at room temperature. After 2h, the reaction mixture was quenched with water (50 mL), extracted with diethyl ether (3×75 mL), and washed with brine (50 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated. The crude product was further purified by flash column chromatography on silica (*n*-hexane/ethyl acetate 15:1). The product was obtained as a colorless liquid (3.7 g, 53%).

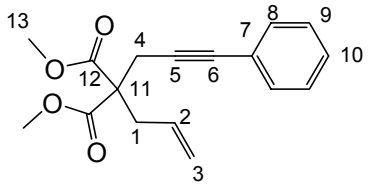


$C_8H_{12}O_4$ (172.18)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 2.65 (tt, 2H, 4), 3.47 (t, 1H, 3), 3.74 (s, 6H, 1), 5.06 (dd, 1H, 6), 5.12 (dd, 1H, 6), 5.76 (m, 1H, 5). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 33.0 (1), 51.5 (4), 52.7 (3), 117.8 (4), 134.0 (5), 169.4 (2). **MS** (+FAB, 3- NBA) m/z: 173 (MH^+, 100), 141 ($C_7H_9O_3^+$, 25.5), 109 (34.8), 41 ($C_3H_5^+$, 22.5). **IR** (NaCl): $\tilde{\nu}$ = 3081w (ν_{CH}, C=C), 3004 (ν_{CH}, C=C), 2956w (ν_{CH}, CH_3), 2365w, 1742s (ν_{CO}), 1644w, 1439m (δ_{CH}, CH_3), 1343m (δ_{CH}, CH_2), 1276m, 1240m, 1200m, 1159m, 1059w, 1026w, 924w (δ_{CH}, C=C), 853w, 462s$_{br}$. **TLC** (*n*-hexane/ethyl acetate 15:1) $R_f = 0.13$.

2-Allyl-2-(3-phenyl-prop-2-ynyl)-malonic acid dimethyl ester (S3)

To a suspension of NaH (288 mg, 12 mmol) in THF (10 mL) was added 2-allyl dimethyl malonate **168** (1.69 g, 9.81 mmol) in THF (15 mL) at 0°C. After stirring for additional 2 h at room temperature, 3-phenyl-prop-2-ynyl-bromide **164** (2.1 g, 10.8 mmol) in THF (15 mL) was added dropwise. After 1.5 h the reaction mixture was poured to saturated of NH_4Cl (30 mL) and extracted with diethyl ether (3×50 mL). The combined organic layers were dried over $MgSO_4$. Flash column chromatography on silica (*n*-hexane: ethyl acetate, 4:1) followed by Kugelrohr destillation (200°C, 10^{-1} mbar) afforded the product as a colourless oil (2.77g, 99 %).



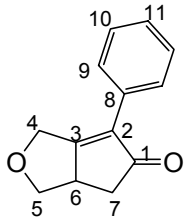
$C_{17}H_{18}O_4$ (286.32)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 2.86 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 1), 3.01 (s, 2H, 4), 3.76 (s, 3H, 13), 5.13 (dd, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 2 Hz, 3), 5.20 (dd, $^3J_{HH}$ = 17 Hz, $^2J_{HH}$ = 2 Hz, 3), 5.67 (ddt, $^3J_{HH}$ = 17, 10, 7.3 Hz, 2), 7.27-7.29 (m, 3H, 8&10), 7.35-7.38 (m, 2H, 9). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 23.8 (4), 36.9 (1), 52.9 (13), 57.4 (11), 83.8 (6), 84.3 (5), 120.0 (3), 123.3 (7), 128.2 (10), 128.4 (8), 131.8 (9), 132.0 (2), 170.5 (12). **MS** (+FAB, 3-NBA) m/z: 287 (MH^+, 100%), 227 (38.51%), 167 (24.35%), 147 (68.40%), 115 (30.43%). **IR** (NaCl): $\tilde{\nu}$ = 2954w, 2364w, 1740s, 1438m, 1327w, 1291m, 1217s, 1114w, 1067w, 926w, 757m, 690w. **TLC** (*n*-hexane: ethyl acetate, 4:1) R_f = 0.31.

7.5.2 Products of ACPKR

2-Phenyl-7-oxabicyclo[3,3,0]oct-1-en-3-one (P1)

The synthesis was performed according to *general procedure 15*.



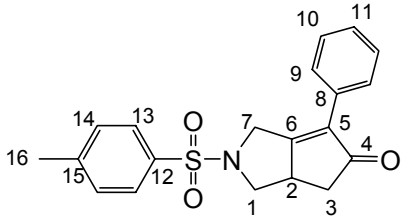
$C_{13}H_{12}O_2$ (200.23)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 2.35 (dd, $^2J_{HH}$ = 17.7 Hz, $^3J_{HH}$ = 3.8 Hz, 1H, 7), 2.87 (dd, $^2J_{HH}$ = 17.7 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, 7), 3.25 (dd, $^3J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, 5), 3.33 (m, ^{1}H, 6), 4.38 (*pst*, $^3J_{HH}$ = 7.6 Hz, 1H, 5), 4.60 (d, $^3J_{HH}$ = 16.4 Hz, 1H, 4), 4.95(d, $^3J_{HH}$ = 16.2 Hz, 1H, 4), 7.34-7.37 (m, 1H, 11), 7.40-7.44 (m, 2H, 9), 7.51-7.54 (m, 2H, 10). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 40.5 (7), 43.5 (6), 66.5 (5), 71.5 (4), 128.2 (9), 128.8 (10), 130.7 (11), 134.9 (8), 177.5 (2),207.0 (1). **MS** (+EI) m/z: 200.1 (M^+, 85.1), 170.0 (43.4), 158.1 ($C_{11}H_{10}O^+$, 49.9), 141.1 (100), 128.1 (45.6), 115.1 (61.1), 105.0 (59.2), 77 (Ph^+, 32.5). **IR** (NaCl): $\tilde{\nu}$ = 3057m, 2977m, 2851m, 2236w, 1985w, 1890w, 1806w, 1707s, 1658s, 1602w, 1496m, 1445m, 1411m, 1352m, 1352m, 1296m, 1241w, 1204w, 1165m, 1119m, 1081w, 1026s, 968w, 906s,766s, 696s, 660m.**TLC** (*n*-hexane/ethyl acetate; 2:1) R_f =

0.3. **HPLC** Daicel Chiracel AD (25 cm×0.46 cm), *n*-heptane:*i*-propanol (90:10), 20 °C, 1.0 mL/min, 220nm/254nm: 11.1 min (*R*), 14.6min (*S*).

6-Phenyl-2-(toluene-4-sulfonyl)-2,3,3a,4-tetrahydro-1H-cyclopenta[c]pyrrol-5-one (P2)

The synthesis was performed according to *general procedure 15*.

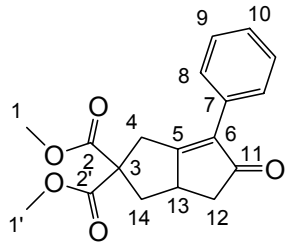


$C_{20}H_{19}NO_3S$ (353.43)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 2.25 (dd, 1H, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 3.5 Hz, 3), 2.41 (s, 3H, 16), 2.61 (dd, 1H, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 9.3, 1), 2.80 (dd, 1H, $^2J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 6.3 Hz, 3), 3.21 (m_{br}, 1H, 2), 4.08 (m, 2H, 1/7), 4.64 (dd, 1H, $^2J_{HH}$ = 17.0 Hz, $^4J_{HH}$ = 1.8, 7) 7.31 (d, 2H, $^3J_{HH}$ = 8.1 Hz, 14), 7.36-7.46 (m, 5H, 9-11), 7.72 (d, 2H, $^3J_{HH}$ = 8.1 Hz, 13). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 21.7 (16), 40.9 (2), 42.0 (3), 48.5 (7), 52.2 (1), 127.5 (13), 128.3 (9), 128.9 (10), 129.1 (11), 130.0 (5), 130.2 (14), 133.8 (8), 136.3 (12), 144.2 (15), 172.0 (6), 205.6 (4). **MS** (+FAB, 3-NBA) m/z: 354 (MH^+, 100), 198 ($C_{13}H_{12}NO^+$, 66.3), 115 (17.9), 91 ($C_7H_7^+$, 69). **IR** (KBr): $\tilde{\nu}$ = 3427m_{br}, 1348m, 3845m, 1702s, 1936m, 1596m, 1492m, 1442s, 1346s, 1282m, 1214m, 1159s, 1089m, 1044s, 918m, 811s, 765s, 692s, 659s, 610m, 552s. **m.p.** 144-145 °C. **TLC** (*n*-hexane:ethyl acetate 2:1) R_f = 0.15. **HPLC** Daicel Chiracel AD (25 cm×0.46 cm), *n*-heptane:*i*-propanol (80:20), 20 °C, 1.0 mL/min, 220nm/254nm: 19.1 min (ma*J*or), 22.7min (minor). **EA** % found (calcd): C: 67.74 (67.97), H: 5.55 (5.42), N: 3.92 (3.96), O: 13.57 (13.58).

5-Oxo-6-phenyl-3,3a,4,5-tetrahydro-1H-pentalene-2,2-dicarboxylic acid dimethyl ester (P3)

The synthesis was performed according to *general procedure 15*.

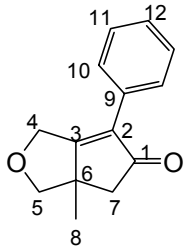


$C_{18}H_{18}O_5$ (314.33)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 1.77 (*pst*, $^{3}J_{HH}$ = 12.6 Hz, 1H, 14), 2.31 (dd, 1H, 12), 2.8-2.87 (m, 2H, 12/14), 3.14 (m_{br}, 1H, 13), 3.30 (d, $^{2}J_{HH}$ = 19.2 Hz, 1H, 4), 3.66 (d, $^{2}J_{HH}$ = 19.2 Hz, 1H, 4), 3.72 (s, 3H, 1), 3.83 (s, 3H, 1'), 7.33 (m, 1H, 10), 7.39-7.42 (m, 2H, 8), 7.54-7.57 (m, 1H, 9). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 300K): δ = 36.1 (4), 39.0 (14), 42.8 (12), 43.0 (13), 53.3 (1), 53.5 (1'), 61.3 (3), 128.4 (10), 128.6 (8), 128.6 (9), 131.0 (7), 135.7 (6), 171.3 (2), 172.2 (2'), 178.8 (5), 207.2 (11). **MS** (+EI) m/z: 314 (M^+, 38.7), 254.2 ($C_{16}H_{14}O_3^+$, 100), 195.1 ($C_{14}H_{11}O^+$, 75.4), 167.1 ($C_{13}H_{11}^+$, 39.6). **IR** (NaCl): $\tilde{\nu}$ = 2956m, 2364w, 1736s, 1706s, 1652m, 1601w, 1495w, 1439m, 1274s, 1197s, 1159s, 1121m, 1061m, 1004w, 938w, 883w, 853w, 765m, 698m. **TLC** (*n*-hexane:ethyl acetate 2:1) R_f = 0.22. **HPLC** Daicel Chiracel AS (25 cm×0.46 cm), *n*-heptane:*i*-propanol (90:10), 20 °C, 1.0 mL/min, 220nm/254nm: 15.0 min (minor), 24.3min (ma*J*or).

