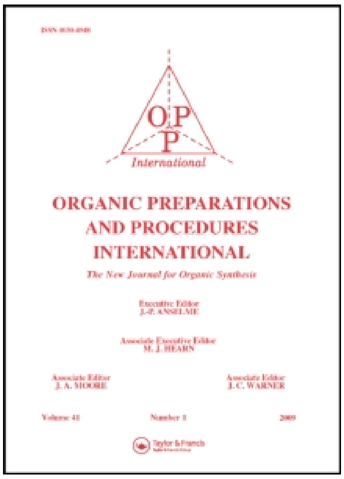

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SYNTHESIS OF POLYPODAL DIPHENYLPHOSPHINE LIGANDS. A REVIEW

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SYNTHESIS OF POLYPODAL DIPHENYLPHOSPHINE LIGANDS. A REVIEW

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INTRODUCTION

The synthesis and use of functional phosphine ligands is a continuing central theme in molecular chemistry with important implications in homogeneous catalysis, in particular for the discovery of highly selective catalytic reactions. For example, asymmetric catalysis by transition metal complexes with chelating bisphosphines has provided practical syntheses of many enantiomerically pure substances. The commonly used ligands are 1,2-, 1,3- and 1,4-bisphosphines which lead to chelates of five- six- and seven-membered rings.

The principal method for introducing the diphenylphosphino group is based on the reaction of an alkyl sulfonate with an alkali diphenylphosphide. This substitution occurs with complete inversion of stereochemistry.[1] Lithium diphenylphosphide is often obtained by reductive cleavage of triphenylphosphine with lithium. Bosnich has proposed to decompose the phenyllithium by the addition of *tert*-butyl chloride.[2]

$$\mathrm{Ph_3P} + 2\,\mathrm{Li} \xrightarrow[\mathrm{THF}]{25 \rightarrow 55°} \mathrm{Ph_2PLi} + \mathrm{PhLi} \xrightarrow[25 \rightarrow 65°]{t\text{-}\mathrm{BuCl}} \mathrm{Ph_2PLi} \tag{1}$$

Other methods involve the action of *n*-butyllithium on diphenylphosphine,[3] or the lithium metal on *P*-chlorodiphenylphosphine.[4] Some authors, following Kagan and Dang,[5] used sodium diphenylphosphide.

$$\mathrm{Ph_2PH} + n\text{-}\mathrm{BuLi} \xrightarrow[\mathrm{THF}]{-\,90°} \mathrm{Ph_2PLi} \tag{2}$$

$$\mathrm{Ph_2PCl} + 2\,\mathrm{Li} \xrightarrow[\mathrm{THF}]{} \mathrm{Ph_2PLi} + \mathrm{LiCl} \tag{3}$$

$$\mathrm{Ph_2PCl} + 2\,\mathrm{Na} \xrightarrow[\mathrm{Dioxane}]{100°} \mathrm{Ph_2PNa} + \mathrm{NaCl} \tag{4}$$

The use of the phosphine-borane complexes has been widely developed recently.[6] An efficient procedure entails sequential reaction of a tosylate with the diarylphosphine-borane anion followed by BH_3 decomplexation mediated by HBF_4-OMe_2 or Et_2NH.[7,8] It is a little-known fact that the BH_3 group in phosphine-boranes has, for much discussed but still unclear reasons, lost its hydride activity to such an extent that it is even stable towards acids, bases[9] and even oxidizing reagents.[10]

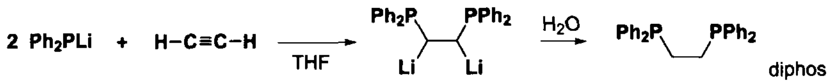
Optically active phosphines[11] have been used as ligands in transition metal complexes having good catalytic properties such as for the asymmetric hydrogenation with Ru or Rh complexes, for example. The preparation of such chelating phosphanes[12] can result from the surprisingly facile resolution of the corresponding phosphine oxides with an ethanolic solution of L-(−)- or D-(+)-O,O'-dibenzoyl-tartaric acid (DBT). The less soluble diastereoisomer is then treated with KOH to remove DBT.[13]

I. SYNTHESIS OF *bis*(DIPHENYLPHOSPHINE) LIGANDS

1. Synthesis of 1,2-*bis*(Diphenylphosphino)ethanes

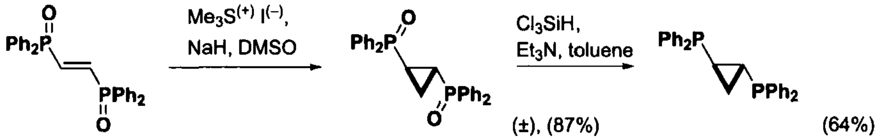
a. 1,2-bis(Diphenylphosphino)ethanes

Bubbling acetylene into a solution of lithium diphenylphosphide leads to 1,2-*bis*(diphenylphosphino)ethane (diphos).[14]



(5)

Cyclopropanation of *trans*-1,2-*bis*(diphenylphosphinoyl)ethylene gives rise to *trans*-1,2-*bis*-(diphenylphosphino)cyclopropane after reduction with trichlorosilane.[15]



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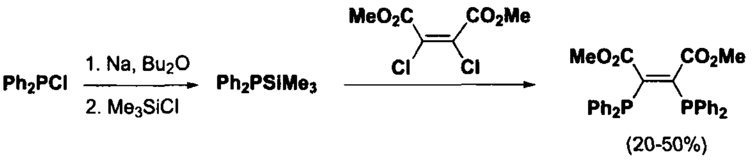
Some diphenylphosphino derivatives of dicarboxylic acids can be obtained by the aid of diphenyl(trimethylsilyl)phosphine.[16,17]



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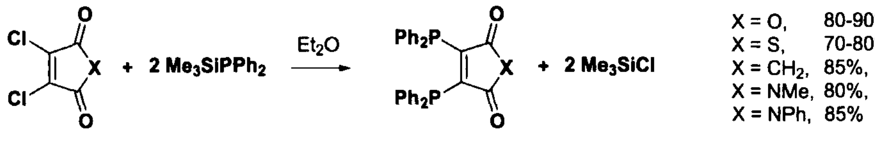
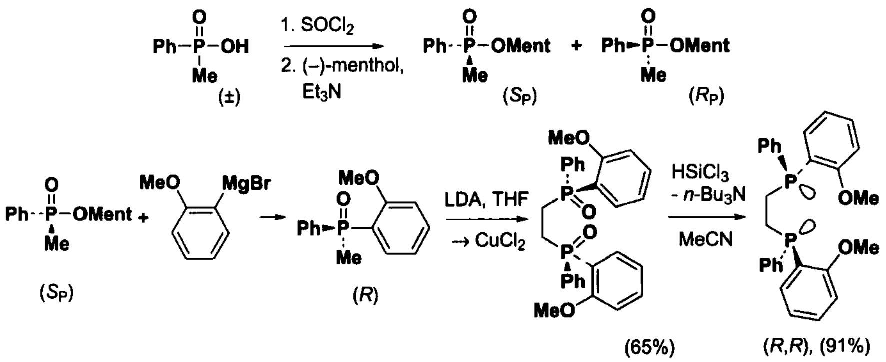


(8)

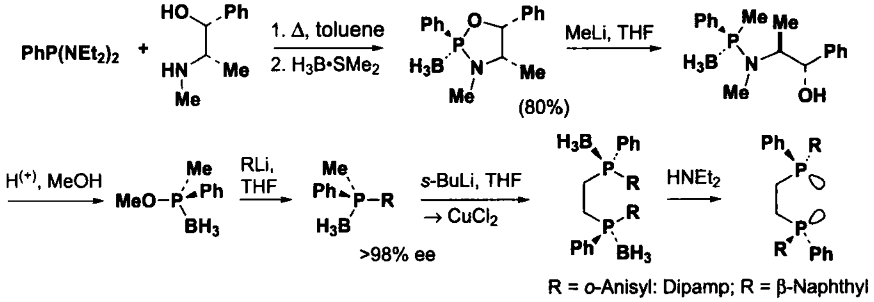
b. P-Chiral 1,2-bis(Diarylphosphino)ethanes

The (*R*,*R*)-1,2-ethanediyl*bis*[(*o*-methoxyphenyl)phenylphosphine [(*R*,*R*)-DIPAMP] was prepared from the (R_P)-menthyl methylphenylphosphinate.[18] The phosphine oxide was reduced with inversion at the phosphorus center.



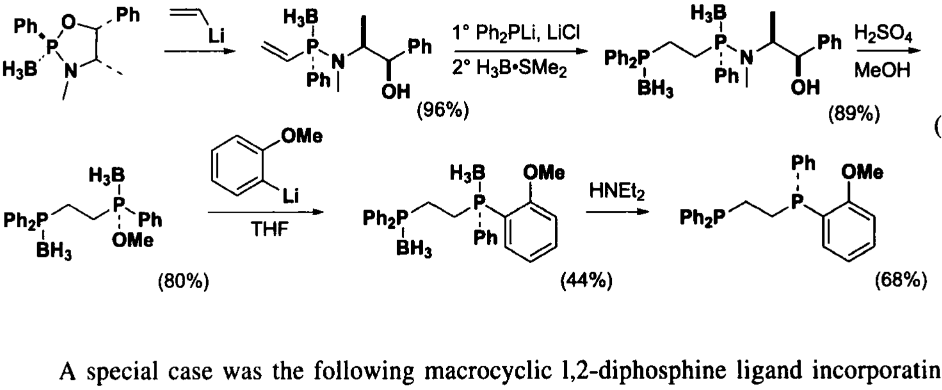
(9)

Jugé and Genet have proposed a general method for the asymmetric synthesis of phosphines involving the formation of oxazaphospholidine complexes from (–)-ephedrine.[19]



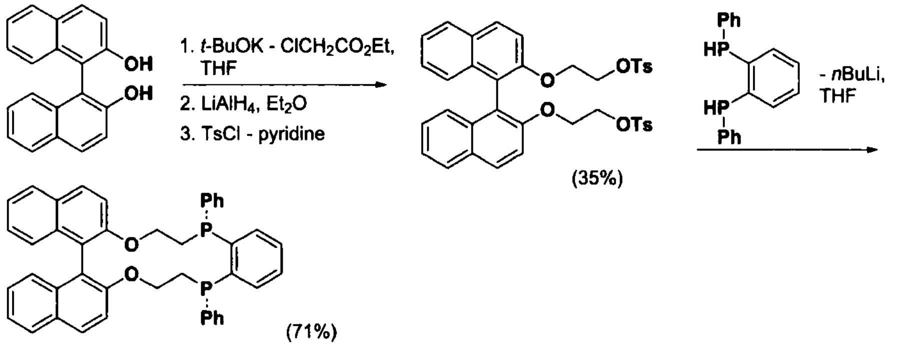
(10)

The Jugé-Genet route has been used for the preparation of (R_p)-(2-methoxyphenyl)-P-phenyl-P-(2'-diphenylphosphino)ethylphosphine.[20]



(11)

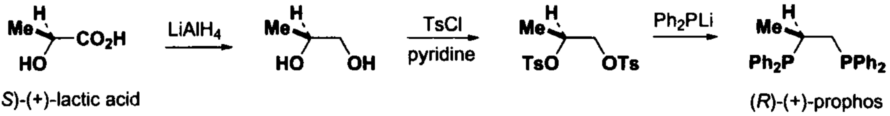
A special case was the following macrocyclic 1,2-diphosphine ligand incorporating a binaphthyl unit. The relative configuration of the two Ph groups attached to the P-atoms was postulated to be *cis*.[21]



(12)

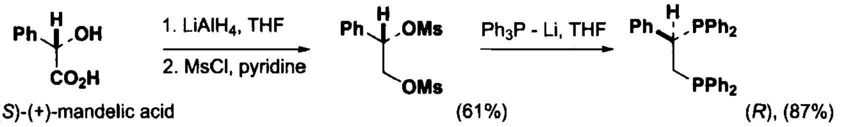
c. *Optically Active 1,2-bis(Diphenylphosphino)ethanes*

The chiral ligand (*R*)-1,2-*bis*(diphenylphosphino)propane, (*R*)-prophos, has been prepared by Fryzuk and Bosnich from (*S*)-lactic acid.[22]



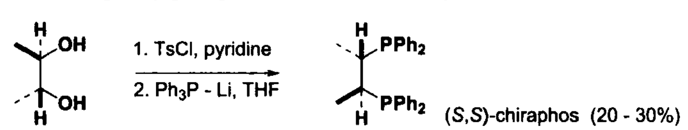
(13)

Similarly, the (*R*)-1,2-*bis*(diphenylphosphino)phenylethane has been synthesized from (*S*)-mandelic acid.[23]



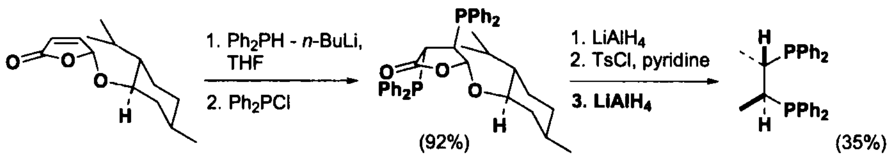
(14)

Concerning the preparation of (2*S*,3*S*)-*bis*(diphenylphosphino)butane, (*S*,*S*)-chiraphos, Bosnich and co-workers observed that tosylation of (2*R*,3*R*)-butanediol proceeds quantitatively but that substitution by lithium diphenylphosphide occurred in low yield.[2]



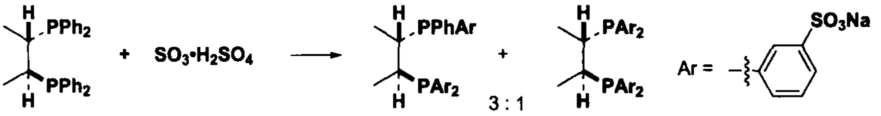
(15)

(*S*,*S*)-Chiraphos was obtained by Feringa and his group from γ-menthoxybutenolide.[3]



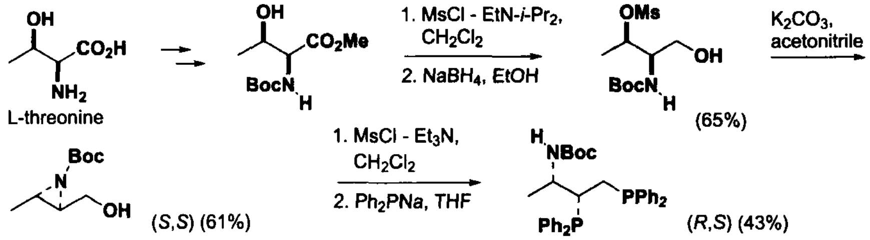
(16)

Sulfonation of chiraphos affords a mixture of sulfonated chiraphos which are water-soluble chiral diphosphine and have been widely used for numerous transition metal mediated process carried out in water.[24]



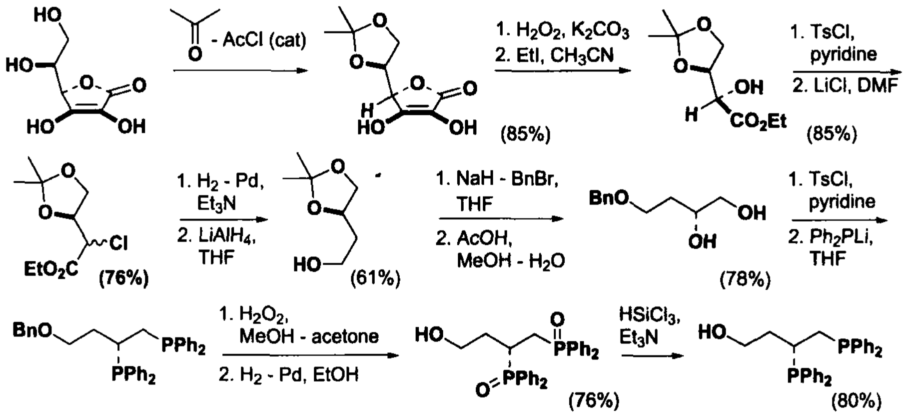
(17)

The chiral bisphosphine, (2*R*,3*S*)-1,2-*bis*(diphenylphosphino)-3-*t*-Boc-aminobutane, was prepared from L-threonine.[25]



(18)

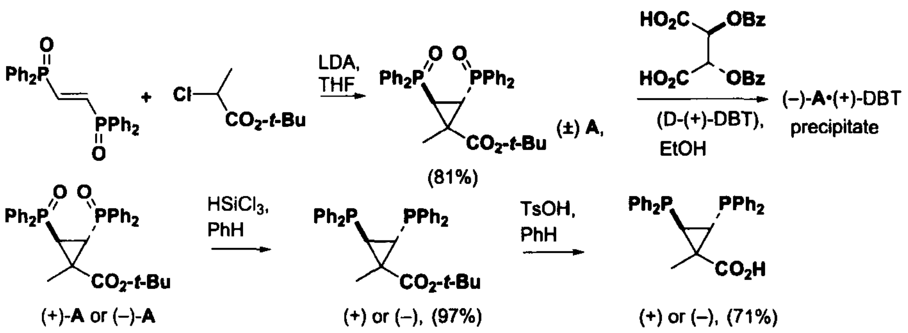
A straightforward procedure for the synthesis of (*S*)-*bis*(diphenylphosphino)butan-4-ol from L-ascorbic acid has been described.[4]



(19)

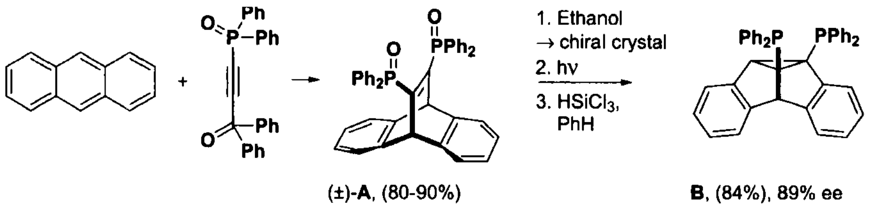
d. Optically Active 1,2-bis(Diphenylphosphino)cycloalkanes

