P-Heterocycles as Ligands in Homogeneous Catalytic Reactions†

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Received November 5, 2009

Contents

1. Introduction

Ligands with phosphorus donor atoms have probably been the most studied ones in transition metal catalyzed reactions. Because of the recognition of the carbon−metal bonding properties and the mechanistic understanding of the basic catalytic reactions, the application of homogeneous catalytic reactions is steadily emerging. The definition of the scope and limitations has rendered many of the transition metal−phosphorus ligand catalytic systems the most efficient solution to practical problems.

Most of the "textbook" homogeneous catalytic reactions, among them enantioselective reactions, apply tertiary phosphines as most conventional ligands. Among the ligands with phosphorus of sp^3 hybridization, the cyclic ligands have reached an impressive maturity. In spite of this fact, in general, the chemistry of phosphorus heterocycles is much less developed than the analogous nitrogen chemistry. It is especially true in the area of coordination chemistry, even though cyclic phosphines proved to be excellent ligands for catalysis.[1−5]

Thus, the main objective of this review is to shed some more light into the synthesis, coordination chemistry, and catalysis of some 3-, 4-, 5-, 6-, and 7-membered *P*-heterocycles of unprecedented structure not reviewed before. The objective of this paper *is not to present a full coverage of P(III) derivatives*, since several aspects of these types of *P*-heterocycles such as theoretical background, synthesis,

György Keglevich was born in Budapest, Hungary, in 1957. He received his M.Sc. under the supervision of Professors L. Tőke and Imre Petneházy from the Technical University of Budapest in 1981. After getting the Ph.D., he was a postdoctoral fellow with Professor L. D. Quin (at Duke University, Durham, NC). In 1994, he received his D.Sc. from the Hungarian Academy of Sciences. After different teaching positions, he was appointed full professor at the Department of Organic Chemical Technology, Budapest University of Technology and Economics, in 1996, and he was the head of this Department in the period of 1999−2006. After a fusion in 2007, he has been the head of the Department of Organic Chemistry and Technology. His research interests include organophosphorus and environmentally friendly chemistry comprising *P*-heterocycles, low-coordinated P-fragments, P(III)-ligands, their borane- and transition metal complexes, catalytic reactions, selective syntheses, resolution of P(IV) compounds, microwave synthesis, ionic liquids, and optimization of reactions by on-line methods.

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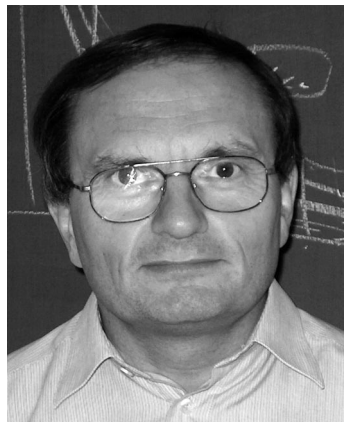
† This paper is dedicated to the memory of Professor Pascal Le Floch.

10.1021/cr900364c
Published on Web 04/12/2010



László Kollár was born in Kaposvár, Hungary. He studied chemical engineering at the University of Veszprém, where he received his diploma in 1979 and the doctoral degree in 1983, working under the direction of László Markó and Bálint Heil on enantioselective hydrogenation of ketones with rhodium complexes. For postdoctoral studies, he spent two years with Piero Pino and Giambattista Consiglio at the ETH, Zurich, being involved in enantioselective hydroformylation of unsaturated esters with platinum−phosphine−tin(II)chloride system. He began independent research on the asymmetric hydroformylation of vinyl aromatics and some mechanistic investigations of platinum−phosphine−tin(II)chloride systems, as well as transition metal catalyzed functionalization of steroids. He was appointed Associate Professor at the University of Veszprém in 1993. In 1996 he moved to Pécs (southern Transdanubia, Hungary), where he has been full Professor since 1997 at the University of Pécs. The main efforts of his current research are platinum, palladium, and rhodium complexes of heterobidentate and multidentate ligands, mechanistic aspects of carbonylation reactions, coordination chemistry in ionic liquids, and "host−guest" interactions.

application,[6] coordination chemistry, and catalysis have been reviewed some years ago. Recently, the review of Le Floch,[7] as well as many research papers, demonstrates the increasing role of transition metal complexes containing *P*-heterocyclic ligands with sp^2 hybridization (phospholide ligands, phosphinines) in homogeneous catalysis.

The main goal of this contribution is to show the novel coordination and catalytic features of the catalytic systems containing *P*-heterocyclic ligands including both low-coordinated phosphorus and those ones with pyramidal character. The structural variability of these transition metal complexes, depending on the systematically modified *P*-heterocycles, enables the fine-tuning of the chemo-, regio-, and (in appropriate cases) enantioselectivities of homogeneous catalytic reactions. This paper is intended to discuss some peculiarities of these reactions catalyzed both by "preformed" and in situ catalysts. The literature until June 2009 is covered with special focus on the last 5 years.

2. Synthesis of P-Heterocyclic Ligands and Their Transition Metal Complexes

A short description of the ligands including structural modifications related to previously known parent compounds will be given in this section. As for the synthetic details, only the most relevant features will be described. However, the ligands will be classified according to their ring size (for the parent structures, see Figure 1), the number of phosphorus donor atoms, or further donor atoms (potential heterobidentate- or heteropolydentate-type ligands). The catalytic relevance of these (potential) ligands is described in the next section (section 3).

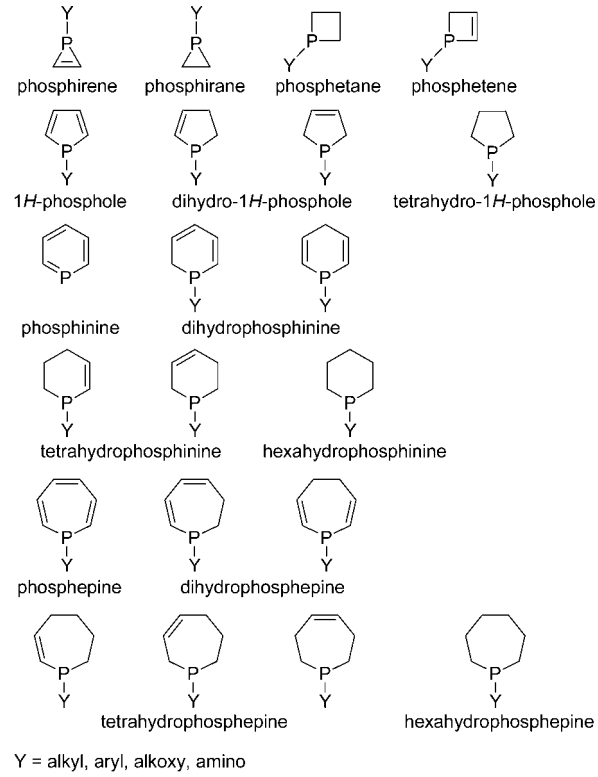


Figure 1. Variation of cyclic *P*-ligands.

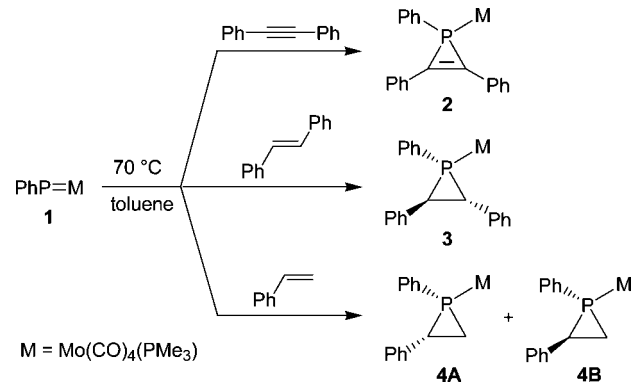
2.1. Three-Membered *P*-Heterocycles (Phosphiranes) and Their Complexes

Although sporadic results have been published with the smallest *P*-heterocycle, a short overview of their synthesis and coordination chemistry is given below. 1-Trimethylsilylphosphirane has been prepared from $P(SiMe_3)_3$ via the 2-chloroethyl substituted derivative. Its protonation led to the thermally highly unstable parent phosphirane. The *P*-trimethylsilyl derivative forms stable neutral tricarbonyl complexes $M(CO)_3L_3$ (M = Cr, Mo) and ionic cp-complexes such as $[Fe(cp)L_3]^+$.[8]

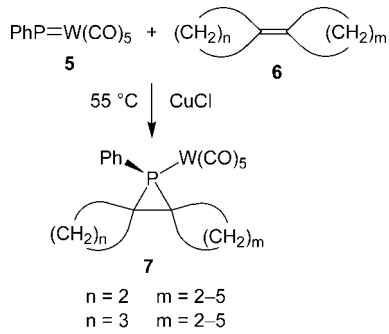
Transition metal phosphinidene complexes add to C=C and C≡C bonds to give the corresponding phosphiranes and phosphirenes. The target *P*-heterocycles (**2**, **3**, **4**, **7**, **9**, **11**, and **17**) were prepared via Mo- (Scheme 1),[9] Zr-,[10] W- (Scheme 2),[11,12] (Scheme 3),[13] (Scheme 4),[14] and Ni- (Scheme 5)[15] complexes.

It was proved that the phosphirane synthesis via the Mo−phosphinidene addition to C=C double bonds goes

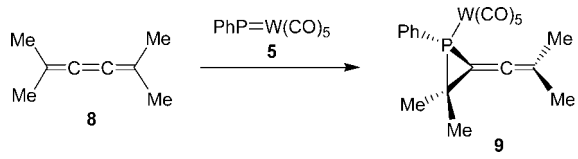
Scheme 1. Synthesis of Phosphiranes Based on Mo=P Derivatives



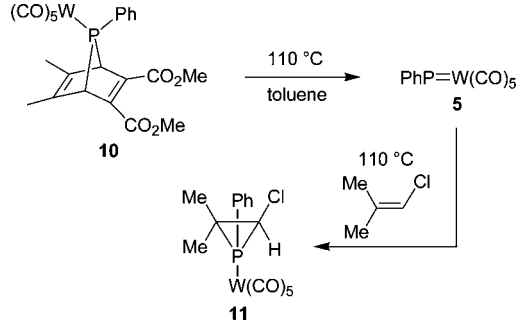
Scheme 2. Synthesis of Phosphiranes Based on W=P Derivatives I



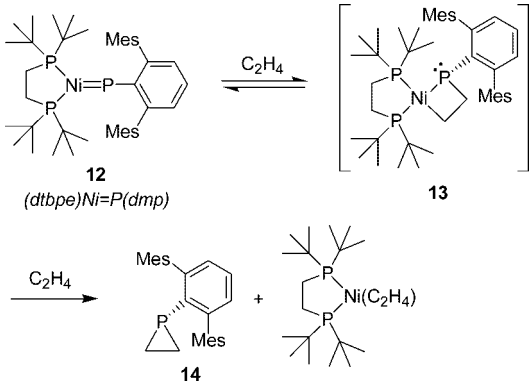
Scheme 3. Synthesis of Phosphiranes Based on W=P Derivatives II



Scheme 4. Synthesis of Phosphiranes Based on W=P Derivatives III

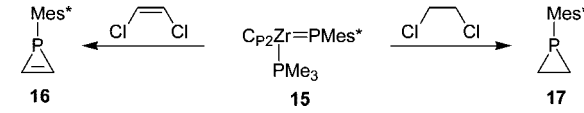


Scheme 5. Synthesis of *P*-(2,6-Dimesitylphenyl)phosphirane Based on a Nickelacycle Intermediate

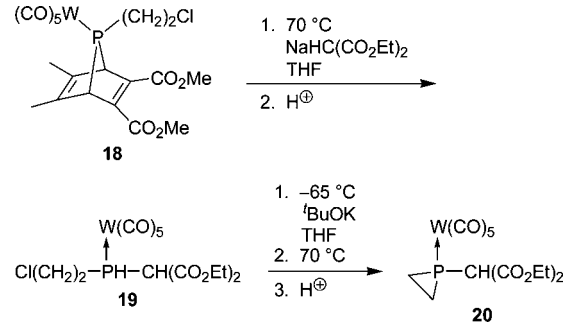


through the formation of a Mo−phosphirane−PMe_3 complex. The *cis*-PMe_3 ligand weakens the interaction between Mo and the three-membered ring, and even under mild CO pressure, the $Mo(CO)_4(PMe_3)$ fragment detaches from the P of the phosphirane by selective CO substitution.[9] In this way, the $Mo(CO)_5(PMe_3)$ by-product can be reused several times. The employment of phosphazirconacycles in metallacycle transfer reactions was shown in the seminal work of Stephan et al.[10] A density functional study on the reactivity of 1,2-dichloroethane was carried out, and the special reactivity of the 16-electron $(Cp)_2Zr{=}PH$ species was highlighted (Scheme 6).[16]

Scheme 6. Synthesis of Phosphiranes Based on Zr=P Derivatives



Scheme 7. Cyclization Approach to a Phosphirane in the Coordination Sphere of W



The dispirophosphiranes (**7**) (Scheme 2) contain a central phosphirane ring that is sprirofused on both sides to 3−6-membered rings. Their X-ray structure and computed geometries for simplified structures suggest that spirofusion with small rings and larger (5-, 6-membered) rings results in tightening or relaxation of the central phosphirane geometry.[12] The alkenylidenephosphirane complexes (**9**), generated from the 1,2-addition of the phosphinidene complex (**5**) to the terminal bond of tetramethylcumulene (Scheme 3), rearrange to the corresponding phospha[3]radiales.[13] The Ph−P moiety is preferably obtained from a 7-phenyl-7-phosphanorbornadiene precursor (**10**), as depicted for the tungsten−phosphirane complexes (Scheme 4). It has to be added that the phosphirane intermediate undergoes concerted migration of chlorine resulting in the formation of the corresponding (phenyl)(vinyl)chlorophosphine.[14]

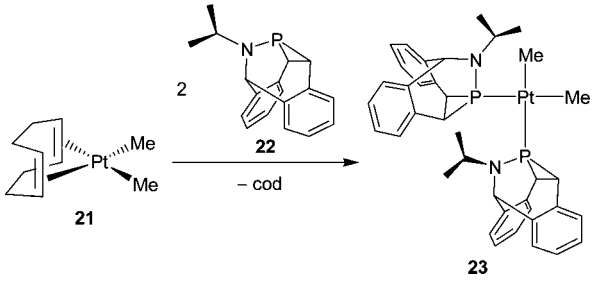
Investigating the group transfer from Ni−phosphinidene complexes to ethylene, the reaction was monitored by low temperature (−28 °C, toluene-d_8) ^1H and ^{13}C NMR measurements. The intermediate formation consistent with the structure of a metallacycle (**13**) was observed (Scheme 5). The reactions carried out with *trans*-ethylene-d_2 revealed that, if the reaction proceeds via [2 + 2]-cycloaddition intermediates, the reductive elimination should occur with retention of configuration.[15]

Combining phosphinidene units, formed from **18**, with malonate anion, the latter trapped the $[ClCH_2CH_2P{-}W(CO)_5]$, giving rise to the corresponding phosphirane complex **20** (Scheme 7). By using other substituents on the P of the phosphinidene moiety, the functional secondary phosphine complexes, $(RP(H)(CH(COOEt)_2)W(CO)_5$, were obtained.[17]

A highly stable polycyclic phosphirane (BABAR-Phos) (**22**) was easily synthesized in a few steps from dibenzosuberone.[18] Both of its Pt(II) (**23**) (Scheme 8)[19] and Pt(0) complexes[20] were prepared. It was found that this type of phosphirane acts as a relatively good electron donor while its electron-acceptor properties are not significantly different from those of phosphines. Several further BABAR-Phos analogues (**28**) were synthesized by using the dibenzosuberone (**24**)−chloro/amino-dibenzocycloheptatriene (**25/26**) pathway (Scheme 9).

A close analogue of BABAR-Phos, dibenzosemibullvalene (**31**), was synthesized from the 5-bis(trimethylsilyl)phospha-

Scheme 8. Synthesis of Pt(II)−(BABAR-Phos)



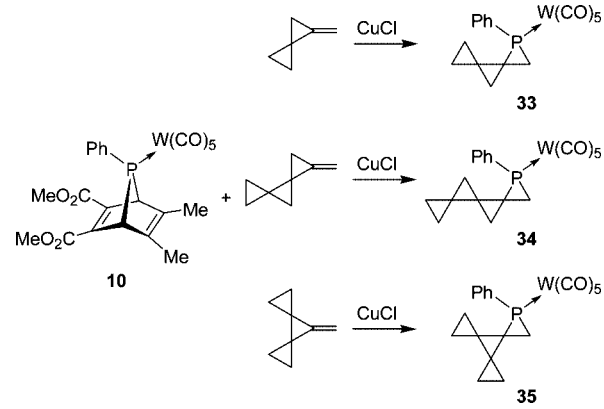
nyl-5*H*-dibenzo[*a,d*]cycloheptene (**29**), which was converted to a highly air-, moisture-, and temperature-sensitive chloro-derivative (**30**) in nearly quantitative reaction (Scheme 10).[21] A definitive proof for the dibenzo-1-phosphasemibullvalene structure was obtained in a complexation reaction with $W(CO)_5$(thf). The resulting $W(CO)_5$ complex (**32**) was characterized by X-ray structure analysis.

Mono- and diphospha[*n*]triangulanes (**33**−**35**) were synthesized from spirocyclopropanated methylenecyclopropanes and bicyclopropylidenes in copper-catalyzed reaction (Scheme 11).[22] Pentacarbonyl−tungsten complexes of a phospha[3]-triangulene ligand were synthesized and their X-ray structure was determined. The tightening of the phosphirane ring was observed when the number of spiro atoms was increased.[23]

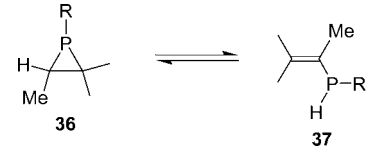
The radical ring-opening polymerization of methylphosphirane, -phosphetane, and -phospholane was studied via high-level ab initio calculations. The reaction is the fastest with phosphetanes, reflecting the compromise between the strain in the transition structure and the strain released by the partially broken bond. Although much slower, radical ring-opening of the phosphirane should also occur.[24] A density functional theory (DFT) study on the Cope rearrangements of *cis*-2,3-divinylphosphirane and related compounds was carried out. It was stated that the minimum energy path proceeds through an *endo*-boat-like aromatic transition structure.[25]

The thermal fragmentation of *P*-phenylphosphirane to phenylphosphinidene and ethylene was studied by electronic structure calculations.[26] A contrasting mechanism of hydrogen migration was observed by theoretical calculations on

Scheme 11. Synthesis of Phospha[*n*]triangulanes and Their W-Complexes



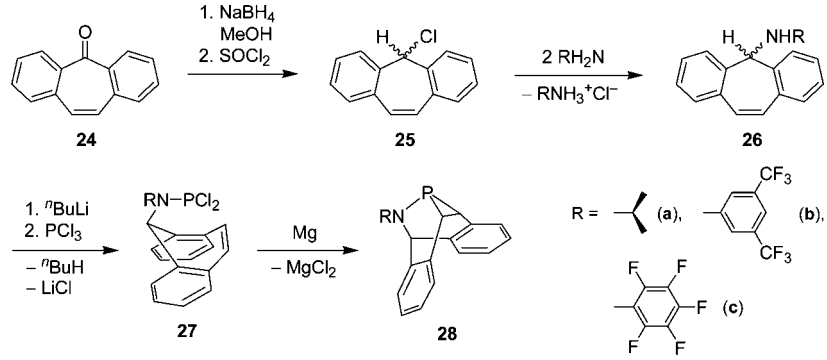
Scheme 12. Ring-Opening of Phosphiranes



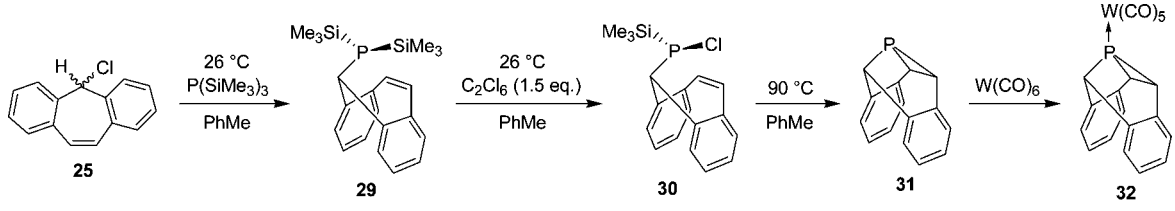
the ring-opening of phosphirane and silirane. It was confirmed that the phosphirane (**36**) ring-opening induced by C−P bond cleavage was accompanied by a hydrogen migration from C to P, yielding vinylphosphine (**37**) (Scheme 12).[27]

The platinum(II) dithiolato complexes (**38a**−**38c**) were prepared containing 1-(9-anthracene)phosphirane ligands. Significant intermolecular π-stacking between the anthracene rings of the phosphirane ligands were observed in the *cis*-bis(phosphirane) complex (Figure 2).[28] All of these complexes are stable to air and moisture. After preparative thin-layer chromatography (TLC) purification, the complexes were characterized by $^1J(^{195}Pt,^{31}P)$ couplings of diagnostic value of the ^{31}P NMR, and **38c** was also characterized by X-ray crystallography.

Scheme 9. Synthesis of BABAR-Phos Derivatives



Scheme 10. Synthesis of Dibenzo-1-phosphasemibullvalene and Its W-Complex



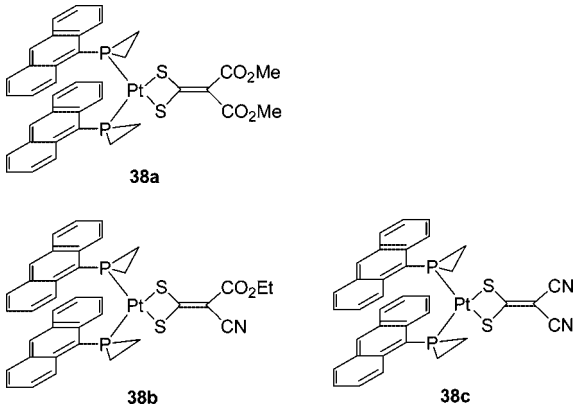
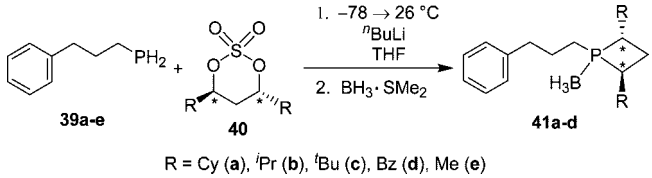


Figure 2. Pt(II)−Phosphirane Complexes.

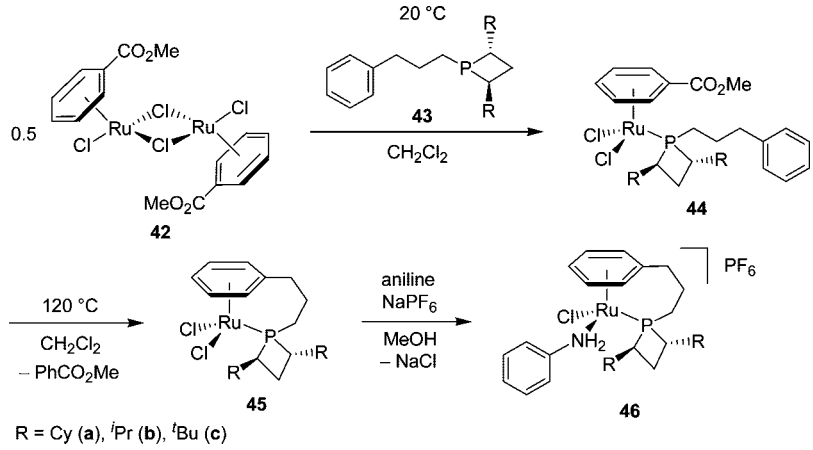
2.2. Four-Membered *P*-Heterocycles (Phosphetanes, Phosphetenes) and Their Complexes

Enantomerically pure cyclic sulfates (**40**) were transformed to enantiopure phosphetane ligands (**41a**−**41d**) (Scheme 13). Diastereoselective synthesis of their ruthenium(II) arene complexes containing chiral phosphetane-based tethers (**46**) was carried out (Scheme 14).[29] The nucleophilic substitution of the chloro ligand by aniline in the presence of Na[PF_6] resulted in the formation of the diastereomeric complex salts

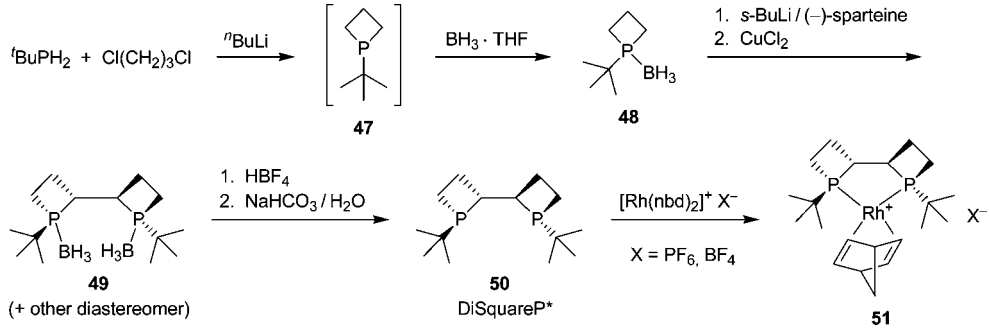
Scheme 13. Synthesis of Enantiopure Phosphetanes



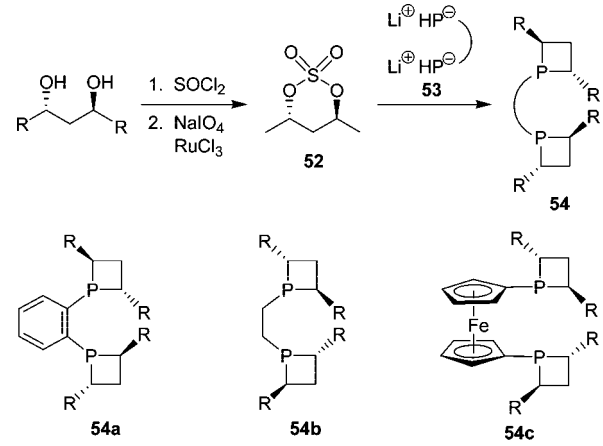
Scheme 14. Synthesis of Ru(II)−Arene Complexes



Scheme 15. Synthesis of a Cyclic Diphosphetane−Rhodium Complex



Scheme 16. Synthesis of Bisphosphetane Derivatives



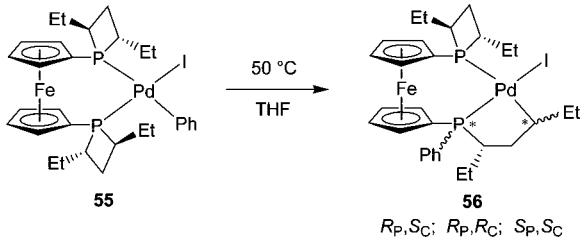
with hexafluorophosphate counterion. Diastereoselectivities up to 88% were obtained. The major diastereoisomers were characterized by X-ray analysis, and R_{Ru},S_C,S_C configurations were obtained in all cases.

Optically active 1,1′-di-*tert*-butyl-2,2′-diphosphetanyl (**50**) was synthesized from *tert*-butylphosphine via enantioselective deprotonation of the borane adduct (**48**) with *s*-BuLi/sparteine and homocoupling with $CuCl_2$ (Scheme 15).[30]

Enantomerically pure monophosphines, diphosphines (**54**), and *P,N*-heterobidentate ligands bearing phosphetane units were prepared from primary phosphines and cyclic sulfates of *anti*-1,3-diols (Scheme 16).[31] The X-ray structural characterization of the ruthenium and rhodium complexes of one of these ligands (**54c**, R = *i*Pr, *i*Pr-FerroTANE) was reported. It shows that both complexes adopt delta conformations as a result of the (*S*,*S*)-configuration of the phosphetane moiety.

The palladium-mediated ring-opening of the Et-FerroTANE ligand bound to Pd(II) (**55**) enabled the synthesis of

Scheme 17. Pd(II)−Et−FerroTANE Complexes



a *P*-stereogenic diphosphine ligand with an alkyl moiety resulting in tridentate coordination (**56**) (Scheme 17).[32] The NMR data and crystal structure of **56** (R_P,S_C), the diastereomer most easily removed by crystallization, showed that the complex was formed via cleavage of the phosphetane P−C bond and concominant phenyl migration to P. It has to be added that the absolute configurations given in Scheme 17 refer to the newly generated *P*-stereogenic center and one of the modified phosphetane stereocenters, which is now bound to Pd.

2.3. Five-Membered *P*-Heterocycles (Phospholes, Phospholenes, Phospholanes) and Their Complexes

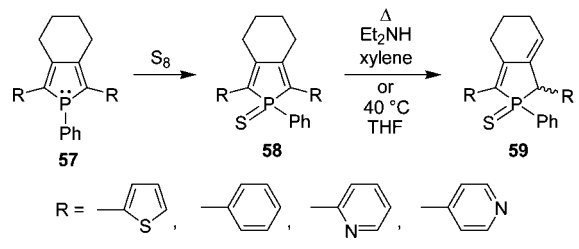
Among the *P*-heterocycles, phospholes and their derivatives are in the forefront both from the point of view of their coordination chemistry and their catalytic application.[33−35]

2.3.1. Phospholes and Their Complexes

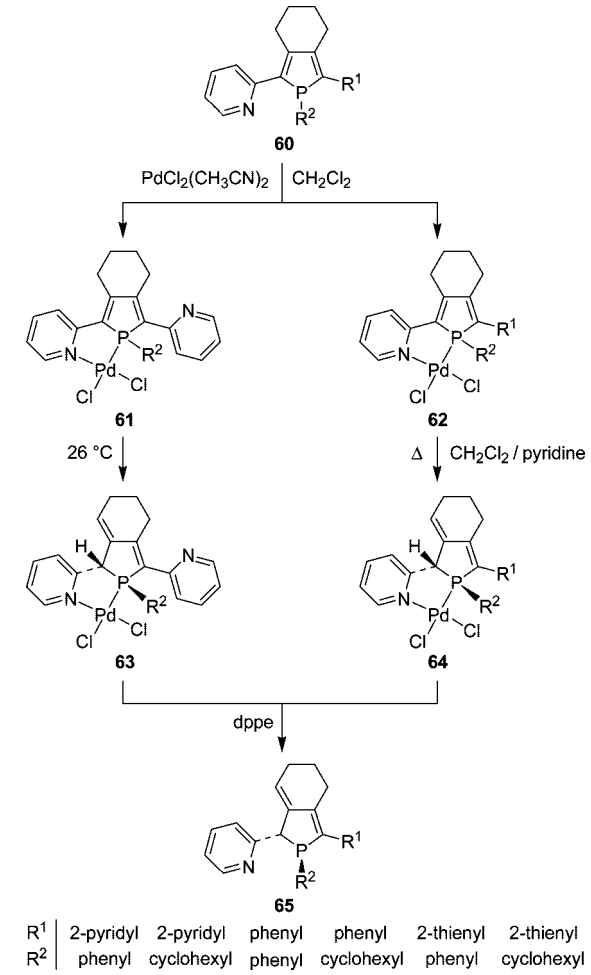
The aromaticity and antiaromaticity of phospholes have been the subject of several recent papers. The oxidation of the P-atom of slightly aromatic σ^3-phospholes affords σ^4-derivatives exhibiting a small antiaromatic character.[36] In spite of the small switch in aromatic−antiaromatic character, this change in the mode of delocalization (i.e., the stabilization of the phospholene isomers) alters substantially the chemical behavior of the parent compounds.[37] From the variety of 2,5-diaryl substituted phospholes (**57**), the 2-pyridyl substituted derivatives of the above parent phosphole, those were transformed also to the corresponding sulfides (**58**, **59**), (Scheme 18).[38]

The corresponding 2-pyridyl-2-phospholene derivatives, which act as S,N-chelates, were formed in the coordination sphere of Pd(II) and Pt(II). The free phospholene ligands (**65**) can be obtained upon addition of dppe to the $Pd(P-N)Cl_2$ complexes (**63**, **64**) (Scheme 19).[38] The isomerization of phospholes lacking pendant 2-pyridyl substituents was accomplished by adding pyridine to the reaction media. The stereochemistry of the Pd(II)−P,N complexes was established by X-ray diffraction studies. The stereochemistry of the process is preserved under the new reaction conditions used and was proved by multinuclear NMR. It is worth noting that the above transformation could not be carried out with 2-(2-pyridyl)phospholes, even at high temperature. It was confirmed by DFT calculations that the coordination to Pd(II) or Pt(II) centers is required to make the isomerization feasible.

Scheme 18. Synthesis of 2,5-Disubstituted Phospholes



Scheme 19. Pt(II) Complexes of 2,5-Disubstituted Phospholes and Phospholenes



1-Arylphospholes with bulky substituents at the 2- and 6-positions show an increased aromaticity due to the reduced pyramidal character of the phosphorus.