2-Phenyl-5-methyl-7-oxabicyclo[3,3,0]oct-1-en-3-one (P4)

The synthesis was performed according to *general procedure 15*.



$C_{14}H_{14}O_2$ (214.26)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 1.3 (s, 3H, 8), 2.58 (2×d, $^{2}J_{HH}$ = 17.2 Hz, 2H, 7), 3.43 (d, $^{2}J_{HH}$ = 7.8 Hz, 1H, 5), 4.04 (d, $^{2}J_{HH}$ = 8.1 Hz, 1H, 5), 4.44 (d, $^{2}J_{HH}$ = 16.4 Hz, 1H, 4), 4.95 (d, $^{2}J_{HH}$ = 16.1 Hz, lH, 4), 7.35-7.55 (m, 5H, 10-12). **TLC** (*n*-hexane/ethyl acetate; 2 : 1) R_f = 0.3. **HPLC** Daicel Chiracel AD (25 cm×0.46 cm), *n*-heptane:*i*-propanol (90:10), 20°C, 1.0 mL/min, 220nm/254nm: 7.9-8.2 min (ma*J*or *R*), 16.9-17.7 min (minor *S*).

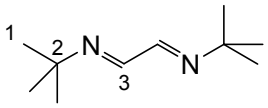
7.6 Rhodium-Silylene Complexes

7.6.1 Synthesis of Silylenes

$NaBAr_F$ was prepared as previously described.[225] $[Rh(cod)Cl]_2$ was purchased from Strem. 1,5-Cyclooctadiene was purchased from Fluka and distilled prior to use.

N,N'-Di-*tert*-butyl-ethylendiimin (179)[200]

To a solution of *tert*-butylamine (73.1 mL, 696 mmol) in water (50 mL) was added dropwise at 0°C an aqueous 40% glyoxal solution (40 mL,348 mmol). After the resulting white suspension was stirred for an additional 45 min, the product was filtered and recrystallized from ethanol and water (1:1). Subsequent sublimation afforded the product as colorless crystals (53 g, 90%).

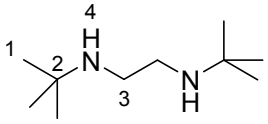


$C_{10}H_{20}N_2$ (168.28)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 1.25 (s, 18H, 1), 7.93 (s, 2H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 29.5 (1), 58.4 (2), 158.1 (3). **MS** (+FAB, 3-NBA) m/z: 41 (16.7), 57.1 ($C_4H_9^+$, 100), 97.1 (23.54), 112.1 (MH^+-C_4H_9, 20.6), 141.2 (9.5). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 2968.1m, 1631.0m, 1475.5m, 1361.6m, 1304.0w, 1213.1s, 933.2m, 879.0m, 746.2m, 594.5w, 482.0m. **m.p**. 51°C. **EA** %found (calcd): C: 71.20 (71.37), H: 11.71 (11.98), N: 16.40 (16.65).

N,N'-Di-*tert*-butyl-ethylendiamine (182)[204b]

Dibromoethane (6.5 mL, 75 mmol), *tert*-butylamine (39.4 mL, 375 mmol), hexane (10 mL), and water (10 mL) were heated to reflux for three days. During this time, a prcipitate formed and two layers became apparent. After refluxing, the mixture was colled in an ice bath and three portion s of NaOH (3×2.7 g) were sequentially added to the reaction mixture. The exothermic reaction made the solution reflux anew. After coooling, the hexane layer was stored over NaOH. This organic layer was then distilled to remove the hexane and any unreacted dibromoethane or *tert*-butylamine. The distillation was then continued under vacuum to yield the product as a colorless liquid (11.05 g, 85.5%). Noteworthy, in the presence of water the product crystallizes as a white solid (**m.p.** 46°C).

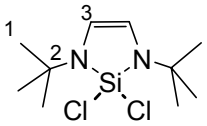


$C_{10}H_{24}N_2$ (172.31)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 1.09 (s, 18H, 1), 2.64 (s, 2H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 300K): δ = 29.4 (1), 43.5 (2), 50.2 (3).

N,N'-1,3-Di-*tert*-butyl-2,2-dichloro-2,3-dihydro-1*H*-[1,3,2]diazasilole (180)[206]

N,N'-Di-*tert*-butyl-ethylendiimin **179** (10.05 g, 59.7 mmol) was dissolved in THF (100 mL) and cooled to -78°C. Small chunks of lithim wire (0.93 g, 133.7 mmol) were added, whereupon the mixture gradually darkened to a red solution. If reaction did not take place, it could be initialized by means of ultrason. The solution was allowed to warm to room temperature for 24 h. The reaction mixture was then frozen with a liquid nitrogen bath, and $SiCl_4$ () was added. The resulting mixture was allowed to warm to room temperature over night. Then the mixture was filtered and all volatiles were evaporated. Subsequent distillation (95°C, 0.1 mbar) afforded a colorless, air-sensitive crystalline solid (11.47 g, 71%).

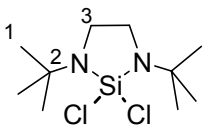


$C_{10}H_{20}Cl_2N_2Si$ (267.27)

^{1}H NMR (400.1 MHz, C_6D_6, 300K): δ = 1.24 (s, 18H, 3), 5.75 (s, 2H, 1). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 300K): δ = 30.9 (3), 53.2 (2), 113.3 (1). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3360.1s_{br}, 2977.4 s, 1731.0w, 1624.6w, 1473.2w, 1379.2m, 1197.7m, 1099.9m, 937.5w, 685.3w, 545.8w. **m.p**. 72-73°C. **EA** %found (calcd): C: 44.34 (44.94), H: 7.57 (7.54), N: 10.24 (10.48).

N,N'-1,3-Di-*tert*-butyl-2,2-dichloro-1*H*-[1,3,2]diazasilole (183)[210b]

N,N'-Di-*tert*-butyl-ethylendiamine **182** (1 g, 5.8 mmol) was dissolved in hexane (12.5 mL). At 0°C, $SiCl_4$ (1.5 mL, 6 mmol) was added *via* syringe. The solution was then allowed to warm to room temperature, at which time triethylamine (2 mL, 14.3 mmol) was added. The solution was heated to reflux and stirred overnight. After cooling to room temperature, the reacton mixture was filtered and washed with hexane (8 mL). The volatiles of the filtrate were evaporated. Distillation of the remaining solid afforded a white crystalline air-sensitive solid (1.05 g, 67 %).

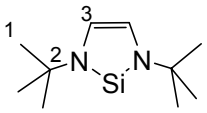


$C_{10}H_{22}Cl_2N_2Si$ (269,29)

^{1}H NMR (400.1 MHz, C_6D_6, 300K): δ = 1.28 (s, 4H, 3), 3.08 (s, 4H, 1). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 300K): δ = 29.1 (3), 41.8 (1), 52.0 (2). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 3406s, 29.76s, 28.74m, 1781m, 2467w, 2361w, 1582w, 1474m, 1385m, 1217s, 1059s, 963m, 871w, 807w, 672s, 536s, 466w. **m.p.** 64-65°C. **EA** %found (calcd): C: 42.16 (44.60), H: 8.09 (8.23), N: 9.65 (10.40).

1,3-Di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene (171)[40]

In the glovebox KC_8 (2.5 g, 18.4 mmol) is added to a stirred solution of *N,N'*-1,3-di-*tert*-butyl-2,2-dichloro-2,3-dihydro-1*H*-[1,3,2]diazasilole **180** (2 g, 7.4 mmol) in THF (20 mL). The resulting solution is stirred at room temperature for approximately 18 h. The conversion is monitored by ^{1}H NMR. The solution is filtered over celite, and the volatiles are evaporated. The crude product is purified by sublimation (60-75°C, 0.1 mbar). The silylene is obtained as a colorless solid (730 mg, 3.72 mmol, 50%).

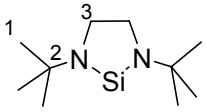


$C_{10}H_{20}N_2Si$ (196,36)

^{1}H NMR (400.1 MHz, C_6D_6, 300K): δ = 1.41 (s, 18H, 1), 6.76 (s, 2H, 3). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 300K): δ = 33.1 (1), 54.1 (2), 120.1 (3). **^{29}Si NMR** (90 MHz, C_6D_6, 300K): δ = 78.0.

1,3-Di-*tert*-butyl-2,3-[1,3,2]-diazasilolidine-2-ylidene (172)

To a solution of NaK_2 from sodium (0.06 g, 2.6mmol) and potassium (0.2 g, 5.1 mmol) in THF (5 mL) and triethylamine (2 mL) was added a solution of *N,N'*-1,3-di-*tert*-butyl-2,2-dichloro-1*H*-[1,3,2]diazasilole **183** (1 g, 3.71 mmol) in THF (10 mL) *via* cannula at -78°C. The conversion is monitored by ^{1}H NMR and filtered when complete after approximately 3 h. The filtrate was concentrated. The product was obtained as yellow crystals which turned red upon standing (340 mg, 46%).



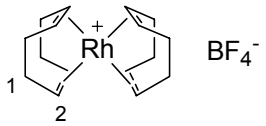
$C_{10}H_{22}N_2Si$ (198,38)

^{1}H NMR (400.1 MHz, *d*$_8$-THF, 300K): δ = 1.29 (s, 18H, 1), 3.31 (s, 4H, 3). **^{29}Si NMR** (90 MHz, *d*$_8$-THF, 300K): δ = 31.9 (1), 47.0 (3), 53.1 (2).

7.6.2 Synthesis of Complexprecursors

Bis-η^4-(1,5-cyclooctadiene) rhodium(I) tetrafluoroborate (184)

To a solution of $[Rh(cod)Cl]_2$ (735 mg, 1.49 mmol) in CH_2Cl_2 (10 mL) was added subsequently 1,5-cyclooctadiene (0.55 mL, 4.49 mmol) and a solution of $AgBF_4$ (665 mg, 3.42 mmol) in acetone (5 mL). The dark-red suspension was stirred for 30 min at room temperature and then filtered through a plug of celite. After evaporation of the volatiles the solid was suspended in THF (10 mL), and filtered. After washing with THF (10 mL) and diethyl ether (5 mL) the dark-red solid was air-dried to yield (1.01 g, 83%).