(−)-*trans*-2,3-*bis*(Diphenylphosphino)-1-methyl-1-cyclopropanecarboxylic acid was obtained by cyclopropanation of *trans*-1,2-*bis*(diphenylphosphinyl)ethene.[26]



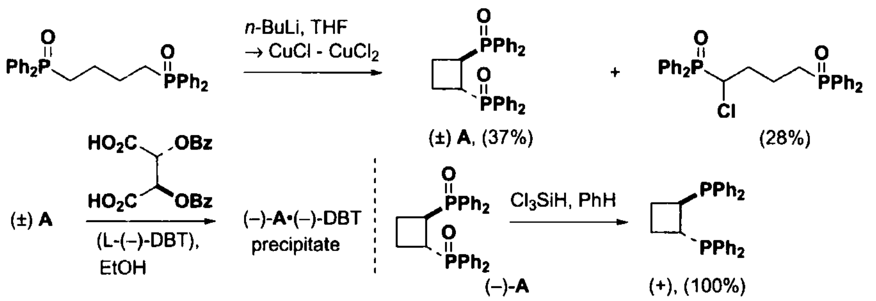
(20)

The ethanol complex of the coordinatoclathrate **A** undergoes an absolute asymmetric di-π-methane photorearrangement giving rise to the dibenzosemibullvalene **B**.[27]



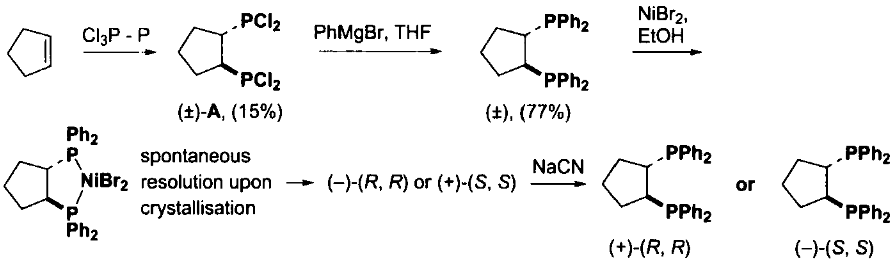
(21)

The *trans*-1,2-*bis*(diphenylphosphino)cyclobutane was prepared *via* an intramolecular oxidative cyclization mediated by copper salts.[28]



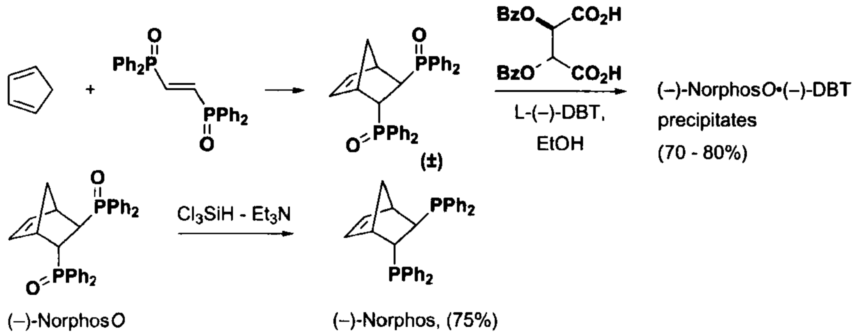
(22)

Heating of white phosphorus, PCl_3, and cyclopentene gives cyclopentane derivative **A**. *trans*-1,2-*bis*(Diphenylphosphino)cyclopentane forms an adduct with $NiBr_2$ which crystallizes as a conglomerate, and the pure enantiomers may be separated by hand.[29]



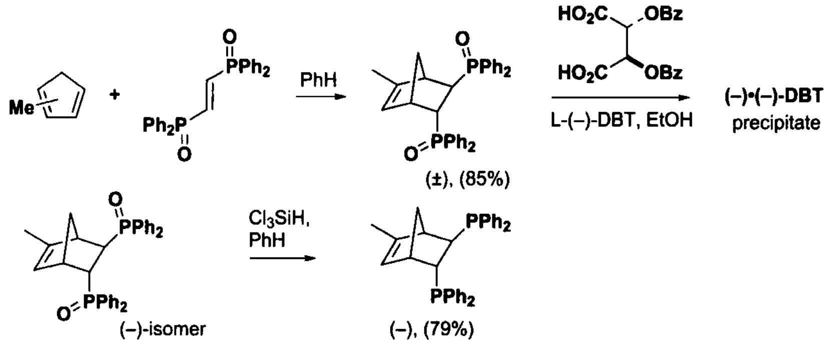
(23)

Norphos is a chelating chiral diphosphine prepared by Brunner and co-workers which gave excellent results in asymmetric hydrogenation.[13]



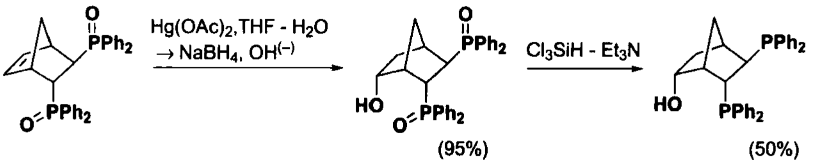
(24)

(±)-MeNorphos*O* has been resolved into its optically pure components by (–)-DBT.[30]



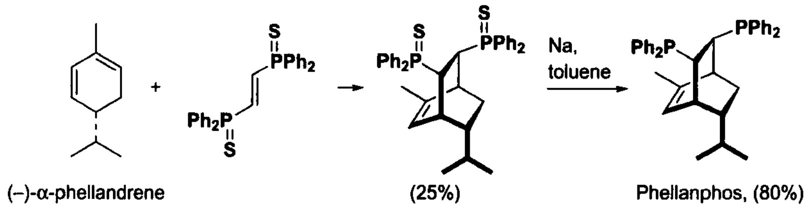
(25)

From (–)-norphos dioxide, Kagan and his group, obtained 6-*endo*-hydroxy norphos.[31]



(26)

Two chiral 1,2-diphosphines were prepared by Diels-Alder reaction between 1,2-*bis*-(diphenylphosphino)ethylene disulfide and chiral dienes (–)-α-phellandrene[32] or nopadiene.[33]



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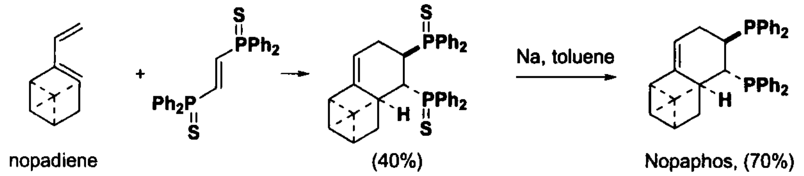
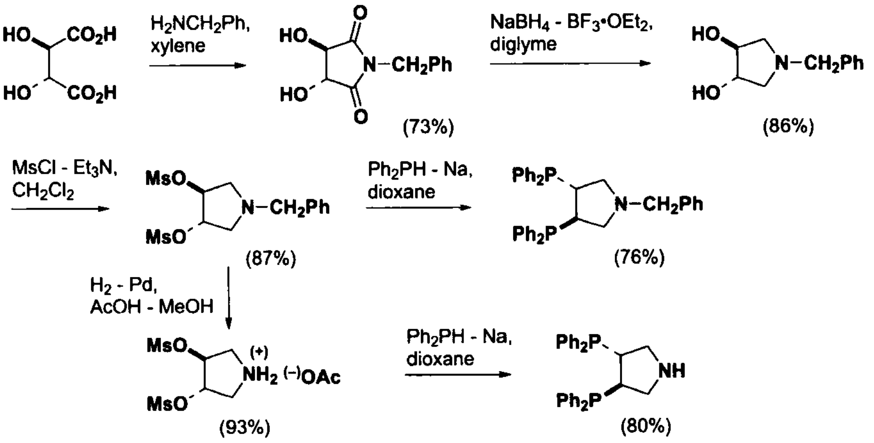


(28)

e. Optically Active 1,2-bis(Diphenylphosphino)heterocycloalkanes

The (*R*,*R*)-3,4-*bis*(diphenylphosphino)pyrrolidine was prepared from tartaric acid.[34]

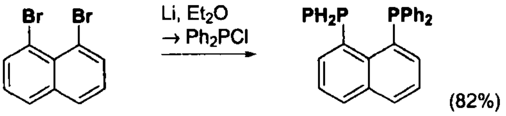


(29)

2. Synthesis of 1,3-*bis*(Diphenylphosphino)propanes

a. 1,3-bis(Diphenylphosphino)propanes

The 1,8-*bis*(diphenylphosphino)naphthalene, a rigid chelating diphosphine analogue of proton sponge, has been prepared from 1,8-dibromo- or 1-bromonaphthalene.[35,36]



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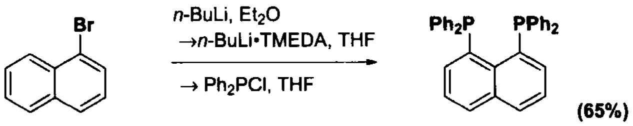
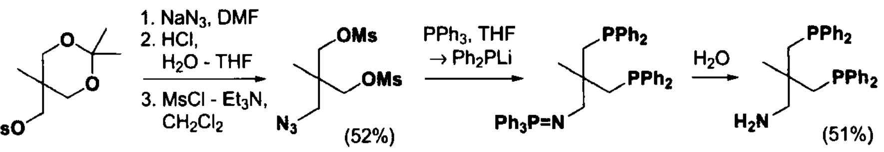


(31)

Some amino-containing 1,3-diphosphines were prepared.[37,38]



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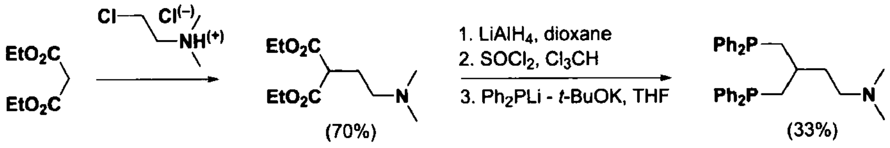
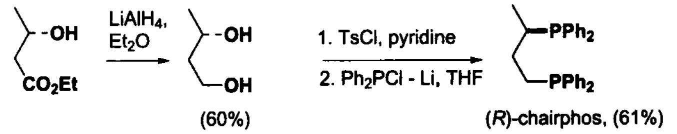


(33)

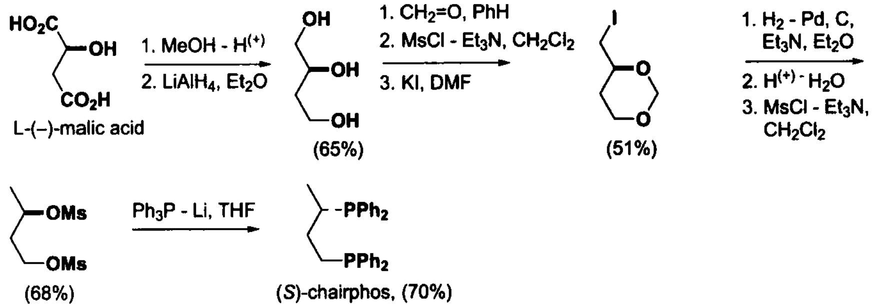
b. Optically Active 1,3-bis(Diphenylphosphino)propanes

The (*R*)-1,3-*bis*(diphenylphosphino)butane, (*R*)-chairphos, was first prepared by Kagan and his group from (*S*)-3-hydroxybutyrate.[39]



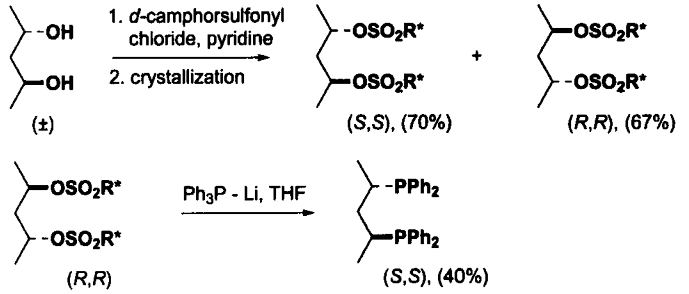
(34)

The opposite enantiomer was obtained by Bosnich and co-workers from L-(–)-malic acid.[40]



(35)

The 2,4-*bis*(diphenylphosphino)pentane or BDPP (or "Skewphos") is able to form a six-membered chelate ring with a metal. Two synthetic procedures have been described by Bosnich and co-workers[40] and Bakos and his group.[41]



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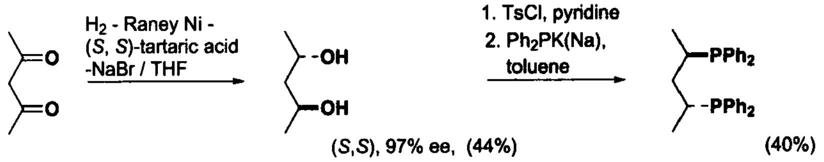
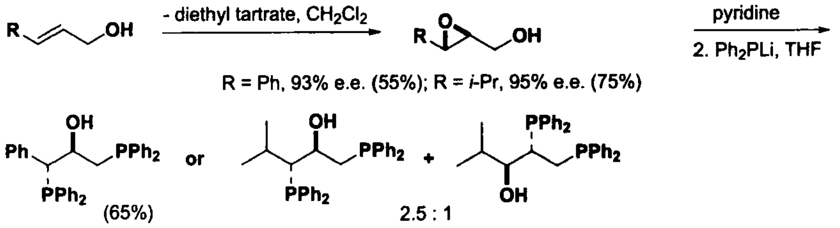


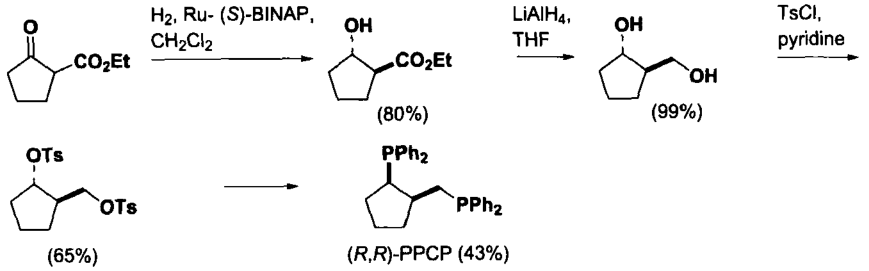
(37)

Optically active 1,3-diphosphines have been obtained *via* Sharpless epoxidation.[42]



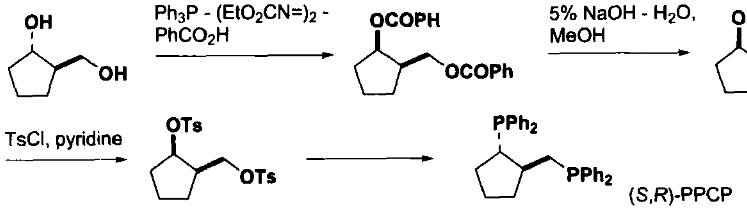
(38)

The (1*R*,2*R*)-1-diphenylphosphino-2-(diphenylphosphinomethyl)cyclopentane [(*R*,*R*)-PPCP], which was designed to form favorable skew conformation of the six-membered chelate with rhodium, has been prepared from Dieckmann ester.[43]



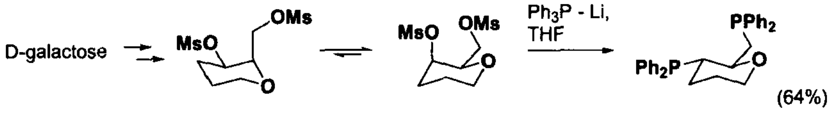
(39)

The (*S*,*R*)-PPCP can be prepared from (*R*,*R*)-2-hydroxymethylcyclopentanol (yields not given).[44]



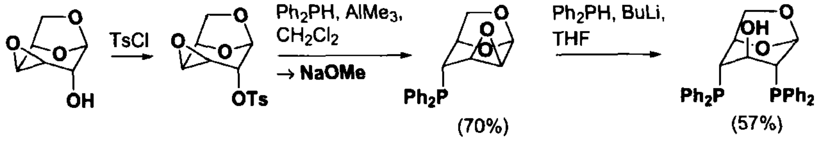
(40)

(2*R*,3*S*)-2-diphenylphosphinomethyl-3-diphenylphosphinotetrahydropyran has been prepared from D-galactose.[45]



(41)

The 1,6-anhydro-2,4-dideoxy-2,4-*bis*(diphenylphosphino)-β-D-glucopyranose was obtained from 1,6-anhydro-β-D-glucopyranose (levoglucosan).[46]

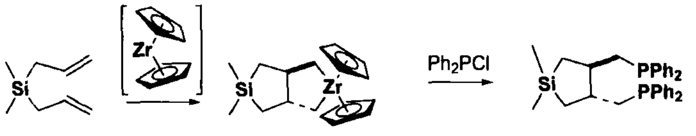


(42)

3. Synthesis of 1,4-*bis*(diphenylphosphino)butanes

a. *1,4-bis(Diphenylphosphino)butanes*

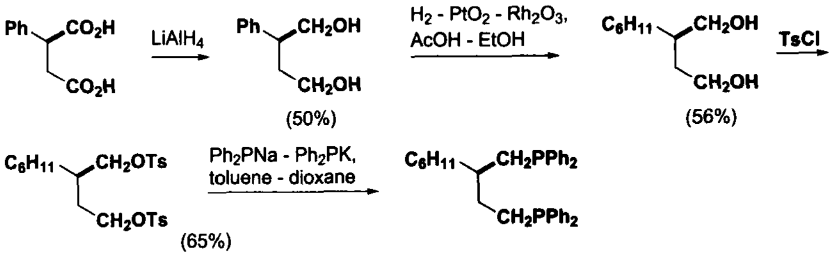
The reaction of zirconocene with bisallylsilane followed by electrophilic substitution led to racemic 1,4-diphosphine.[47]