The sterically most hindered 1-(2′,4′,6′-tri-*tert*-butyl)phenyl-3-methylphosphole (**66**) undergoes acylation favorably at the 2- and 5-positions of the phosphole ring (**67**) (Scheme 20). Interestingly, only 5-acylphospholes can be transformed to diacyl derivatives possessing the "second" acyl group at the "supermesityl" moiety (**68**).[39]

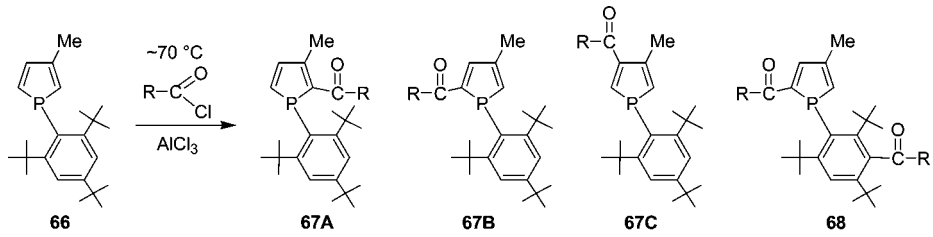
Phospholes of related structure (**69**) react readily with maleic acid derivatives such as amides and anhydrides. The stereoselectivity is influenced by both the aryl substituents and the structure of the maleic derivative. Interestingly, the formation of the *exo*-isomer (**71A**, **73A**) is highly favored with less hindered (mesityl) and most hindered ("supermesityl") *P*-substituents (Scheme 21).[40]

1-(2′,4′,6′-tri-isopropyl)phenyl-3-methylphosphole (**74**) reacts with diphenylacetylene as dienophile, resulting in a 1-phosphanorbornadiene derivative (**76**) (Scheme 22).[41]

The reaction of 1-(2′,4′,6′-tri-*tert*-butyl)phenyl-3-methylphosphole (**66**) with PBr_3 resulted in a key intermediate (**77**) toward various $P(NR_2)_2$- (**78**, **79**), $PH(NR_2)$- (**83**), and PH(OR)-functionalized (**82**) phospholes (Scheme 23).[42]

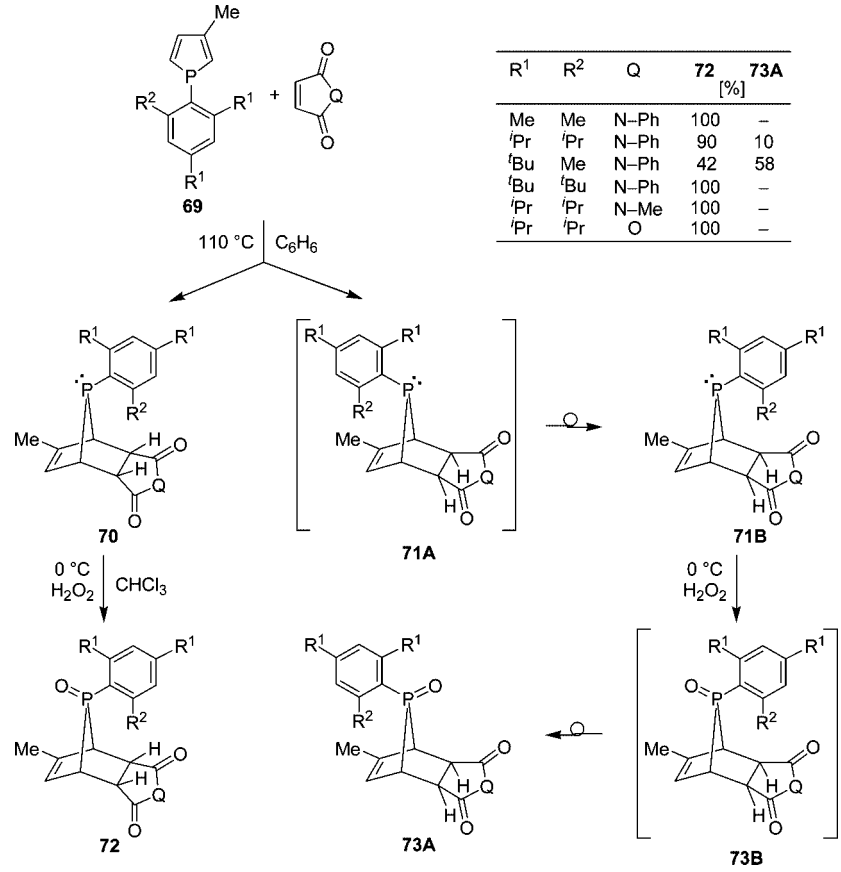
However, phospholes with less bulky 1-aryl substituents react with PBr_3, yielding 2-PBr_2-substituted derivatives (**84**)

Scheme 20. Acylation of Sterically Congested Phospholes



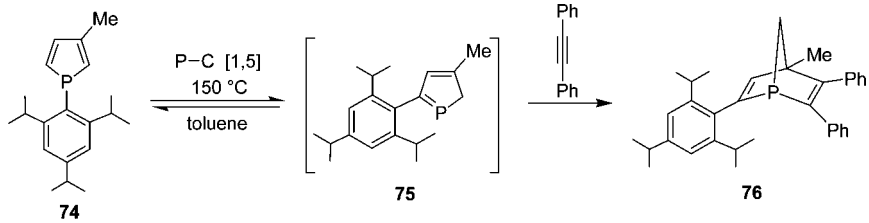
R	Product composition [%]				Yield [%]
	67A	**67B**	**67C**	**68**	
Me	31	9	16	44	~21%
Et	~60	*	*	~40	~50%
^{n}Pr	~60	*	*	~40	~50%

Scheme 21. Cycloaddition Reactions with 1-Arylphospholes Bearing Bulky Aryl Substituent



R^1	R^2	Q	**72**	**73A**
			[%]	
Me	Me	N–Ph	100	–
^{i}Pr	^{i}Pr	N–Ph	90	10
^{t}Bu	Me	N–Ph	42	58
^{t}Bu	^{t}Bu	N–Ph	100	–
^{i}Pr	^{i}Pr	N–Me	100	–
^{i}Pr	^{i}Pr	O	100	–

Scheme 22. Cycloaddition Reactions with 1-Arylphosphole and Diphenylacetylene



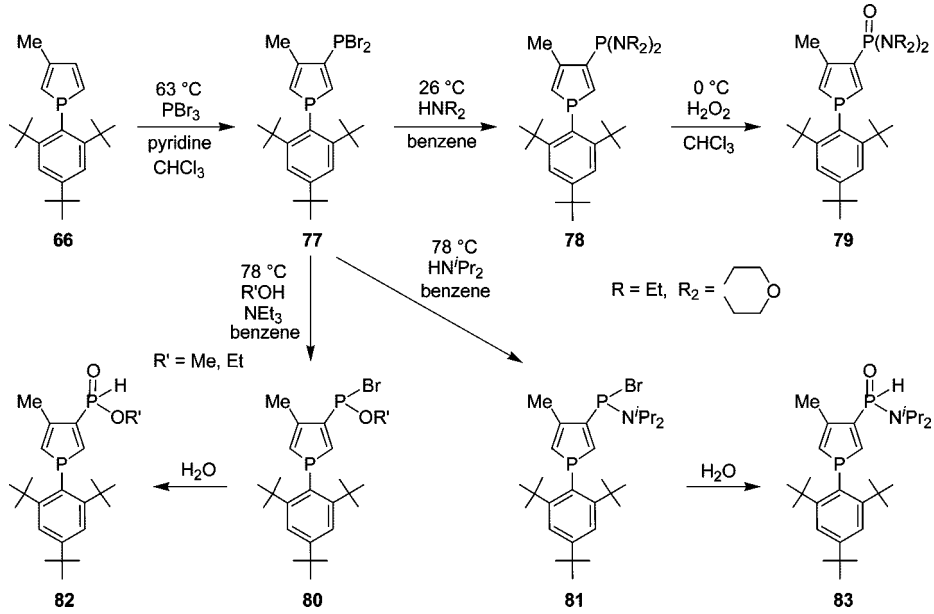
that can be transformed to the corresponding *P*-amides (**87**) and esters (**88**) (Scheme 24).[43]

The similar reaction of 1-(2′,4′-di-*tert*-butyl-6′-methyl)phenyl-3-methylphosphole (**89**) brought about the nearly equimolar mixture of the corresponding 2- and 3-functionalized phospholes (**95** and **92**, respectively) (Scheme 25).[44,45]

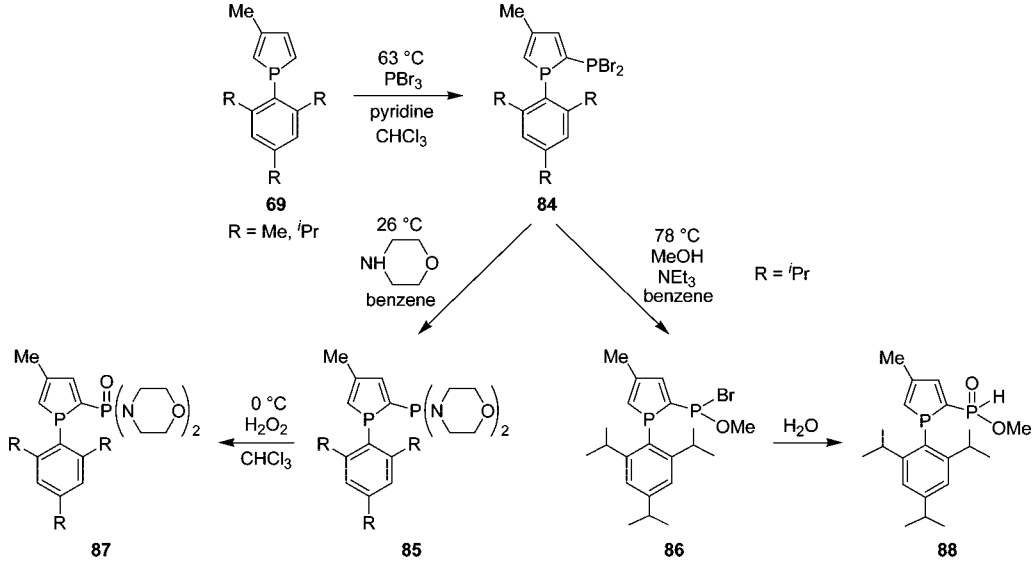
The above parent phospholes with increased aromaticity act as weak σ-donor ligands both with platinum(II)[46] and rhodium(III)−Cp* complexes (**96**) (Scheme 26).[47,36] It was revealed by detailed ^{31}P and ^{1}H NMR studies that even the $PtCl_2$(PhCN)(phosphole) type derivatives are available by the reaction of $PtCl_2(PhCN)_2$ precursor with phospholes possessing sterically bulky (e.g., supermesityl) *P*-substituents.[46]

The "Mathey-phosphole", 1-phenyl-3,4-dimethylphosphole (**97**), provides a diphosphide dianion (**99**) upon heating and

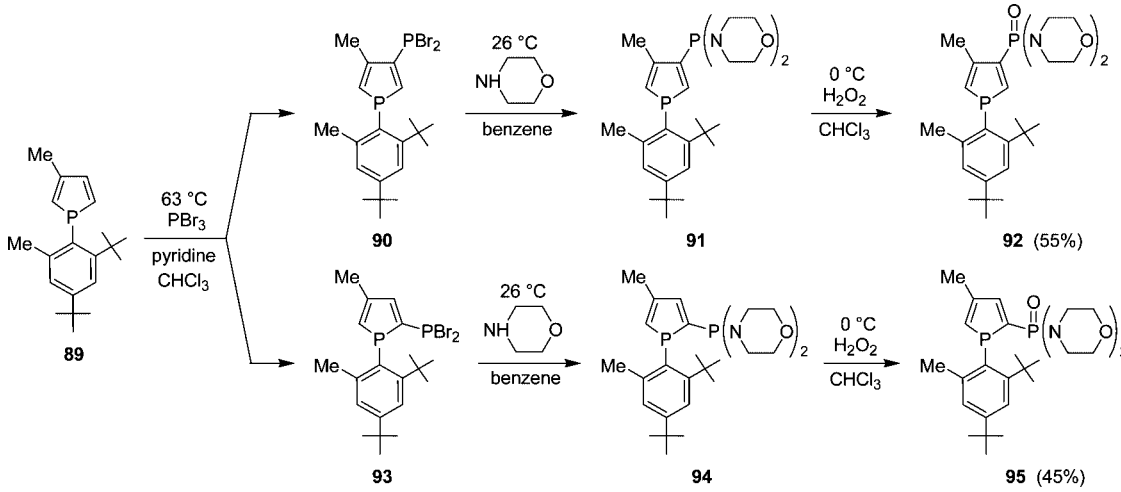
Scheme 23. Synthesis of Phospholes with P-Containing Substituents I



Scheme 24. Synthesis of Phospholes with P-Containing Substituents II

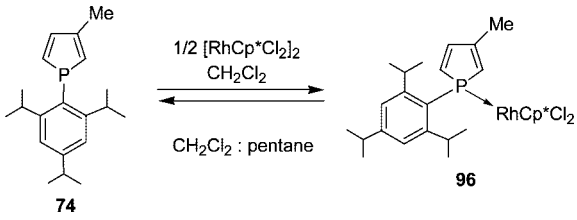


Scheme 25. Synthesis of Phospholes with P-Containing Substituents III



treating with sodium naphthalene. This key intermediate was reacted with chiral ditosylates, providing a chiral ligand with 2,2′-diphosphole moiety (**100**). The enantiopure platinum(II) complexes (**101**) were synthesized, through a dual-chirality

Scheme 26. Synthesis of Rhodium(III)−Phosphole Complexes



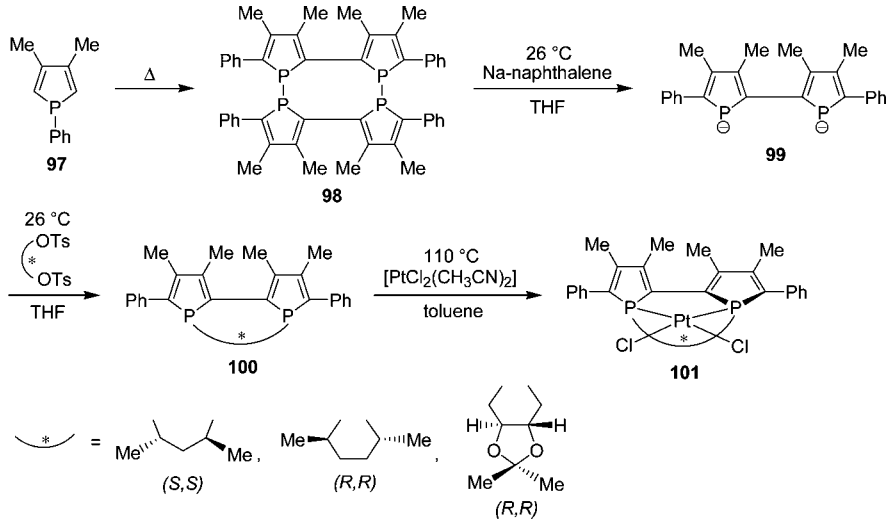
control of the axial and central elements of chirality, with chiral diphosphine and diphosphinite ligands derived from 2,2′-diphosphole (Scheme 27).[48] The molecular structures of **101** with pentan-2,4-diyl and hexan-2,5-diyl moieties were established by X-ray diffraction studies.

The above dianion (**99**) reacts readily with bromocyane. The 1,1′-dicyanodiphosphole (**102**) was treated with chiral lithium diolates, yielding the novel chiral diphoshinite ligands with C2 symmetry (**103**). Their platinum(II) complexes (**104**) were readily prepared by the standard benzonitrile ligand substitution (Scheme 28).[48] It is worth noting that the diphosphinite complexes, contrary to that of the diphospholes above, give broad signals in ^{31}P and ^{1}H NMR. This phenomenon was explained by aggregation in solution.

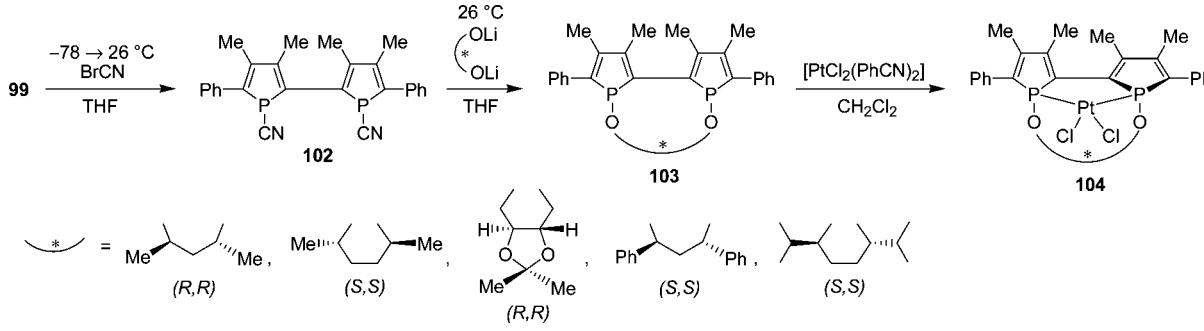
2.3.2. Phospholenes and Their Complexes

The optical resolution of phospholene oxides (**105**) was carried out by using optically active diols (**106**). The efficiency of the resolution was dependent on the *P*-

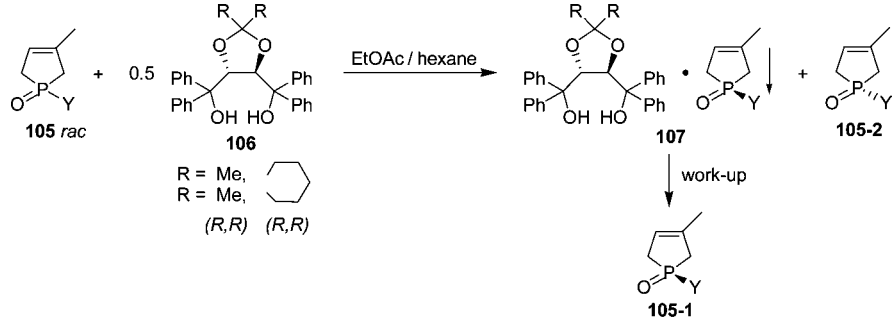
Scheme 27. Synthesis of Platinum(II)−Diphosphole Complexes I



Scheme 28. Synthesis of Platinum(II)−Diphosphole Complexes II

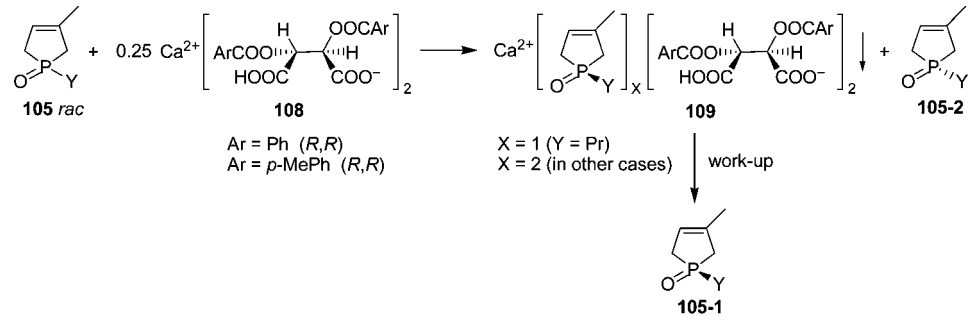


Scheme 29. Optical Resolution of 3-Methyl-3-phospholene Oxides I



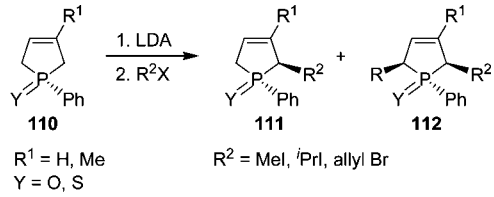
Y	Ph	1-Naph	2-MePh	4-MePh	Et	Pr	EtO	2-PrO
ee (%)	>99	>99	>99	>99	58	95	95	>99
Abs. config. of resolved antipode	*S*		*S*	*S*	*R*	*R*	*R*	*R*

Scheme 30. Optical Resolution of 3-Methyl-3-phospholene Oxides II

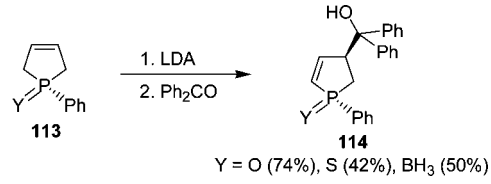


Y	Ph	1-Naph	2-MePh	4-MePh	Et	Pr	EtO	2-PrO
ee (%)	96	99	93	44	73	96	91	92
Abs. config. of resolved antipode	*R*		*R*	*S*	*S*	*S*	*R*	*S*

Scheme 31. Synthesis of Substituted Phospholene Oxides via Alkylation I



Scheme 32. Synthesis of Substituted Phospholene Oxides via Alkylation II



substituent. The highest enantiomeric excesses (ee's) were obtained with *P*-aryl derivatives (Scheme 29).[49,50]

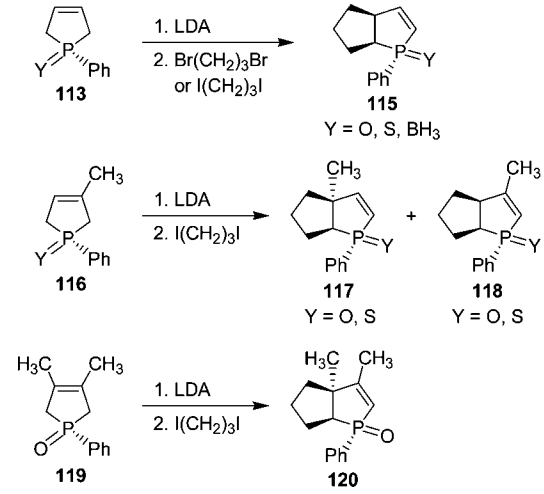
The similar enantiomeric separation of phospholenes (**105**) was carried out with *O,O′*-diacyl-tartrates (**108**). As previously, the best resolutions were achieved with *P*-aryl derivatives (Scheme 30).[51]

The great variety of substituted phospholene oxides were synthesized via deprotonation with lithium diisopropylamide (LDA), followed by alkylation. 3,4-Disubstituted phospholenes were alkylated at 2- and 5-positions (**111**, **112**). As for the stereochemistry of the alkylation, only *trans*-substitution in relation to the P−Ph group was observed (Scheme 31).[52]

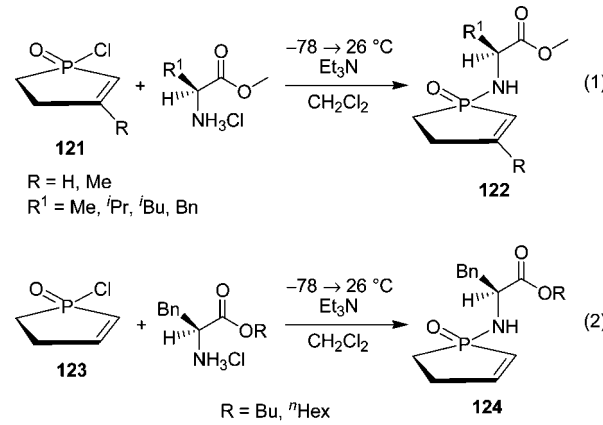
A similar methodology was followed for the alkylation of 3-phospholene derivatives (**113**). The application of benzophenone as carbonyl electrophile resulted in the formation of 4-(hydroxydiphenylmethyl)-2-phospholenes (**114**) as sole reaction products (Scheme 32).[52]

The alkylation with propylene dihalides resulted in the formation of cyclopentane-annulated phosphole oxides (**115**, **117**, **118**, and **120**) by using unsubstituted (**113**), 3-substituted (**116**), and 3,4-disubstituted phospholenes (**119**) (Scheme 33).[52] The annulation occurred with high regio- and stereoselectivities. While 1,3-dibromopropane yielded the expected bicyclic product **115** together with inseparable monocyclic mono- and dialkylation byproducts, the application of 1,3-diiodopropane led to the formation of the pentannulated product **120**, exclusively. The *cis*-ring junction in the annulated products was unequivocally proved, confirmed by

Scheme 33. Synthesis of Bicyclic Phospholenes



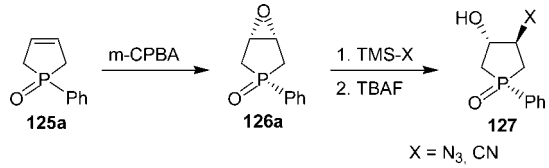
Scheme 34. Synthesis of 1-Substituted Chiral Phospholenes



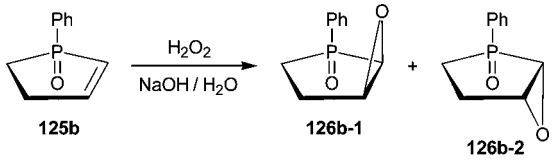
X-ray studies.[53] The absolute configuration of phospholene chalcogenides was determined by the ^{1}H, ^{13}C, and ^{31}P NMR in the presence of dinuclear rhodium complexes, $Rh_2((R)\text{-MTPA})_4$ (MTPA = methoxytrifluoromethylphenylacetic acid, Mosher's acid) by correlation method.[54]

P-Chloro-2-phospholenes (**121**, **123**) were reacted with amino acid esters, resulting in the corresponding 1-*L*-α-amino acid derivatives of phospholene oxides as chiral *P*−*N* phospholenes (**122**, **124**). The two diastereomers were separated by column chromatography (Scheme 34).[55] The configuration at P atom of the two diastereomers was ascertained from their ^{1}H NMR. The C(α)−H proton of one isomer was clearly shifted to downfield from the other

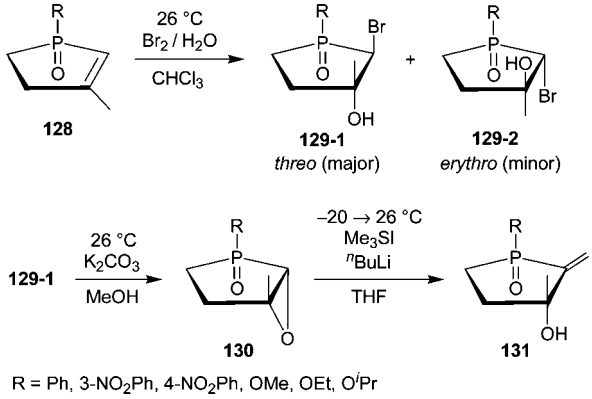
Scheme 35. Synthesis of 3,4-Substituted Phosphole Oxides



Scheme 36. Synthesis of 2,3-Epoxyphospholes I



Scheme 37. Synthesis of 2,3-Epoxyphospholes II



isomer, because this proton is deshielded due to the effect exerted by P═O; thus, it represents C(α)−H and P═O coplanar arrangement.

Starting with 3-phospholene oxides (e.g., **125a**), the epoxidation−ring-opening reaction sequence provided chiral 3,4-disubstituted phospholanes (**127**). Trimethylsilyl azide and trimethylsilyl cyanide were used as nucleophiles and chiral salen-Al complexes or TADDOL-Ti systems as chiral inducers (Scheme 35).[56] Enantioselectivities up to 72% were achieved.

1-Phenyl-2-phospholene oxide (**125b**) was transformed to the mixture of diastereoisomers of 2,3-epoxides (**126b-1**, **126b-2**) (Scheme 36). The diastereoselectivity showed a strong dependence on the reaction time and the concentration of hydrogen peroxide and base.[57] The diastereomer ratio of *erythro* and *threo* isomers was also controlled by the solvent type, so *erythro*- and *threo*-rich epoxides can be easily produced by changing the experimental conditions.

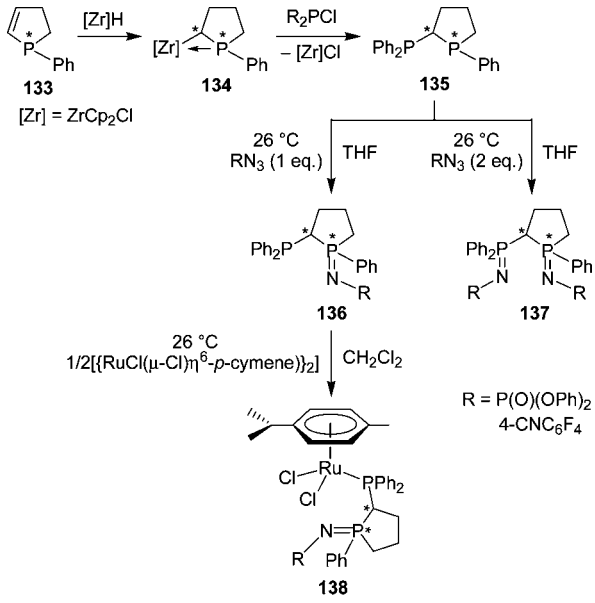
The 3-methyl derivative of the phosphole (**128**) underwent hypobromite addition resulting in the mixture of *threo* (**129-1**) as major and *erythro* (**129-2**) as minor isomer. The dehydrobromination of the epibromohydrin derivative furnishes the epoxide (**130**), the key compound toward the 2-exomethylene derivative (**131**) formed via the reaction with in situ formed dimethylsulfonium methylide (Scheme 37).[58] In this way, a novel synthetic route for the incorporation of one more carbon at C-2 position of the phospholane ring was developed.

1,4-Dialkoxy-2,3-epoxiphospholane oxides (**132-1, 132-2**) also underwent epoxide opening reaction. In this way, several new classes of deoxy phospha−sugar derivatives (**132-5**−**132-8**), analogues of normal sugar derivatives, were synthesized as depicted in Figure 3.[59]

A novel reaction of 1-(2,4,6-trialkylphenyl)phospholene and phospholane oxides with dimethyl acetylenedicarboxylate afforded β-oxophosphoranes.[60,61]

Optically active 1-phenyl-2-phospholene (**133**) was reacted with $Zr(Cp)_2Cl(H)$, resulting in a diastereomeric alkyl species that can be transformed to the 1-phenyl-2-diphenylphosphinophospholane (**135**). Its treatment with 1 or 2 equiv of an azide derivative furnishes the mono- (**136**) or bisimino (**137**) derivatives. The monoimine, bearing a diphenylphosphino substituent, was coordinated to Ru(II) as a monodentate ligand (**138**). Following this approach, a large variety of neutral and cationic mono- and dinuclear η^6-arene−Ru(II) complexes containing iminophosphorane phosphine ligands were prepared (Scheme 38).[62]

Scheme 38. Synthesis of Ruthenium(II)−*p*-Cymene Complexes Containing Iminophosphorane Ligands



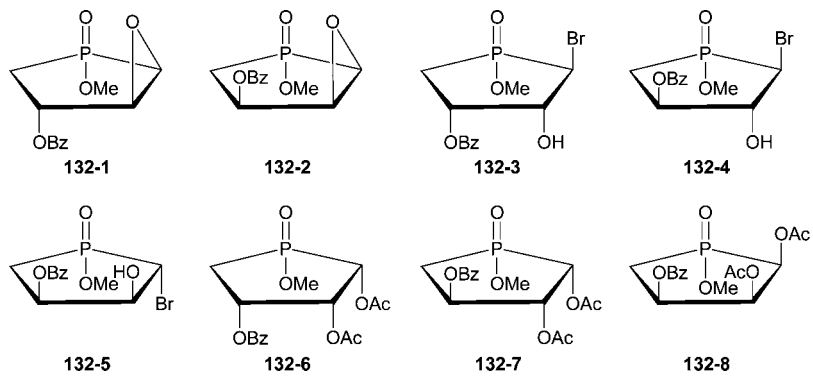
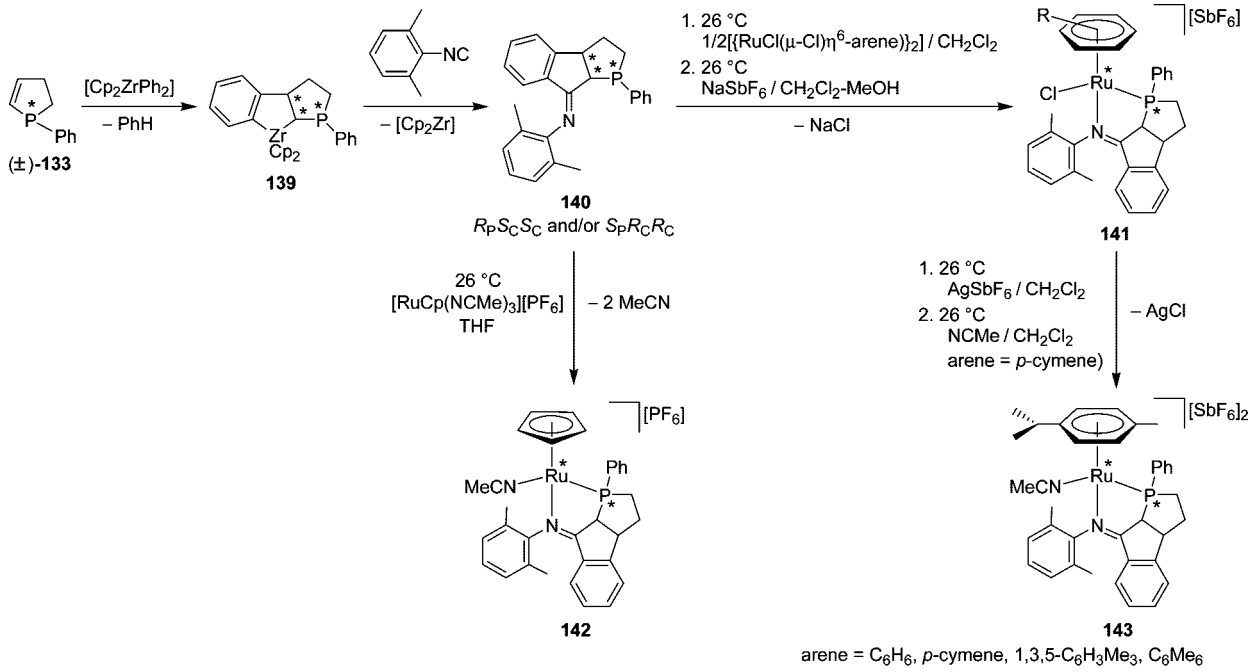
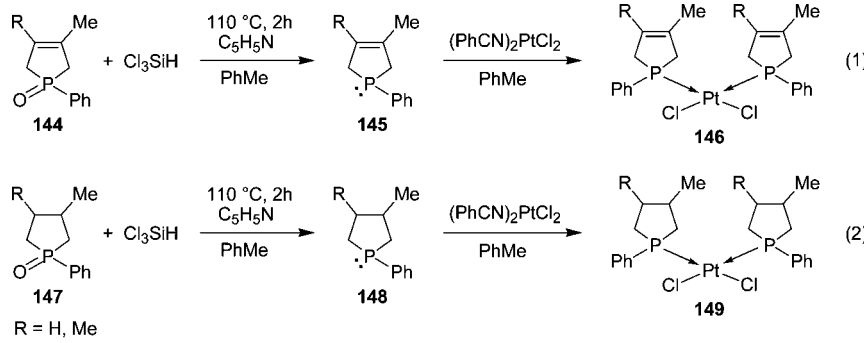


Figure 3. Phospha−Sugar Epimers.