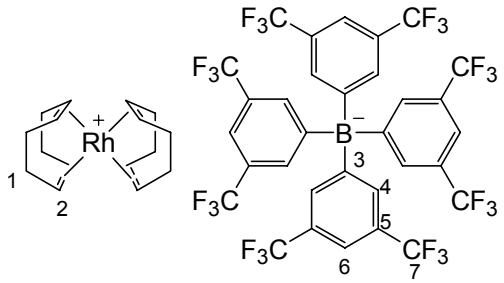


$C_{16}H_{24}BF_4Rh$ (406.07)

^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ = 2.5 (m_{br}, 4H, 1), 2.63 (m_{br}, 4H, 1), 5.37 (s, 4H, 2). **^{13}C{^{1}H} NMR** (100.6 MHz, CD_2Cl_2, 300K): δ = 30.1 (1), 108.0 (2). **MS** (+ESI) m/z: 320 (MH^+, 51.5), 274 ($[M(MeOH)_2]^+$-cod, 100).

Bis-η^4-(1,5-cyclooctadiene) rhodium(I) tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate (185)

To a solution of $[Rh(cod)Cl]_2$ (100 mg, 0.2 mmol) in CH_2Cl_2 (3 mL) was added solid $NaBAr_F$ (363 mg, 0.41 mmol). Addition of 1,5-cyclooctadiene (75 µL, 0.6 mmol) to the orange reaction mixture resulted in immediate formation of a dark-red suspension, which was stirred for 30 min at room-temperature and then filtered through a plug of celite. Evaporation of the volatiles afforded the product (387 mg, 81 % yield). The dark-red solid was recrystallized from CH_2Cl_2/hexane to give dark-red needles (320 mg, 67% yield).



$C_{48}H_{36}BF_{24}Rh$ (1182.48)

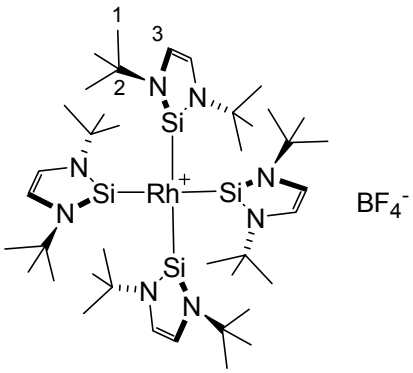
^{1}H NMR (400.1 MHz, CD_2Cl_2, 300K): δ = 2.42 (s, 8H, 1); 5.11 (s, 4H, 2), 7.54 (s, 4H, 6), 7.69 (s, 8H, 4). **^{13}C{^{1}H} NMR** (100.6 MHz, CD_2Cl_2, 300K): δ = 29.9 (1), 108.0 (d, $^1J_{C\text{-}Rh}$ = 7.7 Hz, 2), 117.9 (6), 125.0 (q, $^1J_{F\text{-}C}$ = 272 Hz, 7), 129.0 (3), 135.1 (4), ~162 (q, $^1J_{B\text{-}C}$ = 50 Hz,

3) not observed. **MS** (+FAB, 3-NBA) m/z: 319 (M^+, 100), 211 (M^+-cod, 42.2.). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 2936.5m, 1896.7m, 2845.4w, 1612.4m, 1432.7w, 1358.7s, 1280.9s, 1121.1s_{br}, 986.5w, 889.1m, 836.3m, 780.1w, 711.8m, 674.1m. **m.p**. 175 °C (decomposition). **EA** %found (calcd): C: 48.62 (48.76), H: 3.07 (3.07).

7.6.3 Synthesis of Silylene Complexes

Tetrakis-(1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene) rhodium(I) tetrakis tetrafluoroborate (186)

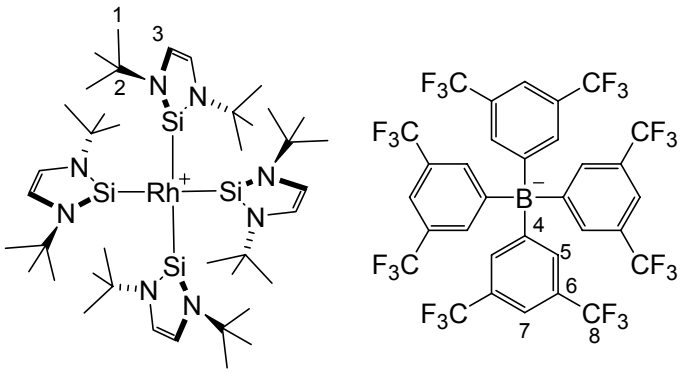
Silylene **171** (10.4 mg, 52 μmol) was dissolved in benzene-d_6 (0.6 mL). Addition of solid $[Rh(cod)_2]BF_4$ (5 mg, 12.5 μmol) gave an orange-red suspension. After standing for 20 hours at room temperature, the solvent was decanted from the orange solid. The residue was diluted in CD_2Cl_2 for NMR-analysis.



^{1}H NMR (400 MHz, CD_2Cl_2, 300K): δ = 1.53 (s, 72H, 1), 6.86 (s, 8H, 3). **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2, 300K): δ = 34.0 (1), 56.4 (2), 121.2 (3). **^{29}Si NMR** (99 MHz, CD_2Cl_2, 300K): δ = 93.5 ($^1J_{Si\text{-}Rh}$ = 82 Hz).

Tetrakis-(1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene) rhodium(I) tetrakis -[3,5-bis(trifluoromethyl)phenyl]borate (187)

$[Rh(cod)_2]BAr_F$ (98 mg, 0.075 mmol) was weighed into a Schlenk tube suspended in hexane (2 mL). Addition of solid silylene **171** (60 mg, 0.306 mmol) afforded an orange suspension after stirring for 14 hours. The resulting solid was separated by filtration and washed three times with small amounts of hexane. After drying under high-vacuum the product was obtained in quantitative yield (based on ^{1}H NMR) as a light-orange powder, which showed essentially the same NMR spectrum as recrystallized material. The extreme air-sensitivity of the powderous compound results in fuming and immediate decomposition when in contact with air. The product was recrystallized from CH_2Cl_2/hexane to afford dark-orange crystals.



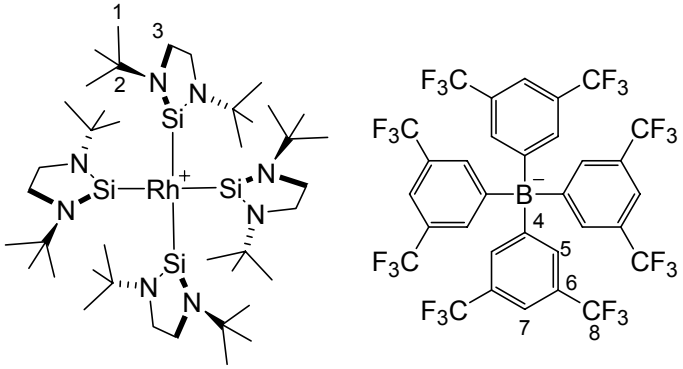
$C_{72}H_{92}BF_{24}N_8RhSi_4$ (1751.57)

^{1}H NMR (500 MHz, THF-d_8, 300K): δ = 1.5 (s, 72H, 1), 6.83 (s, 8H, 3), 7.6 (s, 4H, 7), 7.76 (t, $^4J_{H\text{-}F}$ = 2.5 Hz, 8H, 5). **^{13}C{^{1}H} NMR** (125 MHz, THF-d_8, 300K): δ = 30.1 (1), 55.8 (2), 117.2 (7), 120.8 (3), 124.5 (q, $^1J_{F\text{-}C}$ = 272 Hz, 8), 129.0 (6), 134.6 (5), 161.8 (q, $^1J_{B\text{-}C}$ = 50 Hz, 4). **^{29}Si NMR** (99 MHz, THF-d_8, 300K): δ = 95.6 ($^1J_{Si\text{-}Rh}$ = 82.5 Hz). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 2977s, 1611w, 1466m, 1396w, 1356m, 1279s, 1207m, 1123s$_{br}$, 1000w, 885m, 839m, 809w, 738m, 713m, 659s. **m.p.** 200°C (decomposition). **EA** %found (calcd): C: 49.31 (49.37), H: 5.15 (5.29), N: 6.30 (6.40).

Tetrakis-(1,3-di-*tert*-butyl-2,3-[1,3,2]-diazasilolidine-2-ylidene) rhodium (I) tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (188)

The complex was synthesized as described above, starting from 98 mg (0.075 mmol) of $[Rh(cod)_2]BAr_F$ and 60 mg (0.3 mmol) of **172**. From the resulting bright-yellow suspension after complex **5** was obtained in quantitative yield (based on ^{1}H NMR) as a yellow powder, which was recrystallized from CH_2Cl_2/hexane to give light orange crystals.

$C_{72}H_{100}BF_{24}N_8RhSi_4$ (1759,64)



^{1}H NMR (500 MHz, THF-d_8, 300K): δ = 1.38 (s, 72H, 1), 3.28 (m, 16H, 3), 7.55 (s, 4H, 7), 7.72 (m, 8H, 5). **^{13}C{^{1}H} NMR** (125 MHz, THF-d_8, 300K): δ = 32.0 (1), 46.6 (3), 54.1 (2), 117.4 (7), 120.8 (3), 124.0 (q, $^1J_{F\text{-}C}$ = 272 Hz, 8), 128.8 (6), 134.7 (5), 161.8 (q, $^1J_{B\text{-}C}$ = 50 Hz,

4). **^{29}Si NMR** (99 MHz, THF-d_8, 300K): δ = 134.5 ($^{1}J_{Si-Rh}$ = 76.6 Hz). **IR** (KBr): $\tilde{\nu}$ [cm^{-1}] = 2976m, 1611w, 1474m, 1396w, 1355m, 1279s, 1126s$_{br}$, 1036w, 973m, 887m, 838m, 803w, 744w, 713m, 682m. **m.p.** ~195 °C (decomposition). **EA** %found (calcd): C: 48.74 (49.14), H: 5.57 (5.73), N: 6.13 (6.37).