(43)

b. *Optically Active 1,4-bis(Diphenylphosphino)butanes*

From the corresponding substituted succinic acids, Krause and co-workers prepared chiral 1,4-*bis*(diphenylphosphino)butane derivatives.[48]



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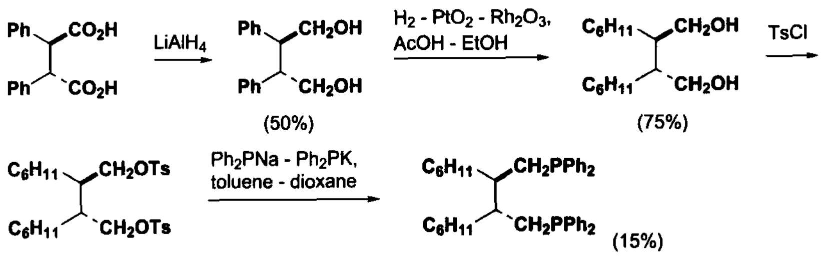
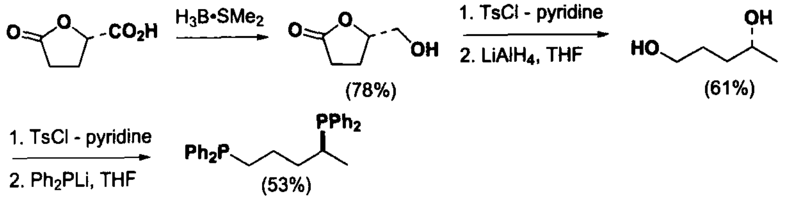


(45)

From (*S*)-(+)-5-oxotetrahydrofuran-2-carboxylic acid, Brunner and co-workers have prepared some chiral bisphosphines.[49]



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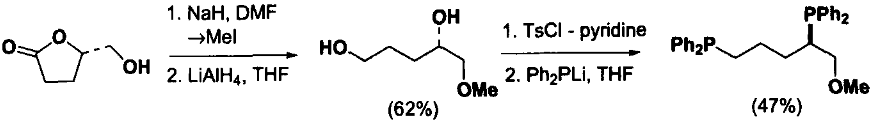
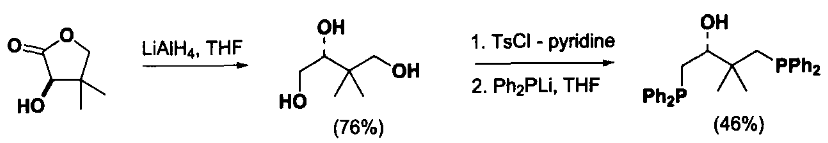


(47)

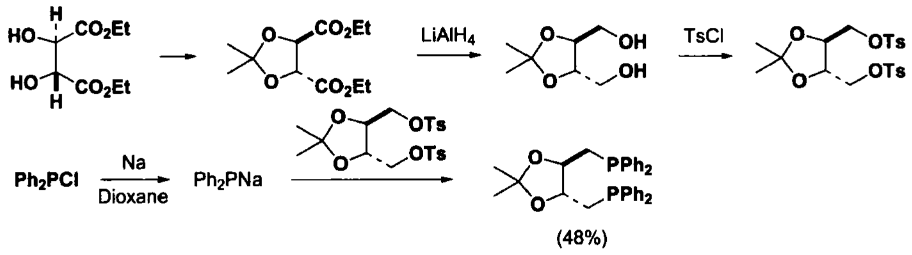
Similarly, (*R*)-3,3-dimethyl-1,4-*bis*(diphenylphosphino)butan-2-ol has been prepared from (*R*)-(–)-pentolactone.[49]



(48)

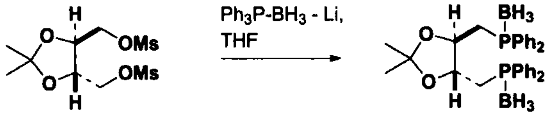
α. Dioxolane Derivatives

In 1971, Kagan and his group have prepared the (–)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-*bis*(diphenylphosphino)butane, (–)-diop, which combined with rhodium(I) was able to induce several asymmetric reductions giving the highest optical yields so far obtained.[50]



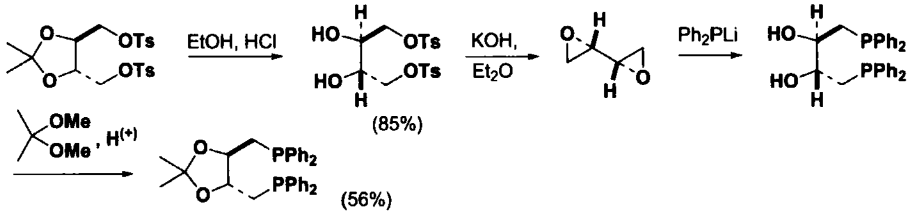
(49)

Diop-borane complex can also be obtained from the corresponding dimesylate.[51]



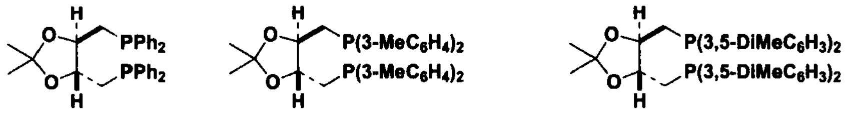
(50)

Diop has been prepared by a different procedure.[52]

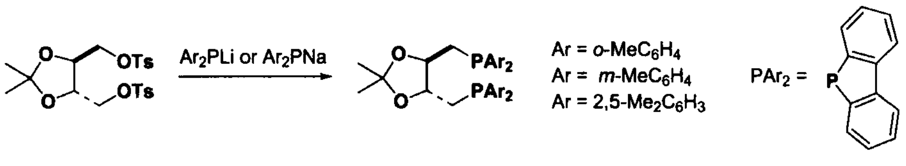


(51)

Various other Diop derivatives have been prepared.[53,54]

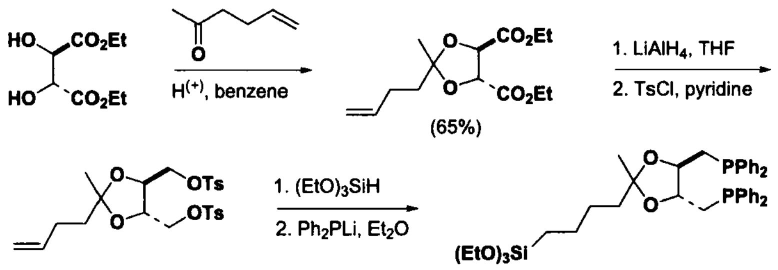


(52)



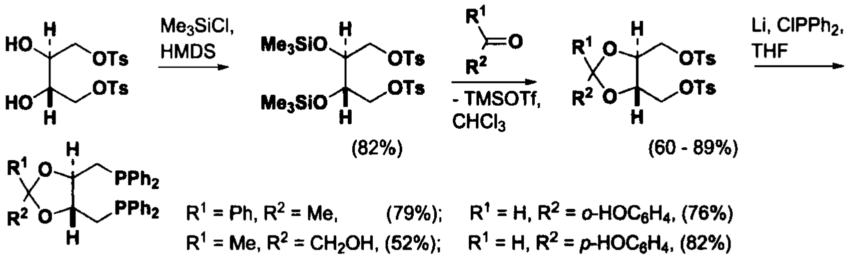
(53)

The preparation of Diop derivatives bearing a tethered hydroxy group able to bond to the surface of one support has been reported.[55]



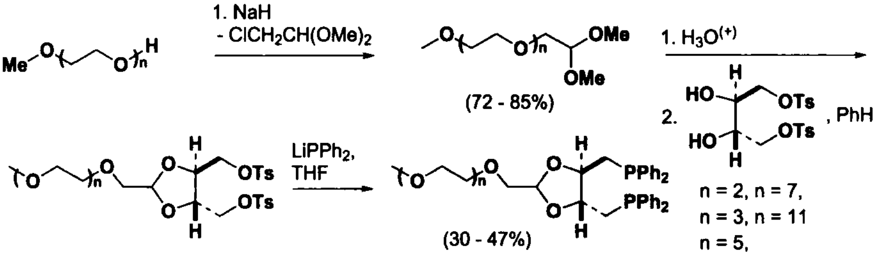
(54)

Some diphosphines related to the diop bearing a hydroxyl group in a rigid backbone have been described.[56]



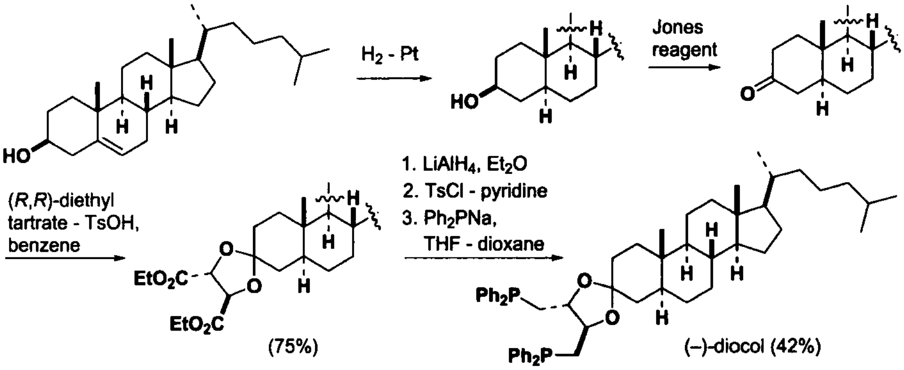
(55)

Polyoxadiphosphines, water soluble diphosphines, were proposed by Sinou and co-workers.[57]



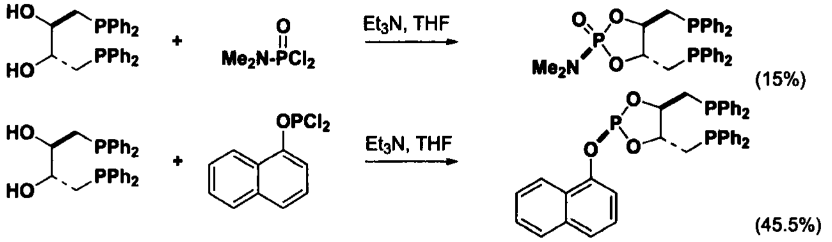
(56)

A chiral phosphine, (–)-diocol, was prepared using cholesterol as starting product.[58]



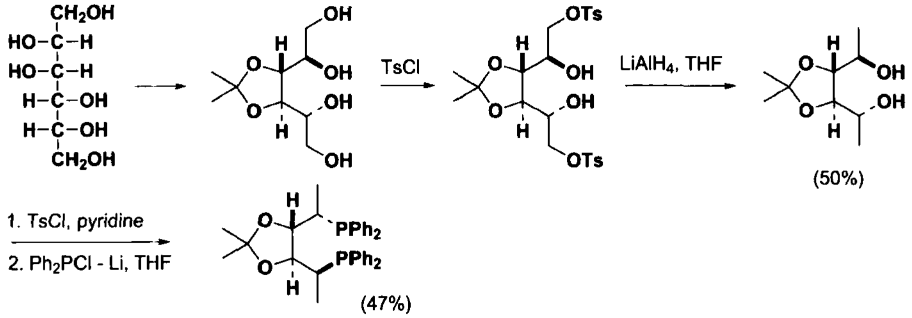
(57)

Analogues of diop bearing a dioxaphospholane cycle were prepared by Börner and his group.[59]



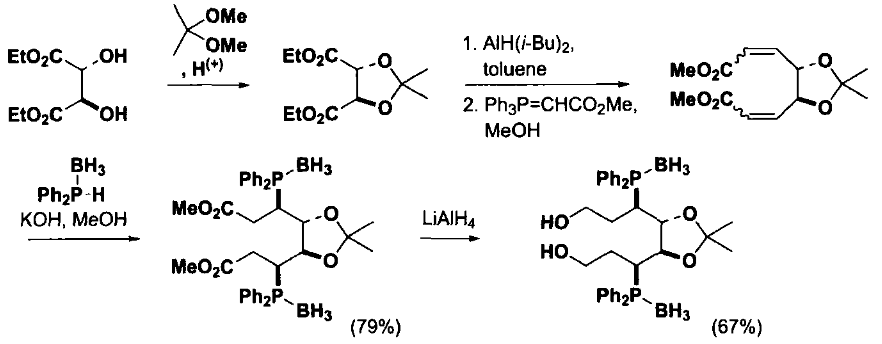
(58)

Analogues of diop with chiral center close to the phosphorus atoms have been prepared by Kagan and co-workers.[39]

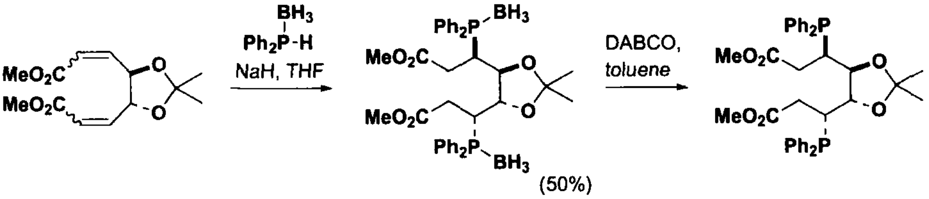


(59)

In the course of the preparation of the following diop derivatives, the diphenylphosphino group was introduced by conjugate addition to activated double bond.[60,61]



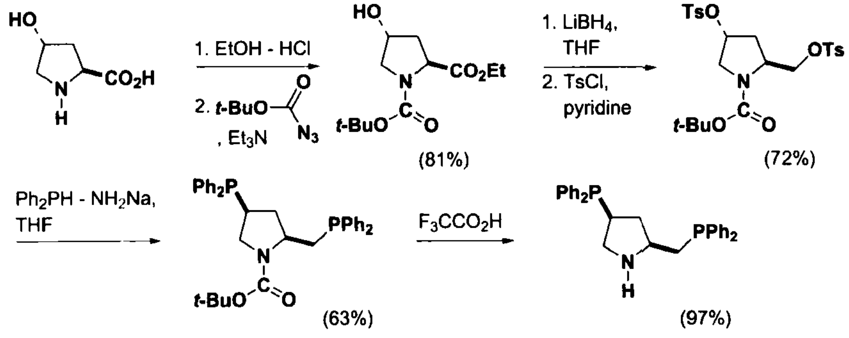
(60)



(61)

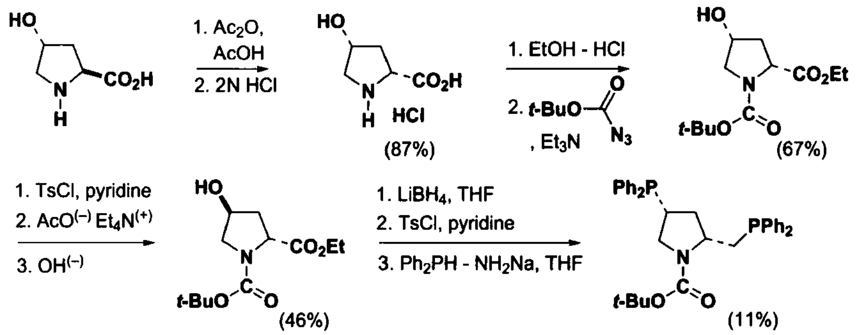
β. Pyrrolidine Derivatives

The (2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine was synthesized from 4-hydroxy-L-proline.[62,63]



(62)

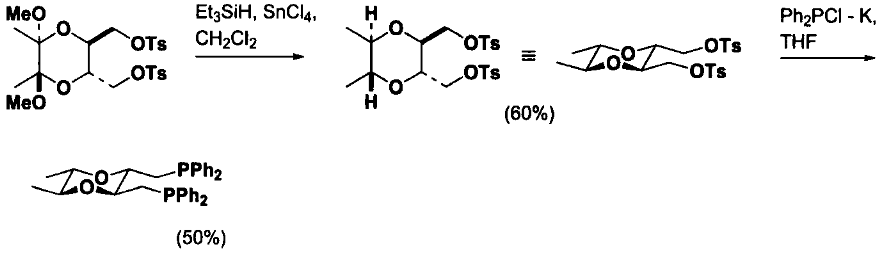
The (2*R*,4*R*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine was also prepared from 4-hydroxy-L-proline. The first step was an epimerization to the *cis* isomer.[62]



(63)

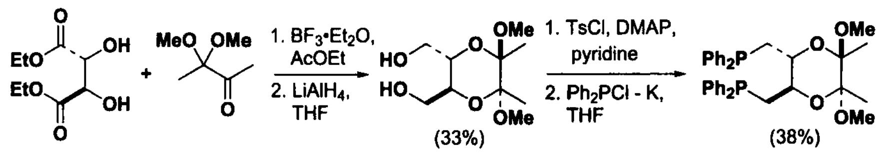
γ. Dioxane Derivatives

The following dioxane derivative lacking any axial group was prepared by reduction of a cyclic bisacetal.[64]



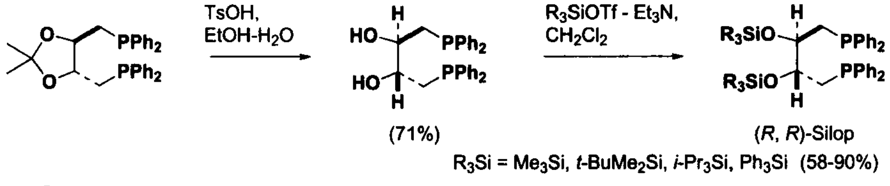
(64)

Reaction of diethyl tartrate with 3,3-dimethoxybutan-2-one gave a dioxane which was transformed into diphosphine.[65]



(65)