Scheme 39. Synthesis of Ruthenium(II)−Cp and −*p*-Cymene Complexes Containing Phosphole-Based P−N Ligands



Scheme 40. Synthesis of Platinum(II)−Phosphole Complexes



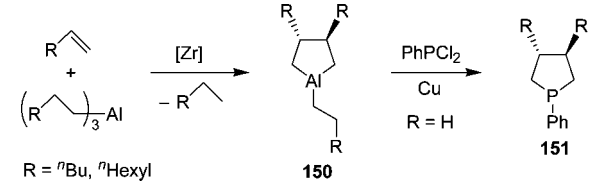
Racemic 1-phenyl-2-phospholene (**133**) was reacted with $Zr(Cp)_2Ph_2$, yielding an annulated zirkonacyclopentene (**139**). Its reaction with 2,6-dimethylbenzonitrile brought about the formation of the corresponding annulated cyclopentenone imine (**140**). This compound coordinates as heterobidentate chiral tricyclic β-iminophosphine ligand to Ru(II) containing either Cp (**142**) or cymene (**143**) ligands via κ^2-*P,N*-coordination manner, providing excellent yields (Scheme 39).[63] The structures of the mono- and dicationic cymene derivatives have been confirmed by X-ray crystallography. Remarkably, the chelate coordination of the iminophosphine ligand **140** to Ru takes place in all cases with complete diastereoselectivity, due probably to the high rigidity and steric requirement of the ligand.

3-Methyl- and 3,4-dimethyl-1-phenylphospholenes (**144**, **147**), as well as their saturated phospholane analogues were coordinated to Pt(II). The formation of the *cis*-Pt(ligand)$_2$Cl$_2$ complexes (**146**, **149**) is highly favored in all cases (Scheme 40).[64]

2.3.3. Phospholanes and Their Complexes

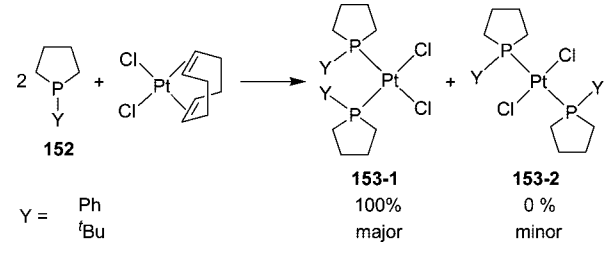
Several novel synthetic strategies based on the application of organometallic reagents turned up recently for the synthesis of a phospholane ring. Trialkylaluminum and a terminal alkene furnishes the substituted aluminacyclopentanes (**150**) as common intermediates in the presence of zirconium complexes. The aluminacycle was transformed to the 1,3,4-trisubstituted phospholane (**151**) by using dichlorophenylphosphine (Scheme 41).[65] This novel one-pot reaction is based on the in situ generated chiral aluminacyclopentanes.

Scheme 41. Synthesis of Chiral 3,4-Substituted Phospholanes

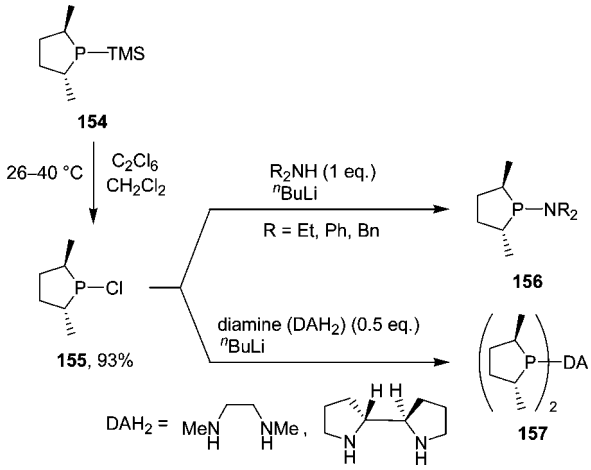


1-Phenyl- and 1-*tert*-butylphospholane (**152**) act as monodentate ligands in Pt(II) complexes (**153**). While with the

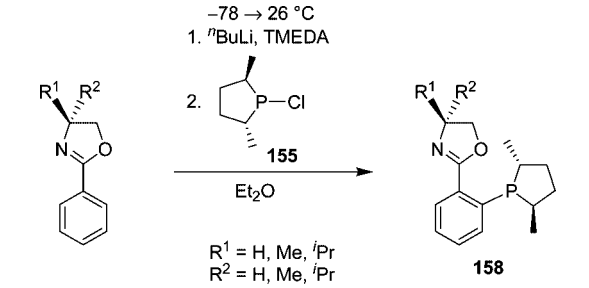
Scheme 42. Synthesis of Platinum−Phospholane Complexes



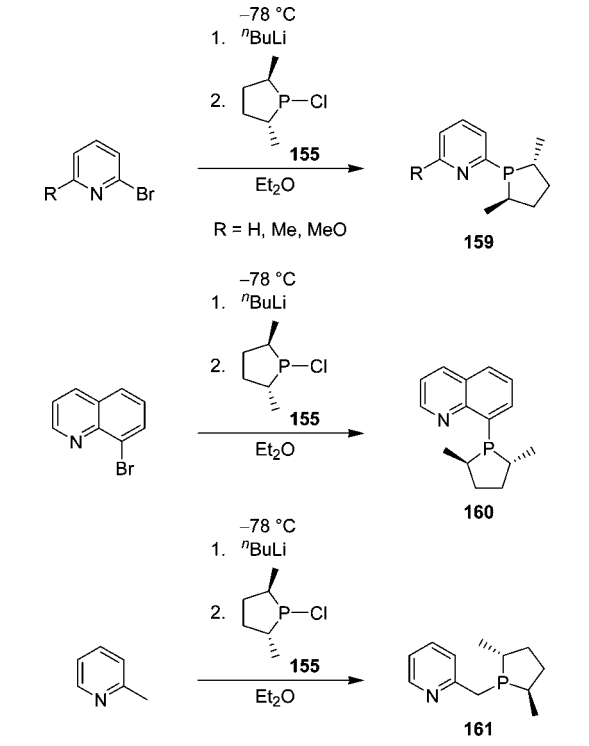
Scheme 43. Synthesis of Chiral Phospholane-Based P−N Derivatives



Scheme 44. Synthesis of Heterobidentate Ligands Possessing Phospholane and Oxazoline Moieties



Scheme 45. Synthesis of Chiral Phospholanes with N-Aromatic Substituents



phenyl derivative the *cis*-complex (**153**-**1**) was formed exclusively, the use of the *tert*-butyl derivative resulted in the mixture of the *cis/trans* complexes (Scheme 42).[66] The geometries were ascertained from the ^1J(Pt,P) coupling constants and proved also by X-ray crystallography.

1-Trimethylsilyl-2,5-dimethylphospholane (**154**) proved to be a useful precursor for the synthesis of monophosphole chiral *P*-amido derivatives (**156**) and those ones containing a diamino linker (**157**). The key to these compounds is the facile synthesis of the enantiomerically pure *P*-chloro derivative (**155**) by treating 1-trimethylsilyl-2,5-dimethylphospholane with chlorinated hydrocarbons (Scheme 43).[67] The large-scale availability of 1-trimethylsilylphospholane **154** and the facile chlorination procedure toward **155** opened up a new way to the synthesis of new phospholanes with relevance to organocatalysis and to transition metal catalysis.

The above *P*-chlorophospholane (**155**) served as enantiopure starting compound also for the synthesis of 1-(oxazolin-2-yl)-2-(2,5-dimethylphosphan-1-yl)benzene (**158**) (Scheme 44), as well as *P*-substituted pyridyl- (**159**), quinolinyl- (**160**), and pyridylmethyl (**161**) phospholanes (Scheme 45).[67]

The same enantiopure (2*R*,5*R*)-*P*-chlorophospholane (**155**) enabled the facile synthesis of various potential heterobidentate ligands such as those ones bearing 2-pyridyl (**162**), thiazoline-2-yl (**163**), and isoquinolin-2-yl (**164**) substituents at the ring phosphorus. The lithium organic reagent was prepared by the reaction of the corresponding bromide and butyl lithium (Scheme 46).[68]

2,5-Diphenylphospholane (**167**) was synthesized by the reduction of the P−Cl bond formed by the chlorination of the corresponding chiral enantiopure phospholanic acid (**165**) (Scheme 47).[69,70] Reduction of **166** with $LiAlH_4$ gave **167** in enantiopure form in quantitative yield. Because of the sensitivity of **167** toward oxidation, it was immediately converted to a $[Rh(COD)(\mathbf{167})_2][BF_4]$ ionic complex. which was characterized by its ^1J(Rh,P) = 142 Hz coupling constant.

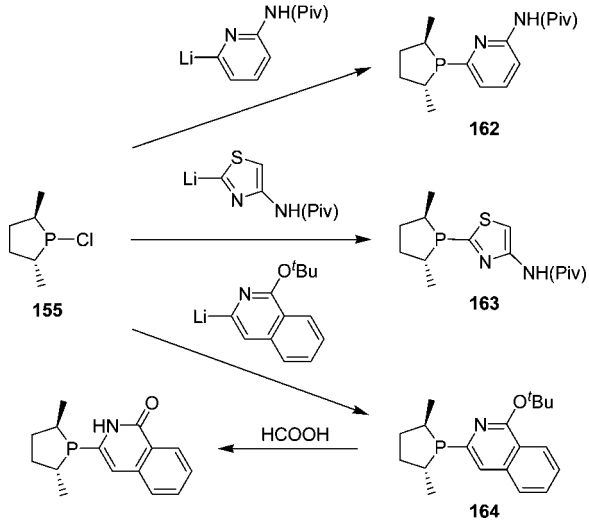
The P−Cl compound (**166**) served as key intermediate for the arylation with a great variety of lithium aryls (Scheme 48).[71] Enantiopure phospholane oxides (**168**) and boranes were obtained in organocuprate or palladium-catalyzed C−P cross-coupling reactions in moderate to high yields.

The parent phospholane (secondary phosphine) was alkylated by alkyl triflates toward the enantiopure 1-alkyl-2,5-diphenylphospholanium salts (**169**) (Scheme 49) and the resulting *P*-alkyl derivative (**170**) (Scheme 50) further to the chiral quaternary phosphonium derivatives (**171**, **173**) (Schemes 51 and 52).[72] It was demonstrated that the enantiopure phospholane can be alkylated in a facile reaction to form enantiopure phospholanium salts as a protected form of electron-rich chiral ligands.

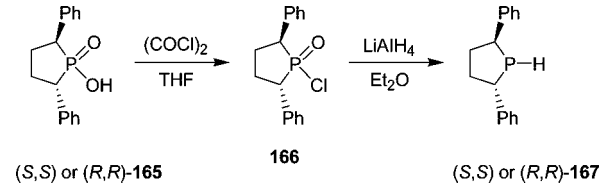
The parent compound, the chiral enantiopure secondary phospholane, 2,5-diphenylphospholane (**165**), was used for the synthesis of cationic Rh(I) complexes with tetrafluoroborate counterion (**174**) (Scheme 53).[69]

The phospholanic acid derivative was synthesized in a multistep reaction starting with a ring-closure reaction with 1,4-diphenylbutadiene.[70,73] It was reduced to the phospholane oxide, which was arylated with a 2-iodopyridine derivative. The reduction of the P═O moiety of **178** furnished 1-(2-pyridyl)-2,5-diphenylphospholane (**180**) (Scheme 54). The size and substitution pattern and, more importantly, the heterocyclic substituent linked to phosphorus were varied. In the rhodium complexes formed with these ligands, the nature of the substituents makes a sharp difference: while the pyridone units of two ligands can assemble by hydrogen bonding and form chelates, the alkoxypyridine moieties are not able to aggregate via intramolecular hydrogen bonding.

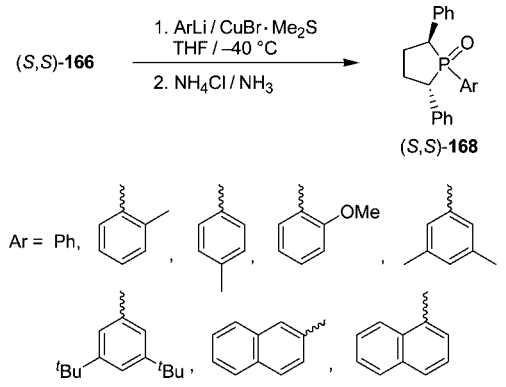
Scheme 46. Synthesis of Enantiomerically Pure Phospholanes Bearing *P*-Heteroaryl Substituents



Scheme 47. Synthesis of Enantiomerically Pure Phospholanes



Scheme 48. Synthesis of Enantiomerically Pure Phospholane Oxides

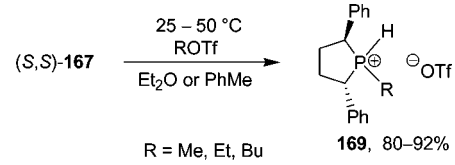


2,5-Diphenylphospholane oxide (**175**) was arylated via palladium-catalyzed C−P bond formation. The chiral 2,5-diarylphosphane oxide was coupled with various aryl and heteroaryl iodides, bromides, and triflates in good yields ranging from 47% to 81%. The reduction of the phospholane oxide derivative led to the corresponding tertiary phosphine−borane adduct (**183**) (Scheme 55).[71] The same adduct can be synthesized in an independent way in Pd(0)-catalyzed arylation of the borane protected chiral 2,5-diphenylphospholane (**185**). In the case of the *P*-phenyl derivative (**168**, Ar = Ph), its rhodium-catalyzed reduction and consecutive stoichiometric reduction led to **182** and borane protected electron-rich ligand (**184**), respectively.

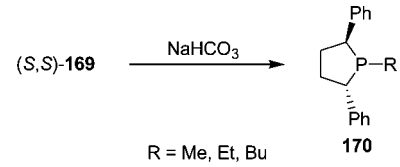
1-Phenyl-2,5-dimethylphospholane (**186**) was reacted by $PdCl_2(PhCN)_2$, resulting in a square-planar *trans*-complex (**187**) (Scheme 56).[74]

The same compound served as a ligand in a Rh(I)−cp complex (**188**), which underwent oxidative addition in the presence of a cyclic boronate ester (Scheme 57).[75] The chiral

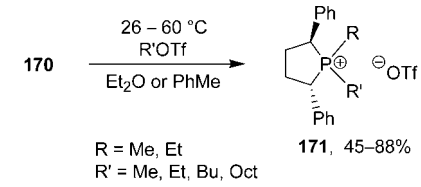
Scheme 49. *P*-Alkylation of an Enantiomerically Pure Phospholane I



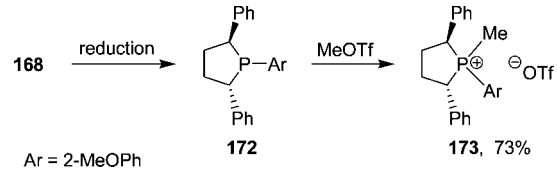
Scheme 50. *P*-Alkylation of an Enantiomerically Pure Phospholane II



Scheme 51. *P*-Alkylation of an Enantiomerically Pure Phospholane III



Scheme 52. *P*-Alkylation of an Enantiomerically Pure Phospholane IV



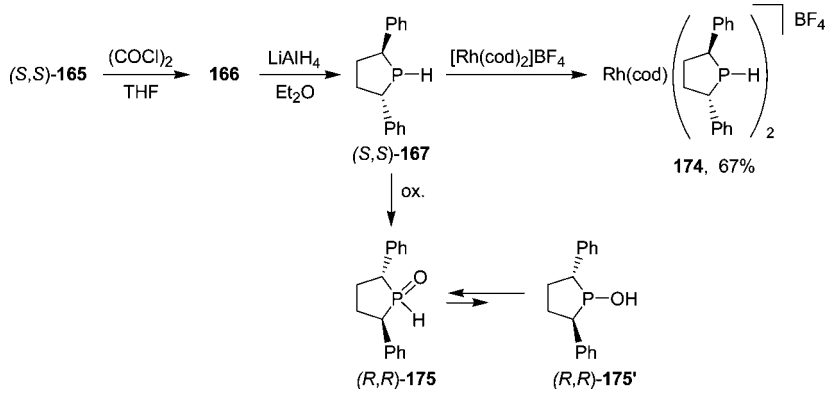
rhodium boryl hydride complex obtained with pinacolborane shows remarkable stereochemical nonrigidity. Experimental and computational studies are reported on the photochemical reaction of these two distinguishable phospholane−hydrido half-sandwich complexes (**189**, **189′**) that undergo intramolecular exchange.

On the one hand, *P*-chlorophospholane oxide (**166**) was subjected to reduction to give P−H species **167**, affording the P−Cl derivative (**190**) by reaction with phosphorus pentachloride. On the other hand, intermediate **166** underwent alcoholate substitution, forming alkyl and aryl phosphinates **191** and **192**, respectively (Scheme 58).[76]

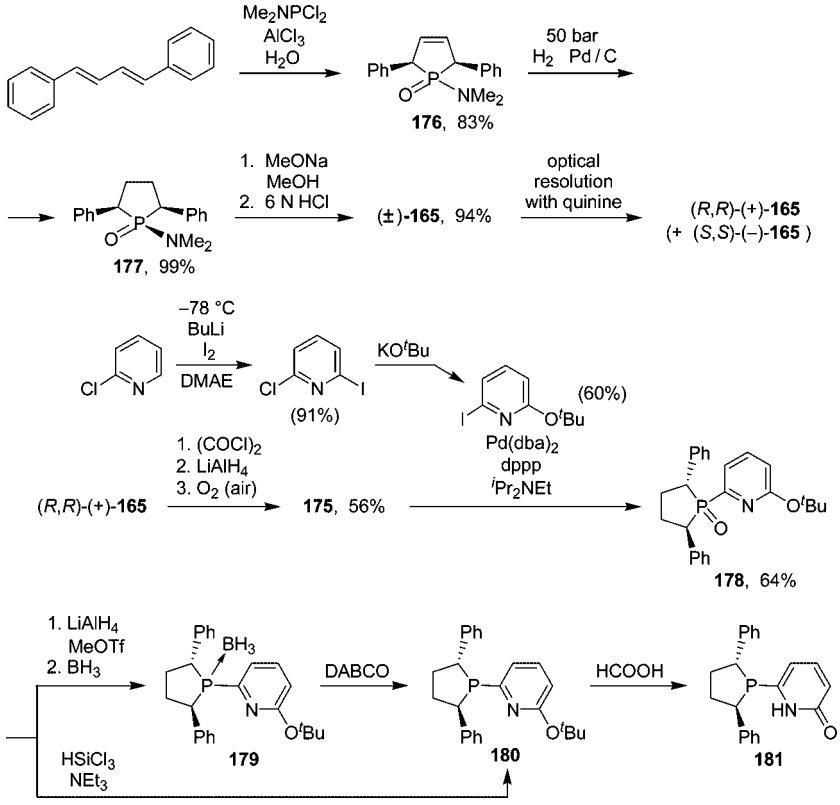
The similar substitution of optically active *P*-chloro-2,5-diphenylphospholane (**190**) was carried out, furnishing the chiral enantiopure *P*-alkoxy/aryloxyphospholane (alkyl/aryl phosphinite, **194** and **193**, respectively) (Scheme 59).[76] Its Rh(I)−bis(phosphinite) complexes (**197**) were synthesized by using the $[Rh(COD)_2][BF_4]$ precursor. The highly sensitive phosphinite was transformed to its borane adduct (**196**) by treating **195** with borane−dimethyl sulfide complex (Scheme 60). Deboronation could be carried out by dimethylamino-functionalized polystyrene or with HBF_4 (Scheme 61). In the latter case, the *P*-alkoxy/aryloxy derivatives were protonated by HBF_4. However, the corresponding benzyloxy derivative (**199**) suffered an O−Bn splitting, resulting in the quantitative formation of the secondary phospholane oxide−BF_3 complex (**200**) as a result of the weakness of the benzylic C−O bond toward acid (Scheme 62).[76]

The synthesis of chiral 2,5-disubstituted phospholanes and their application in homogeneous catalysis have been the subject of many papers (see section 3.2).

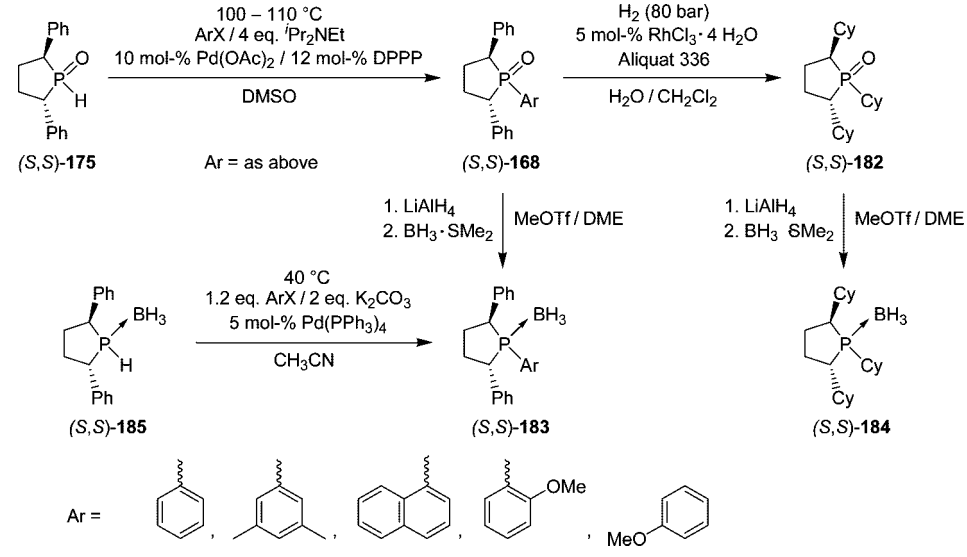
Scheme 53. Synthesis of Rh(I) Complexes Containing Phospholane Ligands



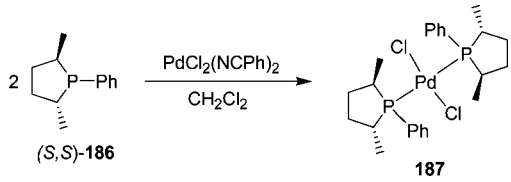
Scheme 54. Synthesis of Enantiomerically Pure *P*-Heteroarylphospholanes



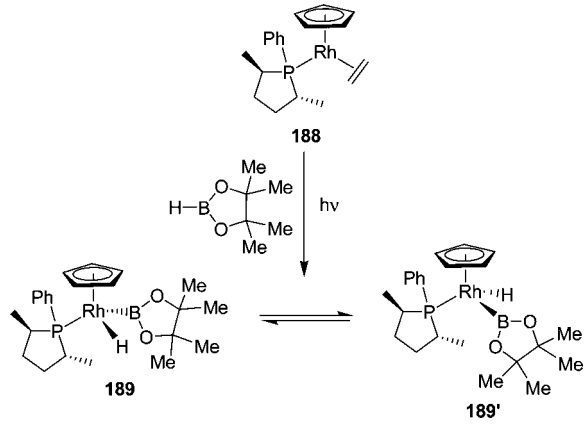
Scheme 55. Synthesis of Enantiomerically Pure *P*-Substituted Phospholanes



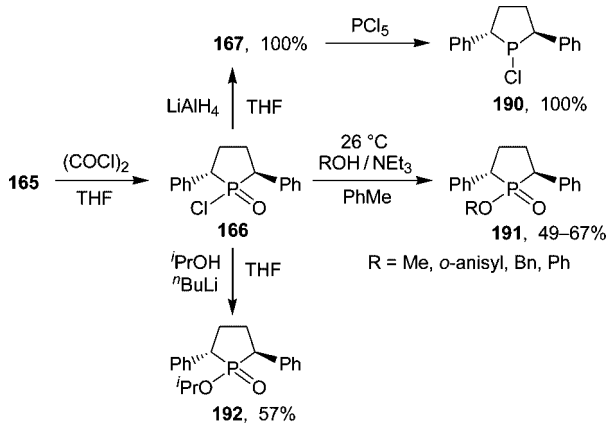
Scheme 56. Synthesis of Pd(II) Optically Active Phospholane Complexes



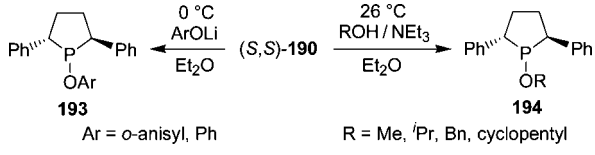
Scheme 57. Synthesis of Rh(III) Complexes Bearing Enantiomerically Pure *P*-Phospholanes



Scheme 58. Synthesis of Cyclic Phosphinates



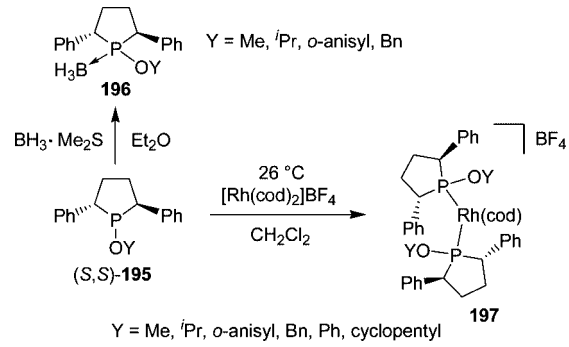
Scheme 59. Synthesis of Enantiomerically Pure Cyclic Phosphinites



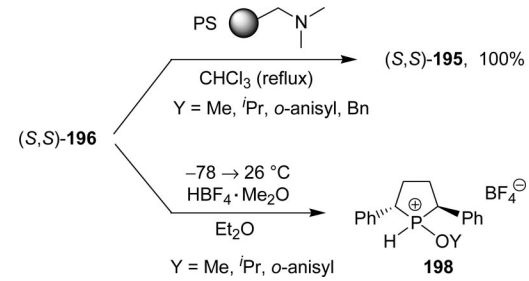
Phenylene- and ferrocene-1,1′-diyl-backboned bidentate ligands (**201** and **202**) were synthesized by using the diphenylphosphino−alkyl bromide precursor, which was transformed to the compound with PH_2 moiety (**204**). The latter functionality served as a center for cyclization with the appropriate cyclic sulfate providing the diphosphine derivative with diphenylphosphino and phospholan-1-yl moieties (**206**) (Scheme 63).[77]

Both the phenylene- and ferrocene-based ligands were coordinated to Pt(II) (**207**) and Rh(I) (**208**) using the corresponding transition metal−diene precursor (Scheme 64).[77] The X-ray crystallographic analysis of **207** (with the *o*-phenylene-based diphosphine as bidentate ligand) revealed that only one quadrant is blocked, and as a consequence of that, the quadrant diagrams enable rationalization of the catalytic results (see section 3.2).

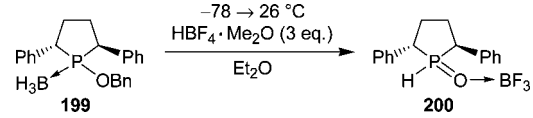
Scheme 60. Synthesis of Rh(I) Complexes Possessing Enantiomerically Pure Phosphinites



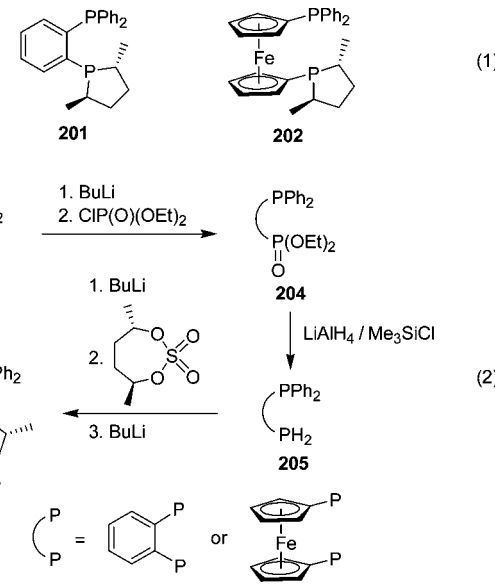
Scheme 61. Deboronation of Borane Adduct of Enantiomerically Pure Phosphinites I



Scheme 62. Deboronation of Borane Adduct of Enantiomerically Pure Phosphinites II

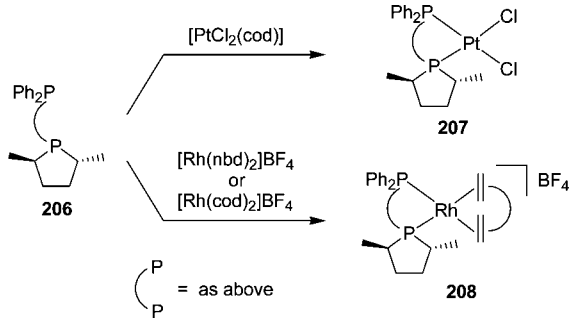


Scheme 63. Synthesis of Arene-Based Heterobidentate Ligands

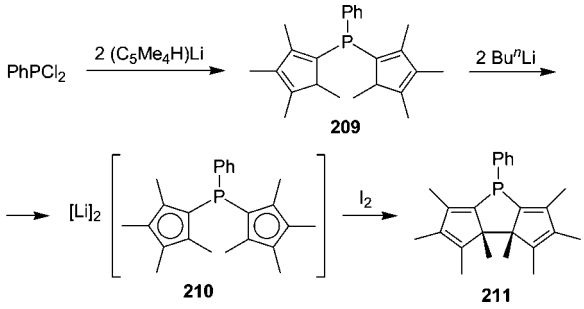


The cyclopentadiene anellated analogues of the known dibenzophosphole derivatives were synthesized from bis(tetramethylcyclopentadienyl)phenylphosphine (**209**) via the corresponding dianion (**210**) (Scheme 65).[78] The phosphines derived from intramolecular C−C coupling of tetramethylcyclopentadienyl groups were evaluated by X-ray crystal-

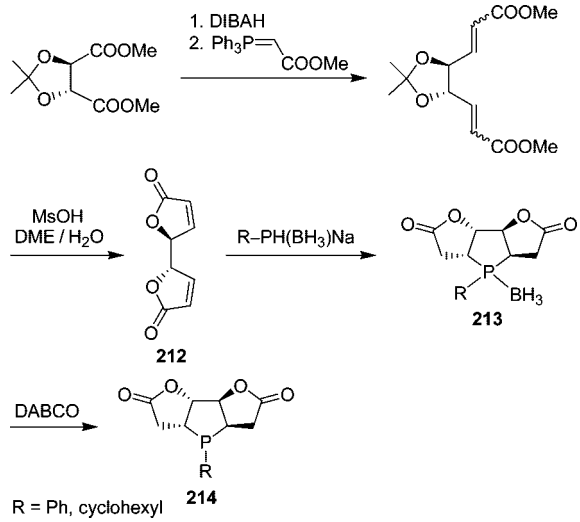
Scheme 64. Synthesis of Pt(II) and Rh(I) Complexes Containing Phosphine−Phospholane Bidentate Ligands



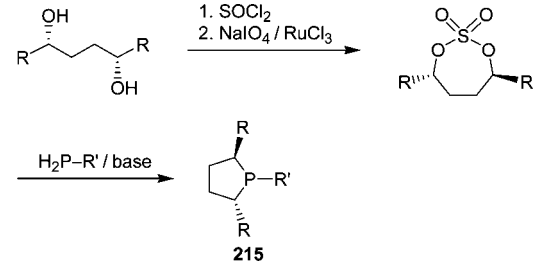
Scheme 65. Synthesis of Dicyclopentadiene-fused *P*-Phenylphospholane



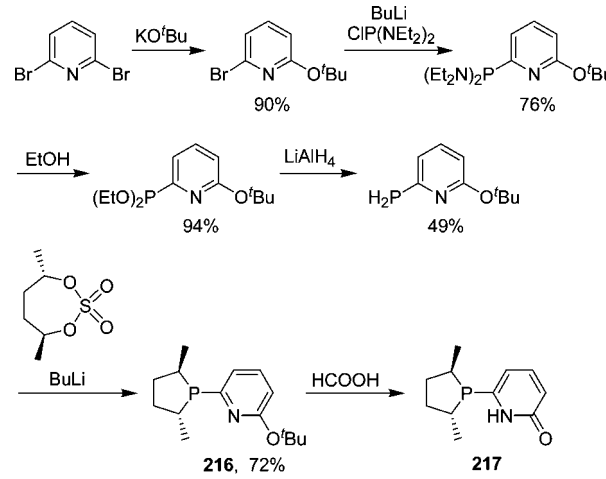
Scheme 66. Synthesis of Bislactone-fused Phospholane



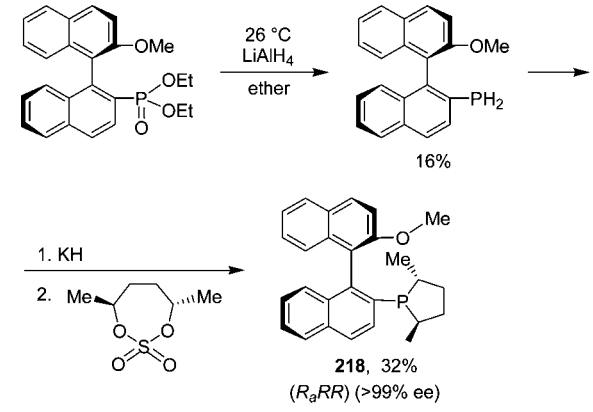
Scheme 67. Synthesis of Enantiopure Phospholanes by Using the Corresponding Cyclic Sulfates I



Scheme 68. Synthesis of Enantiopure Phospholanes by Using the Corresponding Cyclic Sulfates II



Scheme 69. Synthesis of Enantiopure Phospholanes by Using the Corresponding Cyclic Sulfates III



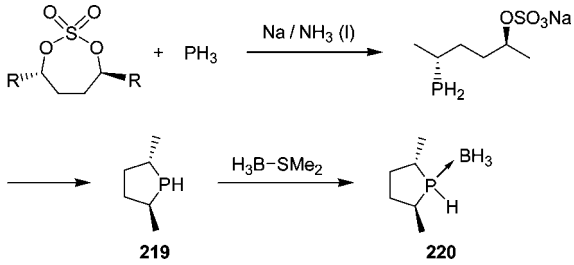
lography. The steric and electronic properties of **211** are determined to be intermediate between those of PPh_2Me and PPh_3. Thus, the crystallographic cone angle was found to be 140.2° (PPh_2Me: 134.5°; PPh_3: 148.2°). It is worth noting that **211** has a smaller cone angle and is less electron donating than the similar parent compound, 1-phenyl-2,5-dimethylphospholane (**186**).