Chapter 8

Appendix

8 Appendix

8.1 X-Ray Crystal Structures

Single crystals were usually obtained through crystallization by dissolving the product in a small quantitiy of dichloromethan and carefully adding a layer of a non-solvent, such as hexane. The crystals were mounted with paraffin on a glass fibre goniometer head. This was attached to the KappaCCD diffractometer. Measurement were recorded at 173K. The space group was determined the systematic extinction by means of the "Collect" data collection software (Nonius BV, 2002). Collect can use either the HKL software (denzo/scalepack/xdisp) for integration[226], or the dirax/view/EvalCCD programs from Utrecht University.[227] The structure was solved with either SIR92[228] or SIR97[229] and refined in Crystals.[230] The absolute configuration and enantiopurity could be determined by refinement of the flack parameter.[231] The refined structures were checked with checkcif.[232]

Table 8.1

	80	**82**
empirical formula	$C_{24}H_{44}IrNOP$, $C_{32}H_{12}BF_{24}$	$C_{26}H_{40}IrNOP$, $C_{32}H_{12}BF_{24}$
formula weight [g mol^{-1}]	1449.02	1469.01
shape	plate	plate
color	orange	orange
temperature [K]	173	173
radiation type	$Mo_{K\alpha}$	$Mo_{K\alpha}$
wavelength [Å]	0.710730	0.710730
crystal size	0.13×0.20×0.20 mm	0.10×0.20×0.20 mm
crystal system	orthorhombic	monoclinic
space group	P 2_1 2_1 2_1	P 1 2_1 1
a [Å]	a = 19.156(5)	12.7512(2)
b [Å]	b = 24.665(4)	18.2817(3)
c [Å]	c = 24.8124(16)	12.9646(2)
α [°]	90	90
β [°]	90	101.601(8)
γ [°]	90	90
unit cell volume [Å^3]	11723.4(39)	2960.49(8)
Z	8	2
calcd density [g cm^{-3}]	1.642	1.648
absorption coeff. μ[mm^{-1}]	2.421	2.399
F(000)	5760	1456
limiting indices (measured)	h = ±25, k = ±32, l_{min}, l_{max} = -32, 28	h = ±16, k = ±23, l = ±16
reflections collected/unique	123531/28180	25750/13531
θ range for data collection	3.151° to 28.003°	1.603° to 27.493°
completeness to θ_{max}	0.997	0.999
data/parameters	21928 (I>3σ(I)), 1451	11099 (I>3σ(I)), 840
goodness-of-fit on F	1.001	1.1352
R	3.83	4.49
R_w	4.29	5.02
Flack parameter	-0.007(4)	0.007(7)

Table 8.2

	83	**88**
empirical formula	$C_{23}H_{22}IrNOP$, $C_{32}H_{12}BF_{24}$	$C_{29}H_{38}IrNOP$, $C_{32}H_{12}BF_{24}$
formula weight [g mol^{-1}]	1435.00	1573.94
Shape	block	plate
color	orange	orange
temperature [K]	173	173
radiation type	$Mo_{K\alpha}$	$Mo_{K\alpha}$
wavelength [Å]	0.710730	0.710730
crystal size	0.28×0.28×0.24	0.31×0.18×0.09
crystal system	orthorhombic	orthorhombic
space group	P 2_1 2_1 2_1	P 2_1 2_1 2_1
a [Å]	18.974 (10)	12747 (2)
b [Å]	24.5613 (2)	18.7599 (2)
c [Å]	25.2943 (10)	26.2140 (3)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
unit cell volume [$Å^3$]	11787.80 (12)	6266.85 (14)
Z	8	4
calcd density [g cm^{-3}]	1.617	1.668
absorption coeff. μ[mm^{-1}]	2.407	2.355
F(000)	5696	3112
limiting indices (measured)	h = ±24, k = ±31, l = ±32	h = ±16, k = ±24, l = ±34
reflections collected/unique	85676/26991	54640/14867
θ range for data collection	1.156 to 27.493°	1.335 to 28.848°
completeness to θ_{max}	0.999	0.998
data/parameters	19985 (I>3σ(I)), 1676	9028 (I>3σ(I)), 875
goodness-of-fit on F	1.0351	1.0288
R	3.35	3.39
R_w	4.38	3.78
Flack parameter	0.002	0.020 (7)

Table 8.3

	120*cis*	**133**
empirical formula	$C_{15}H_{24}NO_2P$	$BC_{55}F_{24}H_{46}IrNOP$
formula weight [g mol^{-1}]	281.33	1427.08
Shape	plate	needle
color	yellow	black
temperature [K]	173K	173K
radiation type	$Mo_{K\alpha}$	$Mo_{K\alpha}$
wavelength [Å]	0.710730	0.710730
crystal size	0.08×0.12×0.28	0.12×0.13×0.33
crystal system	monoclinic	orthorhomic
space group	P 1 2_1 1	P 2_1 2 2_1
a [Å]	8.4760(2)	15.7169(16)
b [Å]	6.9815(2)	17.350(2)
c [Å]	14.0521(3)	20.0286(17)
α [°]	90	90
β [°]	107.4342(13)	90
γ [°]	90	90
unit cell volume [Å^3]	793.34(3)	5461.5(10)
Z	2	4
calcd density [g cm^{-3}]	1.178	1.735
absorption coeff. μ[mm^{-1}]	0.172	2.598
F(000)	304	2816.277
limiting indices (measured)	h = ±11, k = ±9, l = ±19	h = ±23, k = ±25, l = ±29
reflections collected/unique	4558/4549 (R_{int} = 0.0)	194150/18927 (R_{int} = 0.08)
θ range for data collection	3.039 to 29.983°	3.022 to 32.003°
completeness to θ_{max}	0.996	0.997
data/parameters	3538 (I>3σ(I)), 172	13443 (I>3σ(I)), 842
goodness-of-fit on F	1.0883	1.088
R	3.69	2.79
R_w	4.18	2.85
Flack parameter	-0.02 (8)	-0.001(4)

Table 8.4

	162	**187**
empirical formula	$C_{26}H_{24}IrNO_3$	$C_{40}H_{80}N_8RhSi_4$, $C_{32}H_{12}BF_{24}$
formula weight [g mol^{-1}]	766.64	1751.59
Shape	plate	plate
color	yellow	orange
temperature [K]	173K	173K
radiation type	$Mo_{K\alpha}$	$Mo_{K\alpha}$
wavelength [Å]	0.71073	0.71073
crystal size	0.09×0.15×0.20	0.23×0.32×0.4 mm
crystal system	monoclinic	monoclinic
space group	P 1 2_1 1	C 2/c
a [Å]	10.2868 (10)	21.827 (2)
b [Å]	9.8003 (10)	19.811 (2)
c [Å]	13.6871 (2)	19.503 (2)
α [°]	90	90
β [°]	90.1135	108.762 (8)°
γ [°]	90	90
unit cell volume [Å^3]	1379.84 (3)	7985 (2)
Z	2	4
calcd density [g cm^{-3}]	1.845	1.457
absorption coeff. μ[mm^{-1}]	5.024	0.376
F(000)	744	3608
limiting indices (measured)	h = ±17, k = ±16, l = ±22	h = ±30, k = ±29, l = ±27
reflections collected/unique	25556/13276 (R_{int} = 0.02)	91539/11663 (R_{int} = 0.06)
θ range for data collection	2.977 to 36.341°	1.424 to 30.039°
completeness to θ_{max}	0.996	0.998
data/parameters	10399 (I>3σ(I)), 417	6679 (I>3σ(I)), 553
goodness-of-fit on F	0.992	1.1384
R	2.66	3.92
R_w	2.71	4.12
Flack parameter	0.001 (4)	-

Table 8.5

	188
empirical formula	$C_{40}H_{88}N_8RhSi_4$, $C_{32}H_{12}BF_{24}$
formula weight [g mol^{-1}]	1759.65
shape	plate
color	yellow
temperature [K]	173K
radiation type	$Mo_{K\alpha}$
wavelength [Å]	0.71073
crystal size	0.3×0.4×0.5 mm
crystal system	monoclinic
space group	C 2/c
a [Å]	20.9469 (6)
b [Å]	20.6092 (6)
c [Å]	19.3746 (4)
α [°]	90
β [°]	103.192 (2)°
γ [°]	90
unit cell volume [Å^3]	8143.3 (4)
Z	4
calcd density [g cm^{-3}]	1.435
absorption coeff. μ[mm^{-1}]	0.369
F(000)	3640
limiting indices (measured)	h = ±29, k = ±28, l = ±27
reflections collected/unique	88079/11880 (R_{int} = 0.08)
θ range for data collection	1.405 to 30.024°
completeness to θ_{max}	0.997
data/parameters	6019 (I>3σ(I)), 552
goodness-of-fit on F	1.026
R	5.04
R_w	5.28
Flack parameter	-

Chapter 9

Bibliography

9 Bibliography

[1] (a) Gold, V.; Loening, K. L.; McNaught, A. D.; Sehmi, P., Editors, International Union of Pure and Applied Chemistry *Compendium of Chemical Terminology* Blackwell Scientific Publications, Oxford, **1987**. (b) Biochemical usage is wider, in that the central entity can be polyatomic: IUPAC-IUBMB Joint Commission on Biochemical Nomenclature (JCBN), and Nomenclature Commission of IUBMB (NC-IUBMB), Newsletter **1992**, *Arch. Biochem. Biophys.,* **1992**, *294*, 322-325; *Biochem. Internat.,* **1992**, *26*, 567-575; *Bioch. J.,* **1992**, *282*, I-III; *Biol. Chem. Hoppe-Seyler,* **1992**, *373*, 1-4; *Chem. Int.,* **1992**, *14*, 140-141; *Eur. J. Biochem.,* **1992**, *204*, 1-3.

[2] Elschenbroich, Ch.; Salzer, A. *Organometallics: A Concise Introduction*, 3rd Edition, Wiley-VCH, Weinheim, **2006**.

[3] Kauffman, G. B. *Alfred Werner: Founder of Coordination Chemistry*. Springer-Verlag, Berlin, Heidelberg, New York, **1966**.

[4] Pfaltz, A.; Drury, W. J. *Proc. Natl. Acad. Sci. USA* **2004**, 101, (*16*), 5723.

[5] Inoguchi, K.; Sakuraba, S.; Achiwa, K. *Synlett* **1992**, (*3*), 169.

[6] Noyori, R. *"Asymmetric Catalysis in Organic Synthesis"*, Wiley & Sons, Inc., New York, **1994**.

[7] Morrison, J. D., Editor *"Asymmetric Synthesis, Vol. 5, Chiral Catalysis"*, Academic Press, Orlando, Florida, **1985**.

[8] Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, 94, (*18*), 6429.

[9] Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, 99, (*18*), 5946.

[10] Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, 102, (*27*), 7932. Noyori, R. *Adv. Synth. Catal.* **2003**, 345, (*1+2*), 15.

[11] Yoon, T. P.; Jacobsen, E. N. *Science* **2003**, 299, (*5613*), 1691.

[12] Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, 23, (*10*), 345.

[13] Brunkan, N. M.; Gagne, M. R. *Organometallics* **2002**, 21, (*8*), 1576. Faller, J. W.; Grimmond, B. J.; D'Alliessi, D. G. *J. Am. Chem. Soc.* **2001**, 123, (*11*), 2525.

[14] Wadamoto, M.; Ozasa, N.; Yanagisawa, A.; Yamamoto, H. *J. Org. Chem.* **2003**, 68, (*14*), 5593.

[15] Pfaltz, A. *Acc. Chem. Res.* **1993**, 26, (*6*), 339.