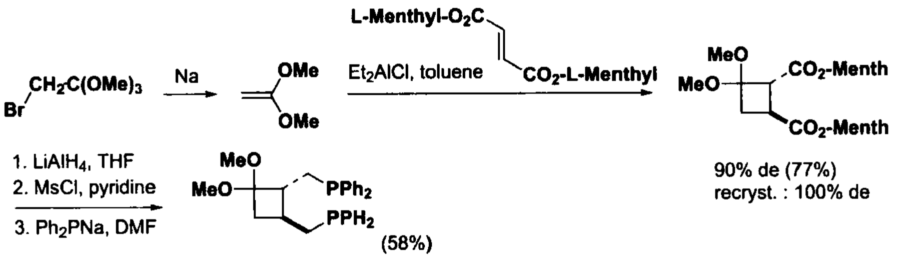
A series of 2,3-*bis*(siloxy)-1,4-*bis*(diphenylphosphino)butanes have been prepared.[66]



(66)

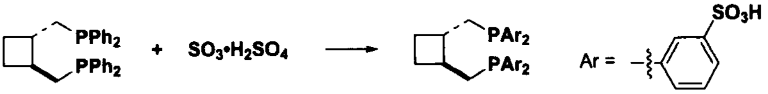
δ. Cyclic Derivatives

A chiral diphosphine ligand bearing a cyclobutane framework was prepared by using diastereoselective [2+2] cycloaddition.[67]



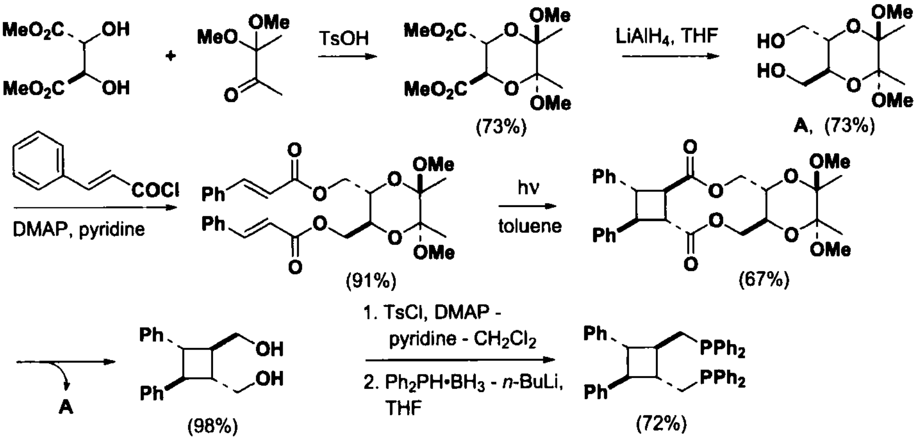
(67)

Tetrasulfonated diarylphosphines cyclobutanediop can be easily obtained.[24]



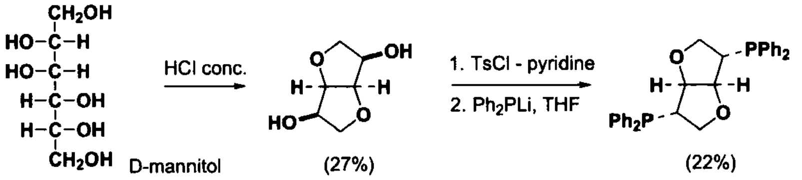
(68)

The asymmetric intramolecular [2+2] photocycloaddition of α,β-enoates gave rise to C_2-symmetric bisphospholanes possessing a cyclobutane backbone.[68]



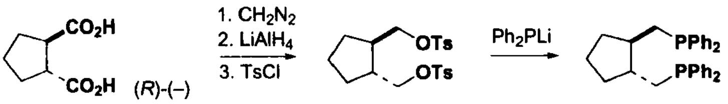
(69)

The 1,4:3,6-dianhydro-2,5-dideoxy-2,5-*bis*(diphenylphosphino)-L-iditol has been prepared from D-mannitol.[69]

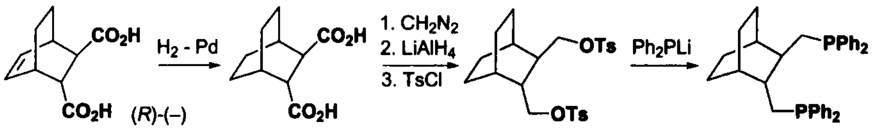


(70)

The hydrocarbonated analogues of diop were obtained by Kagan and co-workers.[54]

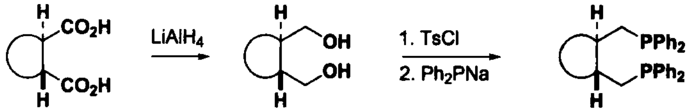


(71)



(72)

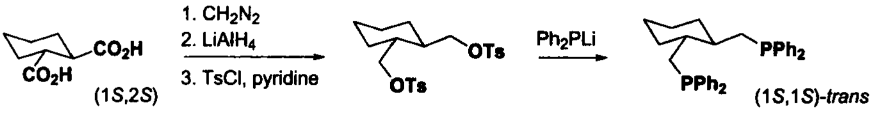
Other chiral diphosphines analogues of diop were also prepared from optically active diacids (yields not indicated).[70]



(73)

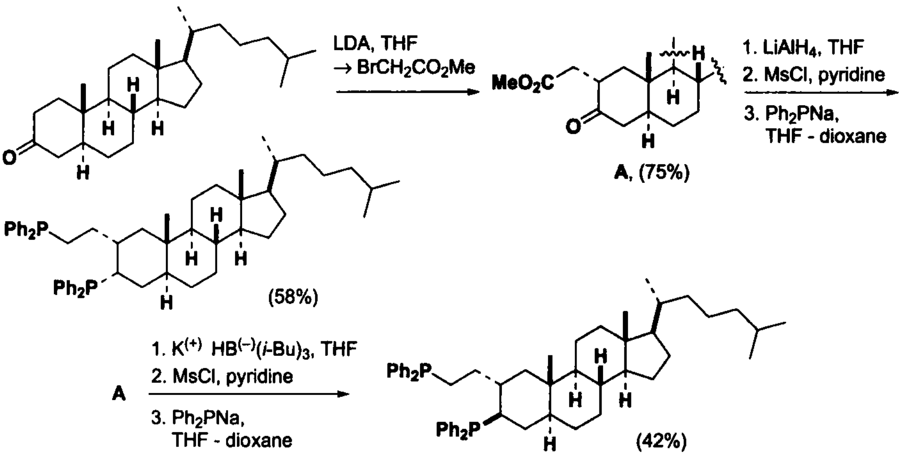
(*R*)-(–)-*trans*-1,2-bis(diphenylphosphinomethyl)cyclobutane
(*S*)-(+)-*trans*-1,2-bis(diphenylphosphinomethyl)cyclopentane
(*R*)-(–)-*trans*-1,2-bis(diphenylphosphinomethyl)cyclohexane

The (1S,2S)-*trans*-1,2-*bis*(diphenylphosphinomethyl)cyclohexane can be prepared from (1*S*,2*S*)-*trans*-1,2-cyclohexanedicarboxylic acid.[71]



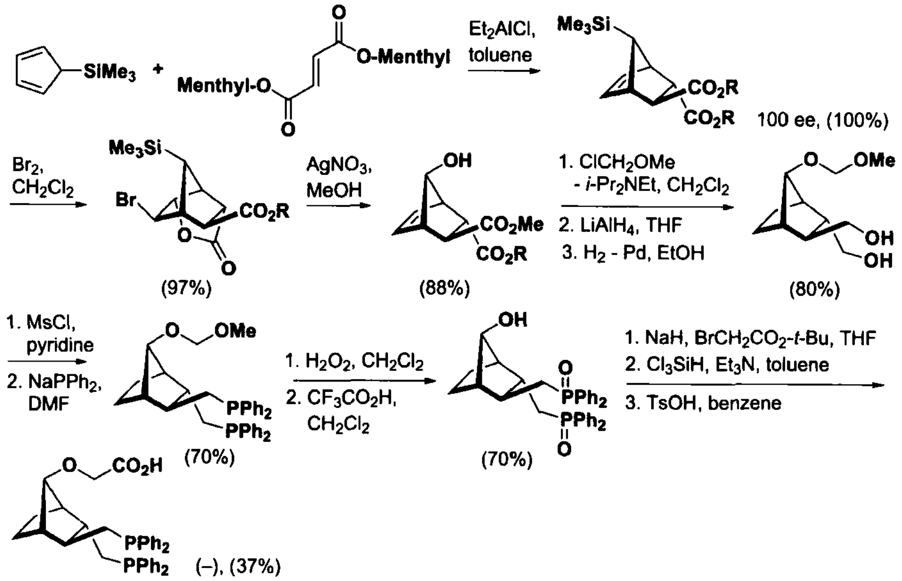
(74)

The 3α- and 3β-diphenylphosphino-2α-(2'-diphenylphosphinoethyl)-5α-cholestanes have been prepared from cholestanone.[72]

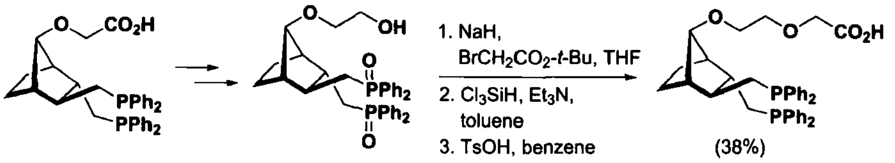


(75)

Chiral bisphosphine ligands bearing hetero-functional groups were prepared by the use of asymmetric Diels-Alder reaction.[73,74]

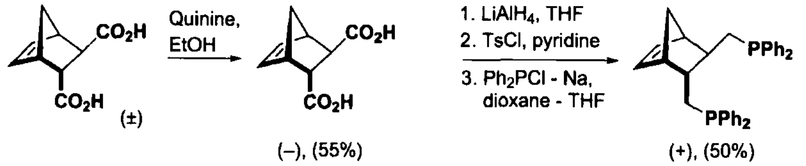


(76)



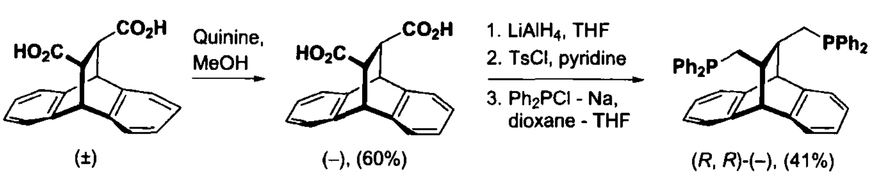
(77)

The enantiomers of *trans*-2,3-(diphenylphosphinomethyl)norbornene have been obtained from norbornene dicarboxylic acid.[75]



(78)

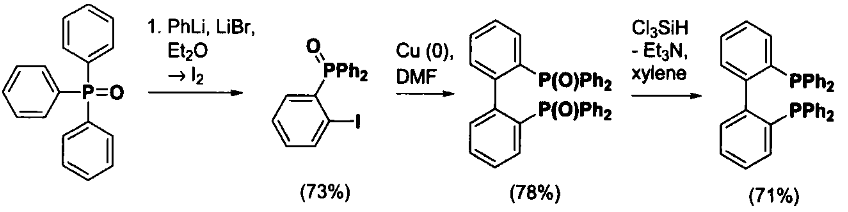
Similarly, enantiomers of *trans*-11,12-*bis*(diphenylphosphinomethyl)-9,10-dihydro-9,10-ethanoanthracene and its perhydrogenated derivatives have been prepared.[76]



(79)

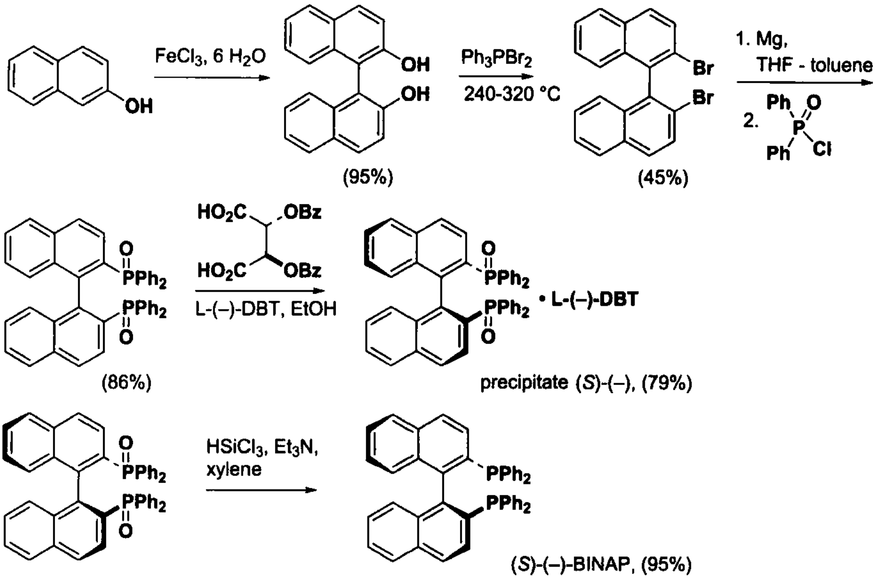
ε. Biphenyl Derivatives

The 1,1'-biphenyl-2,2'-diyl*bis*(diphenylphosphine) can be prepared by Ullmann coupling of 2-iodophenyldiphenylphosphine oxide.[77]



(80)

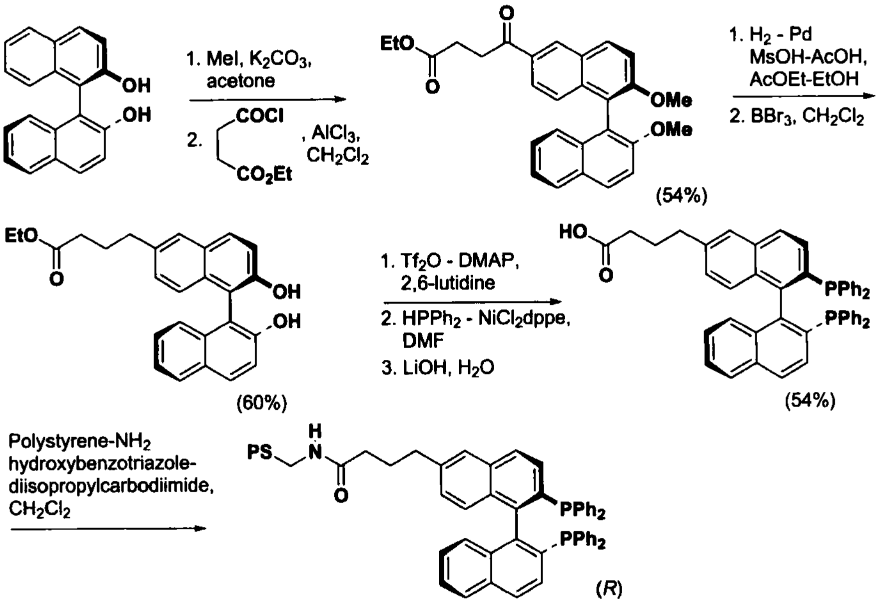
A chiral atropisomeric diphosphine, the 2,2'-*bis*(diphenylphosphino)-1,1'-binaphthalene has been obtained in optically pure form by Noyori and Takaya.[78]



(81)

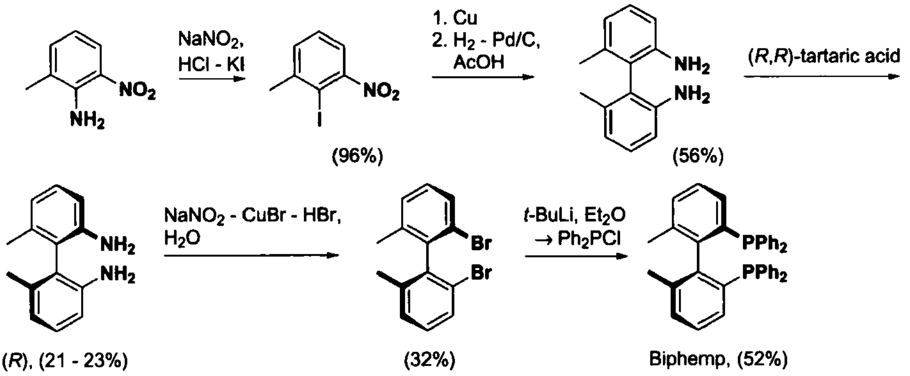
This route has several drawbacks, including a low-yielding bromination reaction. Cai and co-workers have shown that using a nickel catalyzed coupling reaction between ditriflate of 1,1'-binaphtol and diphenylphosphine provided the desired chiral BINAP in 75% yield.[79] There was no racemization during the coupling reaction. Resolution of binaphthol was carried out by complex formation with chiral host compound derived from tartaric acid[80] or *N*-benzylcinchonidinium chloride.[81] The preparation of the ditriflate was described by Mattay and his group.[82]

A BINAP containing an alkyl carbocyclic acid functionality able to incorporate onto an insoluble polymer and provide a reusable catalyst has been prepared.[83]



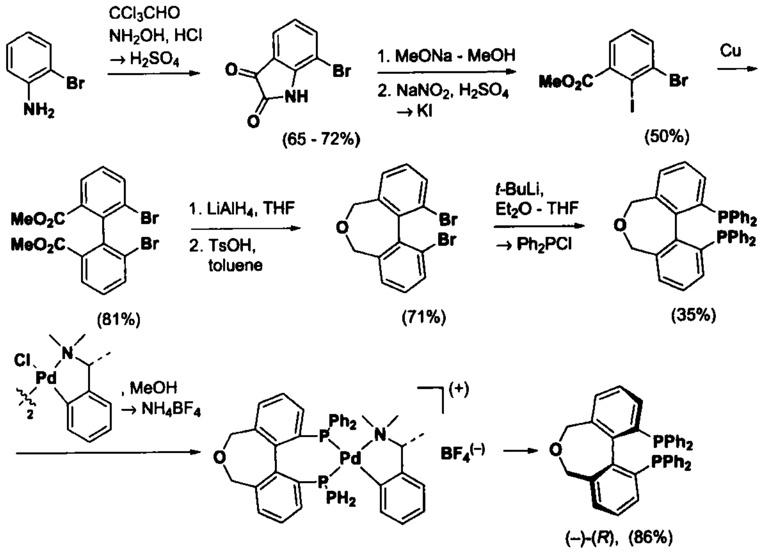
(83)

The (–)-(*R*)- and (+)-(*S*)-(6,6'-dimethylbiphenyl-2,2'-diyl)*bis*(diphenylphosphine) (biphemp) have been synthesized by Schmid and co-workers.[84]



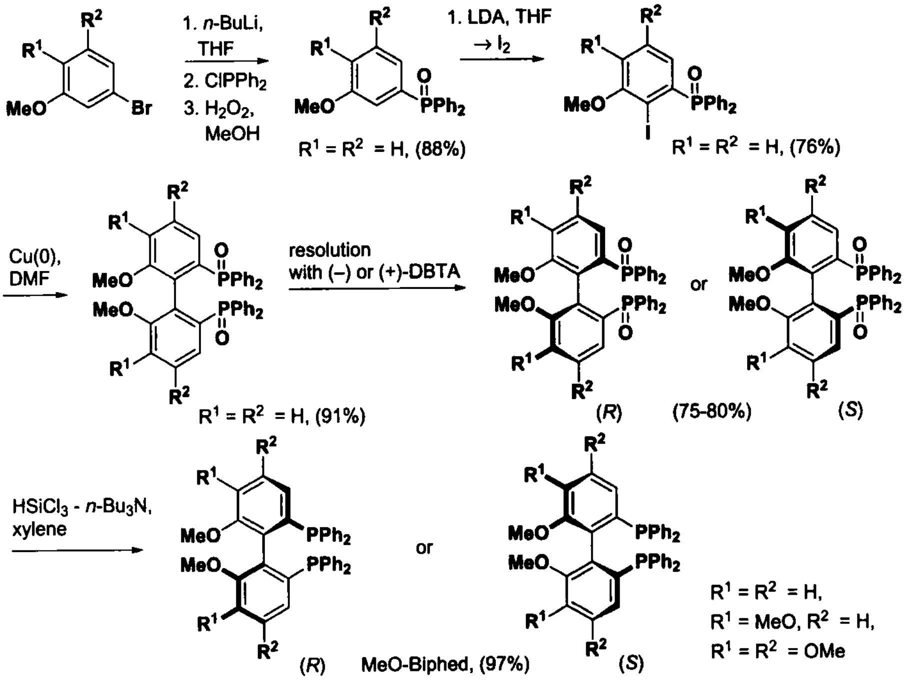
(84)

The same group obtained the 6,6'-bridged analogue, namely the (*R*)-5,7-dihydrodibenz-[*c*,*e*]oxepin-1,11-*bis*(diphenylphosphine).[84a] This was easily resolved *via* the formation of a cationic palladium complex formed from an amino palladacycle.