A bis(lactone) (**212**) was used for the ring-closure reaction upon addition of a phosphide, resulting in a bis(butyrolactone) annulated chiral phospholane (**213**) (Scheme 66).[79] Highly stereoselective double hydrophosphination of unsaturated chiral bis(lactone) served as key reaction in the synthetic sequence. σ-Donor properties of the phospholanes, obtained from both enantiomers of tartaric acid, were estimated by measuring the $^1J(^{31}P,^{77}Se)$ coupling constant of their phosphine selenides.

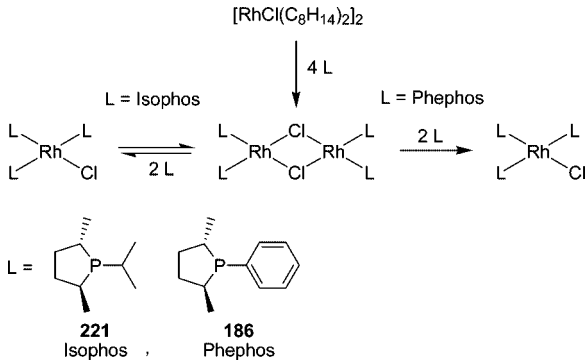
The cyclic sulfate methodology, i.e., the application of cyclic sulfates of 1,4-diols (butane-1,4-diol, hexane-2,5-diol) was used in the seminal works of Burk for the synthesis of a variety of phospholanes (**215**) (Scheme 67).[80] The same reaction was carried out with 2-pyridylphosphine (Scheme 68),[73] binaphthylphosphine (Scheme 69),[81] and the parent PH_3[82] itself, yielding **217**, **218**, and **220**, respectively (Scheme 70).[83] Another synthetic approach leading to product of type **217** is shown in Scheme 54.

1-Phenyl- and 1-isopropyl-2,5-dimethylphospholanes (Phephos (**186**) and Isophos (**221**), respectively) were used as ligands in dinuclear rhodium complexes. While the application of the isopropyl derivative in 3-fold excess to rhodium resulted in an equilibrating mixture between mononuclear and chloro-bridged dinuclear species, the same reaction with Phephos gave the $Rh(Phephos)_3Cl$ mononuclear complex (Scheme 71).[84] The chloro-bridged dimer was also reacted with further Lewis bases (L′) such as carbon monoxide,

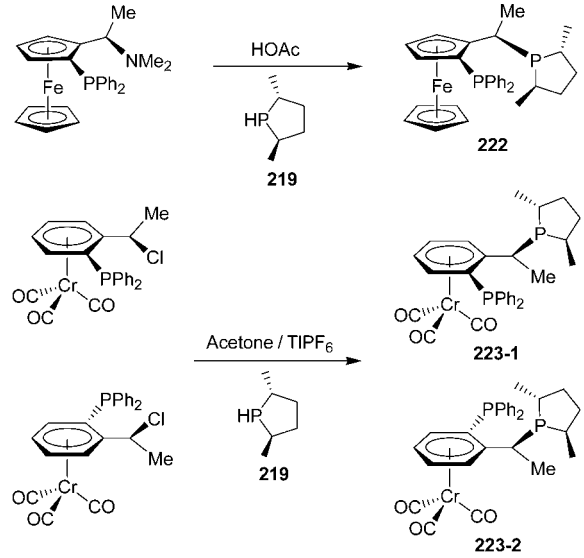
Scheme 70. Synthesis of Enantiopure Phospholanes by Using the Corresponding Cyclic Sulfates IV



Scheme 71. Synthesis of Rh(I)−Enantiopure Phospholane Complexes



Scheme 72. Ferrocene- and Benchrotrene-Based P−P Heterobidentate Ligands

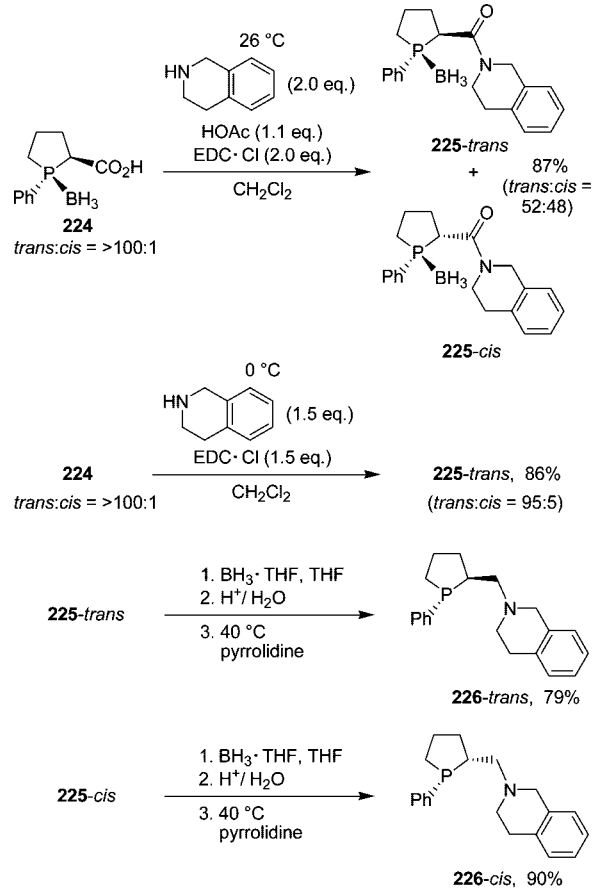


ethylene, and diphenylacetylene, resulting in *trans*-[RhCl(L′)L_2] type complexes.

The easy availability of 2,5-dimethylphospholane (**219**) enabled the facile synthesis of potentially bidentate ligands possessing the chiral phospholane moiety attached to a side-chain bound to the aromatic unit (Scheme 72).[82]

2-Carboxamido-1-phenylphospholanes (**225**) were synthesized from the corresponding phospholane-2-carboxylic acid derivative (**224**) and tetrahydroisoquinoline (Scheme 73).[85] The stereochemistry of the acylation shows strong dependence on the reaction conditions. While at higher temperature nearly a 1/1 mixture of the *cis/trans*-isomers was formed in the presence of acetic acid, the low temperature is in favor of the retention of configuration at position-2. Both *cis*- and *trans*-isomers were reduced to the corresponding amine derivative, resulting in the two diastereoisomers of the *P,N*-heterobidentate ligand (**226**).

Scheme 73. Synthesis of *P,N*-Heterobidentate Ligands with Tetrahydroisoquinoline and Phospholane Moieties



A novel synthetic strategy for the synthesis of 2-trimethylstannyl- (**229**) and 2-carboxy-1-phenylphospholane (**233**) (the phosphorus analogue of proline) was published. The latter compound was synthesized via lithiodestannylation−carboxylation procedure in the presence of a base (nBuLi) and a diamine (TMEDA and its analogues).[86] The key intermediate, the configurationally labile *trans*-1-phenyl-2-phospholanyl lithium borane complex was isolated as a 1,2-dipyperidinylethane (DPE) complex and characterized by X-ray crystallography (Figure 4). The carboxylic acid derivative served as an intermediate for the 2-menthyl ester of the *cis*- and *trans*-isomers (**231**), as well as for that of the enantiomerically pure carbocylic acid via optical resolution with quinine (Scheme 74).

A novel chiral 1,2-bisphospholane ligand, 1,1′-di-*tert*-butyl-[2,2′]-diphospholanyl (TangPhos, **236**) was synthesized by Tang and Zhang. It was prepared from readily accessible compounds by using phosphane sulfides as intermediates. The phosphane sulfide **234** was deprotonated by *n*-BuLi-(−)-sparteine complex and oxidatively coupled by a $CuCl_2$-

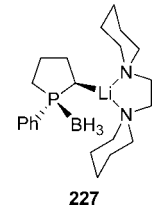
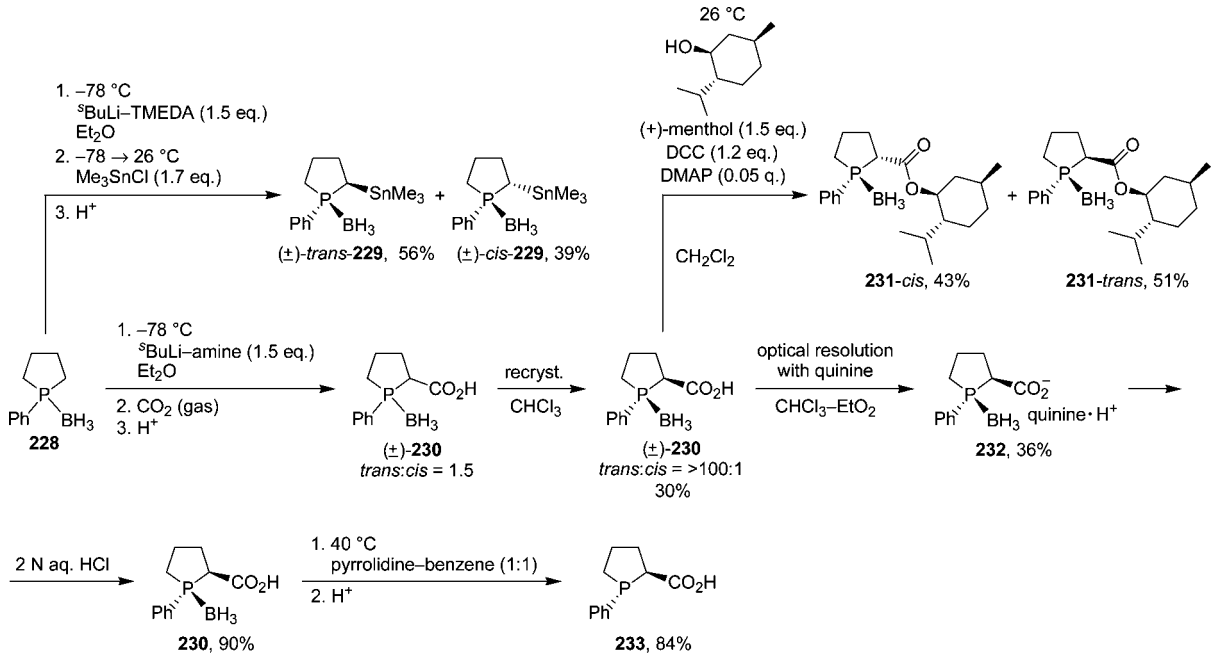
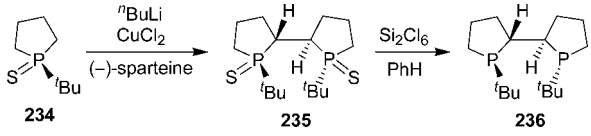


Figure 4. Li−DPE Complex.

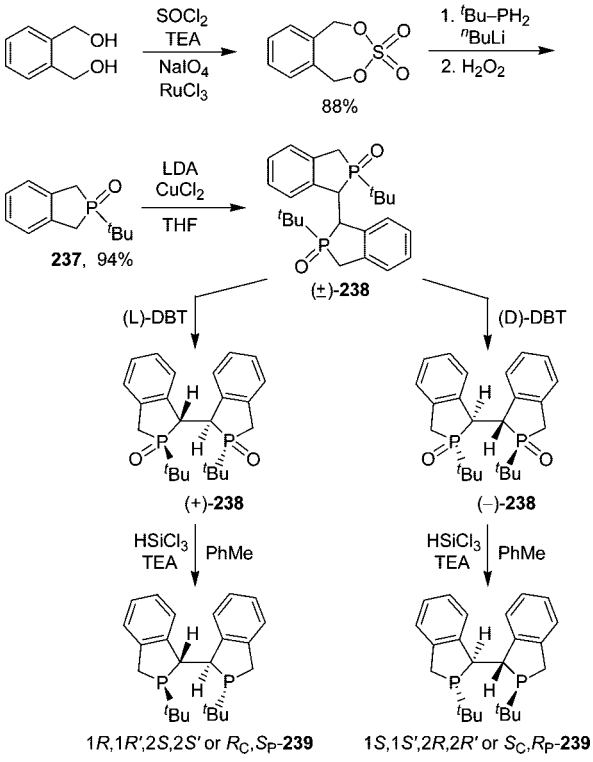
Scheme 74. Synthesis of a *P*-Analogue of Proline



Scheme 75. Synthesis of TangPhos



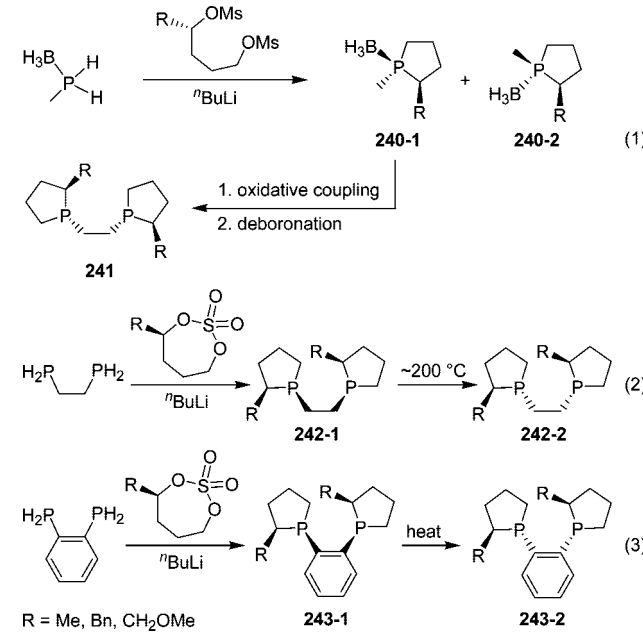
Scheme 76. Synthesis of Enantiopure Bis(benzophospholene) (DuanPhos)



mediated reaction. The desulfurization of the disulfide afforded the air-sensitive TangPhos in excellent yield (Scheme 75).[87]

Benzene-annulated 2,2′-bisphospholene dioxides (**238**) were synthesized by the conversion of the cyclic sulfate to *tert*-butylbenzophospholene oxide and its homocoupling in the presence of LDA and $CuCl_2$. The dioxide was resolved with DBT (dibenzoyl tartaric acid) and reduced to the target compound (**239**, DuanPhos) obtained in both enantiomeric forms (Scheme 76).[88]

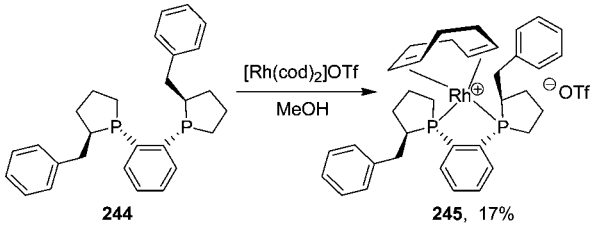
Scheme 77. Synthesis of Ethylene- and 1,2-Phenylene−Bisphospholane Derivatives



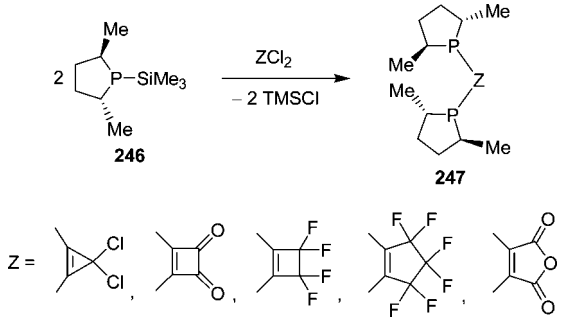
2-Alkyl-1-methylphospholanes (**240**) were synthesized by using a chiral diol dimesylate building block. Its oxidative coupling furnished the *P*-chirogenic ethylene-bridged diphospholane derivative (**241**). The same compound can also be obtained in the reaction of the cyclic sulfate of the above diol and 1,2-diphosphinoethane. The related 1,2-phenylene-bridged compound (**243**) was obtained from the cyclic sulfate and 1,2-diphosphinobenzene (Scheme 77).[89]

An analogue of the above bidentate ligands, 1,2-bis(2-benzyl-phospholan-1-yl)benzene (**244**) as *P*-chirogenic bis-(phospholane) ligand was obtained by stereoselective cy-

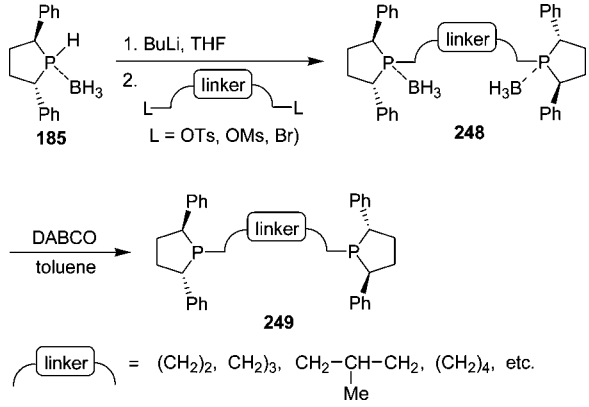
Scheme 78. Synthesis of the Rh(I) Complex of an Enantiopure 1,2-Phenylene-Based Bisphospholane Ligand



Scheme 79. Synthesis of Chiral Bisphospholanes with Various Bridges



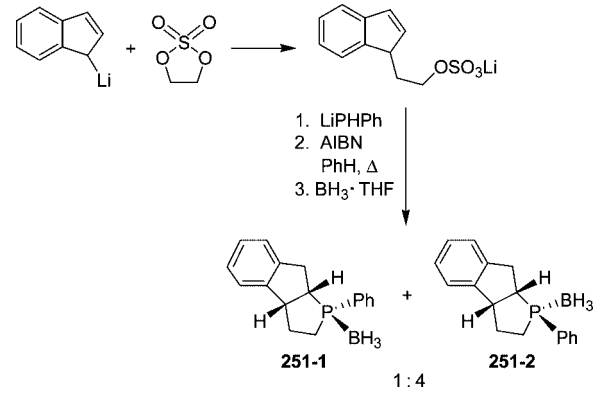
Scheme 80. Synthesis of Bisphospholane Derivatives via Borane Adducts



clization and pyramidal inversion strategies. It was coordinated to Rh(I) via cyclooctadiene substitution of the $[Rh(COD)_2]^+$ precursor, forming a complex cation (**245**) (Scheme 78).[90]

Chiral 2,5-dimethylphospholan-1-yl moiety was attached to different linkers by the coupling reaction of 1-trimethylsilyl-2,5-dimethylphospholane (**246**) with a series of dichlorides. The above bisphospholane ligands (**247**) were prepared by using a highly flexible and convergent approach, enabling the synthesis on an industrially relevant scale (Scheme 79).[91]

Scheme 82. Synthesis of Tricyclic Phospholanes



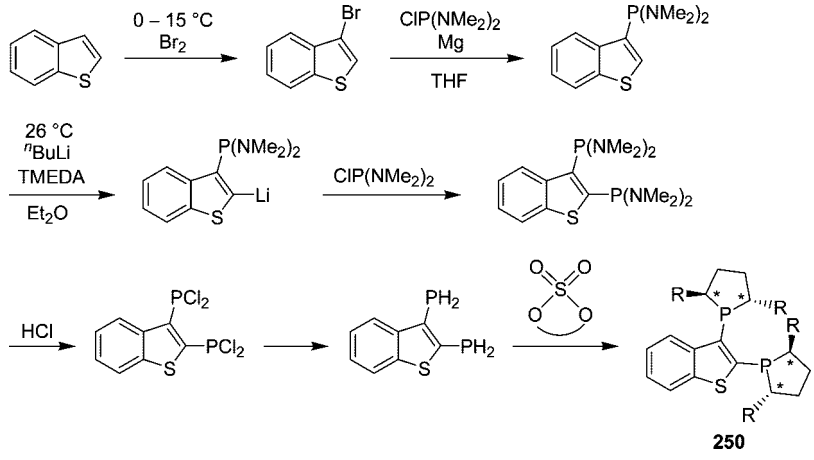
Bis-2,5-diphenylphospholane derivatives (**249**) with various linkers were synthesized with the aim of having a deeper "chiral pocket" when the target ligands are applied in chiral catalysis (see section 3.2). Linkers with appropriate leaving groups and lithium phosphide derivative obtained from the borane adduct of 2,5-diphenylphospholane (**185**) were reacted, resulting in the bis(borane complex) **248**, which was deboronated by a standard methodology (Scheme 80).[92]

Mono- and bidentate phospholane ligands (**250**) based on a benzothiophene scaffold were synthesized with the objective of having ligands that could be modified in terms of the bite angle and the electronic nature of the phosphorus. The multistep synthesis includes the formation of the dimethylaminophosphido-substituted derivatives. The latter ones served as key compounds to obtain the bis(dichlorophosphido) and 2,3-diphosphinobenzothiophene (**250**) derivatives ready for ring-closure reaction, providing the target bisphospholane derivative (Scheme 81).[93]

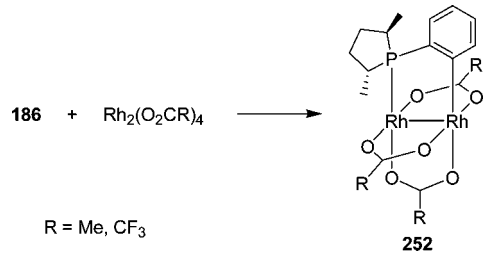
Tricyclic phospholanes with phosphabicyclooctane core such as **251** were obtained as borane adducts. Radical cyclization of indenylethylphosphines (or alkenylphosphines of similar structure), obtained from the lithium sulfate derivative, took place, providing the target compounds as diastereomeric mixtures (Scheme 82).[94]

Chiral 2,5-dimethyl-1-phenylphospholane (**186**) was reacted with dinuclear rhodium complex, $Rh_2(OAc)_4$ or $Rh_2(OOCCF_3)_4$ (Scheme 83).[95] The coordination of the ligand takes place via *ortho*-metalation as PC* chelation (**252**).

Scheme 81. Synthesis of Benzothiophene-Based Bisphospholane Derivatives



Scheme 83. Dinuclear Rh Complexes of Phenylphospholane Derivative



Reacting **252** with a further equivalent of **186**, $Rh_2(O_2CR)_2(PC^*)_2$ complexes were also formed as 3:1 diastereomeric mixture.

2.4. Six-Membered *P*-Heterocycles

Because of the versatile coordination modes of the phosphinine derivatives (Figure 5), the investigation of their transition metal complexes has long been the subject of many studies.

Theoretical studies on the basicity of the parent phosphinine (phosphabenzene) were carried out, reevaluating its proton affinity and gas-phase basicity. Both of these values, 195.8 and 188.1 kcal mol^{-1}, respectively, were in good agreement with previous results. Mass spectrometric and quantum chemical methods were used.[96]

2.4.1. Phosphinines and Their Complexes

The cyclization of aromatic aldehyde and acetophenone derivatives in the presence of HBF_4 resulted in the 2,4,6-trisubstituted pyrylium cation. The key intermediates are the pyrylium salts, which are crystalline and highly fluorescent compounds. The exchange of the oxygen for phosphorus, by using highly nucleophilic PH_3-analogues such as

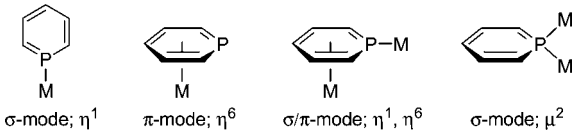
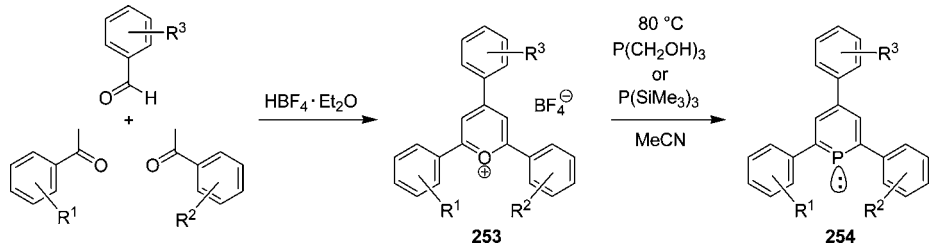
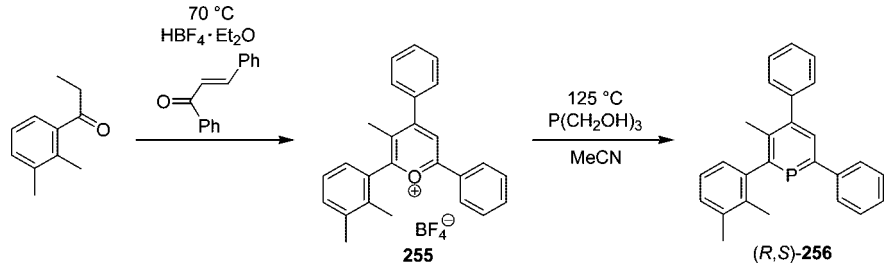


Figure 5. Various coordination modes of phosphinine to transition metals.

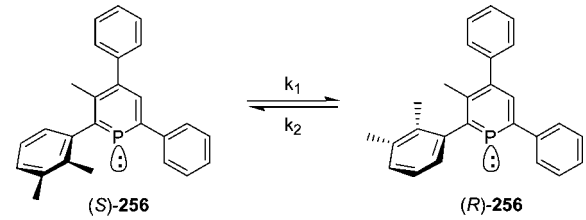
Scheme 84. Synthesis of 2,4,6-Triarylphosphinine Derivatives I



Scheme 85. Synthesis of 2,4,6-Triarylphosphinine Derivatives II



Scheme 86. Equilibrium between Triarylphosphinine Enantiomers



$P(CH_2OH)_3$ or $P(SiMe_3)_3$ as P-source, furnished the 2,4,6-triarylphosphinine (**254**) (Scheme 84).[97]

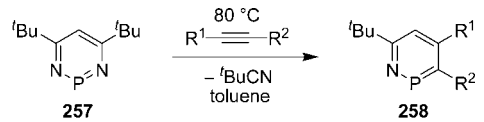
The cyclization can also be carried out by using 2,3-dimethylpropiophenone and 2 equiv of (*E*)-1,3-diphenylpropen-2-one ("chalcone route"), yielding the axially chiral pyrilium ion. The O−P exchange reaction carried out with tris(hydroxymethyl)phosphine furnished the phosphinine **256** (Scheme 85).

The first atropisomeric phosphinine **256** was designed and prepared on the basis of DFT calculations, which predicted the presence of axial chiality.[98] Both enantiomers have been isolated by chiral high-performance liquid chromatography (HPLC) on a chiral stationary phase (Chiralcel OD-H) with *n*-hexane as eluent. The barrier of internal rotation of 109.5 ± 0.5 kJ/mol was found, which shows a good agreement with the theoretically predicted value of 116 kJ/mol (Scheme 86).[99] The assignment of the absolute configurations was achieved by circular dichroism (CD) spectroscopy.

The formation of the parent phosphinine from flash vacuum photolysis of diallylvinylphosphine was investigated. According to these calculations (DFT/B3LYP), the thermal decomposition of diallylvinylphosphine into phosphinine involves the transient formation of 3-phosphabicyclo[3.1.0]hexe-2-ene. Furthermore, it was found that the formation of 1,4-dihydrophosphinine and the elimination of H_2, leading to phosphinine, is a symmetry-forbidden process.[100]

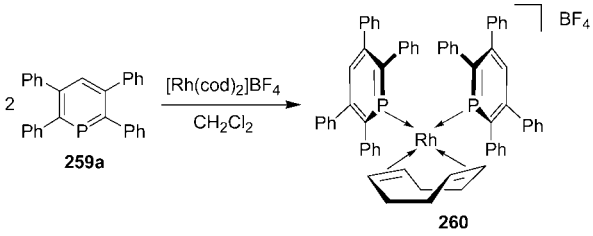
3,5-Di-*tert*-butyl-1,3,2-diazaphosphinine (**257**) was transformed to various 2,3,5,6-tetrasubstituted phosphinines (**259**) via [4 + 2]/retro-[4 + 2]-sequence to produce 1,2-monoazaphosphinines (**258**), which were reacted (without isolation) with the "second" alkyne in the same manner, resulting in the target substituted phosphinines (Scheme 87).[101]

Scheme 87. Synthesis of Phosphinines via Azaphosphinines

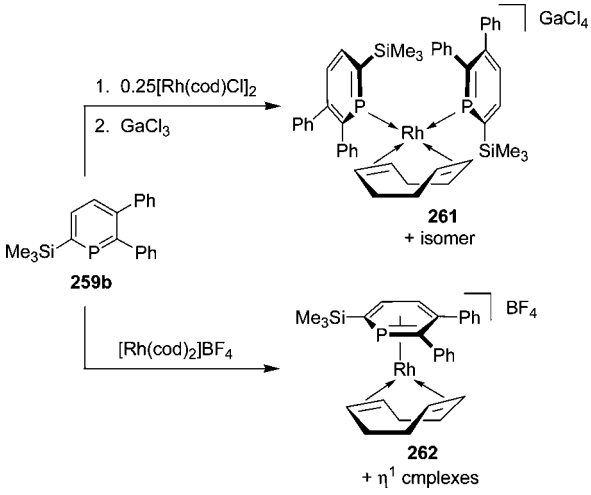


	a	b	c	d
R^1	Ph	Ph	Me	Ph
R^2	Ph	Ph	$SiMe_3$	$SiMe_3$
R^3	Ph	H	Me	Ph
R^4	Ph	$SiMe_3$	$SiMe_3$	$SiMe_3$

Scheme 88. Synthesis of Rh(I) Complexes Containing Tetraarylphosphinine Ligands



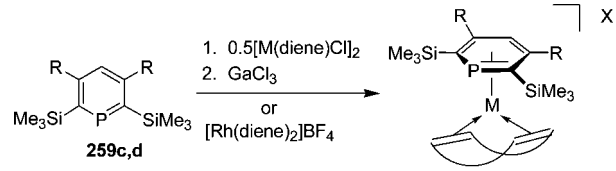
Scheme 89. Synthesis of Rh(I) Complexes Containing Diaryl−trimethylsilyl−Phosphinine Ligand(s)



The above ligands show versatile coordination chemistry. The η^1-type coordination of the tetraphenyl derivative to Rh(I) was observed in a complex cation (**260**) (Scheme 88). This coordination mode is clearly indicated by the large coupling constant ^1J(Rh,P) = 166.5 Hz obtained by ^{31}P NMR. The η^1-type coordination was also confirmed by crystal structure analysis, showing a square-planar geometry around the rhodium center.

The similar [Rh(cod)(ligandum)$_2$]$^+$-type complex cation (**261**) was formed when the chloro-bridged dimer, [Rh(cod)Cl]$_2$, was used as starting complex in the presence of $GaCl_3$ as Lewis acid. The ligandum-to-rhodium ratio was kept at 2/1. However, when the ionic precursor, [Rh(cod)$_2$]BF_4, was used, one of the dienes were substituted for η^6-coordinated 2,3-diphenyl-6-trimethylsilylphosphinine (**262**) (Scheme 89).[101] It is worth noting that the isolation of η^6-complexes was not successful due to the large amount of byproducts.