[16] Fritschi, H.; Leutenegger, U.; Siegmann, K.; Pfaltz, A.; Keller, W.; Krathy, C. *Helv. Chim. Acta* **1988**, 71, (*6*), 1541. Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, 71, (*6*), 1553. Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Angew. Chem.* **1986**, 98, (*11*), 1028. Leutenegger, U.; Madin, A.; Pfaltz, A. *Angew. Chem.* **1989**, 101, (*1*), 61.

[17] Lowenthal, R. E.; Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1990**, 31, (*42*), 6005. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, 113, (*2*), 726. Evans, D. A.; Woerpel, K. A.; Scott, M. J. *Angew. Chem.* **1992**, 104, (*4*), 439.

[18] Mazet, C.; Kohler, V.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2005**, 44, (*31*), 4888.

[19] Glos, M.; Reiser, O. *Org. Lett.* **2000**, 2, (*14*), 2045. Werner, H.; Vicha, R.; Gissibl, A.; Reiser, O. *J. Org. Chem.* **2003**, 68, (*26*), 10166. Gissibl, A.; Finn, M. G.; Reiser, O. *Org. Lett.* **2005**, 7, (*12*), 2325.

[20] Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, 33, (*6*), 336.

[21] Williams, J. M. J. *Synlett* **1996**, (*8*), 705.

[22] Pfaltz, A., Lautens, M. in: Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H.; Editors, *Comprehensive Asymmetric Catalysis I-III, (Vol.2)*, **1999**; 833.

[23] Ward, T. R. *Organometallics* **1996**, 15, (*12*), 2836.

[24] Vasse, J.-L.; Stranne, R.; Zalubovskis, R.; Gayet, C.; Moberg, C. *J. Org. Chem.* **2003**, 68, (*8*), 3258.

[25] Schultz, T.; Schmees, N.; Pfaltz, A. *Appl. Organomet. Chem.* **2004**, 18, (*11*), 595.

[26] Stohler, R.; Wahl, F.; Pfaltz, A. *Synthesis* **2005**, (*9*), 1431.

[27] Pfaltz, A.; Blankenstein, J.; Hilgraf, R.; Hormann, E.; McIntyre, S.; Menges, F.; Schönleber, M.; Smidt, S. P.; Wüstenberg, B.; Zimmermann, N. *Adv. Synth. Catal.* **2003**, 345, (*1+2*), 33.

[28] Wanzlick, H. W.; Schoenherr, H. J. *Angew. Chem., Int. Ed.* **1968**, 7, (*2*), 141.

[29] Oefele, K. *J. Organomet. Chem.* **1968**, 12, (*3*), 42.

[30] Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, 113, (*1*), 361.

[31] Enders, D.; Gielen, H.; Breuer, K. *Tetrahedron: Asymmetry* **1997**, 8, (*21*), 3571.

[32] Herrmann, W. A.; Goossen, L. J.; Koecher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed.* **1997**, 35, (*23/24*), 2805. Herrmann, W. A.; Elison, M.; Fischer, J.; Koecher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed.* **1995**, 34, (*21*), 2371.

[33] Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, 37, (*18*), 2490. Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, 3, (*20*), 3225.

[34] Bonnet, L. G.; Douthwaite, R. E.; Kariuki, B. M. *Organometallics* **2003**, 22, (*21*), 4187.

[35] Seo, H.; Kim, B. Y.; Lee, J. H.; Park, H.-J.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, 22, (*23*), 4783.

[36] Alexakis, A.; Winn, C. L.; Guillen, F.; Pytkowicz, J.; Roland, S.; Mangeney, P. *Adv. Synth. Catal.* **2003**, 345, (*3*), 345. Guillen, F.; Winn, C. L.; Alexakis, A. *Tetrahedron: Asymmetry* **2001**, 12, (*15*), 2083.

[37] Focken, T.; Raabe, G.; Bolm, C. *Tetrahedron: Asymmetry* **2004**, 15, (*11*), 1693. Bolm, C.; Focken, T.; Raabe, G. *Tetrahedron: Asymmetry* **2003**, 14, (*12*), 1733.

[38] Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, 123, (*36*), 8878.

[39] Hill, N. J.; West, R. *J. Org. Chem.* **2004**, 689, (*24*), 4165.

[40] Fürstner, A.; Krause, H.; Lehmann, C. W. *Chem. Commun.* **2001**, (*22*), 2372.

[41] Brown, J. M. in: Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H.; Editors, *Comprehensive Asymmetric Catalysis I-III, (Vol.1)*, **1999**; 487.

[42] Blaser, H. U.; Spindler, F.; Studer, M. *Appl. Catal., A: General* **2001,** 221, (*1-2*), 119. Blaser, H.-U.; Pugin, B.; Spindler, F. *J. Mol. Cat. A: Chemical* **2005,** 231, (*1-2*), 1.

[43] Halpern, J.; Harrod, J. F.; James, B. R. *J. Am. Chem. Soc.* **1961,** 83, 753.

[44] Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, (*12*), 1711.

[45] Ireland, R. E.; Bey, P. *Org. Synth.* **1973,** 53, 63.

[46] Knowles, W. S.; Sabacky, M. J. *Chem. Commun.* **1968**, (*22*), 1445.

[47] Horner, L.; Buethe, H.; Siegel, H. *Tetrahedron Lett.* **1968**, (*37*), 4023; Horner, L.; Siegel, H.; Buethe, H. *Angew. Chem., Int. Ed.* **1968,** 7, (*12*), 942.

[48] Knowles, W. S. *Acc. Chem. Res.* **1983,** 16, (*3*), 106. Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1975,** 97, (*9*), 2567.

[49] Ikariya, T.; Ishii, Y.; Kawano, H.; Arai, T.; Saburi, M.; Yoshikawa, S.; Akutagawa, S. *Chem. Commun.* **1985**, (*13*), 922.

[50] Ohta, T.; Takaya, H.; Kitamura, M.; Nagai, K.; Noyori, R. *J. Org. Chem.* **1987,** 52, (*14*), 3174. Noyori, R.; Ohta, M.; Hsiao, Y.; Kitamura, M.; Ohta, T.; Takaya, H. *J.*

Am. Chem. Soc. **1986,** 108, (*22*), 7117. Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Inoue, S.; Kasahara, I.; Noyori, R. *J. Am. Chem. Soc.* **1987,** 109, (*5*), 1596. Kitamura, M.; Hsiao, Y.; Noyori, R.; Takaya, H. *Tetrahedron Lett.* **1987,** 28, (*41*), 4829.

[51] Horner, L.; Siegel, H.; Buethe, H. *Angew. Chem., Int. Ed.* **1968,** 7, (*12*), 942. Hayashi, T.; Tanaka, M.; Ogata, I. *Tetrahedron Lett.* **1977**, (*3*), 295.

[52] Broene, R. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993,** 115, (*26*), 12569.

[53] Troutman, M. V.; Appella, D. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999,** 121, (*20*), 4916.

[54] Crabtree, R. H.; Felkin, H.; Morris, G. E. *Chem. Commun.* **1976**, (*18*), 716.

[55] Lightfoot, A.; Schnider, P.; Pfaltz, A. *Angew. Chem., Int. Ed.* **1998,** 37, (*20*), 2897.

[56] Blackmond, D. G.; Lightfoot, A.; Pfaltz, A.; Rosner, T.; Schnider, P.; Zimmermann, N. *Chirality* **2000,** 12, (*5/6*), 442-449.

[57] a) Escher, I. H.; Pfaltz, A. *Tetrahedron* **2000,** 56, (*18*), 2879. b) Blankenstein, J.; Pfaltz, A. *Angew. Chem. , Int. Ed.* **2001,** 40, (*23*), 4445. c) Menges, F.; Neuburger, M.; Pfaltz, A. *Org. Lett.* **2002,** 4, (*26*), 4713. d) Menges, F.; Pfaltz, A. *Adv. Synth. Catal.* **2002,** 344, (*1*), 40. e) Smidt, S. P.; Menges, F.; Pfaltz, A. *Org. Lett.* **2004,** 6, (*20*), 2023. f) Drury, W. J., III; Zimmermann, N.; Keenan, M.; Hayashi, M.; Kaiser, S.; Goddard, R.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2004,** 43, (*1*), 70.

[58] Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001,** 123, (*36*), 8878. Perry, M. C.; Cui, X.; Powell, M. T.; Hou, D.-R.; Reibenspies, J. H.; Burgess, K. *J. Am. Chem. Soc.* **2003,** 125, (*1*), 113.

[59] Lee, H. M.; Jiang, T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001,** 20, (*6*), 1255. Liu, D.; Dai, Q.; Zhang, X. *Tetrahedron* **2005,** 61, (*26*), 6460. Focken, T.; Raabe, G.; Bolm, C. *Tetrahedron: Asymmetry* **2004,** 15, (*11*), 1693. Bunlaksananusorn, T.; Polborn, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2003,** 42, (*33*), 3941.

[60] Yamagishi, T.; Ohnuki, M.; Kiyooka, T.; Masui, D.; Sato, K.; Yamaguchi, M. *Tetrahedron: Asymmetry* **2003,** 14, (*21*), 3275. Peer, M.; de Jong, J. C.; Kiefer, M.; Langer, T.; Rieck, H.; Schell, H.; Sennhenn, P.; Sprinz, J.; Steinhagen, H. *Tetrahedron* **1996,** 52, (*21*), 7547.

[61] Smidt, S. P. Ph.D. dissertation, University of Basel, **2003**.

[62] Tang, W.; Wang, W.; Zhang, X. *Angew. Chem., Int. Ed.* **2003**, *42*, 943.

[63] Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769. Braunstein, P.; Graiff, C.; Naud, F.; Pfaltz, A.; Tiripicchio, A. *Inorg. Chem.* **2000**, *39*, 4468. Braunstein, P.; Naud, F.; Graiff, C.; Tiripicchio, A. *Chem. Commun.* **2000**, 897. Braunstein, P.; Fryzuk, M. D.; Le Dall, M.; Naud, F.; Rettig, S. J.; Speiser, F. *Dalton* **2000**, 1067.

[64] Danjo, H.; Higuchi, M.; Yada, M.; Imamoto, T. *Tetrahedron Lett.* **2004**, 45, (*3*), 603.

[65] Schultz, T. Ph.D. dissertation, University of Basel, **2004**.

[66] Ebran, J.-P.; Jubault, P.; Pannecoucke, X.; Quirion, J.-C. *Tetrahedron: Asymmetry* **2003**, *14*, 1637.

[67] Konig, W.; Geiger, R., *Chem. Ber.* **1970,** 103, (*3*), 788.

[68] Atkins, G. M., Jr.; Burgess, E. M. *J. Am. Chem. Soc.* **1968,** 90, (*17*), 4744. Atkins, G. M., Jr.; Burgess, E. M. *J. Am. Chem. Soc.* **1972,** 94, (*17*), 6135. Wipf, P.; Miller, C. P. *Tetrahedron Lett.* **1992,** 33, (*7*), 907.