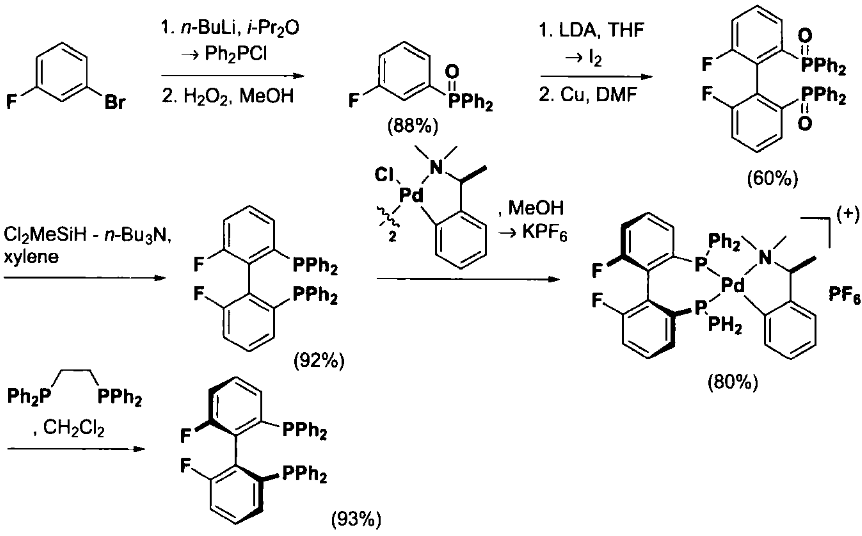
(85)

Some "MeO-biphed" were obtained by Schmid and his group according to the *ortho*-lithation/iodination *Ullmann*-reaction approach.[85]



(86)

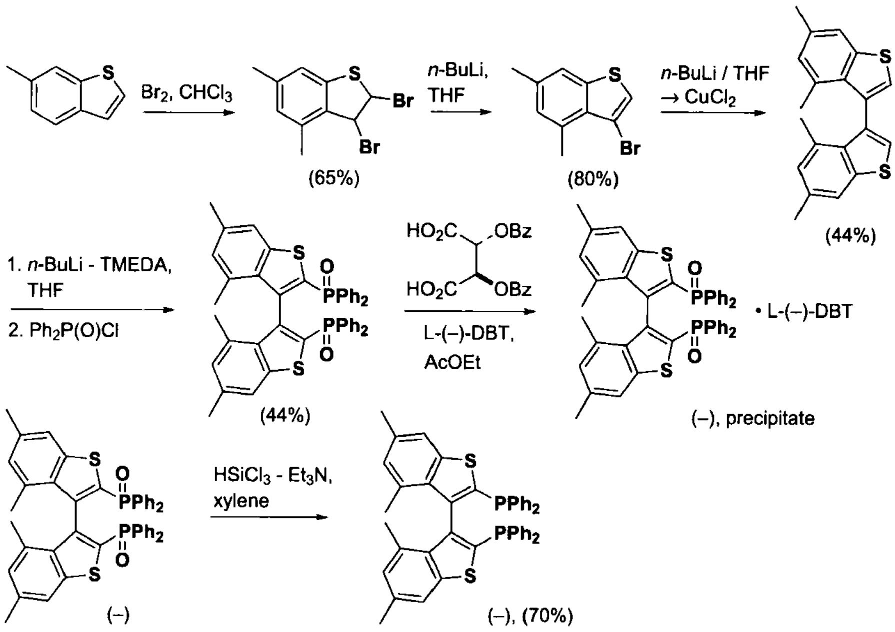
The same procedure has been used by Jendralla for the preparation of (6,6-difluorobiphenyl-2,2'-diyl)*bis*(diphenylphosphine).[86]



(87)

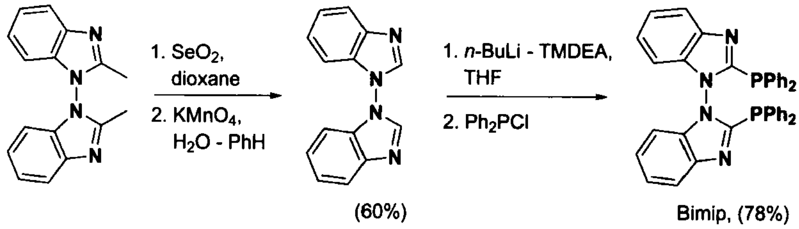
ω. *Biheteroaryl Derivatives*

Some (diphenylphosphino)-biheteroaryls were obtained by Sannicolò and Cesarotti as the 2,2'-*bis*(diphenylphosphino)-4,4',6,6'-tetramethyl-3,3'-bibenzo[*b*]thiophene.[87]



(88)

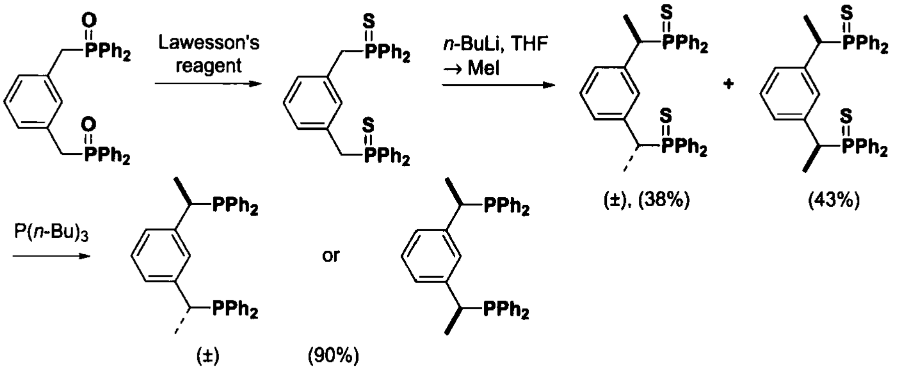
Similarly, the 2,2'-*bis*(diphenylphosphino)-1,1'-bibenzimidazole has been described.[88]

 (89)

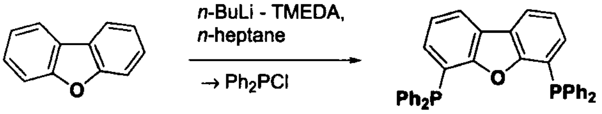
4. Synthesis of 1,5-*bis*(Diphenylphosphino)pentanes

a. *1,5-bis(Diphenylphosphino)pentanes*

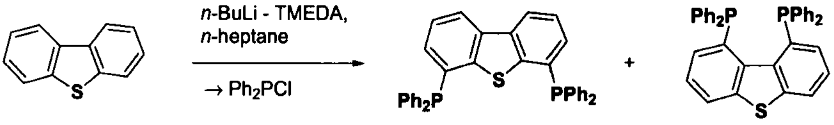
The 1,3-*bis*[1-(diphenylphosphino)ethyl]benzenes were obtained from α,α'-dibromo-*m*-xylene.[89]

 (90)

The synthesis of 4,6-*bis*(diphenylphosphino)dibenzofuran was the result of the twofold lithiation of dibenzofuran and reaction with Ph_2PCl.[90]

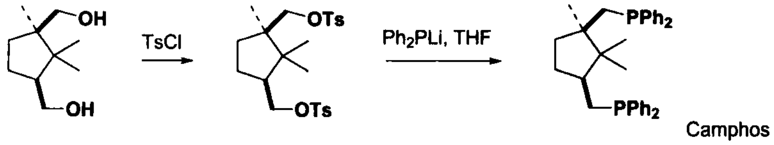
 (91)

In contrast, the lithiation of dibenzothiophene occurs at 4,6- or 1,9-position.[90]

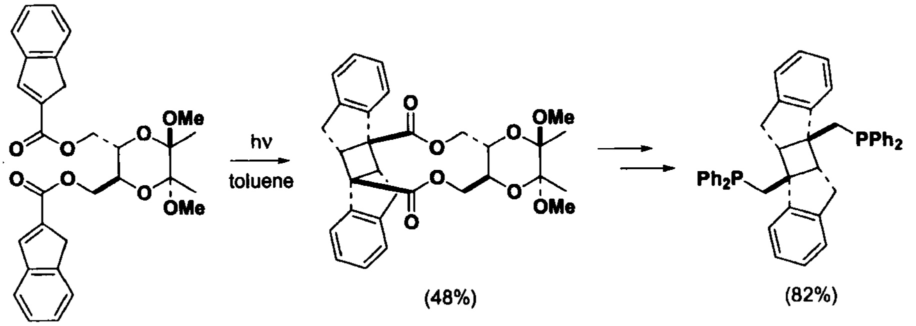
 (92)

b. *Optically Active 1,5-bis(Diphenylphosphino)pentanes and Related Compounds*

The chiral (*1R,3S*)-1,2,2-trimethyl-1,3-*bis*(diphenylphosphinomethyl)methylcyclo-pentane (camphos) has been obtained from (+)-camphoric acid.[91]

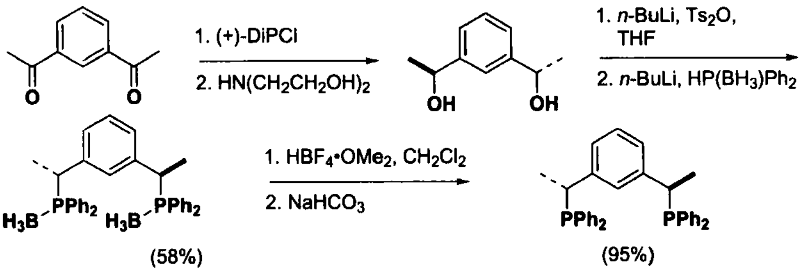
 (93)

The asymmetric intramolecular [2+2] photocycloaddition of diindenecarboxylates led to the *syn*-head-to-tail dimer.[68]



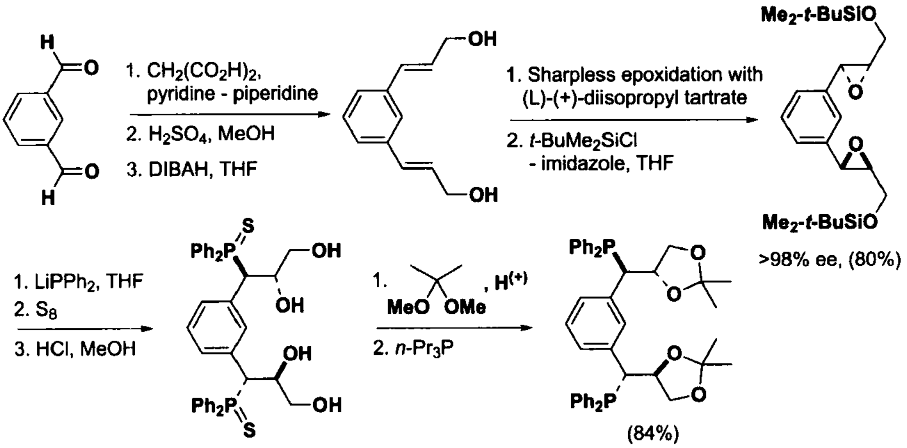
(94)

Chiral reduction of 1,3-diacetylbenzene by (+)-B-chlorodiisopinocampheylborane gave rise to (1*S*,1*S*')-1,3-*bis*(1-hydroxyethyl)benzene. After *in situ* tosylation, the substitution was realized with $Li(BH_3)PPh_2$ to prevent the possible racemization during the nucleophilic attack.[92]



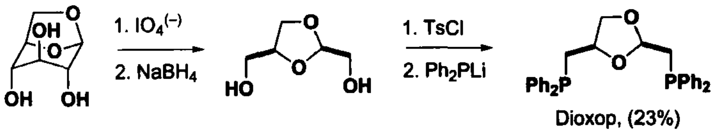
(95)

The selective opening of a bis epoxide resulting from the Sharpless oxidation gave rise to 1,3-*bis*[(1'*S*,2'*S*)-1'-diphenylphosphino)-2',3'-*O*-isopropylidene-2',3'-dihydroxypropyl]-benzene.[93]



(96)

A diphosphine derived from an anhydro sugar (dioxop) has been prepared by Descotes and his group.[94]

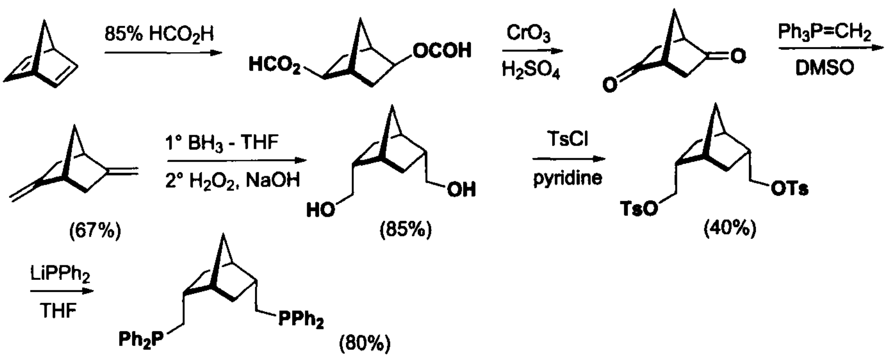


(97)

5. Synthesis of 1,6-*bis*(Diphenylphosphino)hexanes

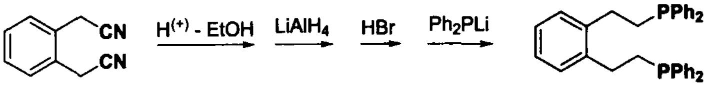
a. 1,6-bis(Diphenylphosphino)hexanes

The bicyclo[2.2.1]heptane-2,5-dione was the starting material for a four step synthesis of *endo,endo*-2,5-*bis*((diphenylphosphino)methyl)bicyclo[2.2.1]heptane based on the diastereo-selective dihydroboration of an exocyclic diene.[95]



(98)

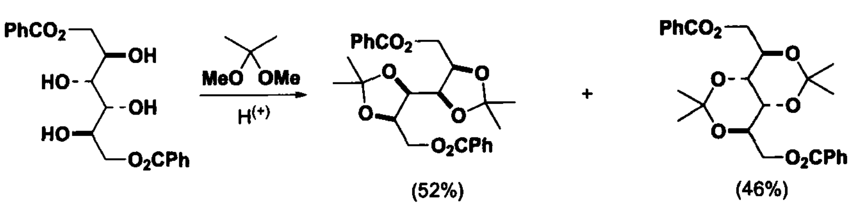
1,2-*bis*(2-Diphenylphosphinoethyl)benzene was prepared starting from 1,2-*bis*(cyanomethyl)benzene.[96]



(99)

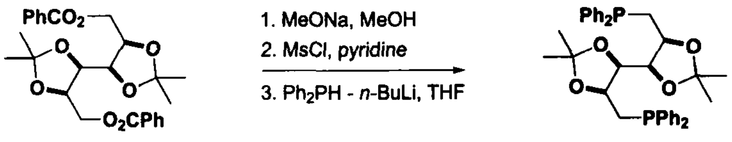
b. Optically Active 1,6-bis(Diphenylphosphino)hexanes

From D-mannitol 1,6-dibenzoate, two cyclic acetals can be prepared.[97]

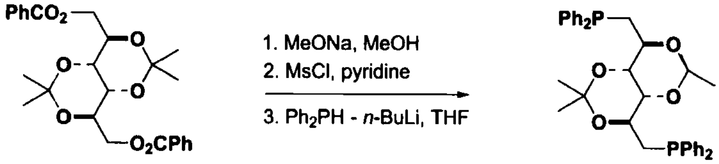


(100)