Scheme 90. Synthesis of Rh(I) and Ir(I) Complexes Containing Tetrasubstituted Phosphinine Ligand(s)

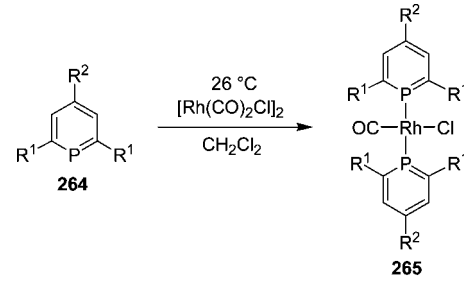


	c	d
R	Me	Ph

	A	B	C	D	E	F
M	Rh	Rh	Rh	Rh	Ir	Ir
R	Me	Ph	Me	Ph	Me	Ph
diene	COD	COD	NBD	NBD	COD	COD

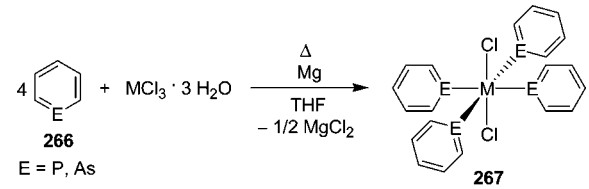
X = BF_4^- or $GaCl_4^-$

Scheme 91. Synthesis of Rh(I) Complexes Containing Triarylphosphinines



R^1	Me	Ph	2-Naphth	Ph	Ph
R^2	Ph	Ph	Ph	4-MeC_6H_4	4-$CF_3C_6H_4$

Scheme 92. Synthesis of Tetraarsenine and Tetraphosphinine Complexes



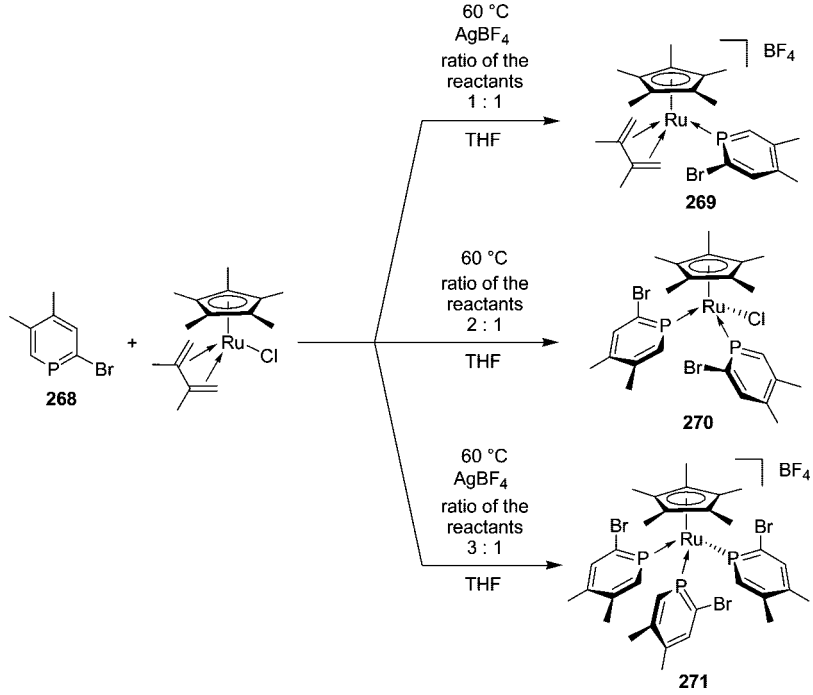
M	E
Ru	P
Os	P
Ru	As

Similarly, the η^6-type coordination of various tetrasubstituted phosphinines was observed in Rh(I) and Ir(I) complex cations (**263**). Depending on the synthetic method, tetrafluoroborate or tetrachlorogallate counterions were used (Scheme 90).[101]

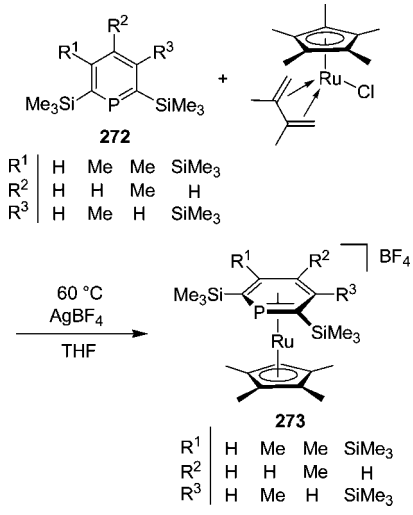
Phosphinines of unprecedented structure were prepared employing the modified version of the original procedure;[102] thus, the corresponding pyrylium tetrafluoroborates were treated with tris(trimethylsilyl)phosphine to produce the target ligands in moderate yields. The η^1-type coordination of 2,4,6-triarylphosphinines was observed in **265** when the neutral chloro-bridged carbonyl complex, [Rh(CO)$_2$Cl]$_2$, was used as precursor (Scheme 91).[103] The *trans*-[(phosphabenzene)$_2$-RhCl(CO)] complexes were characterized by X-ray crystal-structure analysis and NMR spectroscopy.

When the parent unsubstituted phoshinine (or arsenine) (**266**) was reacted with transition metal chlorides ($RuCl_3$ or $OsCl_3$), the *trans*-[MCl_2(ligandum)$_4$] complexes (**267**) were obtained. Magnesium was used as reducing agent to reduce M(III) to M(II). Further reduction of the metals to M(0) failed (Scheme 92).[104] It was revealed by X-ray diffraction analysis that **267** (M = Ru, E = P) features two pairs of coplanar

Scheme 93. Synthesis of Ru(II)−Phosphinine Complexes



Scheme 94. Synthesis of Ru(II)−η^6-Phosphinine Complexes

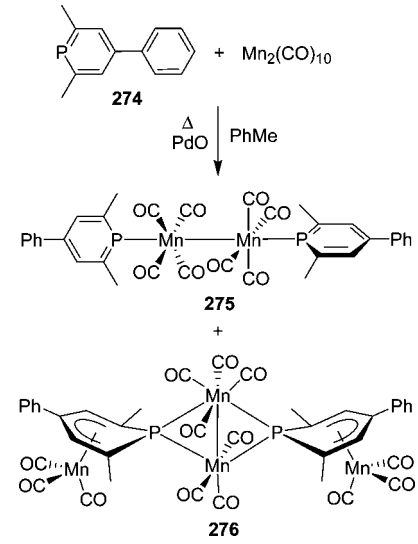


trans-phosphinine ligands, which adopt eclipsed and staggered orientations, respectively.

2-Bromo-4,5-dimethylphosphinine (**268**) was coordinated as η^1-ligand to Ru(II)−Cp*, resulting in either cationic (**269**) or neutral (**270**) complexes by the substitution of the chloro- or the diene ligand, respectively. Combining the two substitution pathways, $[Ru(ligand)_3(Cp^*)]^+$ (**271**) was synthesized when ligand-to-ruthenium ratio of 3 to 1 was used (Scheme 93).[105] In the latter case, the presence of an equimolar amount of $AgBF_4$ is needed in order to achieve complete conversion.

The same authors have shown that the application of 2,6-bis(trimethylsilyl)phosphinines (**272**) possessing electron-releasing substituents resulted in the formation of a Ru(II)-sandwich complex (**273**), i.e., the η^6-type coordination of both Cp* and phosphinine. In order to achieve chloro ligand substitution, $AgBF_4$ had to be used (Scheme 94).[105] Interestingly, the in situ ^{31}P NMR investigations revealed that no stable η^1-phosphinine complexes were formed prior to formation of η^6-complexes.

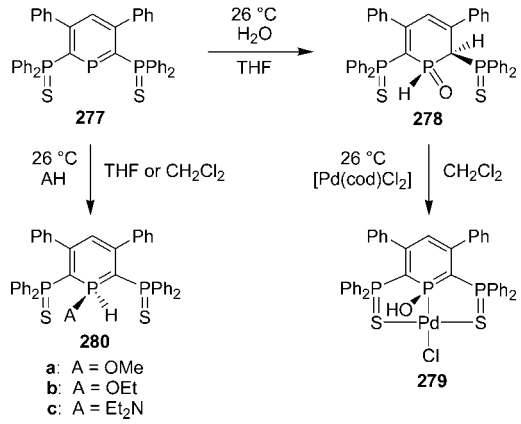
Scheme 95. Synthesis of Mn_2 and Mn_4 Complexes Possessing Phosphinine Ligands of Different Coordination



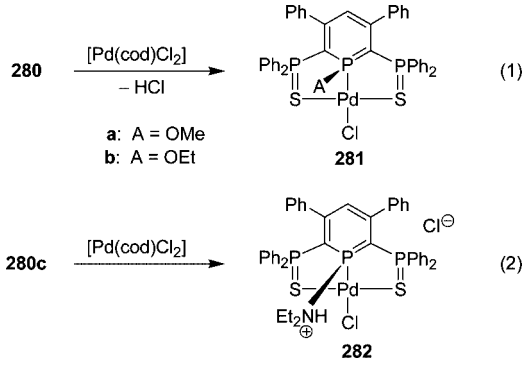
2,6-Dimethyl-4-phenylphosphinine (**274**) was reacted with dimanganese−decacarbonyl in carbonyl substitution reaction. Both the linear P−Mn−Mn−P arrangement (**275**) and the tetramanganese (**276**) compound with bridging phosphinine ligands were obtained. In the latter compound, the open cymantrene-type coordination of $Mn(CO)_3$ to ($5c,6e^-$) system could also be observed (Scheme 95).[106] The structure of both products (**275** and **276**) was determined by X-ray diffraction.

2,6-Bis(diphenylphosphanylsulfide)phosphinine derivatives (SPS-based pincer ligands) were coordinated to Pd(II) (**279**). More precisely, the addition of water furnished the (H)P═O derivative (**278**), which was reacted with $Pd(cod)Cl_2$ precursor upon loss of HCl in pincer-type coordination. The above phosphinine (**277**) reacts also with alcohols and secondary amine, resulting in a phosphinine with P(OMe), P(OEt), and $P(NEt_2)$ moieties (**280**) (Scheme 96).[107]

Scheme 96. Synthesis of Pd(II)−Phosphinine Pincer Complexes I



Scheme 97. Synthesis of Pd(II)−Phosphinine Pincer Complexes I



Their coordination to Pd(II), by using the $Pd(cod)Cl_2$ precursor, yielded the palladium-pincer complex with related structure (**281** and **282**) (Scheme 97).[107]

The coordination of the 2,6-bis(diphenylphosphanylsulfide)phosphinine (**277**) was also investigated. Neutral Pd- (**283**), Pt-, and Ni-pincer complexes (**284**) with two halide atoms attached to ring-phosphorus and transition metal were obtained (Scheme 98). The P−Cl bond underwent ethanolysis, resulting in the P−OEt derivative (**285**).

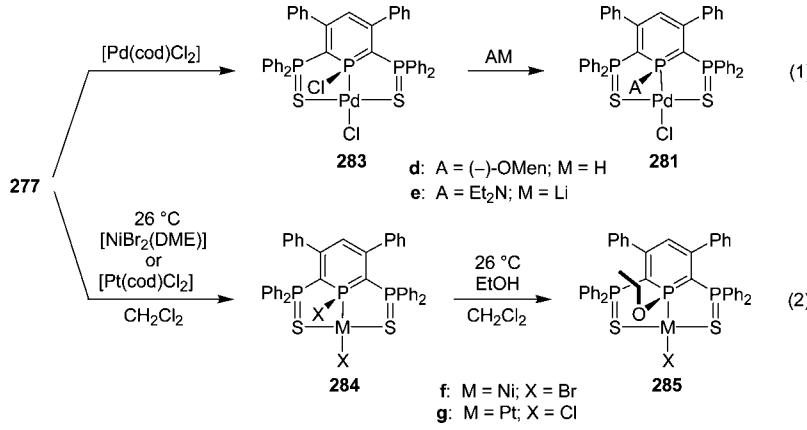
The above starting phosphinine derivative was *P*-butylated by using BuLi. The complexation of the resulting anion (**286**) provided the pincer complexes (**287**) analogous to those ones obtained by direct reaction of the ligand with Pt(II) or Ni(II) precursors (Scheme 99).[107]

The alkylation (methylation)−coordination sequence was also followed in the presence of a Rh(I) dinuclear precursor. However, the expected Rh-pincer motif (**289**), containing a hypervalent phosphorus atom and two phosphine sulfides, was transformed to distorted tetrahedral complexes (**290**−**294**) upon addition of PPh_3. The structure of phosphinine ligand was changed thoroughly, i.e., the planar ligand changed to a C5-delocalized species with the P-donor bending out of the plane. It was reacted with various "small molecules", and the trigonal bipyramidal complexes with carbonyl, sulfur dioxide, carbon disulfide, and dioxygen ligands were characterized (Scheme 100).[108] It was shown by several examples that the SPS ligand is able to adopt the facial coordination mode in trigonal bipyramidal complexes.

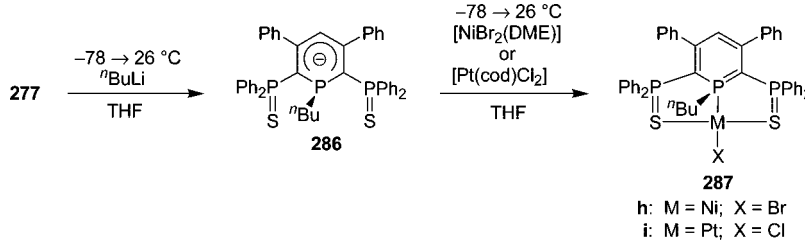
Only the latter type (distorted tetrahedral) structure was obtained with Cu(I). Insoluble dimeric or oligomeric complexes (**296**) were readily cleaved by two-electron donor ligands. Novel complexes (**297**) containing isocyanide as well as phosphine and phosphite ligands were characterized (Scheme 101).[109] The X-ray crystal analysis proved the flexibility of the SPS ligand, which can accommodate square-planar, tetrahedral, octahedral, and trigonal bipyramidal geometries.

Both dinuclear (**298**) and mononuclear (**299**) Au(I) complexes were synthesized with P−S and P coordination of the ligand, respectively. The dimer was cleaved with two electron donors such as PPh_3 and ^{t}BuNC. Linear arrangement of the ligands in bicoordinated Au(I) was found as expected (Scheme 102).[109]

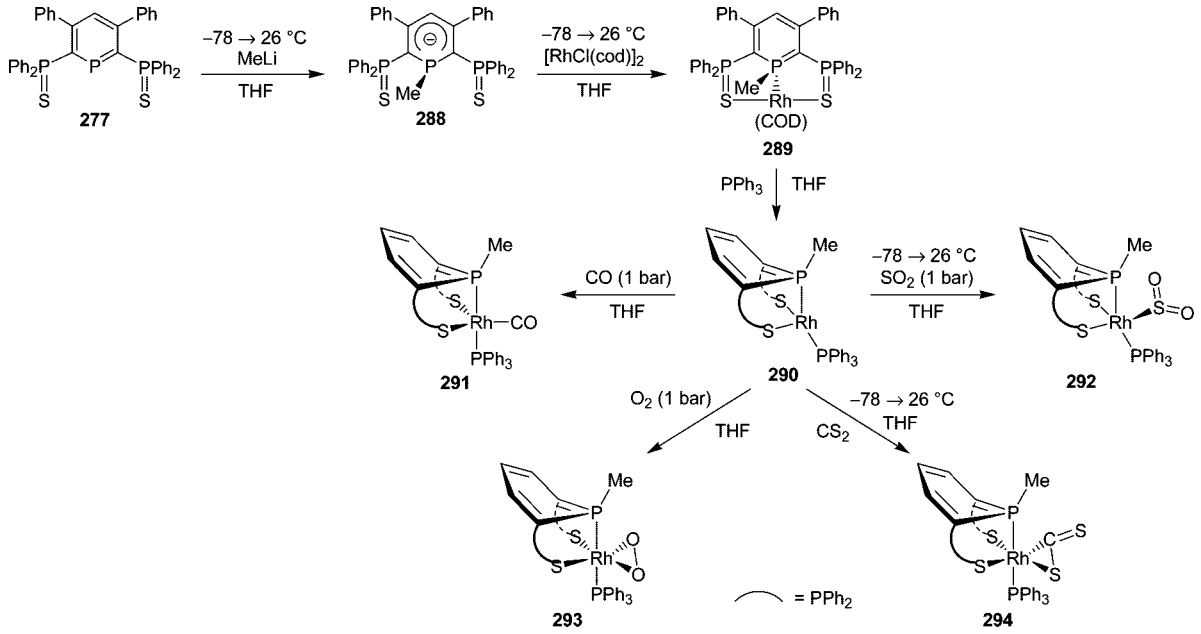
Scheme 98. Synthesis of Pd(II)−Phosphinine Pincer Complexes II



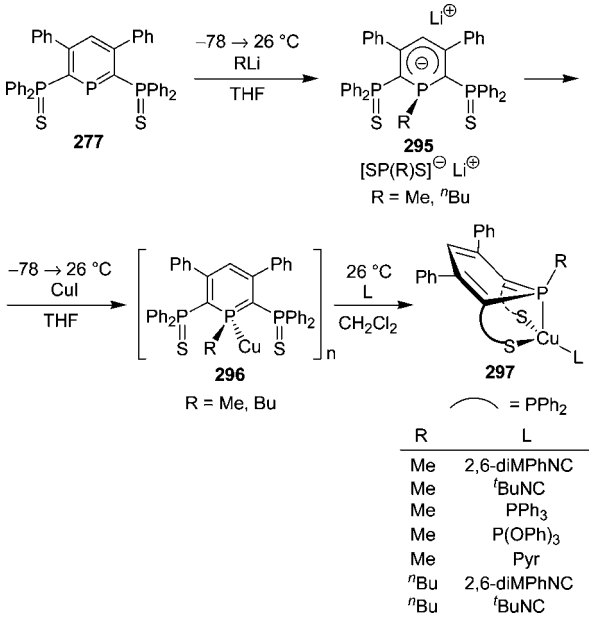
Scheme 99. Synthesis of Pd(II)−Phosphinine Pincer Complexes III



Scheme 100. Synthesis of Rh(I) Phosphinine Complexes Containing P-Donor Bending out of the Plane

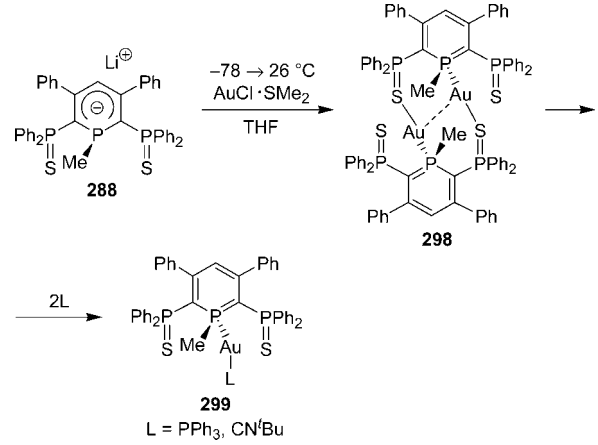


Scheme 101. Synthesis of Cu(I) Phosphinine Complexes Containing P-Donor Bending out of the Plane of the Heterocycle



R	L
Me	2,6-diMPhNC
Me	^{t}BuNC
Me	PPh_3
Me	$P(OPh)_3$
Me	Pyr
^{n}Bu	2,6-diMPhNC
^{n}Bu	^{t}BuNC

Scheme 102. Synthesis of Au(I) Complexes Containing *P*-Methylphosphinide Anion



Lanthanide and uranium complexes with the above-type phosphinine-based SPS pincer ligand, possessing a central hipervalent λ^4-phosphinine ring bearing two *ortho*-positioned diphenylphosphine sulfide side arms, were also synthesized.[110,111]

2,6-Bis(phosphinin-2-yl)pyridine tridentate ligand (**300**) was synthesized from 2,6-diacetylpyridine and chalcon via the bis(pyrylium) salts. A Cu(PNP)Br complex (**301**) was formed by using the appropriate Cu(I) precursor (Scheme 103).[112] The tetrahedral environment of Cu(I) enforces the noncoplanarity of the three heterocycles, leading to interplanar angles for the *P*-heterocycles and *N*-heterocycle between 25.5° and 31.4°. The X-ray crystal analysis of **301** has revealed a remarkable feature of this butterfly structure: the unusual nondirectional coordination mode of the phosphinine rings allowing the distorted tetrahedral geometry.

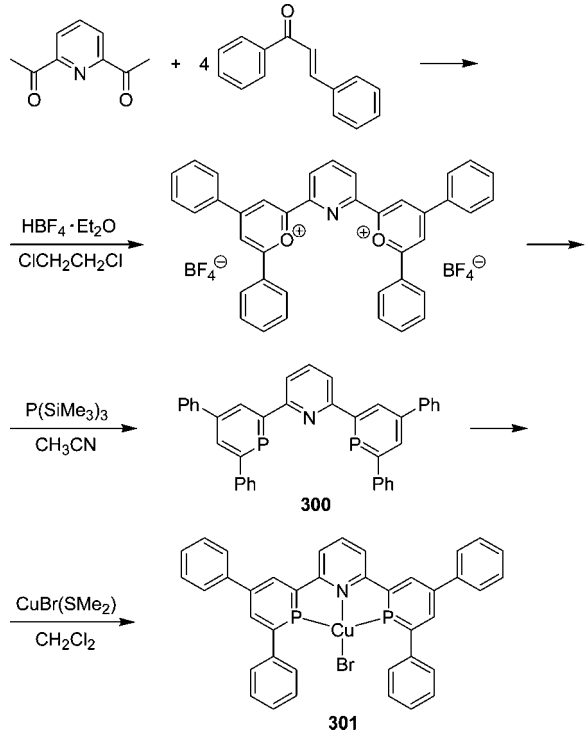
Phenyltripropargylsilane served as a core for the preparation of the tris(phoshinin-2-yl)phenylsilane tripodal ligands (**303**, **304**, **305**). The *tert*-butyl−cyanide−alkyne exchange of the diazaphosphinine building block, i.e., successive [4 + 2]-cycloaddition/cycloreversion sequence, was used as a key reaction for the synthesis. The tungsten−tricarbonyl complex (**306**) of "SiP_3" tripodal ligand **304** was isolated and fully characterized including X-ray crystal analysis (Scheme 104).[113]

A similar methodology was followed for the synthesis of bis(phosphinine) derivatives with SiO−$(CR_2)_n$−OSi linkers of variable length (**307**), providing novel ether macrocycles incorporating phosphinine units (**308**) (Scheme 105).[114]

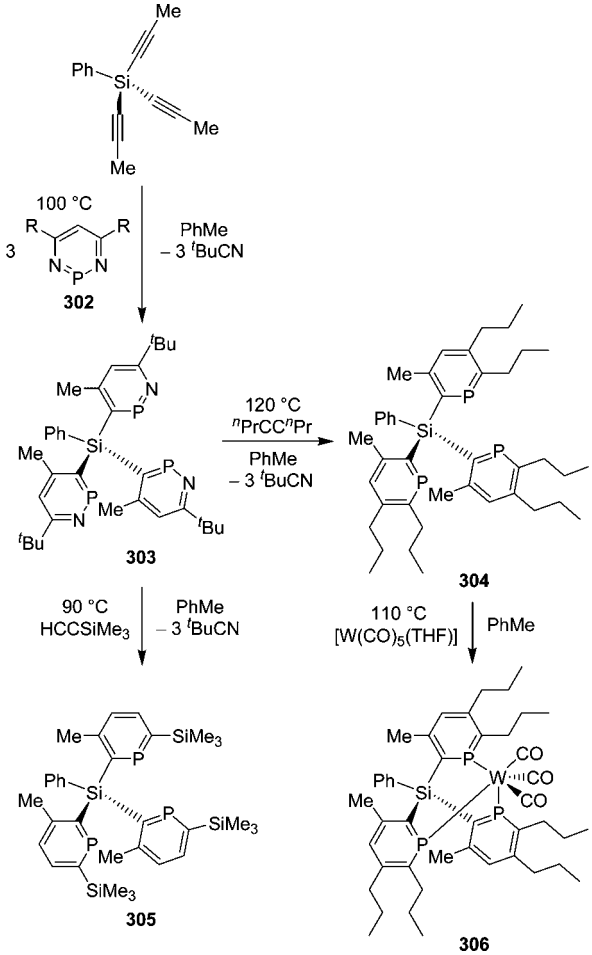
Both the SiOSi linked derivative (**309**) and the 2,6-bis(trimethylsilyl)phosphinine (**311**) were transformed to the dianions (**310** and **312**, respectively) with direct P−P bond (**310**) (Scheme 106 and 107).[115] Although the structure of the monoanion, formed in the first step via one-electron reduction, could be studied by electron paramagnetic resonance (EPR) in the frozen state only, its subsequent reduction led to dianion **310** with direct P−P bond, which could be obtained in crystalline form in the presence of a cryptand.

Even by changing the reaction conditions, the EPR spectrum of the radical monoanion of the dimeric species $(\mathbf{311})_2^{\cdot -}$ obtained from **311** could never be observed. However, the hyperfine interactions in the EPR could be assigned to the dianion in complex **312**.

Scheme 103. Synthesis of a Cu(I)−PNP Complex Containing Pyridine-Based Bisphosphinine Ligand



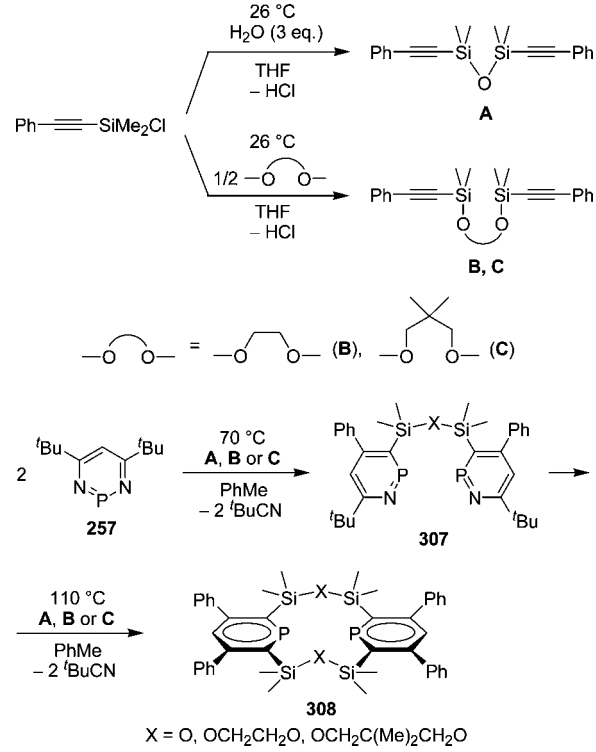
Scheme 104. Synthesis of Tris(phosphinine-2-yl)silane Ligand and Its W(0) Complex



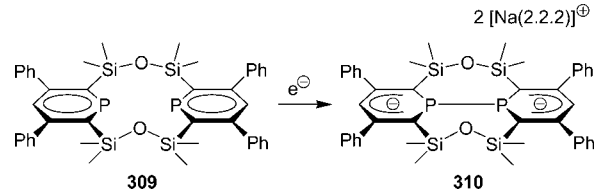
As above, the [4 + 2]/retro-[4 + 2]-reaction sequence, that is, the exchange of the *tert*-BuCN "unit" in diazaphosphinine for alkyne moiety, was followed when a trimeric ring system with SiOSi linkers (**315**) was synthesized. The Cu(I), Ag(I), and Au(I) complexes (**316**) of this potentially terdentate ligand were obtained in the presence of $GaCl_3$ as chloride abstractor (Scheme 108).[116] The phosphinine-based macrocycle was fluxional in solution even at low temperature of −60 °C. The X-ray crystal structure of **316** (M = Cu) revealed a trigonal planar geometry. The detailed examination suggested that the aromaticity of the rings has not been perturbed due to the weak bonding between P and Cu(I).

Similarly, "tetrameric phosphinine" (**317**) and "dimeric phosphinine" (**319**) ring systems with $SiMe_2$ and $SiMe_2$-thiophen-2,5-diyl-$SiMe_2$ linkers were synthesized, respectively. These compounds act as P_4 and P_2S_2 tetradentate ligands, respectively, toward

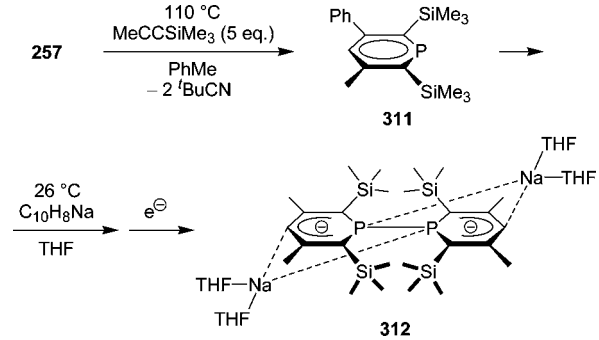
Scheme 105. Synthesis of Bisphosphinines Containing Si-Linkers



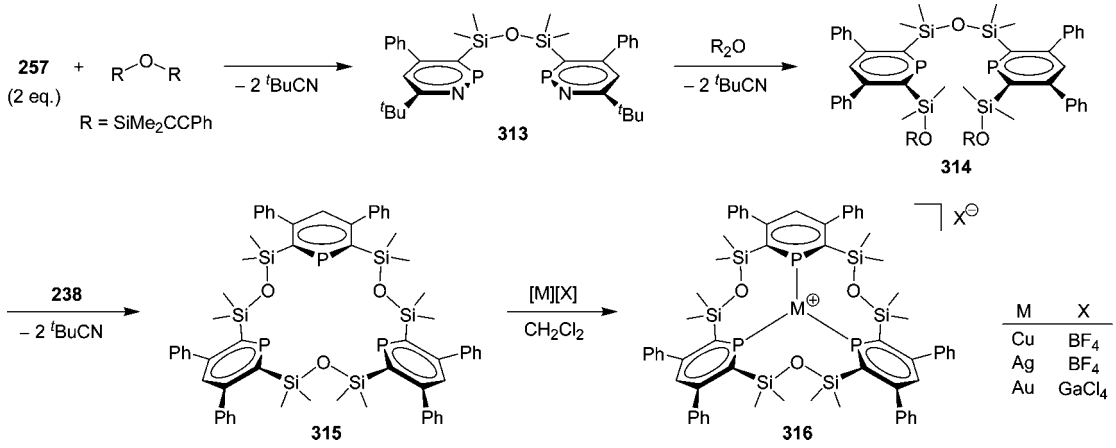
Scheme 106. Synthesis of Bisphosphinine Dianion Containing Si-Linkers



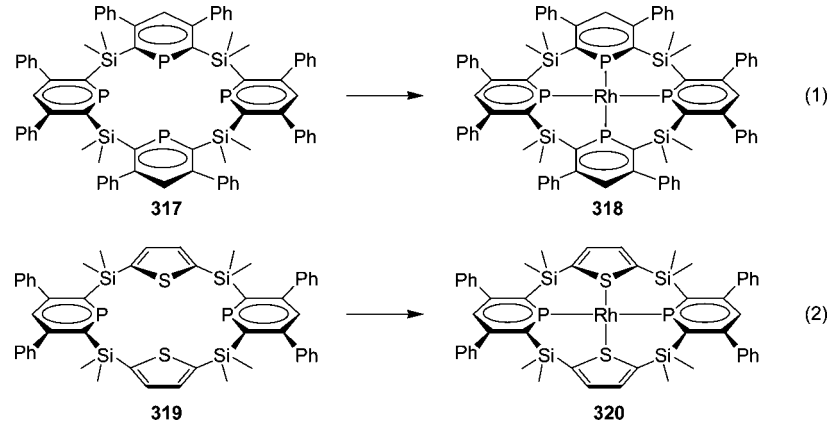
Scheme 107. Synthesis of Bisphosphinine Dianion



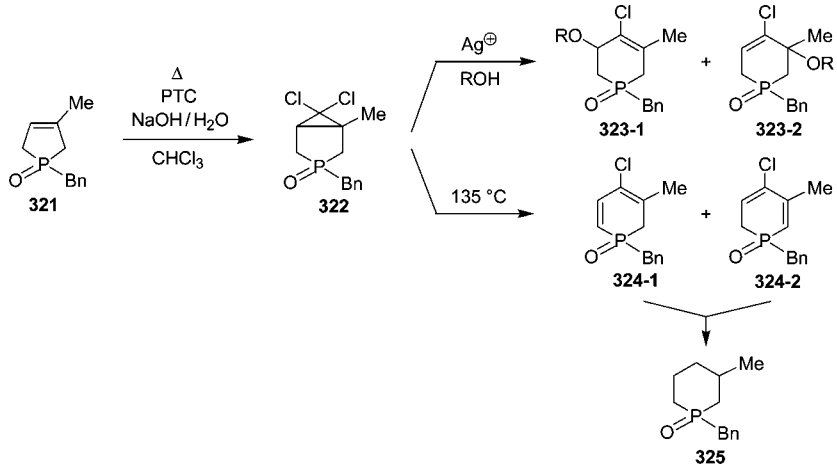
Scheme 108. Synthesis of a Trisphosphinine Ligand with Si-Linkers and Its Cu(I), Ag(I), and Au(I) Complexes



Scheme 109. Synthesis of the Rh-Complexes of Tetrakis−Phosphinine Ligand and That of Its Thiophene Analogue With Si-Linkers



Scheme 110. Synthesis of a Series of 1-Benzylphosphinine Derivatives



Rh(I). EPR investigations and DFT calculations performed on both Rh(I) complexes indicate that the metal coordination is planar. Their electrochemical reduction led to Rh(0), provoking appreciable changes (tetrahedral distortion) in the geometry of the macrocycles (**318** and **320**) (Scheme 109).[117]

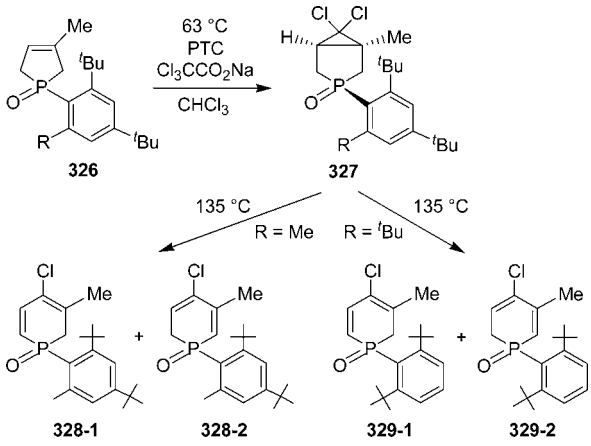
2.4.2. Dihydro-, Tetrahydro-, And Hexahydrophosphinines and Their Complexes

Keglevich and co-workers studied intensively the chemistry of six-membered *P*-heterocycles (phosphinine derivatives).[118−120] 4-Chloro-5-methyl-1-benzyltetrahydrophosphinine oxide isomers with 3-alkoxy substituents (**323**), as well as the corresponding dihydrophosphinine oxide isomers (**324**), were synthesized from 3-methyl-1-benzylphospholene oxide (**321**). The ring enlargement was carried out via dichlorocarbene insertion under phase-transfer catalysis (PTC) conditions. Both isomers were transformed to the saturated 3-methyl-1-benzyl-hexahydrophosphinine oxide (**325**) by hydrogenation combined with hydrogenolysis (Scheme 110).[121]

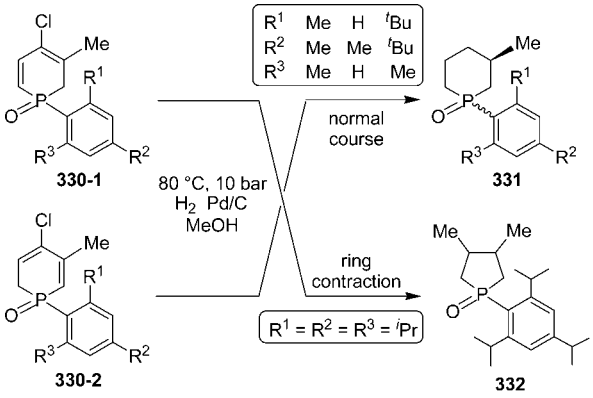
4-Chloro-3-methyl-1,2-dihydrophosphinine oxides possessing sterically bulky aryl substituents (**328**, **329**) were obtained by the above dichlorocarbene insertion−cyclopropane ring-opening reaction sequence (Scheme 111).[122]

Interestingly, while the hydrogenation of the methyl-*tert*-butylphenyl derivatives gave the saturated *P*-aryl−hexahydrophosphinine oxides (**331**) expected, the application

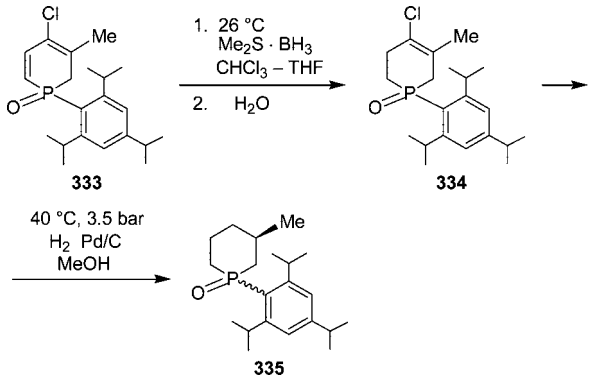
Scheme 111. Synthesis of Aryldihydrophosphinine Oxides



Scheme 112. Hydrogenation of Aryldihydrophosphinine Oxides



Scheme 113. Synthesis of Triisopropylphenyl–Hexahydrophosphinine Oxide

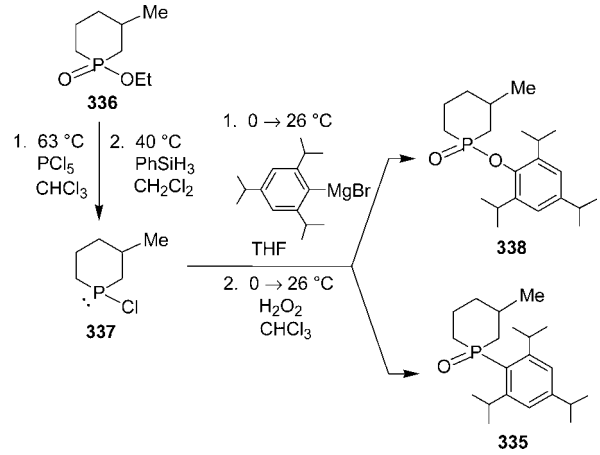


of 2,4,6-trisopropylphenyl derivative led to 3,4-dimethylphospholane (**332**) via ring contraction (Scheme 112).[123]

However, when the hydrogenation of the dihydrophosphinine ring of the 2,4,6-trizopropylphenyl derivative (**333**) was carried out in two steps, i.e., with BH_3 (in the form of its dimethylsulfide adduct) followed by the reduction on Pd/C, the 2,4,6-triisopropylphenyl−hexahydrophosphinine oxide (**335**) was obtained exclusively (Scheme 113).[124]

The P−OEt substituted saturated compound (ethyl phosphinate type compound, **336**) was transformed to the P−Cl derivative by substitution and reduction. The *P*-chlorohexahydrophosphinine (**337**) was reacted with a Grignard reagent with bulky aryl substituent and oxidized with hydrogen peroxide, yielding both triizopropylphenyl- (**335**) and, surprisingly, triisopropylphenoxy-substituted (**338**) phoshinine oxides (Scheme 114).[123]

Scheme 114. Reaction of a Chlorohexahydrophosphinine with Triisopropylphenylmagnesium Bromide



The two double bonds in the ring of 4-dichloromethylene-1-phenyl-3,5-dimethyl-1,4-dihydrophosphinine oxide (**339**) were reduced consecutively with mild reducing agent $Me_2S \cdot BH_3$. The heterogeneous catalytic hydrogenation (Pd/C) yielded the saturated 3,4,5-trimethyl-1-phenylhexahydrophosphinine oxide (**342**) exclusively (Scheme 115).[124]

Both the 3-phosphabicyclo[3.1.0]hexane derivatives (**344**) and a dichloromethylene-1,4-dihydrophosphinine (**346**) were investigated as ligands in Rh(I) and Pd(II) complexes. The 2-methylphenyl-substituted derivatives underwent epimerization at the P stereogenic center. The Rh−Cp* complex was isolated as two diastereoisomers (**345-1**, **345-2**) (Scheme 116). The synthesis of Pd(II) complexes was based on the application of the $Pd(PhCN)_2Cl_2$ precursor. The *trans*-$Pd(ligand)_2Cl_2$ complex (**348**) was formed exclusively (Scheme 117).[125,126] By using $[(Cp^*)RhCl_2]_2$ precursor, **347** was formed as major product.