[69] Streitwieser, A.; McKeown, A. E.; Hasanayn, F.; Davis, N. R. *Org. Lett.* **2005,** 7, (*7*), 1259.

[70] Ohff, M.; Holz, J.; Quirmbach, M.; Boerner, A. *Synthesis* **1998**, (*10*), 1391. Brunel, J. M.; Faure, B.; Maffei, M. *Coord. Chem. Rev.* **1998,** 178-180, (*Pt. 1*), 665. Carboni, B.; Monnier, L. *Tetrahedron* **1999,** 55, (*5*), 1197.

[71] Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990,** 112, (*13*), 5244. Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985,** 107, (*18*), 5301.

[72] McNulty, J.; Zhou, Y. *Tetrahedron Lett.* **2004,** 45, (*2*), 407.

[73] Inoue, I.; Shindo, M.; Koga, K.; Kanai, M.; Tomioka, K. *Tetrahedron: Asymmetry* **1995,** 6, (*10*), 2527.

[74] Williams, D. B. G.; Lombard, H.; van Niekerk, M.; Coetzee, P. P.; Holzapfel, C. W. *Phosphorus, Sulfur and Silicon and the Related Elements* **2002,** 177, (*12*), 2799.

[75] Zhang, K., unpublished results.

[76] Suggs, J. W.; Cox, S. D.; Crabtree, R. H.; Quirk, J. M. *Tetrahedron Lett.* **1981,** 22, (*4*), 303.

[77] Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993,** 93, (*4*), 1307. Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994,** 116, (*9*), 4062.

[78] Kaiser, S. Ph.D. dissertation, University of Basel, **2005**.

[79] a) Crabtree, R. H.; Davis, M. W. *J. Org. Chem.* **1986,** 51, (*14*), 2655. Crabtree, R. H.; Davis, M. W. *Organometallics* **1983,** 2, (*5*), 681. b) Brown, J. M.; Naik, R. G. *Chem. Commun.* **1982**, (*6*), 348-50. Brown, J. M.; Hall, S. A. *J. Organomet. Chem.* **1985,** 285, (*1-3*), 333.

[80] Marcazzan, P.; Patrick, B. O.; James, B. R. *Organometallics* **2003,** 22, (*6*), 1177. James, B. R. *Catalysis Today* **1997,** 37, (*2*), 209.

[81] Vogel, C.; Aebi, R. *Herbicidal N-(alkoxyalkyl)haloacetanilides*. DP 2328340, **1973**.

[82] Blaser, H.-U. *Adv. Synth. Catal.* **2002,** 344, (*1*), 17. Blaser, H.-U.; Spindler, F. *Comprehensive Asymmetric Catalysis I-III* **1999,** 3, 1427.

[83] Schnider, P. Ph.D. dissertation, University of Basel, **1996**.

[84] Jiang, X.; Minnaard, A. J.; Hessen, B.; Feringa, B. L.; Duchateau, A. L. L.; Andrien, J. G. O.; Boogers, J. A. F.; de Vries, J. G. *Org. Lett.* **2003,** 5, (*9*), 1503.

[85] Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994,** 116, (*20*), 8952. Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994,** 116, (*26*), 11703.

[86] POV-Ray 3.5 ed., Persistence of Vision Raytracer, 8 July 2002, http:/www.povray.org.

[87] ORTEP-3 for windows, version 1.076. Farrugia, L. J. *J. App. Crystallogr*. **1997**, *30*, 565.

[88] Flack, H. D., Bernardinelli, G. *J. App. Crystallogr*. **2000**, *33*, 1143.

[89] Gier, T. E. *J. Am. Chem. Soc.* **1961**, 83, 1769.

[90] Märkl, G. *Angew. Chem.* **1966**, 78, (*18-19*), 907.

[91] International Union of Pure and Applied Chemistry, *Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F, and H*, Pergamon Press, Oxford, **1979**. Powell, W. H. *Pure Appl. Chem.* **1982**, 54, 217.

[92] Märkl, G.; Lieb, F.; Merz, A. *Angew. Chem., Int. Ed.* **1967**, 6, (*5*), 458. Märkl, G.; Lieb, F.; Merz, A. *Angew. Chem. Int., Ed. Engl.* **1967**, 6, (*11*), 944.

[93] Ashe, A. J., III *J. Am. Chem. Soc.* **1971**, 93, (*13*), 3293.

[94] Märkl, G. *Lect. Heterocycl. Chem.* **1972**, 1, 69. Dimroth, K. *Fortschr. Chem. Forsch.* **1973**, 38, 147.

[95] De Koe, P.; Bickelhaupt, F. *Angew. Chem., Int. Ed.* **1967**, 6, (*6*), 567. De Koe, P.; Bickelhaupt, F. *Angew. Chem., Int. Ed.* **1968**, 7, (*11*), 889.

[96] Märkl, G.; Merz, A. *Tetrahedron Lett.* **1971**, (*17*), 1215.

[97] Märkl, G.; Dorfmeister, G. *Tetrahedron Lett.* **1987**, 28, (*10*), 1093.

[98] Avarvari, N.; Le Floch, P.; Mathey, F. *J. Am. Chem. Soc.* **1996**, 118, (*47*), 11978.

[99] (a) Märkl, G.; Jin, G. Y.; Silbereisen, E. *Angew. Chem.* **1982**, 94, (*5*), 383. (b) Rösch, W.; Regitz, M. *Z. Naturforsch., Teil B* **1986**, 41B, (*7*), 931. (c) Abbari, M.; Yeung Lam Ko, Y. Y. C.; Carrie, R. *Heteroatom Chemistry* **1991**, 2, (*4*), 439.

[100] For other dienes see: Pellon, P.; Yeung Lam Ko, Y. Y. C.; Cosquer, P.; Hamelin, J.; Carrie, R. *Tetrahedron Lett.* **1986**, 27, (*36*), 4299. Pellon, P.; Hamelin, J. *Tetrahedron Lett.* **1986**, 27, (*46*), 5611. Märkl, G.; Kallmünzer, A. *Tetrahedron Lett.* **1989**, 30, (*39*), 5245. Wrackmeyer, B.; Klaus, U. *J. Organomet. Chem.* **1996**, 520, (*1-2*), 211. Annen, U.; Regitz, M.; Kluge, H. *Chem. Ber.* **1990**, 123, (*4*), 935.

[101] Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, 105, (*10*), 3842.

[102] Wong, T. C.; Bartell, L. S. *J. Chem. Phys.* **1974**, 61, (*7*), 2840. Kuczkowski, R. L.; Ashe, A. J., III *J. Mol. Spectrosc.* **1972**, 42, (*3*), 457. Bart, J. C. J.; Daly, J. J. *J. Chem. Soc. A* **1970**, (*4*), 567.

[103] Ashe, A. J., III *Acc. Chem. Res.* **1978**, 11, (*4*), 153.

[104] Baldridge, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, 110, (*13*), 4204.

[105] Nyulaszi, L.; Veszpremi, T. *J. Phys. Chem.* **1996**, 100, (*16*), 6456. Nyulaszi, L. *Chem. Rev.* **2001**, 101, (*5*), 1229.

[106] Saieswari, A.; Deva Priyakumar, U.; Narahari Sastry, G. *Theochem* **2003**, 663, 145.

[107] Batich, C.; Heilbronner, E.; Hornung, V.; Ashe, A. J., III; Clark, D. T.; Cobley, U. T.; Kilcast, D.; Scanlan, I. *J. Am. Chem. Soc.* **1973**, 95, (*3*), 928. Ashe, A. J., III; Burger, F.; El-Sheik, M. Y.; Heilbronner, E.; Maier, J. P.; Muller, J. F. *Helv. Chim. Acta* **1976**, 59, (*6*), 1944.

[108] Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, 52, (*5*), 2769.

[109] Frison, G.; Sevin, A.; Avarvari, N.; Mathey, F.; Le Floch, P. *J. Org. Chem.* **1999**, 64, (*15*), 5524.

[110] Pham-Tran, N.-N.; Bouchoux, G.; Delaere, D.; Nguyen, M. T. *J. Phys. Chem.* **2005**, 109, (*12*), 2957.

[111] Märkl, G.; Potthast, R. *Angew. Chem., Int. Ed.* **1967**, 6, (*1*), 86. Märkl, G.; Merz, A. *Tetrahedron Lett.* **1968**, (*32*), 3611. Ashe, A. J., III; Smith, T. W. *Tetrahedron Lett.* **1977**, (*5*), 407.

[112] Märkl, G.; Lieb, F.; Merz, A. *Angew. Chem., Int. Ed.* **1967**, 6, (*1*), 87.

[113] Kanter, H.; Mach, W.; Dimroth, K. *Chem. Ber.* **1977**, 110, (*2*), 395.

[114] Dillon, K. B.; Mathey, F.; Nixon, J. F., *Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-organic Chemistry*, Wiley, **1998**, 235. And references therein.

[115] Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1993**, 115, (*23*), 10665. Trauner, H.; Le Floch, P.; Lefour, J.-M.; Ricard, L.; Mathey, F. *Synthesis* **1995**, (*6*), 717.

[116] Märkl, G.; Lieb, F.; Martin, C. *Tetrahedron Lett.* **1971**, (*17*), 1249. Breit, B.; Fuchs, E. *Chem. Commun.* **2004**, (*6*), 694.

[117] Kanter, H.; Dimroth, K. *Tetrahedron Lett.* **1975**, (*8*), 541. Mathey, F.; Le Floch, P. *Chem. Ber.* **1996**, 129, (*3*), 263. Elschenbroich, C.; Voss, S.; Harms, K. *Z. Naturforsch. B* **1999**, 54, (*2*), 209.

[118] Knoch, F.; Kremer, F.; Schmidt, U.; Zenneck, U.; Le Floch, P.; Mathey, F. *Organometallics* **1996**, 15, (*12*), 2713. Le Floch, P.; Knoch, F.; Kremer, F.; Mathey, F.; Scholz, J.; Scholz, W.; Thiele, K. H.; Zenneck, U. *Eur. J. Inorg. Chem.* **1998**, (*1*), 119. Elschenbroich, C.; Nowotny, M.; Metz, B.; Massa, W.; Graulich, J. *Angew. Chem.* **1991**, 103, (*5*), 601. Elschenbroich, C.; Nowotny, M.; Behrendt, A.; Harms, K.; Wocadlo, S.; Pebler, J. *J. Am. Chem. Soc.* **1994**, 116, (*14*), 6217.

[119] Breit, B.; Winde, R.; Mackewitz, T.; Paciello, R.; Harms, K. *Chem. Eur. J.* **2001**, 7, (*14*), 3106.