The dioxolanyl and tetraoxadecalin derivatives were transformed into diphosphines.[97]

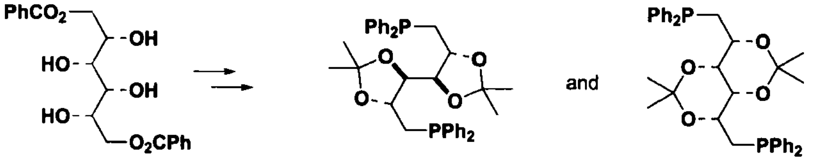


(101)



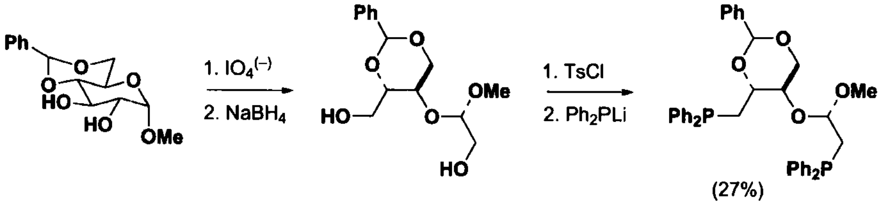
(102)

The same procedure has been used for the preparation of two diphosphines from L-iditol 1,6-dibenzoate.[97]



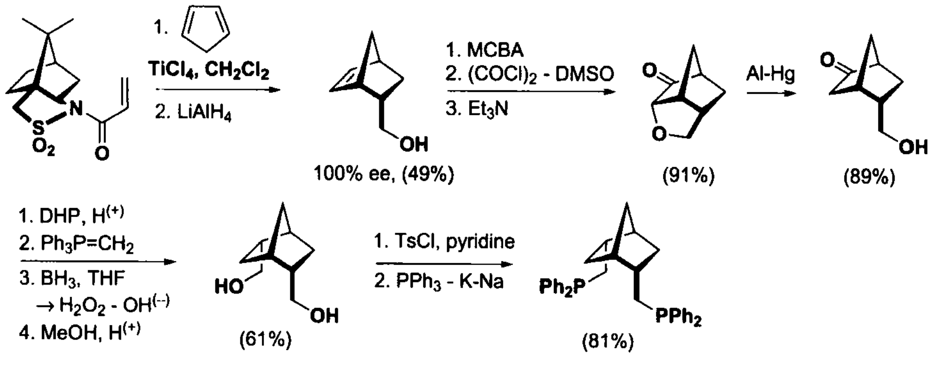
(103)

A diphosphine acetal has been prepared from a protected sugar.[94]



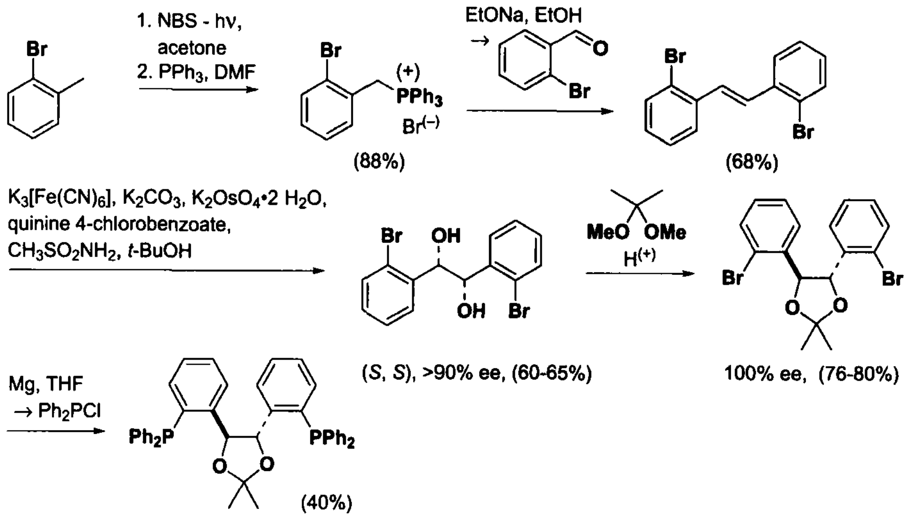
(104)

(1*S*,2*S*,4*S*,5*S*)-2,5-*bis*(diphenylphosphinomethyl)bicyclo[2.2.1]heptane has been prepared by the use of an asymmetric Diels-Alder reaction.[98]



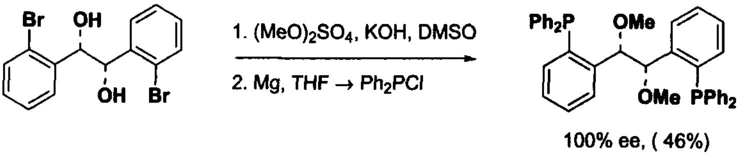
(105)

A ligand homologous of the diop was prepared by Brunner and co-workers. Both enantiomers of the diol were obtained *via* asymmetric dihydroxylation of dibromostilbene by using the esters of 4-chlorobenzoic acid with quinine or quinidine.[99]



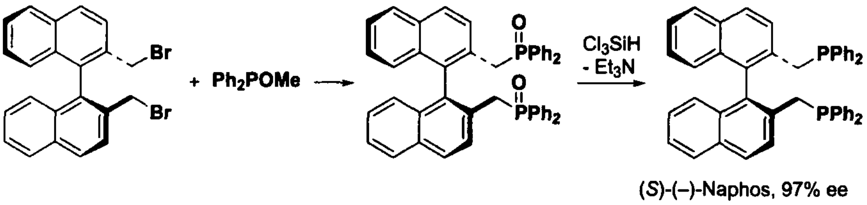
(106)

The dimethoxy derivative has been obtained from the diol.[99]



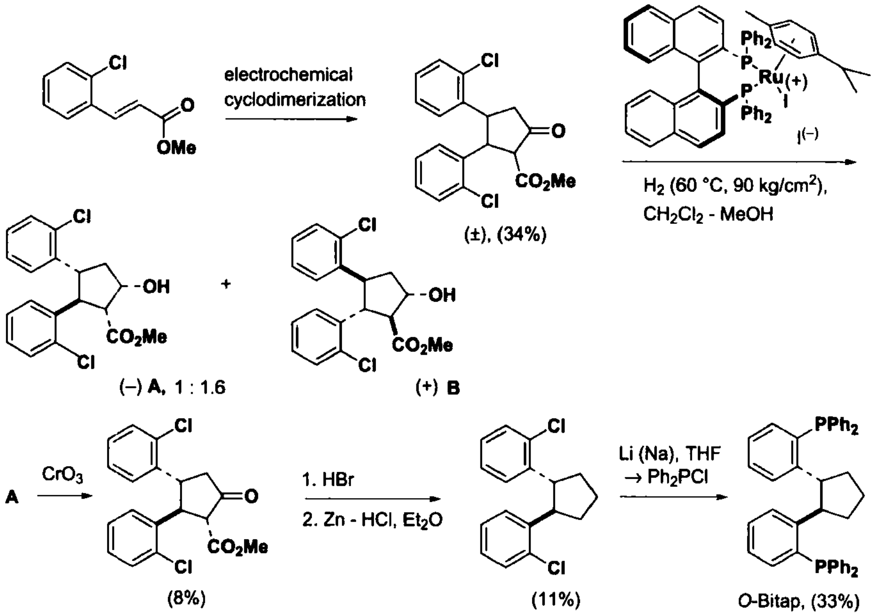
(107)

An optically active binaphthyl derivative has been obtained by Kumada and co-workers from an Arbusov reaction between 2,2'-*bis*(bromomethyl)-1,1-binaphthyl and methyl diphenylphosphinite followed by reduction (no yields given).[100]



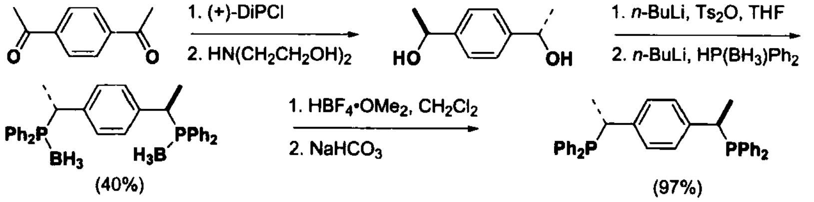
(108)

The (1*R*,2*R*)-*trans*-*bis*(2-diphenylphosphinophenyl)cyclopentane (*O*-bitap) has been prepared in optically pure form based on asymmetric hydrogenation of 4,5-diaryl-2-oxocyclopentanecarboxylates by the BINAP-Ru(II) complex.[101]



(109)

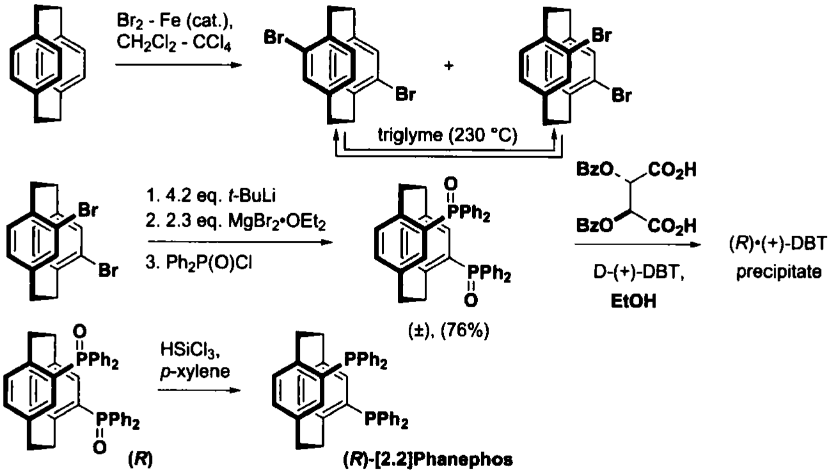
As for the 1,3-diacetylbenzene, chiral reduction of 1,4-diacetylbenzene by (+)-B-chloro diisopino-campheylborane gave rise to (1*S*,1*S*′)-1,4-*bis*(1-hydroxyethyl)benzene precursor of a diphosphine.[92]



(110)

6. Synthesis of Optically Active 1,7-*bis*(Diphenylphosphino)heptanes

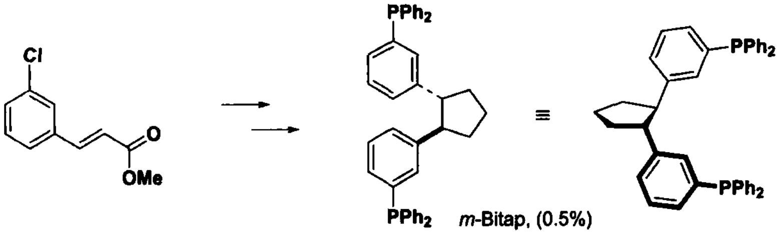
Pye, Rossen and co-workers use a paracyclophane backbone to give a planar chiral C_2 symmetric bisphosphine, the 4,12-*bis*(diphenylphosphino)[2.2]paracyclophane [(*R*)-[2.2]phanephos].[102]



(111)

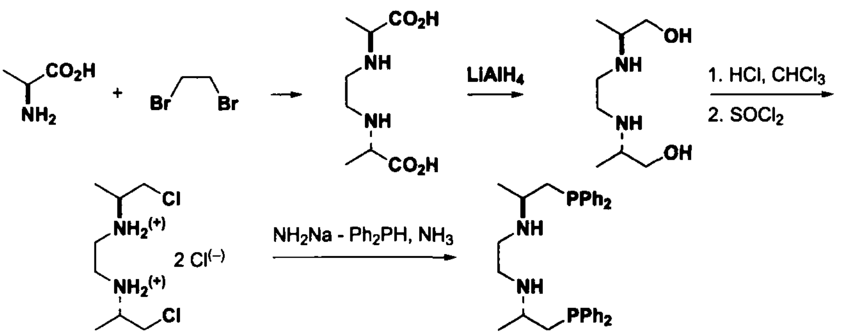
7. Synthesis of 1,n-*bis*(Diphenylphosphino)alkanes and Related Compounds

The (1*R*,2*R*)-*trans*-*bis*(3-diphenylphosphinophenyl)cyclopentane (*m*-bitap) has been obtained according to the same procedure as for the preparation of the (1*R*,2*R*)-*trans*-*bis*(2-diphenylphosphinophenyl)cyclopentane (Scheme 109).[101]



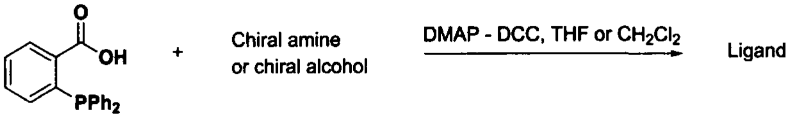
(112)

(2*S*,7*S*)-2,7-Dimethyl-3,6-diaza-1,8-octanediol was prepared from (*S*)-prolinol and transformed into (2*S*,7*S*)-2,7-dimethyl-3,6-diaza-1,8-(diphenylphosphino)octane.[103]



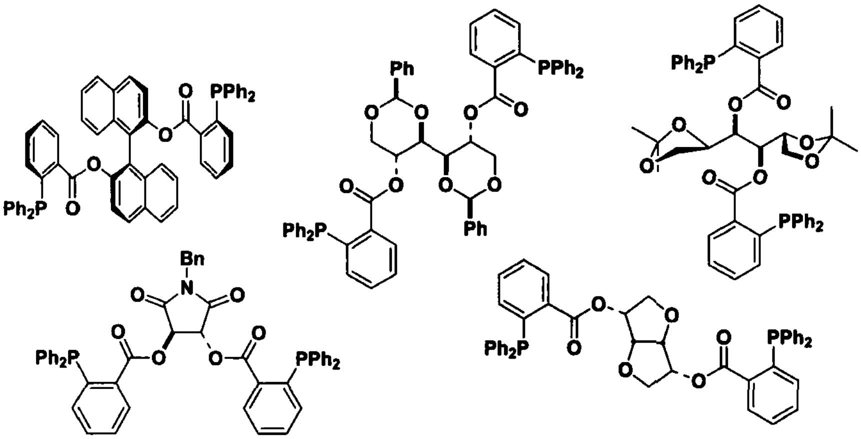
(113)

A modular approach for ligand design has been proposed by Trost and co-workers based on the obtaining of 2-(diphenylphosphino)benzoic esters or amides.[104]



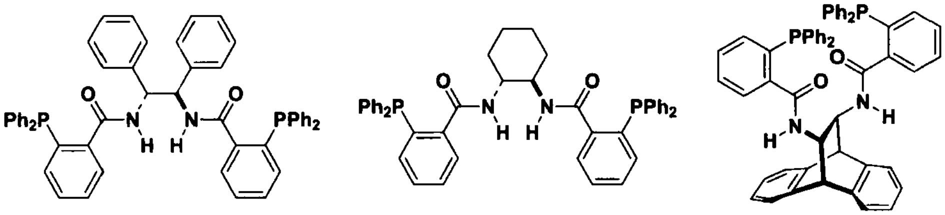
(114)

Some ligands from C_2 symmetrical diols may be easily obtained.[104]



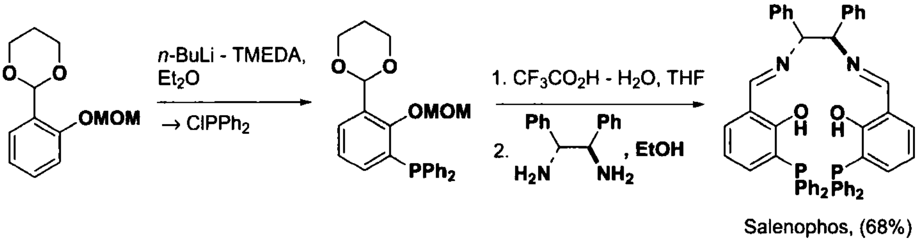
(115)

Similarly, C_2 symmetric 1,2-diamines give rise to bidentate ligands.[105]



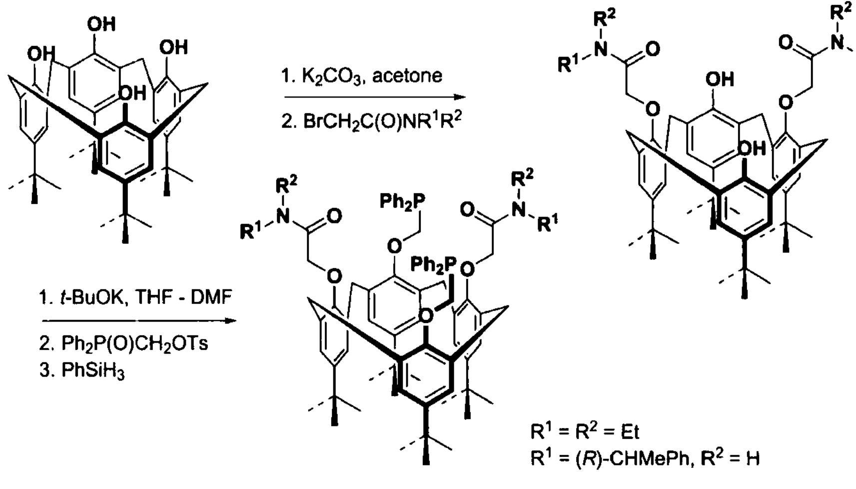
(116)

A chiral ligand bearing hard and soft coordination sites, like salanophos, was obtained from 1,2-diphenylethane-1,2-diamine and *o*-bromophenol.[106]



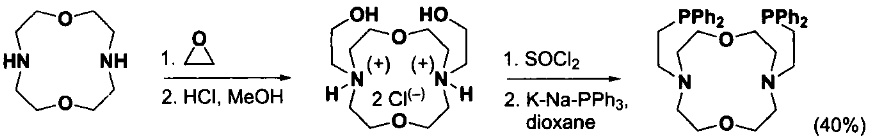
(117)