The *cis*-complex geometry (**349**, **352**) was obtained for various dihydro- and tetrahydrophosphinines when $PtCl_2(PhCN)_2$ was used as the precursor of the platinum moiety (Schemes 118 and 119).[64] The *cis* arrangement of *P*-ligands was unequivocally proved by $^1J(Pt,P)$ couplings.

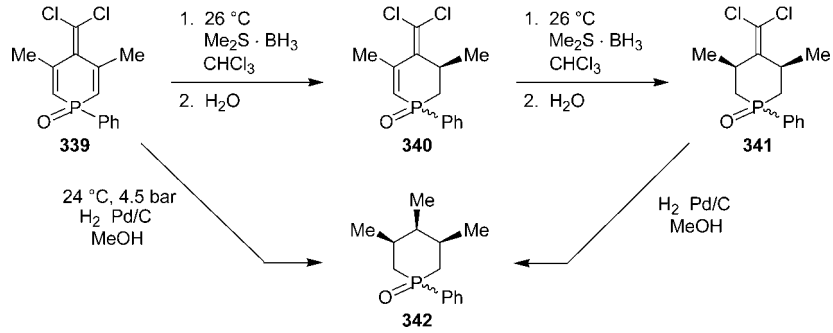
4-Chloro-3-methyl-1,6-dihydrophosphinine oxide (**353**) was tested as diene in Diels−Alder reaction in the presence of dimethyl acetylenedicarboxylate as dienophile. Unexpectedly, no formation of the phosphabicyclo[2.2.2]octadiene (**354**) derivative was observed. However, the corresponding β-ketophosphorane (**355**) was formed in an inverse Wittig-type reaction (Scheme 120).[127,128,60]

The addition of $Z_2P(O)H$ to 1,2-dihydrophosphinine oxides (**356**) took place with high regioselectivity, forming the corresponding 3-substituted 1,2,3,6-tetrahydrophosphinine oxides (**357**) (Scheme 121).[129−131]

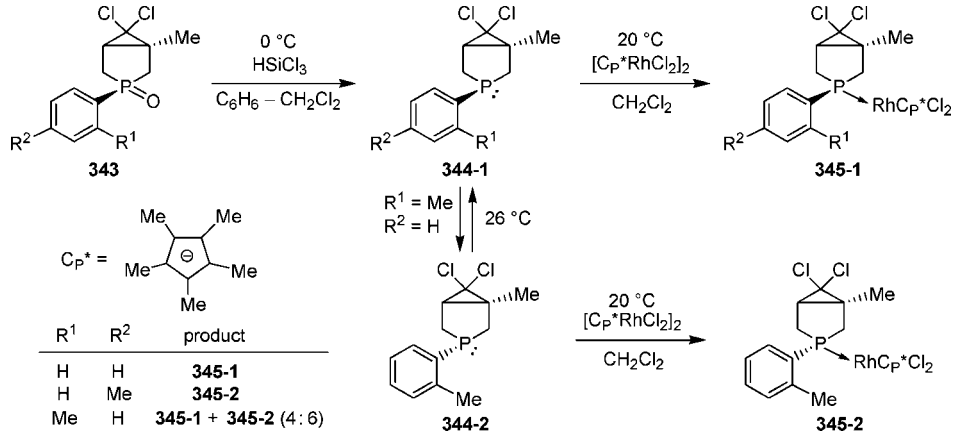
The heterogeneous catalytic hydrogenation of the *P*-phenyl (**358**) and *P*-ethoxy derivatives (**360**) gave pure *cis* diastereomer (**359**) and the 3/1 mixture of *trans/cis*-(**361**) diastereoisomers of the fully saturated hexahydrophosphinine oxides, respectively (Scheme 122).[132,133]

The reduction of the two different P═O functionalities in both the tetrahydrophosphinine (**358**) and the hexahydro derivatives (**359**) was carried out by trichlorosilane. The resulting bidentate diphosphine ligands formed stable square-planar *cis*-chelate complexes with Pt(II) (**363** and **365**, respectively) as characterized by NMR (Scheme 123).[134,135]

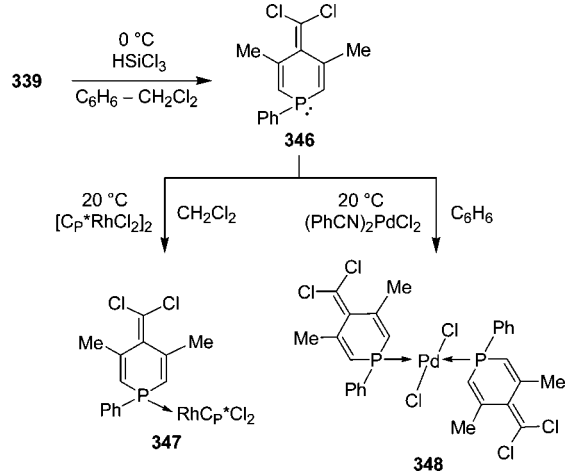
Scheme 115. Reduction of a 4-Dichloromethylene−1,4-Dihydrophosphinine Oxide



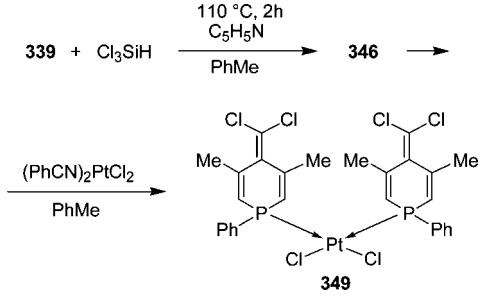
Scheme 116. Synthesis of Rh(III)−Phosphabicyclo[3.1.0]hexane Complexes



Scheme 117. Synthesis of Rh(III) and Pd(II) Complexes Containing 4-Dichloromethylene−1,4-Dihydrophosphinine

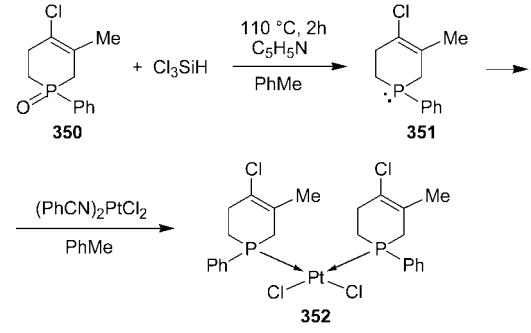


Scheme 118. Synthesis of Pt(II) Complex Containing a 4-Dichloromethylene−1,4-Dihydrophosphinine As the Ligand



Further 3-P functionalized 1,2,3,6-tetrahydrophosphinine oxides were also prepared.[136]

Scheme 119. Synthesis of Pt(II) Complex Containing a 1,2,3,6-Tetrahydrophosphinine As the Ligand



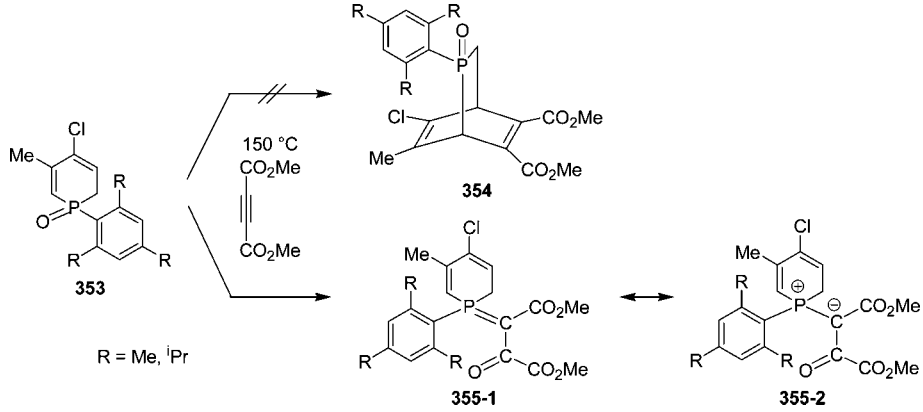
2.5. Seven-Membered *P*-Heterocycles (Phosphepines) and Their Complexes

The most recent synthetic procedures for phosphepine derivatives are generally based on the achievements of organometallic chemistry. Either the phosphorus reactant is coordinated to a transition metal and the reaction takes place on the ligand bound to the metal throughout the reaction *or* a transition metal catalyzed homogeneous reaction is used for the synthesis of the target phosphepine derivative.

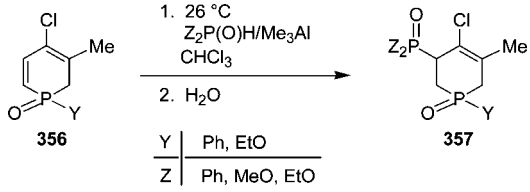
The ruthenium-catalyzed metathesis reaction proved to be a powerful tool in the cyclization of dialkenylphenylphosphines. The application of the borane adduct of bis(3-buten-1-yl)phenylphosphine (**366**) and (4-penten-1-yl)allylphenylphosphine (**368**) in ring-closing metathesis resulted in the formation of symmetric and unsymmetric 1-phenyltetrahydrophosphepines (**367** and **369**), respectively (Scheme 124).[137−139]

The above methodology was used for the ring-closure of bis(3-buten-1-yl)phenylphosphine bound to Pt(II). The *trans*-

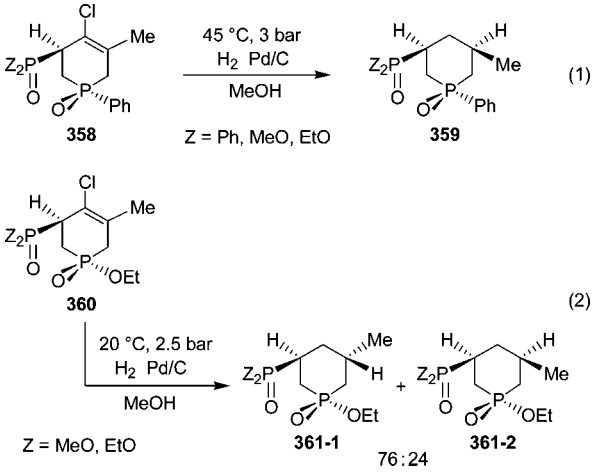
Scheme 120. Reaction of Aryldihydrophosphinine Oxides with Dimethyl Acetylenedicarboxylate



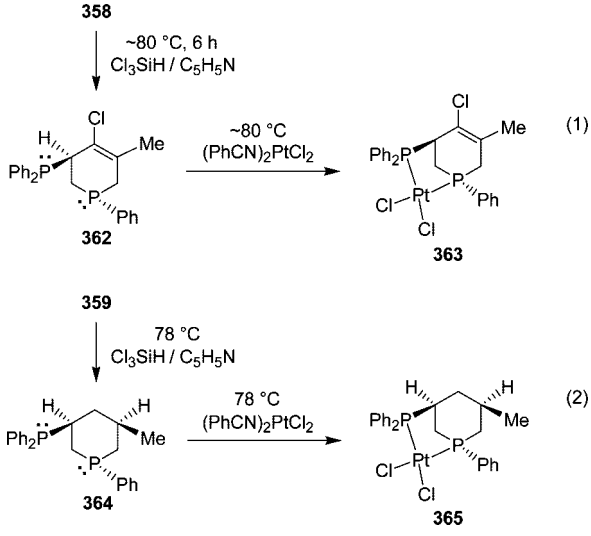
Scheme 121. Synthesis of 3-Substituted 1,2,3,6-Tetrahydrophosphinine Oxides



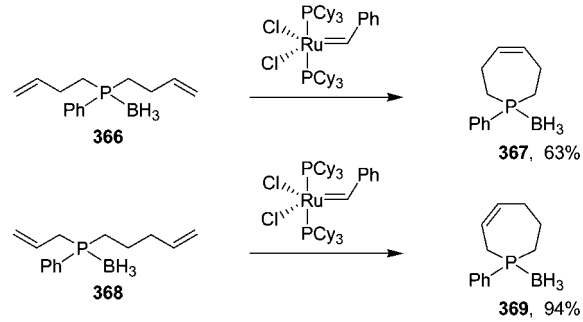
Scheme 122. Synthesis of 3-Substituted Hexahydrophosphinine Oxides via Hydrogenation



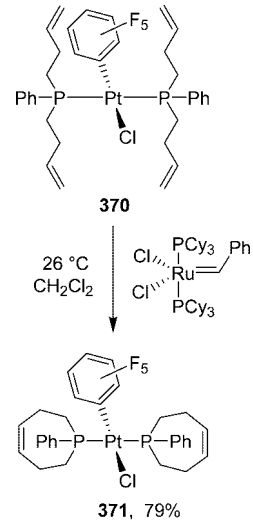
Scheme 123. Synthesis of *cis*-Chelate Pt(II) Complexes



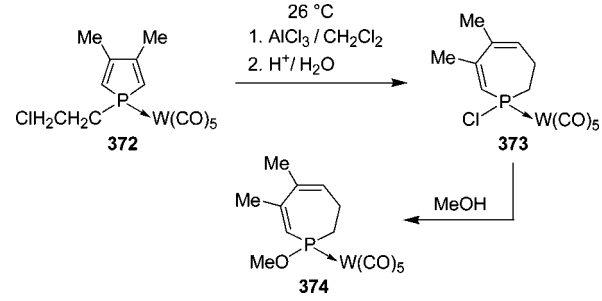
Scheme 124. Synthesis of the Borane Adduct of Tetrahydrophosphepines



Scheme 125. Synthesis of a Pt(II) Complex Containing Tetrahydrophosphepine Ligands

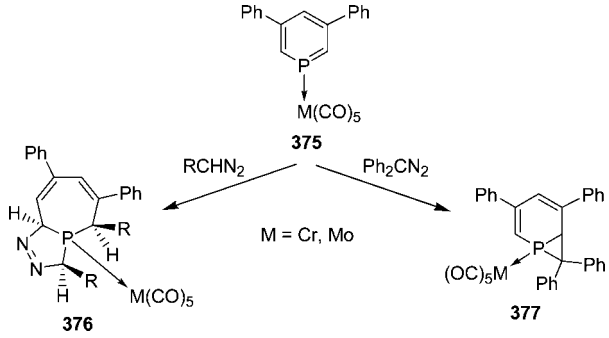


Scheme 126. Synthesis of a W(0) Complex Containing Phosphepine Derivatives As the Ligand

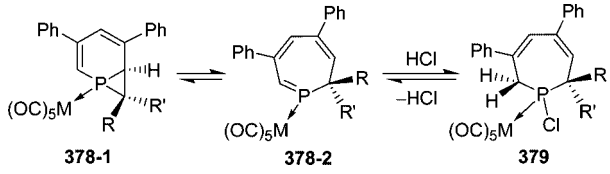


diphosphine−Pt(II) complex (**370**) was transformed to the corresponding *trans*-bis(tetrahydrophosphepine)−Pt(II) (**371**)

Scheme 127. Reaction of Phosphinine−Cr−Carbonyl (Or Mo−Carbonyl) with Carbenes



Scheme 128. Equilibria Involving the Carbonyl Complexes of Phosphepine and Cyclopropanated Phosphinine Derivatives



complex via metathesis catalyzed by Grubbs-type catalyst (Scheme 125).[140]

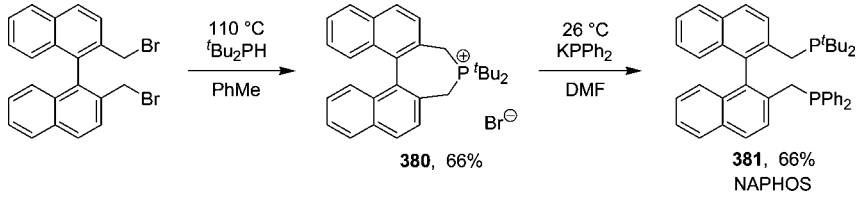
3,4-Dimethyl-1-(2-chloroethyl)phosphole coordinated to a $W(CO)_5$ moiety (**372**) underwent ring-enlargement in the presence of $AlCl_3$.[141] The 1-chloro-3,4-dimethylphosphepine product (**373**) was reacted toward the 1-methoxy derivative (**374**) by methanolysis (Scheme 126).

Chromium− and molybdenum−pentacarbonyl complexes of 3,5-diphenylphosphinine (**375**) were reacted with diazoalkanes. The outcome of the reaction was thoroughly influenced by the structure of the diazo reactant, i.e., by using the diphenyl derivative or monosubstituted diazo derivative, cyclopropanation toward a bycyclic compound (**377**) or ring-enlargement−*P*-alkylation toward a phosphepine derivative (**376**) took place, respectively (Scheme 127).[142] The cyclopropanated derivative (**378-1**) was found to be in equilibrium with the phosphepine (**378-2**) and dihydrophosphepine (**379**) derivatives formed in ring-enlargement (Scheme 128).

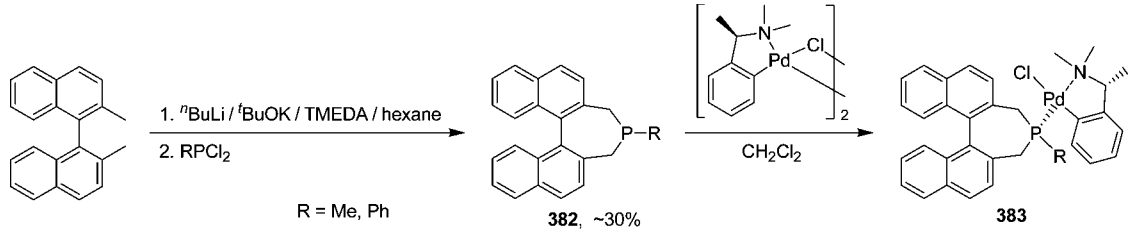
Since chiral dinaphthophosphepines turned to be one of the most successful ligands in various homogeneous catalytic reactions, several new strategies were worked out for their synthesis. 2,2′-Bis(bromomethyl)-1,1′-binaphthyl yielded the corresponding cyclic phosphonium salt (**380**) with secondary amines, which furnished the axially chiral diphosphine (**381**) with two different phosphorus donors (Scheme 129).[143]

2,2′-Dimethyl-1,1′-binaphthyl underwent ring-forming reaction with alkyldichlorophosphine in the presence of a strong base (BuLi). The resulting dinaphthophosphepine (**382**) was coordinated to Pd(II) containing the *ortho*-metalated α-phenylethylamine ligand (**383**) (Scheme 130).[144−146]

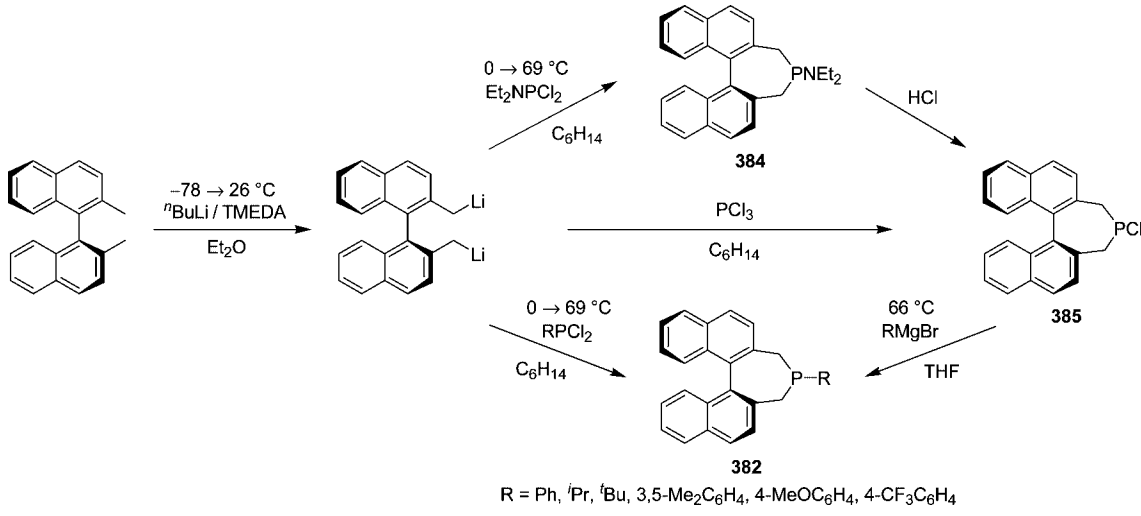
Scheme 129. Synthesis of NAPHOS via Quaternary Phosphonium Derivative



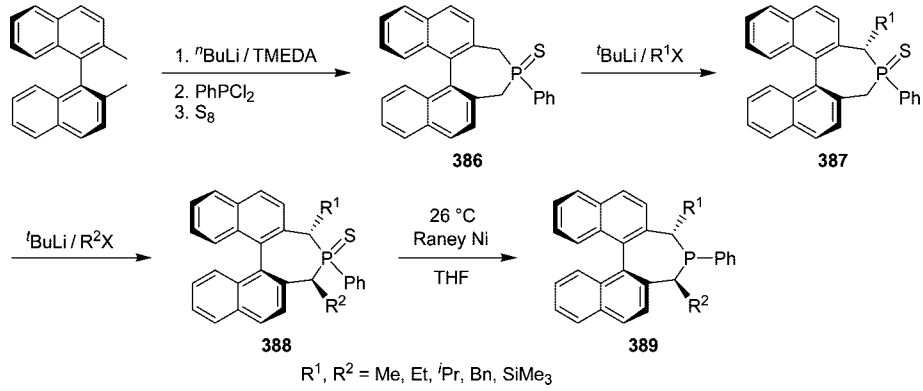
Scheme 130. Synthesis of a Pd(II) Complex Containing Dinaphthophosphepine Derivative



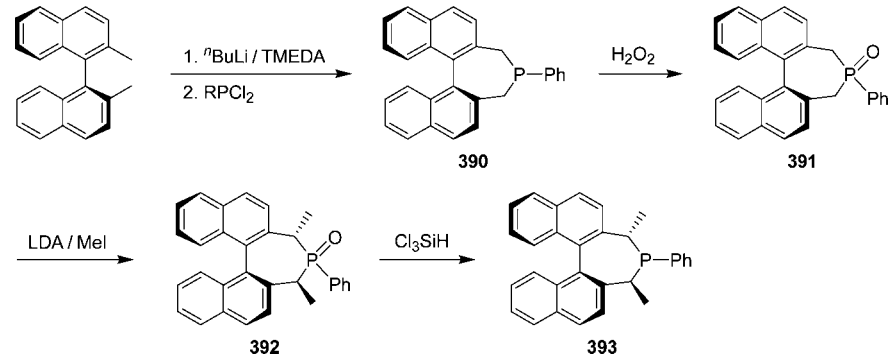
Scheme 131. Synthesis of Dinaphthophosphepine Derivatives with Axial Chirality



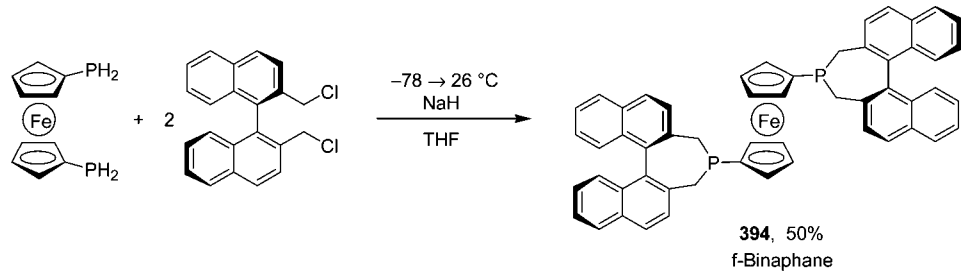
Scheme 132. Synthesis of Dinaphthophosphepine Derivatives with Axial and Central (C Stereogenic Centers) Elements of Chirality I



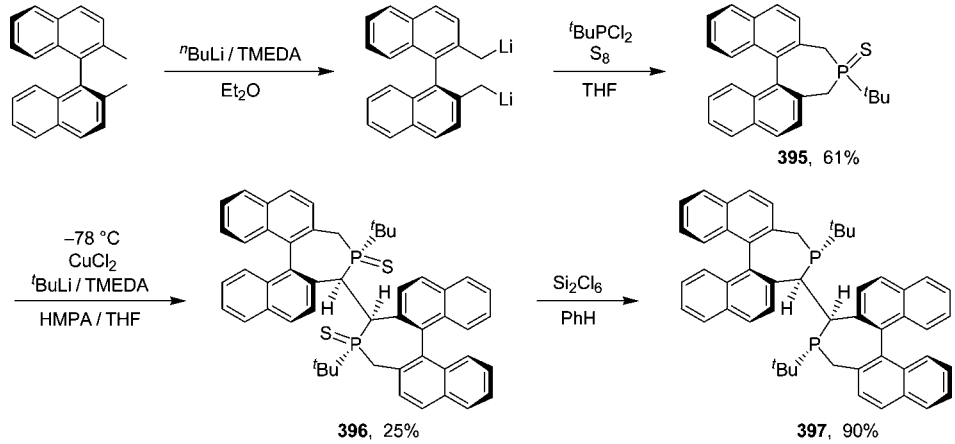
Scheme 133. Synthesis of Dinaphthophosphepine Derivatives with Axial and Central (C Stereogenic Centers) Elements of Chirality II



Scheme 134. Synthesis of Ferrocene-Based Dinaphthophosphepine



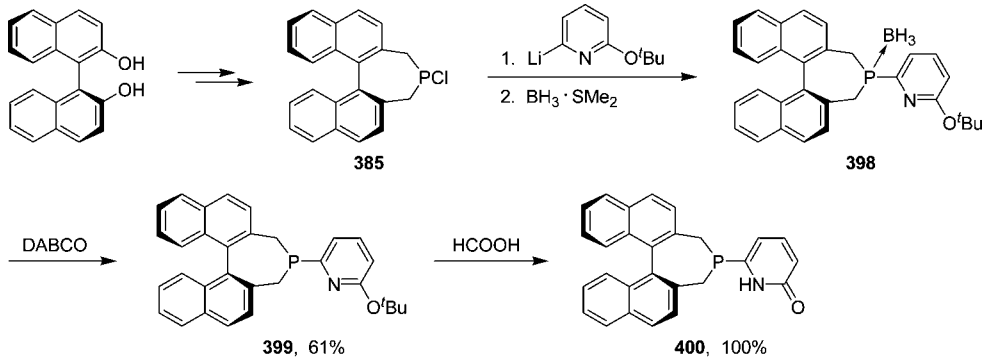
Scheme 135. Synthesis of Dinaphthophosphepine Derivatives with Axial and Central (P and C Stereogenic Centers) Elements of Chirality III



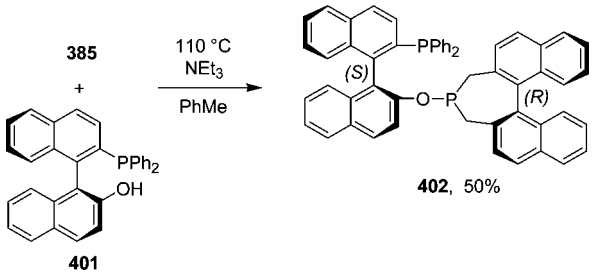
Similarly, the dilithiated compound was reacted with Et_2NPCl_2, resulting in *P*-diethylaminophosphepine derivative (**384**), which provided the P−Cl compound in a facile substitution. The variety of target compounds, the *P*-alkyl/aryl-dinaphthophosphepines (**382**), were synthesized either in the reaction of the P−Cl derivative (**385**) with Grignard reagent or that of the dilithiated intermediate with the corresponding dichlorophosphine (Scheme 131).[147−150]

2,2′-Dimethyl-1,1′-binaphthyl gave the *P*-phenyldinaphthophosphepine sulfide derivative (**386**) in the reaction

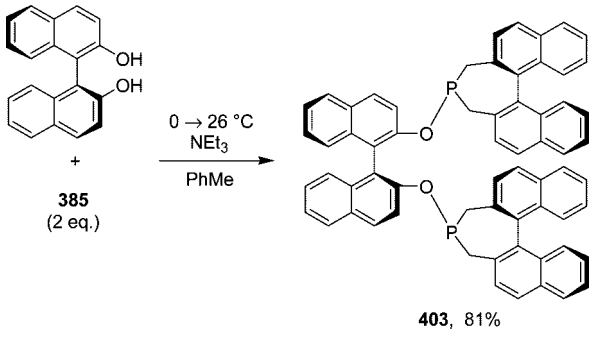
Scheme 136. Synthesis of a Dinaphthophosphepine Derivatives



Scheme 137. Synthesis of a Binaphthyl-Based P−P Heterobidentate Ligand



Scheme 138. Synthesis of a Binaphthyl-Based Diphosphinite Ligand



with dichlorophenylphosphine and sulfur. Consecutive diastereoselective alkylation at the benzylic positions resulted in a monodentate phosphine ligand containing both the axial and central elements of chirality (**389**) (Scheme 132).[151]

The analogous oxide (**391**) was also methylated at the two benzylic positions, yielding *P*-phenyl-2,7-dimethyldinaphthophosphepine (**393**) (Scheme 133).[152]

The bis(primary phosphine), 1,1′-diphosphinoferrocene, was converted to the corresponding bis(phosphepine)ferrocene derivative (**394**) by using 2,2′-bis(chloromethyl)-1,1′-binaphthyl as chiral building block (Scheme 134).[153]

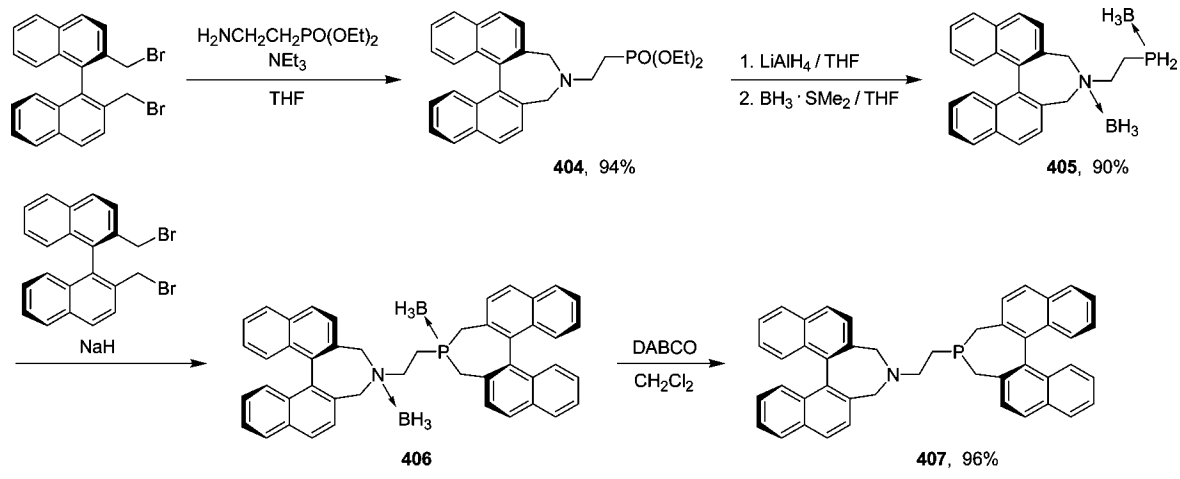
The phosphepine sulfide (**395**), obtained from the dilithiated binaphthyl precursor, was homocoupled at the benzylic positions, resulting in a homobidentate ligand (**397**) with axial and central (C, P) elements of chirality (Scheme 135).[154]

Optically active 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) as an easily available chiral building block was used for the synthesis of the *P*-chlorobinaphthophosphepine (**385**), which was used as a key intermediate either in the coupling reaction with 2-pyridyl lithium (Scheme 136)[74,147,155] or in the coupling with 2-diphenylphosphino-2′-hydroxy-1,1′-binaphthyl (Scheme 137).[156−158] In the latter case, a phosphine−phosphinite type heterobidentate ligand (**402**) was obtained.