[120] Doux, M.; Ricard, L.; Mathey, F.; Le Floch, P.; Mezailles, N. *Eur. J. Inorg. Chem.* **2003**, (*4*), 687.

[121] Schmid, B.; Venanzi, L. M.; Gerfin, T.; Gramlich, V.; Mathey, F. *Inorg. Chem.* **1992**, 31, (*24*), 5117.

[122] DiMauro, E. F.; Kozlowski, M. C. *J. Chem. Soc. Perkin Trans. 1* **2002**, (*3*), 439.

[123] Weber, L. *Angew. Chem., Int. Ed.* **2002**, 41, (*4*), 563.

[124] Breit, B. *J. Mol. Catal. A: Chemical,* **1999,** *143*, 143.

[125] (a) Escher, I. H.; Pfaltz, A. *Tetrahedron* **2000,** 56, (*18*), 2879. (b) Blankenstein, J.; Pfaltz, A. *Angew. Chem. , Int. Ed.* **2001,** 40, (*23*), 4445. (c) Menges, F.; Neuburger, M.; Pfaltz, A. *Org. Lett.* **2002,** 4, (*26*), 4713. (d) Menges, F.; Pfaltz, A. *Adv. Synth. Catal.* **2002,** 344, (*1*), 40. (e) Smidt, S. P.; Menges, F.; Pfaltz, A. *Org. Lett.* **2004,** 6, (*20*), 3653. (f) Drury, W. J., III; Zimmermann, N.; Keenan, M.; Hayashi, M.; Kaiser, S.; Goddard, R.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2004,** 43, (*1*), 70.

[126] Rey, M.; Dunkelblum, E.; Allain, R.; Dreiding, A. S. *Helv. Chim. Acta* **1970**, 53, (*8*), 2159.

[127] Mitsunobu, O.; Yamada, M.; Mukaiyama, T. *Bulletin of the Chemical Society of Japan* **1967**, 40, (*4*), 935.

[128] Atkins, G. M., Jr.; Burgess, E. M. *J. Am. Chem. Soc.* **1968,** 90, (*17*), 4744; Atkins, G. M., Jr.; Burgess, E. M. *J. Am. Chem. Soc.* **1972,** 94, (*17*), 6135; Wipf, P.; Miller, C. P. *Tetrahedron Lett.* **1992,** 33, (*7*), 907.

[129] Karsch, H. H.; Bienlein, F.; Rupprich, T.; Uhlig, F.; Herrmann, E.; Scheer, M. in: Herrmann, W. A.; Brauer, G.; Editors, *Synthetic Methods of Organometallic and Inorganic Chemistry* **1996**, 58.

[130] Becker, G.; Schmidt, H.; Uhl, G.; Uhl, W. *Inorg. Synth.* **1990**, 27, 249.

[131] Rösch, W.; Allspach, T.; Bergsträßer, U.; Regitz, M. in: Herrmann, W. A., Brauer, G.; Editors, *Synthetic Methods of Organometallic and Inorganic Chemistry Vol.3*, **1996**, 11.

[132] Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR-Spektroskopie von Nichtmetallen* (Band 3) Thieme, Stuttgart, **1993**, p.126.

[133] Schmid, B.; Venanzi, L. M.; Albinati, A.; Mathey, F. *Inorg. Chem.* **1991**, 30, (*25*), 4693.

[134] Nief, F.; Fischer, J. *Organometallics* **1986**, 5, (*5*), 877.

[135] Roundhill, D. M.; Sperline, R. P.; Beaulieu, W. B. *Coord. Chem. Rev.* **1978**, 26, (*3*), 263.

[136] λ^5-phosphinines with electronegative substituents show some features of aromaticity. With positive substituents λ^5-phosphinines display only weak or no aromaticity. For details see: Wang, Z.-X.; Schleyer, P. v. R. *Helv. Chim. Acta* **2001**, 84, (*6*), 1578.

[137] (a) Nemoto, T.; Matsumoto, T.; Masuda, T.; Hitomi, T.; Hatano, K.; Hamada, Y. *J. Am. Chem. Soc.* **2004**, *126*, 3690; (b) Dubrovina, N. V.; Boerner, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5883.

[138] Konig, W.; Geiger, R. *Chem. Ber.* **1970,** 103, (*3*), 788.

[139] Boland, N. A.; Casey, M.; Hynes, S. J.; Matthews, J. W.; Smyth, M. P. *J. Org. Chem.* **2002**, 67, (*11*), 3919.

[140] Janssen, J. P.; Helmchen, G. *Tetrahedron Lett.* **1997**, 38, (*46*), 8025.

[141] (a) Bartels, B.; Helmchen, G. *Chem. Commun.* **1999**, (*8*), 741. (b) Bartels, B.; Garcia-Yebra, C.; Helmchen, G. *Eur. J. Org. Chem.* **2003**, (*6*), 1097.

[142] Bartels, B.; Garcia-Yebra, C.; Rominger, F.; Helmchen, G. *Eur. J. Inorg. Chem.* **2002**, (*10*), 2569.

[143] Cramer, R. *J. Am. Chem. Soc.* **1964**, 86, (*2*), 217.

[144] Hayashi, T.; Okada, A.; Suzuka, T.; Kawatsura, M. *Org. Lett.* **2003**, 5, (*10*), 1713.

[145] Bart, J. C. J.; Daly, J. J. *J. Chem. Soc. A* **1970**, (*4*), 567.

[146] Funa, N.; Ohnishi, Y.; Ebizuka, Y.; Horinouchi, S. *J. Bio. Chem.* **2002**, 277, (*7*), 4628.

[147] Huber, U. Ger. Off. 77-2705874, **1977**. Huber, U. U.S. Patent 4,112,003, **1978**.

[148] Hansen, C. A.; Frost, J. W. *J. Am. Chem. Soc.* **2002**, 124, (*21*), 5926.

[149] Fuchs, E. P. O.; Roesch, W.; Regitz, M. *Angew. Chem.* **1987**, 99, (*10*), 1058.

[150] Annen, U.; Regitz, M. *Tetrahedron Lett.* **1988**, 29, (*14*), 1681.

[151] Jiang, X.-B.; Minnaard, A. J.; Hessen, B.; Feringa, B. L.; Duchateau, A. L. L.; Andrien, J. G. O.; Boogers, J. A. F.; de Vries, J. G. *Org. Lett.* **2003**, *5*, 1503.

[152] Ashe, A. J.; Chan, W. T. *Tetrahedron Lett.* **1975**, (*32*), 2749.

[153] Hunter, R. A.; Whitby, R. J.; Light, M. E.; Hursthouse, M. B. *Tetrahedron Lett.* **2004**, 45, (*41*), 7633.

[154] Trost, B. M. *Science* **1991**, 254, (*5037*), 1471.

[155] (a) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, (*9*), 977. (b) Khand, I. U.; Pauson, P. L. *J. Chem. Soc., Perkin Trans. 1* **1976**, (*1*), 30. (c) Pauson, P. L. *Tetrahedron* **1985**, 41, (*24*), 5855.

[156] Pauson, P. L.; Khand, I. U.; Knox, G. R.; Watts, W. E. *Chem. Commun.* **1971**, (*1*), 36.

[157] Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, 46, (*26*), 5436.

[158] Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, 41, (*24*), 5861. Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, 26, (*40*), 4851.

[159] Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, 12, 323.

[160] Hay, A. M.; Kerr, W. J.; Kirk, G. G.; Middlemiss, D. *Organometallics* **1995,** 14, (*11*), 4986. Kerr, W. J.; Kirk, G. G.; Middlemiss, D. *Synlett* **1995**, (*10*), 1085. Hiroi, K.; Watanabe, T.; Kawagishi, R.; Abe, I. *Tetrahedron: Asymmetry* **2000**, 11, (*3*), 797.

[161] (a) Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000,** 56, (*21*), 3263. (b) Gibson, S. E.; Stevenazzi, A. *Angew. Chem., Int. Ed.* **2003,** 42, (*16*), 1800. (c) Blanco-Urgoiti, J.; Anorbe, L.; Perez-Serrano, L.; Dominguez, G.; Perez-Castells, J. *Chem. Soc. Rev.* **2004**, 33, (*1*), 32. (d) Gibson, S. E.; Lewis, S. E.; Mainolfi, N. *J. Organomet. Chem.* **2004**, 689, (*24*), 3873.

[162] (a) Jeong, N.; Hwang, S. H.; Lee, Y.; Chung, Y. K. *J. Am. Chem. Soc.* **1994,** 116, (*7*), 3159. (b) Lee, B. Y.; Chung, Y. K.; Jeong, N.; Lee, Y.; Hwang, S. H. *J. Am. Chem. Soc.* **1994,** 116, (*19*), 8793. (c) Pagenkopf, B. L.; Livinghouse, T. *J. Am. Chem. Soc.* **1996,** 118, (*9*), 2285-6. (d) Lee, N. Y.; Chung, Y. K. *Tetrahedron Lett.* **1996,** 37, (*18*), 3145. (e) Kim, J. W.; Chung, Y. K. *Synthesis* **1998**, (*2*), 142. (f) Belanger, D. B.; O'Mahony, D. J. R.; Livinghouse, T. *Tetrahedron Lett.* **1998,** 39, (*42*), 7637. (g) Belanger, D. B.; Livinghouse, T. *Tetrahedron Lett.* **1998,** 39, (*42*), 7641. (h) Sugihara, T.; Yamaguchi, M. *Synlett* **1998**, (*12*), 1384. (i) Sugihara, T.; Yamaguchi, M., *J. Am. Chem. Soc.* **1998,** 120, (*41*), 10782. (j) Hayashi, M.; Hashimoto, Y.; Yamamoto, Y.; Usuki, J.; Saigo, K. *Angew. Chem., Int. Ed.* **2000,** 39, (*3*), 631.

[163] Pearson, A. J.; Dubbert, R. A. *Organometallics* **1994**, 13, (*5*), 1656.

[164] Zhang, M.; Buchwald, S. L. *J. Org. Chem.* **1996**, 61, (*14*), 4498.

[165] Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996,** 118, (*39*), 9450. Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999,** 121, (*25*), 5881. Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, 121, (*30*), 7026.

[166] Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, 107, (*8*), 2568. Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, 111, (*9*), 3336.

[167] (a) Morimoto, T.; Chatani, N.; Fukumoto, Y.; Mura. S. *J. Org. Chem.* **1997,** 62, (*11*), 3762. (b) Kondo, T.; Suzuki, N.; Okada, T.; Mitsudo, T.-A. *J. Am. Chem. Soc.* **1997,** 119, (*26*), 6187.

[168] (a) Koga, Y.; Kobayashi, T.; Narasaka, K. *Chem. Lett.* **1998**, (*3*), 249; (b) Jeong, N. *Organometallics* **1998,** 17, (*17*), 3642.