Cavity-shaped phosphane ligands based on a calix[4]arene matrix have been prepared by Matt and his group.[107]

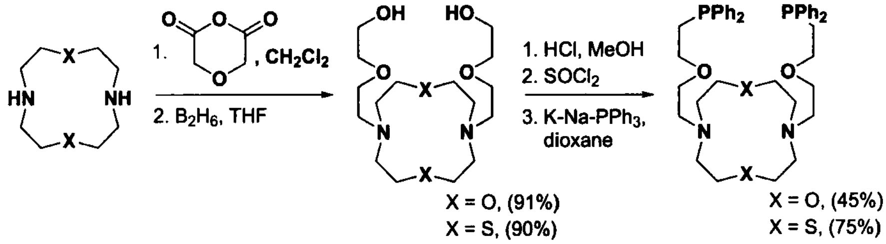


(118)

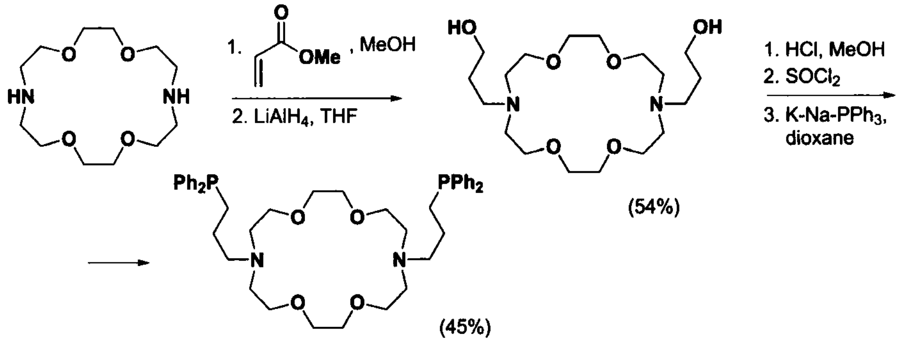
The synthesis of a series of phosphine-functionalized dipodal macrocycles has been described by Lehn, Parker and co-workers.[108]



(119)



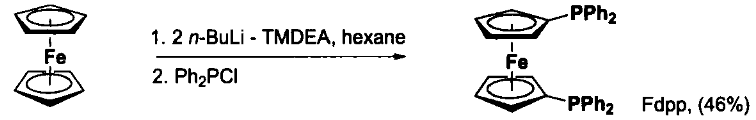
(120)



(121)

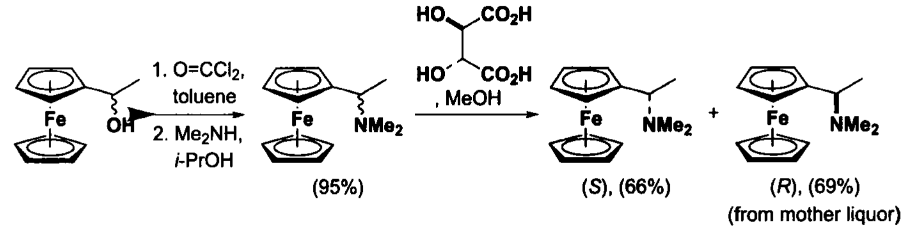
8. Synthesis of Optically Active Ferrocenes or Ruthenocenes[109]

Solutions of *n*-butyllithium and N,N,N',N'-tetramethylethylenediamine (TMEDA) readily dilithiate ferrocene which can be used to prepare ferrocene-1,1'-*bis*(diphenylphosphine).[110] (Tri-*n*-butylstannyl)ferrocene was also used as precursor of monolithioferrocene.[111]



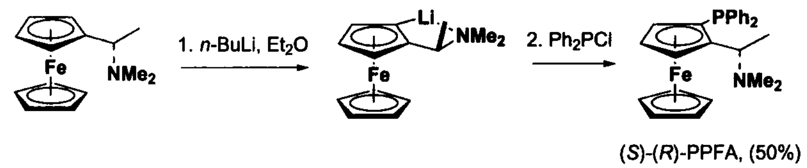
(122)

The resolution of (*S*)- et (*R*)-α-ferrocenylethyldimethylamine with (*R*)-(+)-tartaric acid is one of the cases were both antipodes are obtained in high yield.[112]



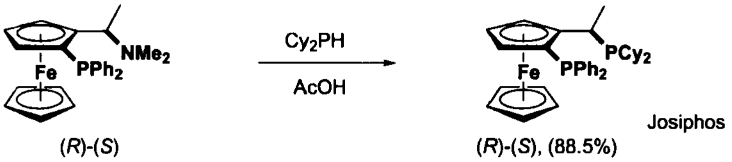
(123)

α-Ferrocenyl tertiary amines are lithiated at the 2-position of the ferrocene because the nitrogen atom of the amino group interacted with the attacking metal. The lithiation of (*S*)-enantiomer led to (*S*)-α-[(*R*)-2-diphenylphosphinoferrocenyl]ethyldimethylamine (PPFA).[113]



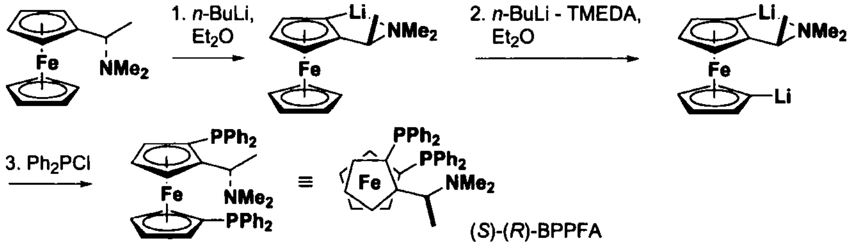
(124)

Synthesis of (*R*)-1-[(*S*)-2diphenylphosphino)ferrocenyl]ethyldicyclohexylphosphine was achieved as illustrated (josiphos).[114]



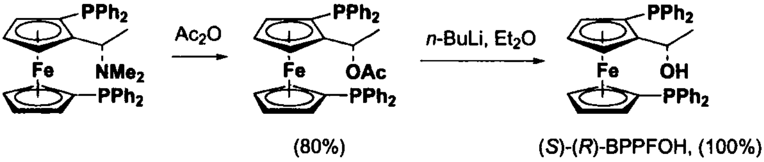
(125)

Synthesis of (*S*)-α-[(*R*)-1',2-*bis*(diphenylphosphino)ferrocenyl]ethyldimethylamine is shown below (BPPFA).[113]



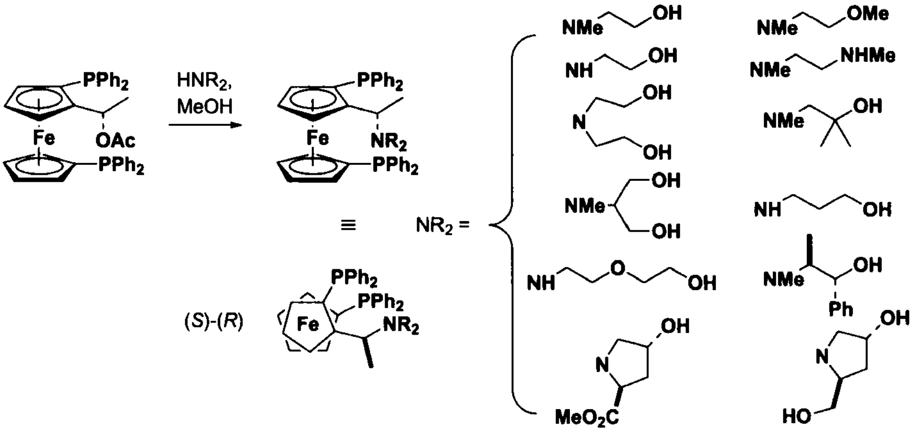
(126)

Synthesis of (*S*)-α-[(*R*)-1',2-*bis*(diphenylphosphino)ferrocenyl]ethanol is outlined (BPPFOH).[115]

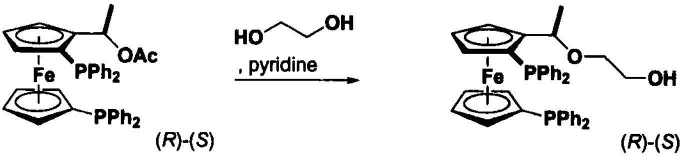


(127)

Synthesis of some (*S*)-α-[(*R*)-1',2-*bis*(diphenylphosphino)ferrocenyl]ethylamines or ethers were obtained after substitution of the ferrocenylethyl acetate.[116]

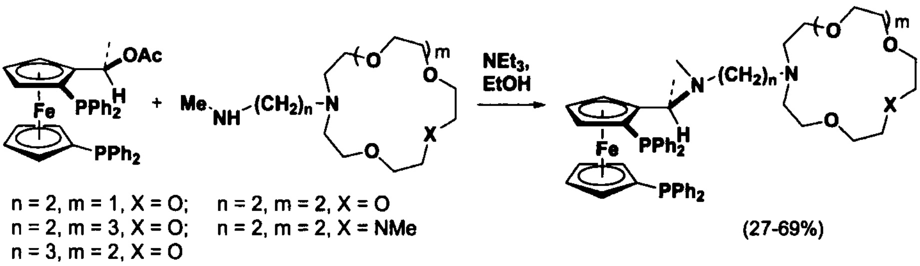


(128)

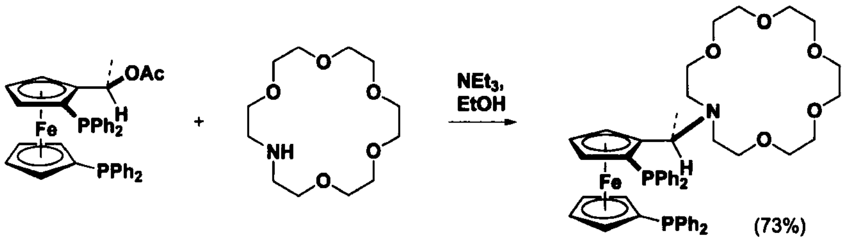


(129)

Chiral ferrocenylphosphine ligands modified by monoaza or diaza crown ethers of various ring sizes and linker chain lengths have been synthesized.[117]

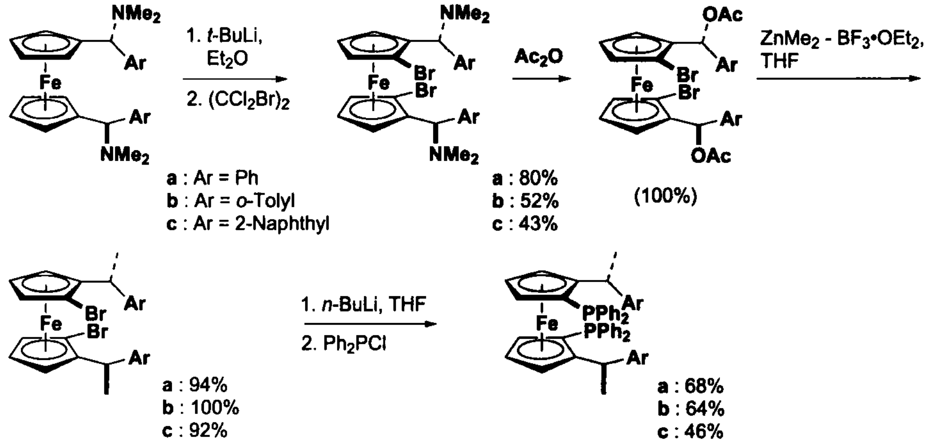


(130)



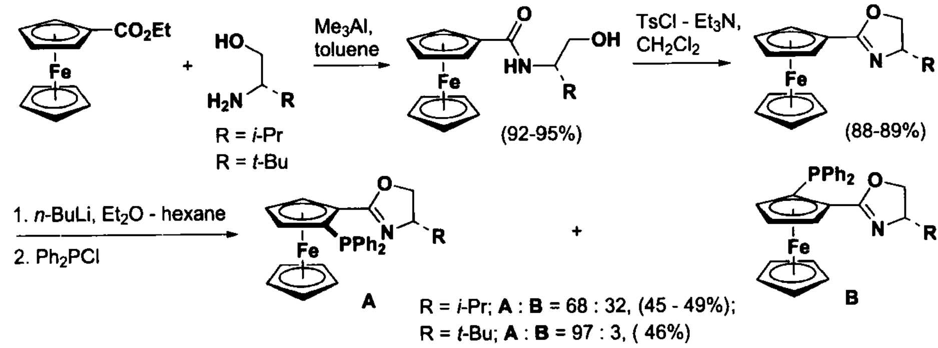
(131)

Chiral C_2-symmetrical ferrocenyl ligands have been prepared by Knochel and co-workers.[118]



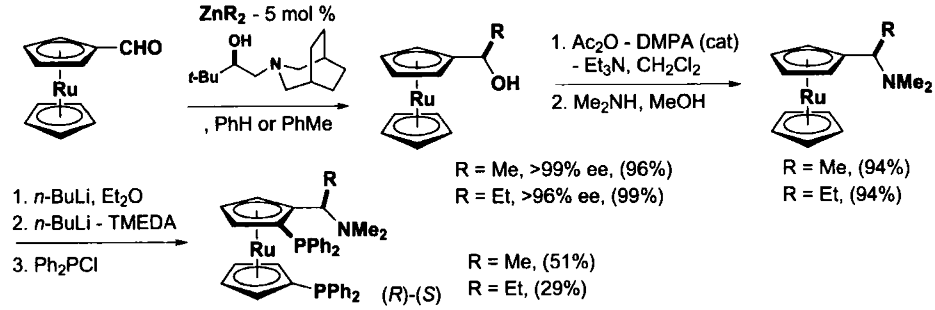
(132)

A series of diphenylphosphino(oxazolinyl)ferrocene ligands has been obtained from ethyl ferrocenecarboxylate and amino acid-derived amino alcohols.[119]



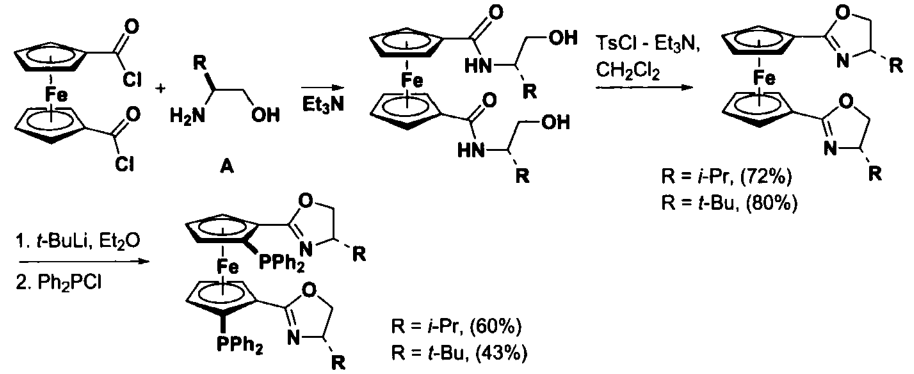
(133)

Optically active ruthenocenyl*bis*(phosphines) were prepared by way of stereoselective lithiation of (*R*)-*N*,*N*-dimethyl-1-ruthenocenylalkylamines.[120]



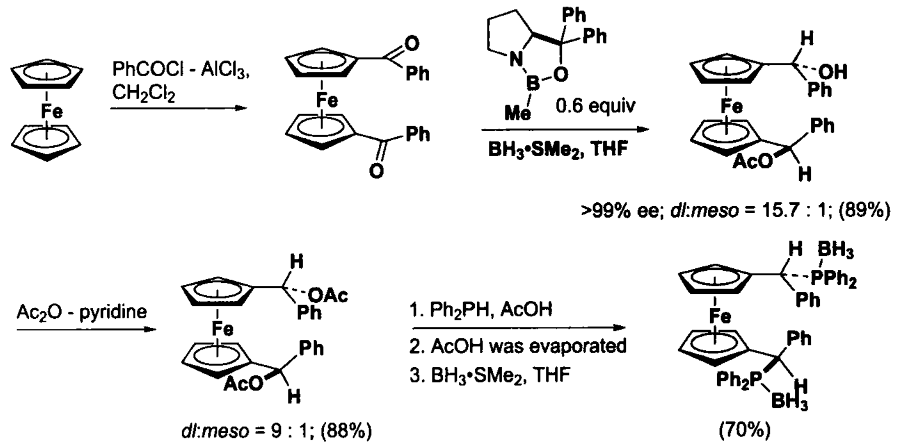
(134)

Ligands which are "*N*,*N*′,*P*,*P*′-type" have been prepared from chiral amino-alcohol A.[121]



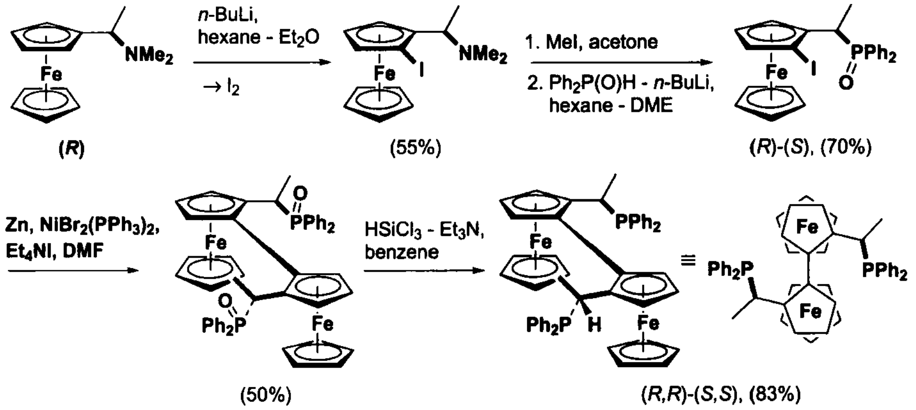
(135)

The synthesis of C_2-symmetrical chiral ferrocenyl (or ruthenocenyl) diphosphines has been described by Knochel and his group.[122]