When *P*-chlorobinaphthophosphepine derivative was used in 2-fold excess to BINOL, a bis(phosphinite) type ligand with three binaphthyl moieties (**403**) was obtained (Scheme 138).[159]

Heterobidentate binaphthyl-based ligands with *P,N*-donors (**405**) were synthesized by using diethyl 2-aminoethylphosphonate. The 2,2′-bis(bromomethyl)-1,1′-binaphthyl was reacted with both the amino- and the phosphino moieties, yielding dihydroazepine and the dihydrophosphepine ring (**407**), respectively (Scheme 139).[160] The *P,N*-heterobidentate ligands (Figure 6) with

Scheme 139. Synthesis of a Binaphthyl-Based *P,N*-Heterobidentate Ligand



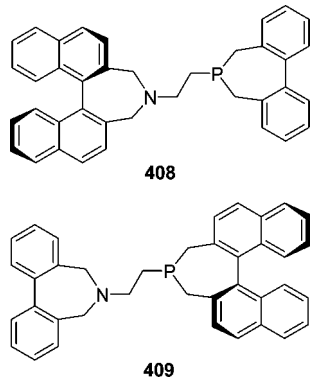
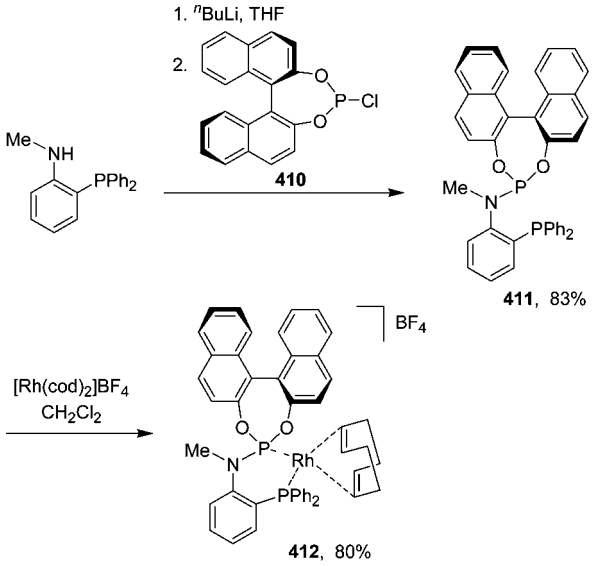
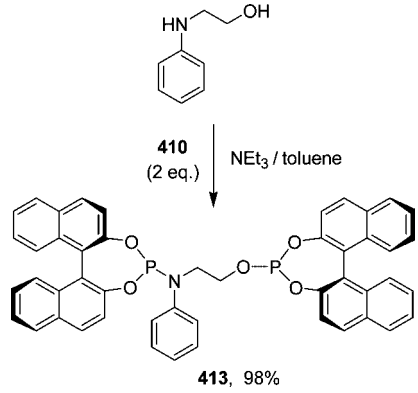


Figure 6. *P*−*N*-heterobidente ligands with binaphthyl and biphenyl moieties.

Scheme 140. Synthesis of a Rh(I) Complex Containing a Phosphine−Phosphoramidate Ligand



Scheme 141. Synthesis of a Binaphthyl-Based Phosphite−Phosphoramidate Ligand



binaphthyl−biphenyl moieties (**408**, **409**) were synthesized by using the same strategy.[161]

The *P*-chlorobinaphthodioxaphosphepine chiral building block (**410**) was coupled either to 2-diphenylphosphino-*N*-methylaniline (Scheme 140) or, in 2-fold excess, to *N*-(2-hydroxyethyl)aniline (Scheme 141), yielding **411** and **413**, respectively. The phosphine−phosphoramidate bidentate ligand was reacted with the $[Rh(cod)_2]BF_4$ precursor, and the $[Rh(P-P)(cod)]BF_4$ ionic complex (**412**) was isolated.[161]

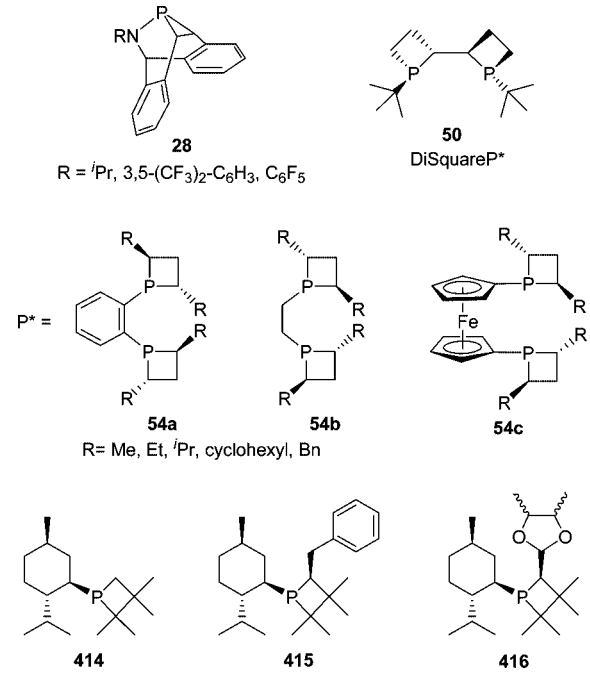


Figure 7. Three- and four-membered *P*-heterocyclic ligands used most frequently in transition metal catalyzed reactions.

3. Transition Metal Catalyzed Homogeneous Catalytic Reactions in the Presence of P-Heterocyclic Ligands

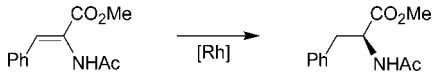
The various *P*-ligands, primarily phosphines, were used in the variety of homogeneous catalytic reactions.[162] Since the present paper is focused only to *P*-heterocycles, their recent catalytic applications will only be mentioned, and for comparison, some milestones of the previous homogeneous catalytic results will also be discussed.

Although most types of homogeneous reactions catalyzed by transition metal−*P*-heterocycles catalysts tend to be summarized, comparisons and some deeper insight will be given only on most investigated benchmark reactions such as asymmetric hydrogenation of dehydroamino acid derivatives, itaconic acid derivatives, or hydroformylation of styrene.

Asymmetric hydrogenation, as the most studied homogeneous catalytic reraction, plays an important role in synthetic chemistry. The continuous development of enantiomerically pure *P*-ligands is a key to the generation of chiral centers selectively. A wide variety of substrates, leading to chiral compounds with pharmaceutical or agrochemical interest or to simple chiral units used as a chiral building block, were used mainly in rhodium- and ruthenium-catalyzed hydrogenations. The efficiency of chiral monodentate ligands, among them various *P*-heterocycles, was shown in a review on asymmetric hydrogenation.[163]

The following subchapter is organized as above, i.e., the catalytic results are arranged according to the *P*-heterocycles of different ring sizes. Although most standard reactions were tested with similar substrates (acetamido acrylates in asymmetric hydrogenation, styrene for carbonylation reactions, etc.), the catalysts and reaction conditions are varied in wide range and are detailed in the tables only. Therefore, when basic homogeneous catalytic reactions are depicted, no details on ligand structure and conditions will be mentioned. In the case of more specific substrates, the catalytic features are given in the text (see Figure 7).

Scheme 142. Rhodium-Catalyzed Hydrogenation of Methyl α-Acylamidocinnamate



3.1. Homogeneous Catalysis Including 3- and 4-Membered *P*-Heterocyclic Ligands

BABAR-Phos type stable phosphiranes (**28**), possessing the PC_2 ring as a part of a polycyclic framework, were used for the synthesis of platinum(0) complexes, which proved to be active hydrosilylation catalyst precursors.[20]

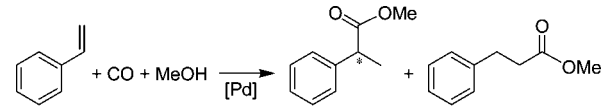
2,2′-Diphosphetanyl derivative (**50**) was used as ligand in highly enantioselective rhodium-catalyzed hydrogenation of α-acylamido acrylates and cinnamates (Scheme 142, Table 1).[30]

Rhodium complexes of 1,1′-bis(phosphetano)ferrocenes (**54c**) were used in enantioselective hydrogenation of various unsaturated substrates such as acetamido acrylates and dimethyl itaconate.[164] The analogous phenylene- and ethylene-based ligands (**54a** and **54b**, respectively) have shown an unusual increase of the optical yields at high hydrogen pressures, especially in case of the cyclohexyl-substituted **54b**.[165]

The ruthenium and rhodium complexes of 1,1′-bis(phosphetano)ferrocenes (**54c**) were used in catalytic hydrogenation of *β*-ketoesters and *N*-acetamidocinnamates, respectively, with moderate to high enantioselectivities.[166]

The use of the same ferrocene-based (FerroTANE) ligands (**54c**) resulted in high ee's in the enantioselective hydrogenation of various prochiral alkenes.[167] While excellent ee's were obtained with Me- and Et-substituted ligands, the application of more bulky substituents resulted in low ee's. Furthermore, Et−FerroTANE ligand (**54c**, R = Et) proved to be more efficient for amido itaconate-type substrate than the Et−DuPHOS (**432**) ligand with 2,5-diethylphospholane moieties (see also section 3.2, Table 2).

Scheme 143. Palladium-Catalyzed Hydromethoxycarbonylation of Styrene



An efficient asymmetric hydrogenation of 2-methylene–succinic acid hemiamide was developed by using the same type of ligand in rhodium catalysts.[168] Again, the increase of the bulkiness of the R group (Et vs *i*Pr) led to lower ee's.

An opposite trend was observed in rhodium-catalyzed asymmetric hydroformylation of styrene and allyl cyanide. The *tert*-butyl substituted FerroTANE-based catalyst provided higher ee's than that of the methyl-substituted ligand.[169]

Electron-rich 2,4-disubstituted phosphetanes (**54a**−**54c**) were used in ruthenium- and rhodium-catalyzed asymmetric hydrogenations. The stereochemical outcome of the reactions was rationalized on the basis of a quadrant-based stereochemical model. Dihydrojasmonate of industrial importance was synthesized in the presence of new chiral cationic ruthenium complexes.[170]

Palladium complexes bearing chiral phosphetanes (**414**−**416**) proved to be active catalysts in hydromethoxycarbonylation of vinylarenes (Scheme 143). Excellent regioselectivities (up to 99%) and moderate ee's were obtained. Phosphetane derivatives provided higher ee's (50% as highest ee in case of 4-methoxystyrene) than the *P*-phenyl-2,5-dimethylphospholane (**186**, see section 3.2, Table 3).[74]

A catalytically active palladium−monodentate phosphetane system was studied by NMR under methoxycarbonylation conditions. It was found that, unlike to the widely used Pd−diphosphine (e.g., bdpp) system, the styrene insertion step into the Pd−H bond is irreversible.[171]

Table 1. Homogeneous Catalysis Including Transition Metal−Phosphetane Ligand Catalytic Systems

reaction	substrate	catalyst precursor	ligand (L)	ee [%]	temp. [°C] (pressure)	conv. (r. time)	ref
C=C hydrogenation	acetamido cinnamate acetamido acrylate	$[Rh(L)(NBD)]PF_6$	**50**	>99	20 (1 bar)	100 (1 h)	30
			50	>99	20 (1 bar)	100 (1 h)	
C=C hydrogenation	acetamido acrylate	$[Rh(COD)_2]OTf$	**54c** (R = Me)	69	20 (4 bar)	100 (18 h)	164
			54c (R = *i*Pr)	94	20 (4 bar)	100 (1 h)	
	dimethyl itaconate		**54c** (R = Me)	91	20 (4 bar)	100 (1 h)	
			54c (R = *i*Pr)	66	20 (4 bar)	100 (1 h)	
C=C hydrogenation	acetamido cinnamate	$[Rh(COD)_2]OTf$	**54a** (R = *i*Pr)	81	20 (10 bar)	not mentioned	165
		$[Rh(COD)_2]OTf$	**54a** (R = *i*Pr)	84	20 (40 bar)		
			54a (R = *i*Pr)	90	20 (100 bar)		
			54b (R = cHex)	15	20 (10 bar)		
			54b (R = cHex)	58	20 (40 bar)		
			54b (R = cHex)	70	20 (100 bar)		
C=C hydrogenation	dimethyl itaconate	$[Rh(L)(COD)]BF_4$	**54c** (R = Me)	91	20	100 (<1 h)	167
			54c (R = Et)	98	20		
			54c (R = Pr)	97	20		
			54c (R = *i*Pr)	78	20		
			54c (R = *t*Bu)	1	20		
C=C hydrogenation	amido itaconate	$[Rh(L)(COD)]BF_4$	**54c** (R = Et)	98	20	100 (1 h)	167
			432 (R = Et)	85	20	5 (1 h)	
C=C hydrogenation	2-methylenesuccinic acid amide	$[Rh(L)(COD)]BF_4$	**54c** (R = Et)	87	20 (4 bar)	>98 (2 h)	168
			54c (R = Et)	72	20 (10 bar)	>98 (0.7 h)	
			54c (R = *i*Pr)	83	20 (4 bar)	>98 (2 h)	
hydroalkoxycarbonylation	styrene	$PdCl_2(L)_2$	**414**	0	70	82 (24 h)	74
	styrene		**415**	6	70	99 (24 h)	
	styrene		**416**	29	70	26 (24 h)	
	4-methoxystyrene		**414**	50	60	71 (24 h)	
	4-methylstyrene		**414**	25	60	33 (24 h)	
hydroformylation	styrene	$[Rh(acac)(CO)_2]$	**54c** (R = Me)	55	80 (10 bar)	10 (3 h)	169
	styrene		**54c** (R = *t*Bu)	18	80 (10 bar)	9 (3 h)	
	allyl cyanide		**54c** (R = Me)	73	80 (10 bar)	31 (3 h)	
	allyl cyanide		**54c** (R = *t*Bu)	53	80 (10 bar)	28 (3 h)	

Table 2. Homogeneous Catalytic Hydrogenation of C=C Double Bonds in the Presence of Transition Metal−Phosphol (Phospholane) Ligand Catalytic Systems

substrate	catalyst precursor	ligand (L)	ee [%]	temp. [°C] (pressure)	conv. (r. time [h])	ref.
itaconic acid	$[Rh(L)_2(COD)]BF_4$	**167**	52	20 (1 bar)	100 (<1 h)	69
dimethyl itaconate	$[Rh(L)_2(COD)]BF_4$	**167**	39	20 (1 bar)	100 (<1 h)	
acetamido cinnamic acid	$[Rh(L)_2(COD)]BF_4$	**167**	68	20 (1 bar)	100 (<1 h)	
acetamido cinnamate	$[Rh(L)_2(COD)]BF_4$	**167**	82	20 (1 bar)	100 (<1 h)	
acetamido cinnamate	$[Rh(COD)_2]BF_4$	**418**	83	20 (1 bar)	100 (1.5 h)	
itaconic acid	$[Rh(L)(COD)]BF_4$	**201**	82	20 (1 bar)	100 (<1 h)	77
		202	55	20 (1 bar)		
acetamido cinnamic acid		**201**	46	20 (1 bar)		
		202	43	20 (1 bar)		
acetamido cinnamate		**201**	81	20 (1 bar)		
		202	51	20 (1 bar)		
acetamido acrylate	$[Rh(COD)_2]BF_4$	**424**	32	25 (1 bar)	100 (0.06)	73
		425	51		100 (1.33)	
		180	9		100 (1.25)	
		181	16		100 (16)	
acetamido cinnamate	$[Rh(COD)_2]BF_4$	**421**	65	25 (1 bar)	100 (1 h)	79
acetamido acrylate			78	25 (1 bar)	100 (0.1 h)	
dimethyl itaconate	$[Rh(L)(NBD)]BF_4$	**222**	>99	20 (1 bar)??	100 (1 h)	82
		223-1	25	20 (1 bar)??	12 (1 h)	
		223-2	86	20 (1 bar)??	53 (1 h)	
β-acetamido butanoate (*cis*)	$[Rh(L)_2]BF_4$	**247b**	93.6	25 (1 bar)	100 (1 h)	91
		247e	89.9	25 (1 bar)	100 (1 h)	
β-acetamido butanoate (*trans*)		**247b**	99.5			
		247e	99.7			
acetamido acrylate	$[Rh(NBD)L][BF_4]$	**435**	95	20 (2 bar)	100(0.25 h)	89
acetamido acrylate	$[Rh(NBD)L][BF_4]$	**244**	98	20 (2 bar)	100(0.25 h)	
acetamido cinnamate	$[Rh(COD)L][BF_4]$	**435**	84	20 (2 bar)	100(0.25 h)	
acetamido cinnamate	$[Rh(COD)L][BF_4]$	**244**	95	20 (2 bar)	100(0.25 h)	
acetamido cinnamate	$[Rh(L)_2(COD)]BF_4$	**420** (R = Me)	31	20 (1 bar)	100 (24 h)	76
		420 (R = *i*Pr)	75	20 (1 bar)	100 (0.8 h)	
		420 (R = Bn)	26	20 (1 bar)	100 (24 h)	
acetamido cinnamate	$[Rh(NBD)L][SbF_6]$	**239**	>99	20 (1.5 bar)	100 (12 h)	88
acetamido acrylate		**239**	>99	20 (1.5 bar)	100 (12 h)	
dimethyl itaconate		**239**	>99	20 (1.5 bar)	100 (12 h)	
dimethyl itaconate		**236**	99	20 (1.5 bar)	100 (12 h)	
α-acetoxy-4-methoxystyrene		**239**	96	20 (1.5 bar)	100 (12 h)	
α-acetoxy-4-methoxystyrene		**236**	80	20 (1.5 bar)	100 (12 h)	
acetamido cinnamate	$[Rh(COD)L][BF_4]$	**439** (R = Me)	94.4	25 (1 bar)	100 (6 h)	93
acetamido cinnamate		**439** (R = Me)	94.9	35 (5 bar)	100 (6 h)	
acetamido acrylate		**439** (R = Me)	98.7	25 (1 bar)	100 (6 h)	
acetamido acrylate		**439** (R = Me)	98.2	35 (5 bar)	100 (6 h)	
2-methylenesuccinic acid amide	$[Rh(L)(COD)]BF_4$	**432** (R = Et)	93	0 (4 bar)	33 (18 h)	168
		432 (R = Et)	94	20 (4 bar)	>98 (4 h)	
		432 (R = Et)	96	45 (4 bar)	>98 (2 h)	

Table 3. Homogeneous Catalytic Carbonylations (Hydroformylation and Hydroalkoxycarbonylation) in the Presence of Transition Metal−Phosphol (Phospholane) Ligand Catalytic Systems

reaction	substrate	catalyst precursor	ligand (L)	ee [%]	temp. [°C] (pressure)	conv. [%] (r. time [h])	ref
hydroformylation	styrene	$PtCl_2(L)_2$	**100a**	18	20 (100 bar)	14 (72 h)	48
			100a	0	60 (100 bar)	12 (23 h)	
			100b	0	20 (100 bar)	4 (72 h)	
			100b	0	60 (100 bar)	10 (24 h)	
			100c	12	20 (100 bar)	64 (94 h)	
			100c	2	60 (100 bar)	99 (5 h)	
			103b	0	20 (100 bar)	5 (72 h)	
			103c	2	20 (100 bar)	81 (72 h)	
hydroformylation	styrene	$[Rh(acac)(CO)_2]$	**432** (R = Me)	44	80 (10 bar)	10 (3 h)	169
			432 (R = Et)	52	80 (10 bar)	14 (3 h)	
			432 (R = *i*Pr)	83	80 (10 bar)	15 (3 h)	
			434 (R = Me)	43	80 (10 bar)	8 (3 h)	
			434 (R = Et)	55	80 (10 bar)	10 (3 h)	
			434 (R = *i*Pr)	82	80 (10 bar)	11 (3 h)	
			434 (R = Ph)	94	80 (10 bar)	57 (3 h)	
	allyl cyanide	$[Rh(acac)(CO)_2]$	**432** (R = Me)	32	80 (10 bar)	42 (3 h)	
			432 (R = Et)	35		49	
			432 (R = *i*Pr)	82		55	
			434 (R = Me)	37		36	
			434 (R = Et)	49		40	
			434 (R = *i*Pr)	83		48	
			434 (R = Ph)	90		96	
hydroformylation	1-octene	$RhCl(CO)(L)_2$	**417** (R = Ph)		90 (10 bar)	28 (4 h)	66
			417 (R = *t*Bu)		90 (10 bar)	91 (4 h)	
hydromethoxycarbonylation	styrene	$PdCl_2(L)_2$	**186**	4	90 (20 bar)	55	74
		$PdCl_2(L)_2$	**186**	3	90 (35 bar)	81	
		$PdCl_2(L)_2$	**186**	0	90 (50 bar)	97	

High-level ab initio calculations were used to determine the propensities of various phosphetanes toward radical ring-opening polymerization. It was found that, in the case of 1-*tert*-butylphosphetane, homolytic substitution of the propagating radical with *tert*-butyl substituents at phosphorus will be competitive with the propagation. The calculations also suggest that, for chiral phosphetanes, the ring-opening reaction is enantioselective at P and the polymer is expected to be isotactic.[172]

3.2. Homogeneous Catalysis Including Five-Membered *P*-Heterocyclic Ligands

The application of phospholes in homogeneous catalysis turned up already in the early 1980s, when the dibenzophospholyl moiety and various chiral skeletons of natural origin were merged and resulted in ligands showing excellent performance in asymmetric hydroformylation. Rigid structures like that of the DIOP family, as well as the ability of forming 7-membered platinum−diphosphine chelates, were kept in bicyclooctane (BCO)-based ligands.

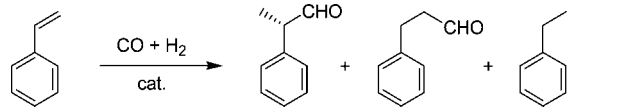
As in the case of several other enantioselective homogeneous reactions, DIOP as chiral bidentate phosphine with C_2 symmetry was used also in platinum-catalyzed enantioselective hydroformylation.[173] In spite of the high ee's obtained in hydrogenation of various C=C, C=O, and C=N double bonds with rhodium catalysts, rather low enantioselectivity (26%), accompanied by low branched selectivity as well, has been obtained in enantioselective hydroformylation of styrene. Much better enantioselections were achieved by tuning of the ligand, i.e., by the substitution of the diphenylphosphino group either with 5*H*-benzo[b]phosphoindole (dibenzophospholyl, DBP) or binaphthophospholyl (BNP) moieties.[174] The ee's were increased to 64 and 44%, respectively, accompanied by the prevailing formation of the branched aldehyde regioisomer. It is worth noting that the polymer-bound DBP−DIOP gave nearly the same ee as DIOP itself.[175]

A similar tendency was observed with the BCO ligands possessing diphenylphosphino (BCO−DPP) and dibenzophospholyl (BCO−DBP) groups. The BCO−DBP ligand provided much higher ee (85 vs 25%) and higher regioselectivity toward the chiral branched aldehyde (80 vs 43%) than the corresponding parent diphenylphosphino ligand in enantioselective hydroformylation of styrene (Scheme 144).[176]

On the basis of the previous observations made on other ligands (DIOP, BDPP), the diphenylphosphino moieties of BPPM have been substituted for dibenzophospholyl moieties.[177] The BPPM−DBP−platinum catalytic system gave virtually complete enantioselectivities by conducting the hydroformylation in triethyl-*ortho*-formate, and additionally, the regioselectivity toward branched aldehyde increased considerably (see Figures 8−10).

The enantiopure secondary phospholane, 2,5-diphenylphospholane (**167**), and its oxide (**418**) were used as ligands in rhodium-catalyzed enantioselective hydrogenation of vari-

Scheme 144. Enantioselective Hydroformylation of Styrene



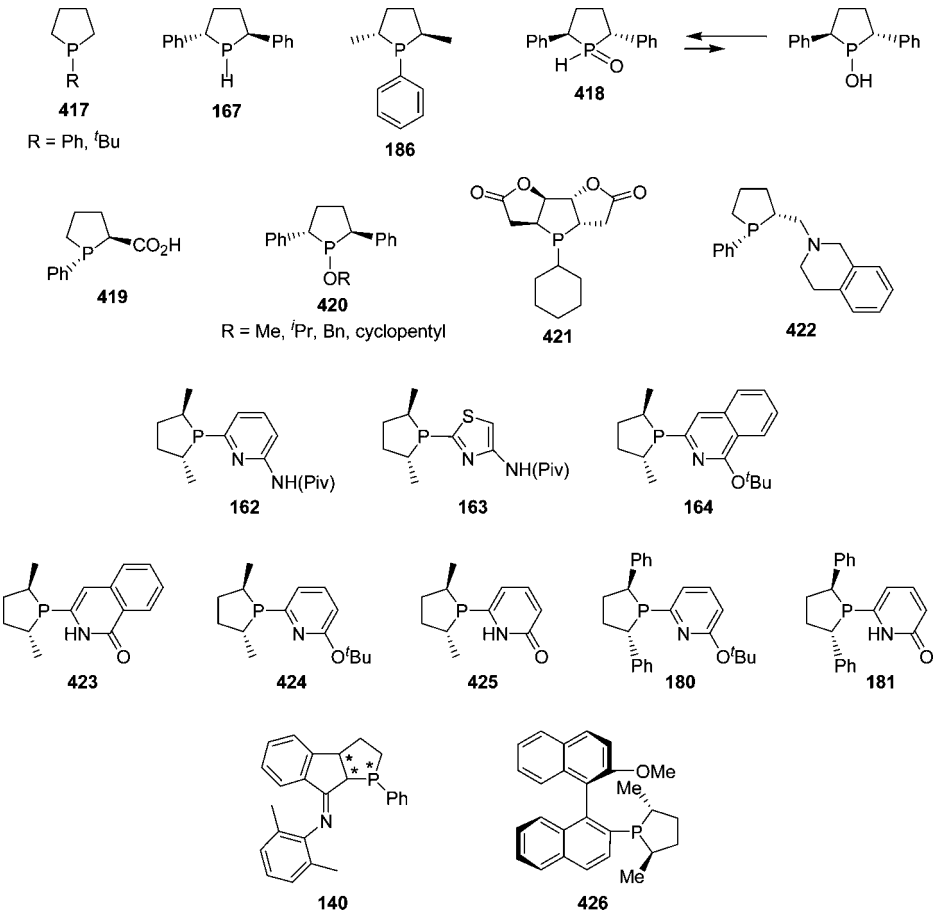


Figure 8. Five-membered *P*-heterocyclic ligands containing one P-donor used most frequently in transition metal catalyzed reactions.

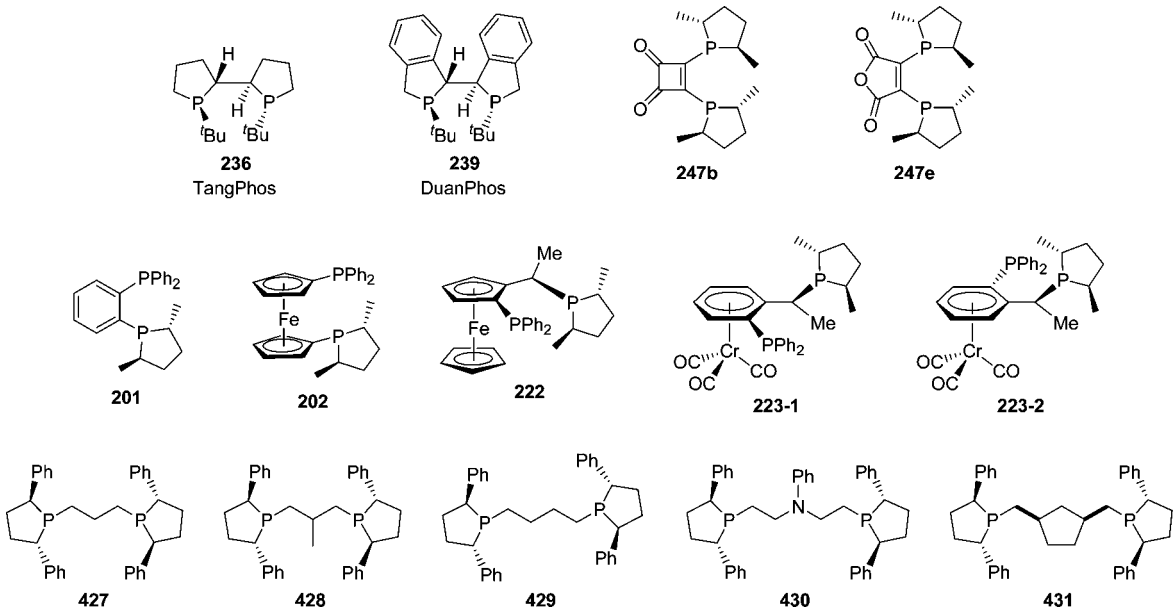


Figure 9. Five-membered *P*-heterocycles with two phosphorus donors used most frequently in transition metal catalyzed reactions I.

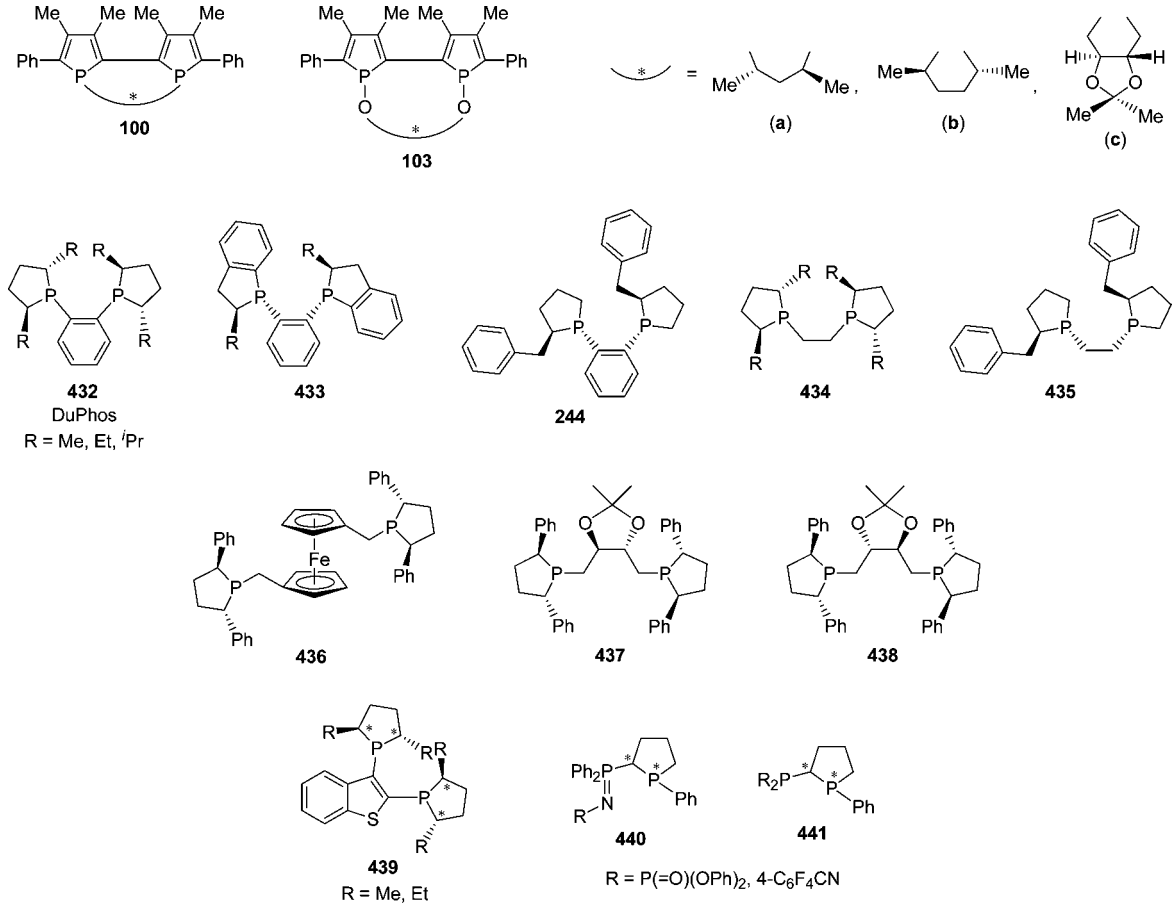


Figure 10. Five-membered *P*-heterocycles containing two phosphorus donors used most frequently in transition metal catalyzed reactions II.