[169] Shibata, T.; Takagi, K. *J. Am. Chem. Soc.* **2000,** 122, (*40*), 9852.

[170] Shibata, T.; Toshida, N.; Takagi, K. *J. Org. Chem.* **2002**, 67, (*21*), 7446. Shibata, T.; Toshida, N.; Takagi, K. *Org. Lett.* **2002**, 4, (*9*), 1619. Morimoto, T.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. *J. Am. Chem. Soc.* **2002**, 124, (*15*), 3806. Kwong, F. Y.; Li, Y. M.; Lam, W. H.; Qiu, L.; Lee, H. W.; Yeung, C. H.; Chan, K. S.; Chan, A. S. C. *Chem. Eur. J.* **2005**, 11, (*13*), 3872.

[171] Grossman, R. B.; Buchwald, S. L. *J. Org. Chem.* **1992**, 57, (*22*), 5803.

[172] Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, 115, (*11*), 4912. Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, 116, (*19*), 8593.

[173] Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996,** 118, (*46*), 11688. Sturla, S. J.; Buchwald, S. L. *J. Org. Chem.* **1999,** 64, (*15*), 5547; Sturla, S. J.; Buchwald, S. L. *Organometallics* **2002,** 21, (*4*), 739.

[174] Kobayashi, T.; Koga, Y.; Narasaka, K. *J. Organomet. Chem.* **2001**, 624, (*1-2*), 73.

[175] Jeong, N.; Sung, B. K.; Choi, Y. K. *J. Am. Chem. Soc.* **2000**, 122, (*28*), 6771.

[176] Shibata, T.; Toshida, N.; Yamasaki, M.; Maekawa, S.; Takagi, K. *Tetrahedron* **2005**, 61, (*42*), 9974.

[177] Lu, Z.-L. postdoctoral report, **2004**, University of Basel.

[178] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, 92, (*10*), 2953.

[179] Cotton, F. A. *Inorg. Chem.* **1964**, 3, (*5*), 702. Strohmeier, W.; Mueller, F. J. *Chem Ber.* **1967**, 100, (*9*), 2812.

[180] Schnider, P.; Koch, G.; Prétôt, R.; Wang, G.; Bohnen, F. M.; Kruger, C.; Pfaltz, A. *Chem. Eur. J.* **1997,** 3, (*6*), 887.

[181] Noth, H.; Schlegel, A.; Knizek, J.; Krossing, I.; Ponikwar, W.; Seifert, T. *Chem. Eur. J.* **1998**, 4, (*11*), 2191. Ivanova, S. M.; Nolan, B. G.; Kobayashi, Y.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Chem. Eur. J.* **2001**, 7, (*2*), 503.

[182] Gaspar, P. P.; West, R. *Chemistry of Organic Silicon Compounds* **1998**, 2, (*Pt. 3*), 2463.

[183] Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1979**, 101, (*18*), 5427.

[184] Lappert, M. F. *Main Group Metal Chemistry* **1994**, 17, (*1-4*), 183.

[185] Jutzi, P.; Kanne, D.; Kruger, C. *Angew. Chem.* **1986**, 98, (*2*), 163.

[186] Karsch, H. H.; Keller, U.; Gamper, S.; Mueller, G. *Angew. Chem.* **1990**, 102, (*3*), 297.

[187] Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, 116, (*6*), 2691.

[188] West, R.; Denk, M. *Pure Appl. Chem.* **1996**, 68, (*4*), 785.

[189] Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaser, D. *Chem. Commun.* **1995**, (*19*), 1931.

[190] Heinicke, J.; Oprea, A.; Kindermann, M. K.; Karpati, T.; Nyulaszi, L.; Veszpremi, T. *Chem. Eur. J.* **1998**, 4, (*3*), 541.

[191] Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, 121, (*41*), 9722.

[192] Lee, G.-H.; West, R.; Mueller, T. *J. Am. Chem. Soc.* **2003**, 125, (*27*), 8114.

[193] (a) Veszpremi, T.; Nyulaszi, L.; Hajgato, B.; Heinicke, J. *Theochem* **1998**, 431, (*1-2*), 1. (b) Urquhart, S. G.; Hitchcock, A. P.; Lehmann, J. F.; Denk, M. *Organometallics* **1998**, 17, (*11*), 2352.

[194] West, R.; Buffy, J. J.; Haaf, M.; Mueller, T.; Gehrhus, B.; Lappert, M. F.; Apeloig, Y. *J. Am. Chem. Soc.* **1998**, 120, (*7*), 1639.

[195] Leites, L. A.; Bukalov, S. S.; Denk, M.; West, R.; Haaf, M. *J. Mol. Struct.* **2000**, 550-551, 329.

[196] Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Mueller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, 121, (*40*), 9479.

[197] Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaeser, D. *J. Organomet. Chem.* **1996**, 521, (*1-2*), 211.

[198] Metzler, N.; Denk, M. *Chem. Commun.* **1996**, (*23*), 2657.

[199] (a) Moser, D. F.; Bosse, T.; Olson, J.; Moser, J. L.; Guzei, I. A.; West, R. *J. Am. Chem. Soc.* **2002**, 124, (*16*), 4186. (b) Su, M.-D. *J. Am. Chem. Soc.* **2003**, 125, (*7*), 1714. (c) Moser, D. F.; Naka, A.; Guzei, I. A.; Mueller, T.; West, R. *J. Am. Chem. Soc.* **2005**, 127, (*42*), 14730. (d) Delawar, M.; Gehrhus, B.; Hitchcock, P. B. *Dalton Trans.* **2005**, (*17*), 2945.

[200] Haaf, M.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk, M.; West, R. *J. Am. Chem. Soc.* **1998**, 120, (*49*), 12714.

[201] (a) Denk, M.; Hayashi, R. K.; West, R. *J. Am. Chem. Soc.* **1994**, 116, (*23*), 10813. (b) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1998**, 17, (*7*), 1378.

[202] Ishida, S.; Iwamoto, T.; Kira, M. *J. Am. Chem. Soc.* **2003**, 125, (*11*), 3212. Cai, X.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Slootweg, J. C. *J. Organomet. Chem.* **2002**, 643-644, 272.

[203] Bharatam, P. V.; Moudgil, R.; Kaur, D. *Organometallics* **2002**, 21, (*18*), 3683.

[204] (a) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, 68, (*4*), 785. (b) Haaf, M.; Schmedake, T. A.; Paradise, B. J.; West, R. *Can. J. Chem.* **2000**, 78, (*11*), 1526. (c) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaser, D. *Chem. Commun.* **1995**, (*19*), 1931. (d) Heinicke, J.; Oprea, A.; Kindermann, M. K.; Karpati, T.; Nyulaszi, L.; Veszpremi, T. *Chem. Eur. J.* **1998**, 4, (*3*), 541.

[205] (a) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, 33, (*10*), 704. (b) Hill, N. J.; West, R. *J. Org. Chem.* **2004**, 689, (*24*), 4165. (c) Lappert, M. F. *J.*

Organomet. Chem. **2000**, 600, (*1-2*), 144. (d) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, 617-618, 209.

[206] (a) Denk, M.; Hayashi, R. K.; West, R. *Chem. Commun.* **1994**, (*1*), 33. (b) Dysard, J. M.; Tilley, T. D. *Organometallics* **2000**, 19, (*23*), 4726. (c) Cai, X.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Can. J. Chem.* **2000**, 78, (*11*), 1484. (d) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Millevolte, A. J.; Powell, D. R.; West, R. *J. Organomet. Chem.* **2001**, 636, (*1-2*), 17. (e) Amoroso, D.; Haaf, M.; Yap, G. P. A.; West, R.; Fogg, D. E. *Organometallics* **2002**, 21, (*3*), 534. (f) Evans, W. J.; Perotti, J. M.; Ziller, J. W.; Moser, D. F.; West, R. *Organometallics* **2003**, 22, (*5*), 1160.

[207] Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Powell, D.; West, R. *Organometallics* **2000**, 19, (*17*), 3263.

[208] Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1998**, 17, (*26*), 5599.

[209] Avent, A. G.; Gerhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *J. Organomet. Chem.* **2003**, 686, 321.

[210] Herrmann, W. A.; Harter, P.; Gstöttmayr, C. W. K.; Bielert, F.; Seeboth, N.; Sirsch, P. *J. Organomet. Chem.* **2002**, 649, (*2*), 141.

[211] Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, 41, (*8*), 1290.

[212] McGuinness, D. S.; Yates, B. F.; Cavell, K. J. *Organometallics* **2002**, 21, (*24*), 5408.

[213] Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, (*12*), 1711.

[214] Schenck, T. G.; Milne, C. R. C.; Sawyer, J. F.; Bosnich, B. *Inorg. Chem.* **1985**, 24, (*15*), 2338.

[215] According to: Green, M.; Kuc, T. A.; Taylor, S. H. *Chem. Commun.* **1970**, *22*, 1553.

[216] (a) Herrmann, W. A.; Goossen, L. J.; Artus, G. R. J., Köcher, C. *Organometallics*, **1997**, *16*, 2472. (b) Köcher, C.; Herrmann, W. A. *J. Organomet. Chem*. **1997**, *532*, 261.

[217] (a) Aizenberg, M. J.; Elsevier, C. J.; Milstein, D. *J. Organomet. Chem*., **1998**, *551*, 81. (b) Thorn, D. L.; Harlow, R. L. *Inorg. Chem*. **1990**, *29*, 2017.

[218] Rosenberg, L.; Fryzuk, M. D.; Rettig, S. J. *Organometallics*, **1999**, *18*, 958 (Supporting Information).

[219] Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, 62, (*21*), 7512.

[220] A. J. Gordon, R. A. Ford, "*The Chemist's Companion*", Wiley and Sons, New York, **1972**.

[221] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, 43, (*14*), 2923.

[[222]] Prétôt, R. Ph.D. dissertation, University of Basel, **1997**.

[223] Becker, G.; Beck, H. P. *Z. Anorg. Allg. Chem.* **1977**, *430*, 66.

[224] Crabtree, R. H.; Morehouse, S. M. *Inorg. Synth.,* Vol 24, 174.

[225] Reger, D. L.; Wright, T. D.; Little, C. A.; Lamba, *J. J.* S.; Smith, M. D. *Inorg. Chem.* **2001**, *40*, 3810.

[226] Otwinowski, Z.; Minor, W. *Methods in Enzymology* **1997**, 276, (*Part A*), 307.

[227] Duisenberg, A. J. M.; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. *J. Appl. Crystallogr.* **2003**, 36, (*2*), 220.

[228] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, 26, (*3*), 343.

[229] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, 32, (*1*), 115.

[230] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, 36, (*6*), 1487.

[231] Flack, H. D., Bernardinelli, G., *J. App. Crystallogr*. **2000**, *33*, 1143.

[232] http://checkcif.iucr.org/