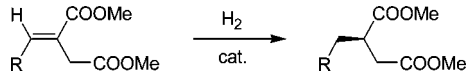
ous olefins including itaconates, α-acetamidoacrylates, and cinnamates, as well as α-acetoxystyrene. Comparing to the most efficient catalysts, moderate ee's but high catalytic activities were obtained.[69]

1-Alkoxy-2,5-diphenylphospholane (**420**) and its phospholanium salts were used in rhodium-catalyzed asymmetric hydrogenation of α-acetamido cinnamates and α-acetamidostyrenes. Moderate and low ee's were obtained especially compared to bidentate diphosphine and bisphospholane ligands.[76]

A highly electron-donating chiral bis(phospholane) ligand (DuanPhos, **239**) formed highly active catalysts for rhodium-catalyzed enantioselective hydrogenation. High enantioselectivities (99% ee or even higher) were obtained for different types of functionalized prochiral alkenes.[88]

Recently, the Rostock group with its industrial partner developed a modular bisphospholane ligand family (for example, **247b**, **247e**) showing exceptionally high activity and enantioselectivity for alkene and ketone reduction.[178,91]

Scheme 145. Enantioselective Hydrogenation of Itaconic Acid Derivatives



These ligands, belonging to the CatASium M series, were used for the synthesis of chiral 2-hydroxy-1-methylpropanoates ("Roche esters") in rhodium-catalyzed asymmetric hydrogenation of 2-hydroxymethylacrylates. ee's up to 99% were achieved in the enantioselective hydrogenation of the parent substrate, and due to a kinetic resolution phenomenon, 96% ee was achieved in the hydrogenation of the analogous 2-(arylhydroxy)methyl derivatives.[179] The same ligands were tested in "standard" enantioselective hydrogenation of methyl α-acetamidocinnamate[180] and α-acetoxyacrylates[181] in propylene carbonate.

Heterobidentate ligands bearing 2,5-dimethylphospholane and diphenylphosphino moieties (**201**, **202**) proved to be efficient in rhodium-catalyzed asymmetric hydrogenation of itaconic acid and acetamido cinnamic acid derivatives. The phenylene-based ligand (**201**) was found to be superior to the ferrocene derivative (**202**).[77]

The heterobidentate ligands with similar donor groups (**222**, **223-1**, **223-2**) were tested in enantioselective hydrogenation of dimethyl itaconate (Scheme 145, R = Me). The ferrocene-based ligand **222** was superior to arene−chromium−tricarbonyl ligands (**223-1**, **223-2**) in terms of both activity and enantioselectivity.[82]

P-Chirogenic ethylene- and 1,2-phenylene-bridged bisphospholane ligands (**435**, **244**) proved to be highly efficient in rhodium-catalyzed asymmetric hydrogenation of α- and *β*-acetamido dehydroamino acid derivatives[89] and that of the pregabalin precursor.[90]

2,5-Dimethylphospholane ligands with 1-*N*-heterocyclic substituents have shown high catalytic activities in rhodium-catalyzed hydrogenation of acetamido acrylates. Moderate ee's were obtained.[73]

Catalysts with high activity were obtained from bislactone-fused phospholane ligands and $[Rh(COD)_2]BF_4$ catalyst precursor. Optical yields of 65 and 78% were obtained with acetamido cinnamate and acrylate substrates. The use of benzyl crotonate instead of the corresponding methylester resulted in an increase in optical yields, i.e., 92% ee was obtained.[79]

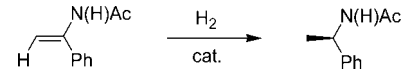
The efficiency of bisphospholanes based on a benzothiophene scaffold was shown in asymmetric homogeneous hydrogenation of acetamido cinnametes, acrylates, enamides, and itaconates. The rhodium-based systems gave ee values of up to 98.7%.[93]

The Et−DuPHOS ligand (**432**) has shown good hydrogenation activity with 2-methylenesuccinic acid amide. Interestingly, the ee's show slight increase with increasing temperature.[168]

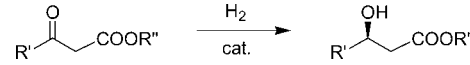
Being two of the most widely used diphosphines, 2,5-disubstituted phospholane based BPE (**434**) and DuPHOS (**432**) type ligands have shown excellent features in various enantioselective catalytic reactions, among them hydrogenations. (It is important to note that the DuPHOS[182−185] and BPE[186,187] ligands are named with reference to the R-substituents on the phospholane ring; thus, when R = Et, the ligands are called Et−DuPHOS and Et−BPE, respectively.)

As was reported more than a decade ago, a large-scale capacity of the BPE−Rh catalytic system was observed in enantioselective hydrogenation of enamides and ketones. (*R,R*)-Me−BPE−Rh catalyst reduced acylated α-arylenamides in high (>95%) ee (Scheme 146).[188]

Scheme 146. Enantioselective Hydrogenation of α-Acetamidostyrene



Scheme 147. Enantioselective Hydrogenation of a *β*-Ketoester



A chiral $RuBr_2$(*i*Pr−BPE) complex proved to be a highly effective catalyst for asymmetric reduction of C=O bonds. A variety of *β*-ketoesters were hydrogenated with high ee's (up to 98%) (Scheme 147).[189]

Similarly, the fine-tuning of the parent DuPHOS ligand resulted in ligands that show superior enantioface discriminating abilities in various reactions, e.g., in enantioselective hydrogenation of α-enamides to produce α-amino acid derivatives (Schemes 148 and 149),[80,190,191] and in enantioselective hydrogenation of the C=N group in the presence of Rh−Et−DuPHOS (**432**, R= Et) catalyst (Scheme 150).[183]

These catalysts are robust and tolerate a broad range of solvents and organic functionalities within the substrate. Their rhodium complexes are also unique in possessing high hydrogenation activity and enantioselectivity in *β*,*β*-disubstituted α-enamides (tetrasubstituted ethylenes). The (*S,S*)-Et−DuPHOS−Rh catalyst gave less than 2% overreduction and excellent isolated yields.

Recently, the first gold asymmetric hydrogenation catalyst was reported by using Me−DuPHOS as chiral ligand.[192] The high reactant control was shown by the fact that the highest stereocontrol was obtained with the substrate possessing the 2-naphthylidenesuccinate moiety.

The (*S,S*)-Me−DuPHOS−Rh catalyst produced chiral allyl alcohols in the asymmetric hydrogenation of enol esters. Under these conditions, the initially formed chiral propargylic acetate was subsequently reduced to yield *Z*-allylic acetate (Scheme 151).[187]

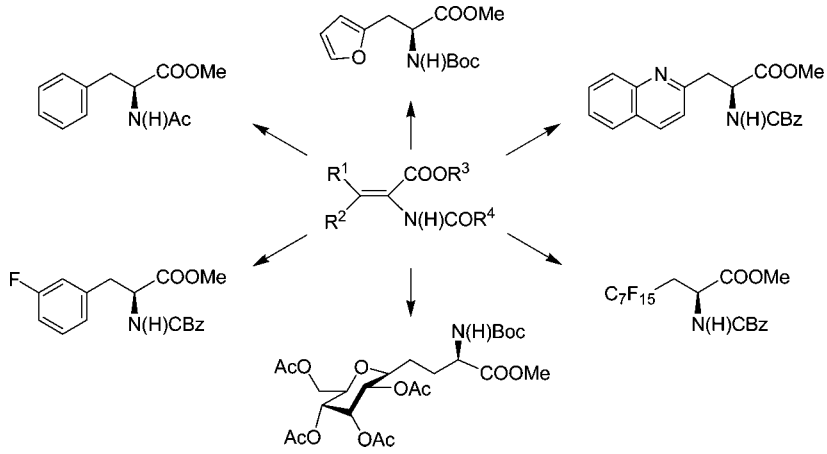
The chiral hydroxyphospholanes derived from D-mannitol (MANPHOS) were used in highly enantioselective rhodium-catalyzed asymmetric hydrogenation of various kinds of functionalized olefins such as dehydroamino acid derivatives and itaconic acid derivatives. An interesting feature of this 3,4-dihydroxyphospholane-based ligand is that excellent ee's (>99%) were recorded also in water as solvent.[193]

1-*tert*-Bu- and Ph-substituted phospholanes (**417**), as well as phoshinanes and phosphepanes (see below), were used as ligands in rhodium-catalyzed hydroformylation of 1-octene (Scheme 152), with the overall conclusion that no special effect of the rings on the hydroformylation was observed. Interestingly, the application of phosphepane-based ligands resulted in high isomerization but low hydroformylation activity.[66]

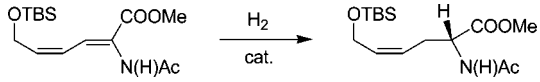
The hydroformylation activity of various platinum and rhodium complexes containing 1-arylphospholes, including 2,4,6-trialkylphenylphospholes of various sterical hindrance on the aryl moiety, were used in the hydroformylation of styrene as test substrate.[194,195] Although the activity of the platinum−phosphole−tin(II)chloride in situ systems were behind most of the platinum−diphosphine systems, excellent regioselectivities toward branched aldehydes were obtained.

Chiral diphosphine and diphosphinite ligands derived from 2,2-biphosphole (**100** and **103**, respectively) were used in platinum-catalyzed enantioselective hydroformylation of

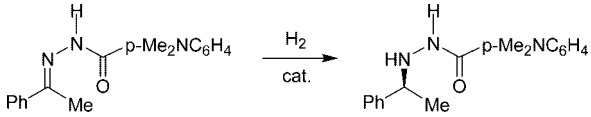
Scheme 148. Enantioselective Hydrogenation of α-Acetamido Unsaturated Esters I



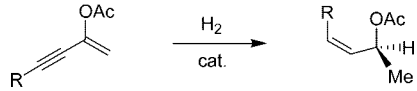
Scheme 149. Enantioselective Hydrogenation of α-Acetamido Unsaturated Esters II



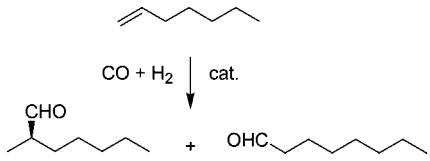
Scheme 150. Enantioselective Hydrogenation of a C=N Double-Bond in a Hydrazone Derivative



Scheme 151. Enantioselective Hydrogenation of an Enine Derivative



Scheme 152. Hydroformylation of 1-Octene



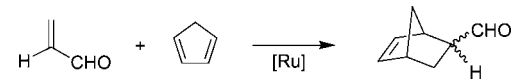
styrene. The high chemoselectivities were accompanied by moderate to high regioselectivities toward aldehydes and low enantioselectivities.[48]

Chiral phospholanes belonging to the DuPHOS and BPE ligand families were tested in rhodium-catalyzed enantioselective hydroformylation of styrene and allyl cyanide.[169] One of the BPE ligands (**434** (R = Ph)) was identified as the most efficient ligand in asymmetric hydroformylation, which gives excellent regio- and enantioselectivities, as well as high turnover rates. These features make these ligands suitable also for industrial application.

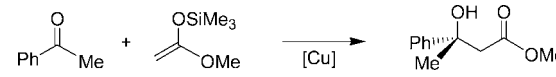
The palladium complex of the chiral monodentate phospholane ligand **186** was used in asymmetric methoxycarbonylation of styrene. Although low ee's were obtained by using this catalyst compared to phosphetanes (see above), the regioselectivity toward branched isomer was high. Interestingly, the reaction is also accompanied by the formation of some α-methoxyethylbenzene (in the range of 5−30%; see Table 4).[74]

The half-sandwich ruthenium(II) complexes containing chiral 2-diphenylphosphino-1-phenylphospholane ligand were

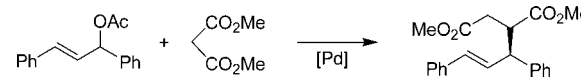
Scheme 153. Ruthenium-Catalyzed Cycloaddition



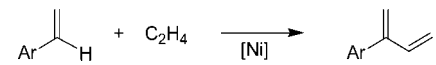
Scheme 154. Copper-Catalyzed Enantioselective Aldol Reaction



Scheme 155. Palladium-Catalyzed Allylic Substitution



Scheme 156. Nickel-Catalyzed Hydrovinylation



also reported as active catalysts in asymmetric Diels−Alder cycloaddition reactions (Scheme 153).[62]

A similar half-sandwich ruthenium(II) catalyst with tricyclic β-iminophosphine **140** was used in Diels−Alder cycloaddition. The reaction goes with moderate diastereoselectivity and complete lack of enantioselectivity.[63]

Bisphospholane ligands *i*Pr−DuPHOS and Ph−BPE families were used in copper-catalyzed enantioselective aldol reaction to ketones (Scheme 154), and good ee's (up to 66%), related to the extremely difficult carbon−carbon bond formation, were obtained.[92]

The novel *P,N* ligands both with *P*-proline (**419**) and tetrahydroisoquinoline backbones were tested in palladium-catalyzed allylic substitutions (Scheme 155). On the basis of the catalytic results, the *P*-monodentate type coordination of the ligand instead of *P,N*-heterobidentate coordination was suggested.[85,86]

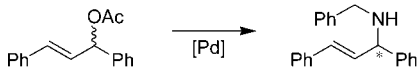
It was proved that the introduction of a chiral phospholane moiety to the axially chiral binaphthyl unit (instead of the diphenylphosphino group of MOP) in **426** has no effect on the enantioselectivity of hydrovinylation (Scheme 156).[81]

New chiral phospholanes possessing various heterocycles attached to phosphorus were tested in palladium-catalyzed allylic amination (Scheme 157), and high ee's (up to 99%) were obtained. Especially high enantioelectivities were obtained by using dimethylphospholane with isoquinoline type *P*-substituent (**164**), which cannot aggregate with a second ligand at the palladium center by hydrogen bonding because of its *O-tert*-butyl protection.[68]

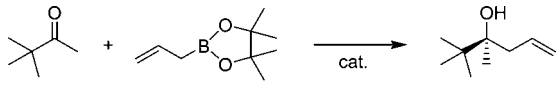
Table 4. Miscellaneous Homogeneous Catalytic Reactions in the Presence of Transition Metal−Phosphol (Phospholane) Ligand Catalytic Systems

reaction	substrate	catalyst precursor	ligand (L)	ee [%]	temp. [°C]	conv. (r. time [h])	ref
Diels−Alder cycloaddition	acrolein + cyclopentadiene	$[RuCl_2(L)(\eta^6\text{-p-cymene})][SbF_6]$	**440** (R = $P(O)(OPh)_2$)	9	−20	86 (46)	62
			440 (R = 4-C_6F_4CN)	7	−20	>99 (91)	
			441	13	−20	>99 (12)	
Diels−Alder cycloaddition	acrolein + cyclopentadiene	$[RuCl(L)(\eta^6\text{-arene})][SbF_6]$	**140** (arene = C_6H_6)	0	−20	92 (20 h)	63
			140 (*p*-cymene)	0	−20	99 (20 h)	
			140 (1,3,5-$Me_3C_6H_3$)	0	−20	90 (20 h)	
		$[Ru(MeCN)(L)(\eta^6\text{-p-cymene})][SbF_6]_2$	**140** (arene = C_6H_6)	0	−20	87 (20 h)	
			140	0	−20	89 (20 h)	
allylic amination	diphenylacetoxyprop-1-ene + benzylamine	$Pd_2(dba)_3 \cdot CHCl_3$	**162**	76	25	100 (not reported)	68
			163	20			
			164	99			
			180	8			
			181	45			
			423	91			
			424	92			
			425	83			
allylic substitution	1,3-difenil-allyl acetate	$[PdCl(\pi\text{-allyl})]_2$	**422** (*trans*)	45	0	48 (0.06)	85
			422 (*trans*)	45		95 (4)	
			422 (*cis*)	94		42 (0.06)	
			422 (*cis*)	94		99 (6)	
allylic substitution	1,3-difenil-allyl acetate	$Pd(dba)_2$	**419**	77	0	86 (6 h)	86
hydrovinylation	6-methoxy-2-vinylnaphthalene	$[(allyl)NiBr]_2$	**426** (R_aRR)	17	−45	99 (2 h)	81
			426 (S_aRR)	4	−45	97 (2 h)	
aldol reaction	acetophenone	$CuF \cdot 3PPh_3 \cdot 2EtOH$	**434** (R = Ph)	24	4	92 (1.2)	92
			427	41		86 (24)	
			428	50		53 (24)	
			429	29		86 (18)	
			430	8		65 (24)	
			431	4		73 (24)	
			436	3		83 (24)	
			437	18		100 (18)	
			438	14		95 (18)	
cyclopropanation	styrene	$Rh_2(OAc)_3(PC^*)$	**252** (R = Me)	17	36	58	95
			252 (R = CF_3)	20	40	66	

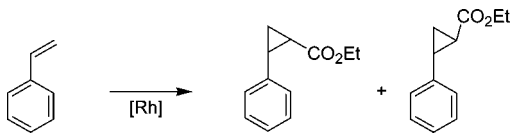
Scheme 157. Palladium-Catalyzed Allylic Amination



Scheme 158. Enantioselective Allylation of *tert*-Butylmethyl Ketone



Scheme 159. Rhodium-Catalyzed Cyclopropanation



The first catalytic enantioselective allylboration of ketones was reported by using (*S,S*)-Me−DuPHOS−Cu catalyst. The wide variety of aromatic, heteroaromatic, α,β-unsaturated, and aliphatic ketones were allylated in the presence of a rare-earth additive under ambient conditions (Scheme 158).[196]

Various chiral nitroalkanes were synthesized with excellent yields and enantioselectivities (up to 95%) in the enantioselective addition of dialkylzinc to β-nitroalkenes. A CuOTf−Me−DuPHOS catalyst in situ catalyst was used.[197]

Mono- and biscyclometalated *P*-phenylphospholane rhodium(II) complexes were tested in cyclopropanation of styrene (Scheme 159). While up to 20% ee's were obtained with dinuclear complexes with one cyclometalated ligand, the cyclometalation of a second *P*-phenyl-phospholane led to moderate to high yields and ee's up to 76% (see Figure 11 and Table 5).[95]

3.3. Homogeneous Catalysis Including Six-Membered *P*-Heterocyclic Ligands

Most homogeneous catalytic results obtained with phosphinine-based ligands were reviewed recently by Müller and Vogt.[97] This review was also focused on the synthesis and coordinating properties of this intriguing class of ligands. Therefore, only the most important preliminaries for comparison and most recent results will be discussed.

The efficiency of chiral BINOL- or TADDOL-substituted phosphinine phosphite (**447** and **448**, respectively) was demonstrated in the enantioselective hydrogenation of standard prochiral alkenes such as dimethyl itaconate and acetamidocinnamate.[97]

A series of novel phosphinines (**443**) were used in rhodium-catalyzed hydroformylation of terminal and internal olefins. It was demonstrated that the catalytic activity is mainly determined by steric parameters, and turnover frequencies up to 45 000 h^{-1} for the hydroformylation of 1-octene were determined. The branched to normal ratio was varied between 0.30 and 0.56 depending on the structure of phosphinine.[103] An excellent performance of the phoshinine-based rhodium catalysts was observed with highly substituted alkenes. Even tetrasubstituted alkenes were hydroformylated in the presence of rhodium−phosphinine systems through isomerization to terminal alkene, whereas the triphenylphosphine systems were completely inactive.

The hydroformylation of 1-octene in the presence of Rh−*P*-substituted hexahydrophosphinine (**442**) in situ

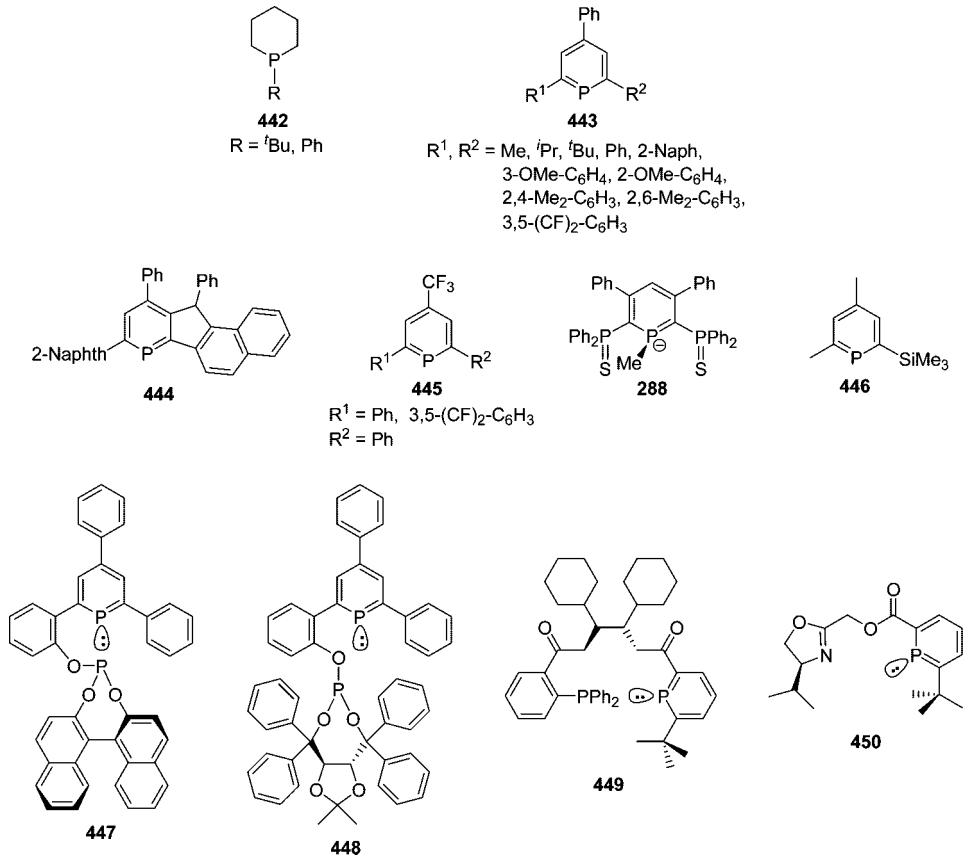


Figure 11. Six-membered *P*-heterocyclic ligands used most frequently in transition metal catalyzed reactions.

Table 5. Homogeneous Catalysis Including Transition Metal−Phosphinine (Or Hexahydrophosphinine) Ligand Catalytic Systems

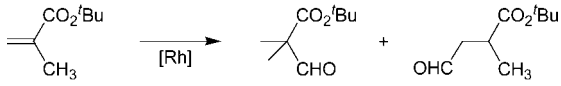
reaction	substrate	catalyst precursor	ligand (L)	br/n[a]	temp. [°C] (pressure)	conv. (r. time [h])	ref
C=C hydrogenation	dimethyl itaconate	$[Rh(L)(COD)]BF_4$	**447**	79 [b]	25 (10 bar)	100 (n.d.) [c]	97
		$[Rh(L)_2COD)]BF_4$	**448**	52 [b]	25 (10 bar)	100 (n.d.)	
	acetamido cinnamate	$[Rh(L)(COD)]BF_4$	**447**	62 [b]	40 (10 bar)	100 (n.d.)	
hydroformylation	1-octene	$[Rh(CO)_2(acac)]$	**443** ($R^1 = R^2 =$ Me)	0.56	90 (10 bar)	28 (20 h)	103
			443 ($R^1 =$ Me, $R^2 =$ Ph)	0.42		25 (20 h)	
			443 ($R^1 = R^2 =$ Ph)	0.50		22 (20 h)	
			443 ($R^1 =$ Ph, $R^2 =$ 2-Naph)	0.53		35 (20 h)	
			443 ($R^1 = R^2 =$ 2-Naph)	0.50		31 (20 h)	
			443 ($R^1 = R^2 =$ *i*Pr)	0.45		34 (20 h)	
			443 ($R^1 = 2,4\text{-}Me_2\text{-}C_6H_3$)	0.30		12 (20 h)	
hydroformylation	*t*butyl methacrylate	$[Rh(acac)(CO)_2]$	**443** ($R^1 = R^2 =$ Ph)	0.57	50 (60 bar)	79 (22 h)	198
			443 ($R^1 = R^2 = 2,4\text{-}Me_2C_6H_3$)	0.76		72 (22 h)	
			PPh_3, 443 ($R^1 = R^2 =$ Ph)	5.4		37 (22 h)	
			PPh_3, 443 ($R^1 = R^2 = 2,4\text{-}Me_2\text{-}C_6H_3$)	8.4		39 (22 h)	
			$PtBu_3$,443 ($R^1 = R^2 =$ Ph)	0.81		69 (22 h)	
			$PtBu_3$, 443 ($R^1 = R^2 = 2,4\text{-}Me_2\text{-}C_6H_3$)	0.73		66 (22 h)	
hydroformylation	styrene	$[Rh(acac)(CO)_2]$	**449**	21.4 [d]	20 (50 bar)	42 (22 h)	97
			450	25 [d]	20 (50 bar)	100 (22 h)	
hydroformylation	1-octene	$RhCl(CO)(L)_2$	**442** (R = Ph)	0.47	90 (10 bar)	19 (4 h)	66
			442 (R = *t*Bu)	0.85		88 (4 h)	
isomerization of allylic alcohols	substituted allylic alcohols	$[Rh(NBD)_2][BF_4]$	**443** ($R^1 = R^2 = 2,4\text{-}Me_2\text{-}C_6H_3$		60 *e*	30 (12) dioxane	200
					60 *f*	100 (1) dioxane	
					23 *e*	1 (16) DCM	
					23 *f*	17 (1) DCM	
Heck-reaction	methyl acrylate; iodobenzene	**287** (M = Pd, X = Cl)	**286**		*c*	TON = 10 000	201
Suzuki−Miyaura	phenylboronic acid + bromoarenes	**287** (M = Pd, X = Cl)	**286**		*c*	TON < 79 900	201

[a] Ratio of regioisomers (branched to normal). [b] Enantiomeric excess. [c] n.d. stands for "not determined". [d] ee = 0%. [e] No H_2 pretreatment. [f] H_2 pretreatment.

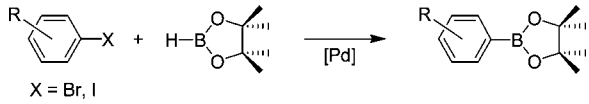
systems was carried out. Relatively low regioselectivities (branched to linear isomer ratio close to 1/1) were obtained. The *tert*-butyl-substituted derivative showed much higher activity than the corresponding phenyl ligand.[66]

A systematic investigation on the influence of the mixtures of various monodentate achiral ligands on the regioselectivity of rhodium-catalyzed hydroformylation of methacrylates was carried out (Scheme 160). One of the most prominent

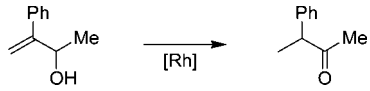
Scheme 160. Rhodium-Catalyzed Hydroformylation of *tert*-Butyl Methacrylate



Scheme 161. Formation of Boronic Esters from Aryl Halides and Pinacolborane



Scheme 162. Rhodium-Catalyzed Isomerization of Allylic Alcohols



heterocombinations was the 1/1 mixture of PPh_3 and 2,6-bis(2,4-dimethylphenyl)-4-phenylphosphinine. In this case, the formation of the "less-branched" formyl regioisomer was dominating by using *tert*-butyl methacrylate as substrate.[198]

Excellent regioselectivities toward branched aldehyde were obtained in rhodium-catalyzed hydroformylation of styrene by using phosphinine-based heterobidentate ligands **449** and **450**.[97] No ee's for 2-phenylpropanal were detected in spite of the application of optically active ligands.

The Miyaura coupling reaction allowed the formation of boronic esters from aryl halides and pinacolborane in the presence of palladium(II) complexes containing phosphinine-based tridentate SPS ligands (Scheme 161).[199] The similar catalysts were active in Suzuki−Miyaura cross-coupling reactions forming biphenyl derivatives from phenylboronic acid and bromoarenes with turnover frequency of up to 8×10^5 h^{-1}.[201]

The isomerization of allylic alcohols to the corresponding unsaturated carbonyl compounds was accomplished with rhodium-trisubstituted phosphinine catalysts (Scheme 162). In order to achieve high conversion, the activation of the rhodium precursor by hydrogen was necessary.[200]

3.4. Homogeneous Catalysis Including Seven-Membered *P*-Heterocyclic Ligands

Dinaphthophosphepine-based ligands were used in palladium-catalyzed enantioselective allylic amination of *rac*-(*E*)-1,3-diphenyl-3-acetoxyprop-1-ene. While the application of *O*-*tert*-butyl-protected pyridinol ligand (**399**), which is not capable of self-assembling, resulted in low ee's, the lactame analogue (**400**) induced high enantioselectivities.[68]

1-*tert*-Bu- and Ph-substituted phosphepanes (**451**, Figure 12) were used as ligands in rhodium-catalyzed hydroformylation of 1-octene, resulting in high isomerization but low hydroformylation activity compared to the analogous phospholanes and phosphinanes (see sections 3.2 and 3.3).[66]

The rhodium(I) complexes of the 1,2-bis(binaphthophosphepino)benzene derivative (BINAPHANE) proved to be efficient catalysts to obtain enantioselectivities of practical importance (ee > 99%) in the hydrogenation of β-substituted aryleneamides. The fine-tuning of the parent ligand by modifying the groups on the aromatic rings provided a general catalytic system for asymmetric hydrogenation.[155] Furthermore, the same ligand was successfully used for the palladium-catalyzed enantioselective cyclization of silyloxy-1,6-enines.[202]

Another bisbinaphthophosphepine ligand of highly electron-donating properties containing a P stereogenic center (**397**, BINAPINE) demonstrated excellent activity and enantioselectivity in rhodium-catalyzed hydrogenation of *Z*-β-aryl-β-acetamido acrylates.[154]

It is interesting to note that the *P*-phenylphosphabicyclo-[3.3.0]octane (PBO) and its benzene anellated derivative (**251**) proved to be efficient nucleophilic catalysts for asymmetric acylation and the chiral resolution of the alcohols by benzoylation.[94]

The search for monodentate phosphines, based on 4,5-dihydro-3*H*-dinaphthophosphepine framework, has long been an interesting field of ligand design for homogeneous catalysis and led to the construction of a ligand library. The potential of these ligands was demonstrated by enantioselective hydrogenation of standard substrates such as dehydroamino acid derivatives, itaconic acid derivatives, ketoesters, and enamides.[203] Recently, enol carbamates were hydrogenated by using this ligand family in rhodium-catalyzed reaction, and enantioselectivities up to 96% ee were achieved (Scheme 163). The *P*-phenyl derivative (**390**) proved to be the most efficient.[203]

The same research groups carried out detailed investigations in rhodium-catalyzed hydroformylation of styrene in the presence of similar monodentate phosphepine-based ligands. The application of various *P*-aryl-4,5-dihydro-3*H*-dinaphthophosphepine ligands (**390**, with various substituents on the P-phenyl ring, as well as its 2,7-dimethyl-substituted

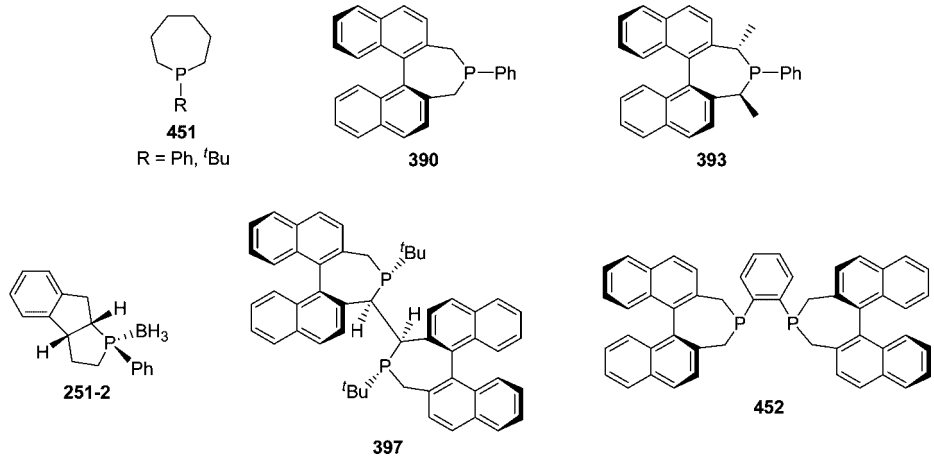
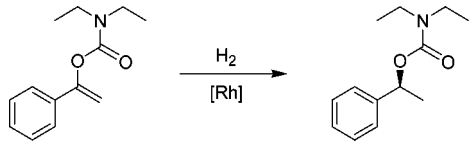


Figure 12. Seven-membered *P*-heterocyclic ligands used most frequently in transition metal catalyzed reactions.

Scheme 163. Asymmetric Hydrogenation of Enol Carbamates



analogue (**393**)) resulted in active catalysts with moderate enantioselectivities. Surprisingly, bidentate ligands containing the same chiral moieties did not result in improved enantioselectivity.[204]

4. Concluding Remarks

Since the discovery of the importance of phosphorus ligands in transition metal catalyzed reactions, large efforts were made in both the synthesis of novel phosphorus compounds and their application in homogeneous catalysis. In finding the right electronic and steric balance of the central transition metal and the *P*-donor ligand(s), the family of *P*-heterocycles has become one of the most important candidates. Phospholes and their saturated chiral derivatives, such as dibenzophospholes attached to chiral backbone, 2,5-disubstituted phospholanes, and dinaphthophosphepines, have gained an important role in asymmetric catalysis and are among the "privileged ligands" in asymmetric catalysis. The detailed investigation of their coordination chemistry and the "tailor-made" ligands based on it led to eantioselective catalysts of practical importance enabling the synthesis of chiral building blocks or intermediates of pharmaceuticals, agrochemicals, and natural compounds.

5. Acknowledgments

The authors thank the Hungarian National Science Foundation (NKTH-OTKA CK78553 and OTKA K067679) for their financial support. A special thanks to Z. Frank for drawing the schemes.

6. References

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CR900364C