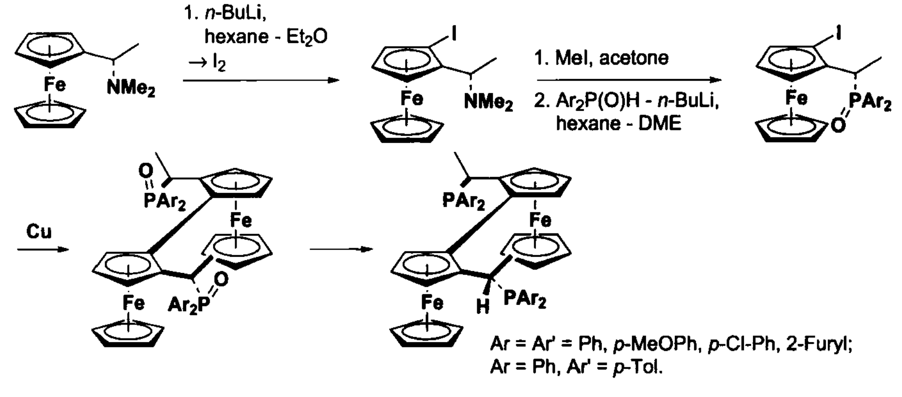
(136)

A chiral diphosphine ligand, (*R*,*R*)-(*S*,*S*)-2,2"-*bis*[1-(diphenylphosphino)ethyl]-1,1"-biferrocene, which possesses both central and planar elements of chirality was synthesized.[123]



(137)

The *trans*-chelating phosphine ligand (*S*,*S*)-(*R*,*R*)-2,2"-*bis*[1-(diarylphosphino)ethyl]-1,1"-biferrocene was synthesized from (*S*)-1-(*N*,*N*-dimethylamino)ethylferrocene.[124]



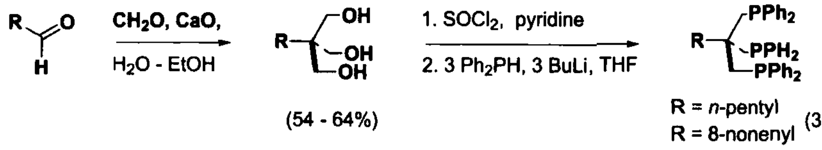
(138)

II. SYNTHESIS OF *tris*(DIPHENYLPHOSPHINE) LIGANDS

1. Synthesis of Triphosphine Ligands

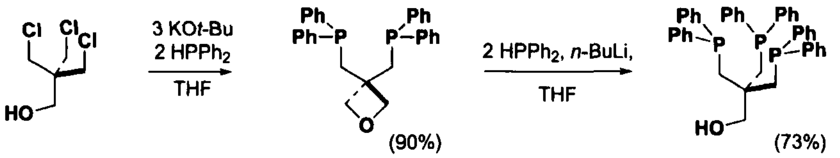
a. *Triphosphine Ligands with a Neopentyl Backbone*

Tripod ligands have been prepared from the corresponding triols.[125]



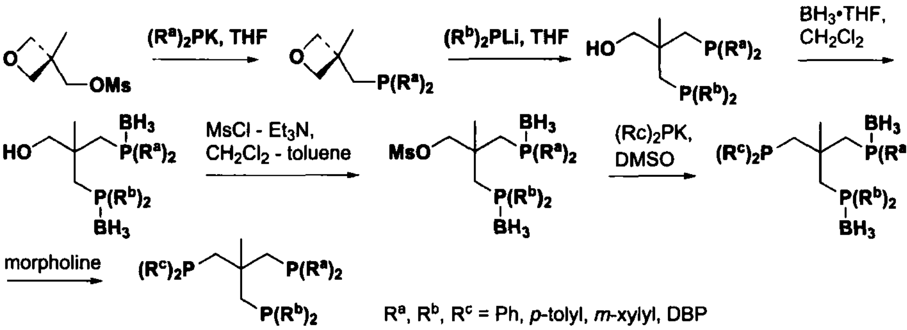
(139)

Starting from pentaerythritol, the synthesis of a hydroxy functionalized tripod ligand was achieved in a few steps.[126]

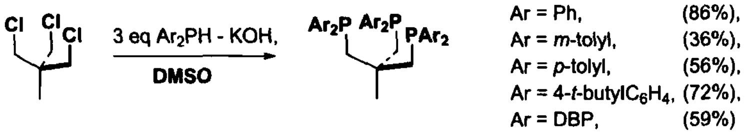


(140)

Tripod ligands containing three different donor groups at their neopentyl backbone have been described by several authors.[127,128]

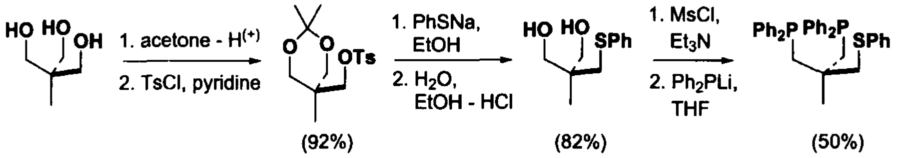


(141)



(142)

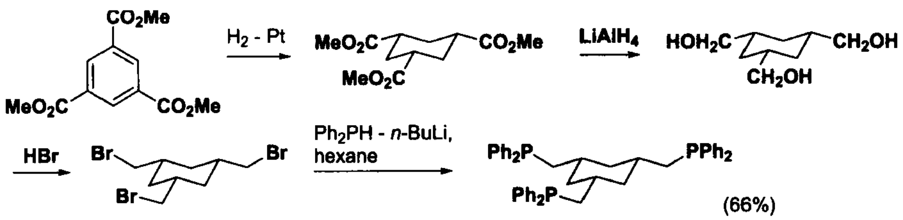
A hybrid tripodal ligand containing phosphorus and sulfur atoms, 2,2-*bis*(diphenylphosphinomethyl)-1-phenylthiopropane was synthesized.[129]



(143)

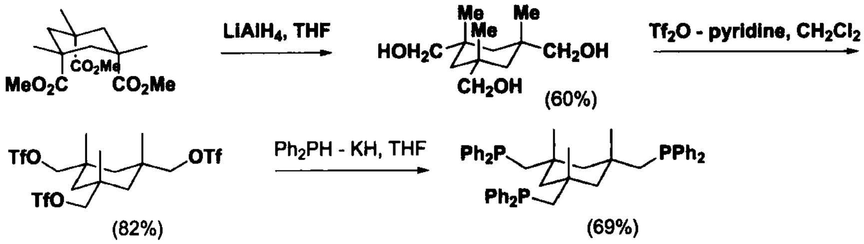
b. *Triphosphine Ligands with a 1,3,5-Cyclohexane Backbone*

The tridentate ligand *cis,cis*-1,3,5-*tris*[(diphenylphosphino)methyl]cyclohexane has been synthesized from the methyl ester of trimesic acid.[130]



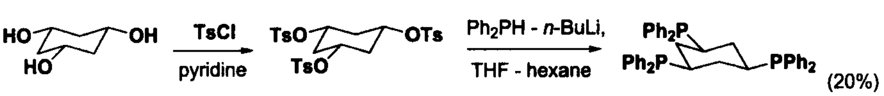
(144)

The *cis,cis*-1,3,5-*tris*[(diphenylphosphino)methyl]-1,3,5-trimethylcyclohexane has been prepared from *cis,cis*-trimethyl ester.[131]



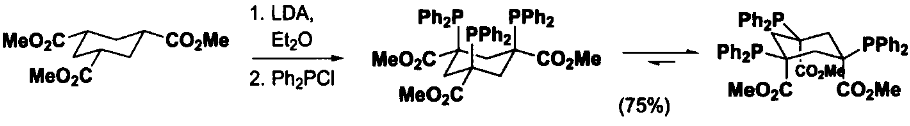
(145)

The *cis,cis*-1,3,5-*tris*(diphenylphosphino)cyclohexane was easily obtained by a two-step procedure from *cis,cis*-1,3,5-cyclohexanetriol.[132]



(146)

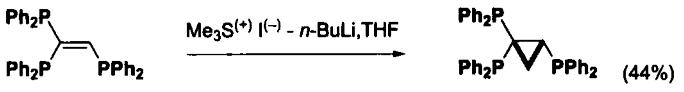
The tripodal *cis,cis*-1,3,5-*tris*(diphenylphosphino)-1,3,5-*tris*(methoxycarbonyl)cyclo-hexane has been synthesized by phosphinylation of the trienolate of the following triester.[133]



(147)

c. Triphosphine Ligands with a Cyclopropane Backbone

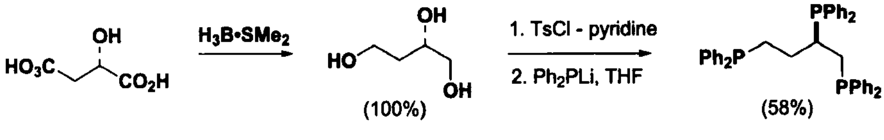
Cyclopropanation of 1,1,2-*tris*(diphenylphosphino)ethene with dimethylsulfonium methylide affords 1,1,2-*tris*(diphenylphosphino)cyclopropane.[134]



(148)

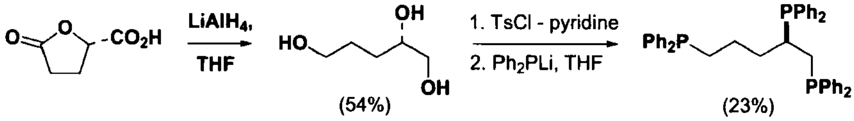
2. Synthesis of Optically Active Triphosphine Ligands

Brunner and co-workers have prepared some optically active *bis* and *tris*(phosphines). Reduction of L-malic acid afforded a triol precursor of the 1,2,4-*tris*(diphenylphosphino)butane.[49]



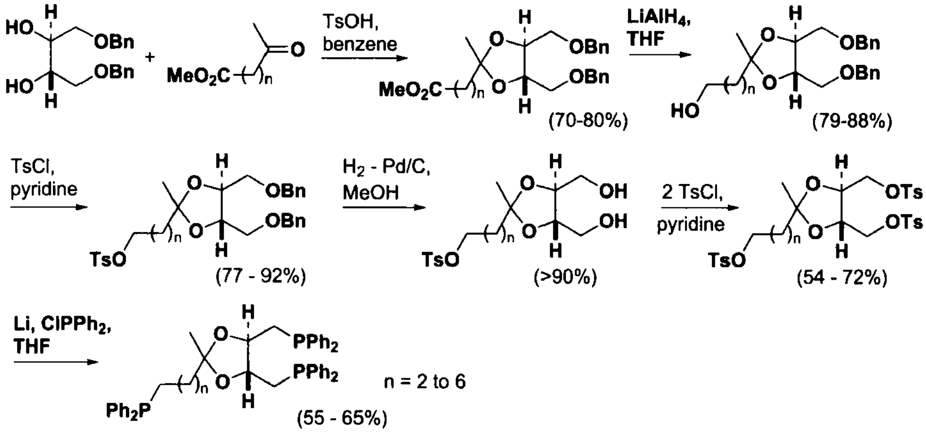
(149)

The corresponding homologue was synthesized from a lactone prepared from L-glutamic acid.[49]



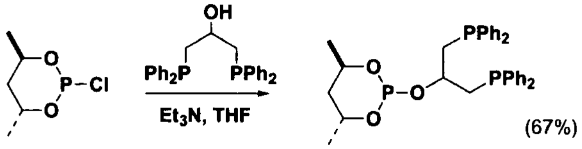
(150)

Some diop derivative triphosphines have been prepared starting from (*R*,*R*)-tartaric acid.[135]



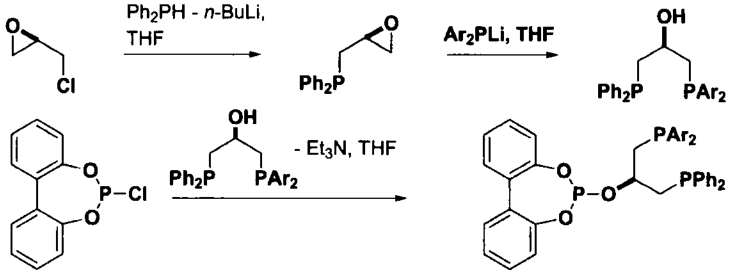
(151)

Chiral tripodal ligand has been obtained from the alcohol resulting of the reaction of epichlorhydrin with lithium diphenylphosphide.[136]



(152)

Successive addition of lithium phosphide to optically active epichlorhydrin led to chiral 1,3-(diarylphosphino)-2-propanols which react with phosphorochloridites to yield mixed donor group tripodal ligands.[137]

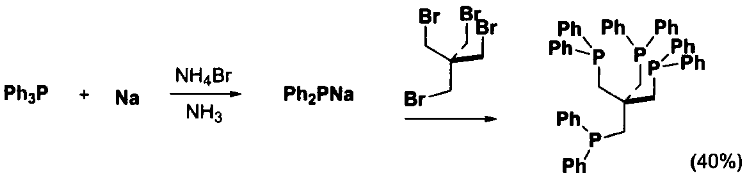


(153)

III. SYNTHESIS OF *tetrakis*(DIPHENYLPHOSPHINE) LIGANDS

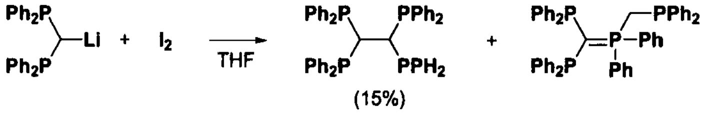
1. Synthesis of Tetraphosphine Ligands

A tetrafunctional ligand was prepared from *tetrakis*(bromomethyl)methane and four equivalents of NaPPh$_2$ in liquid ammonia.[138]



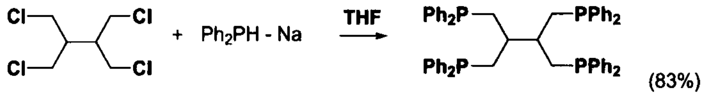
(154)

Oxidation of a THF solution of $LiCH(PPh_2)_2$ with iodine afforded 1,1,2,2-*tetrakis*-(diphenylphosphino)ethane with low yields.[139]



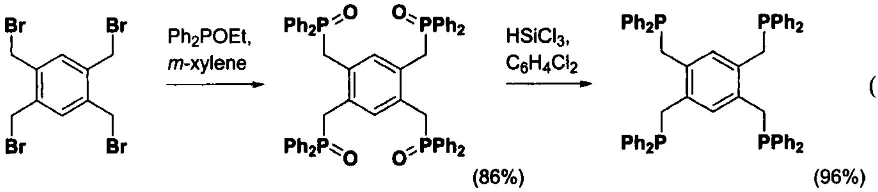
(155)

The 2,3-*bis*[(diphenylphosphino)methyl]-1,4-*bis*(diphenylphosphino)butane has been obtained from tetrachloro analogue.[140]



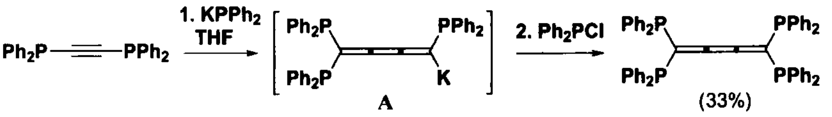
(156)

The 1,3,4,6-*tetrakis*(diphenylmethyl)benzene has been prepared from the Arbuzov reaction of 1,3,4,6-*tetrakis*(bromomethyl)benzene and ethyl diphenylphosphinite.[141]



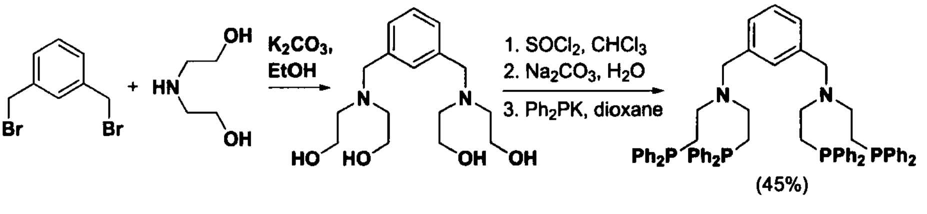
(157)

Treatment of *bis*(diphenylphosphino)ethyne with potassium diphenylphosphide led to potassium derivative which reacted with chlorodiphenylphosphine to give 1,1,4,4-*tetrakis*(diphenylphosphino)butatriene *via* a suspected intermediate **A**.[142]



(158)

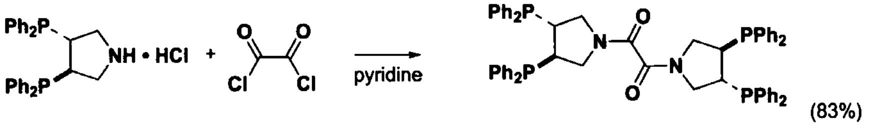
A very simple procedure gave rise to 1,3-*bis*{*bis*[2-(diphenylphosphino)ethyl]aminomethyl}benzene from 1,3-dibromomethylbenzene.[143]



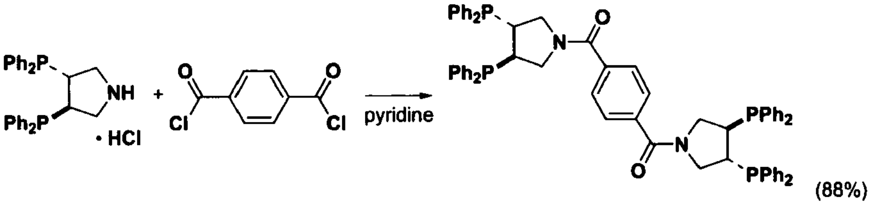
(159)

2. Synthesis of Optically Active Tetraphosphine ligands

The (*R*,*R*)-3,4-*bis*(diphenylphosphino)pyrrolidine, prepared from tartaric acid, reacts with oxalyl chloride or terephthaloyl chloride to give tetraphosphine ligands.[34]



(160)



(161)

IV. CONCLUSION

It should be clear from this review that a great diversity of polyphosphine ligands have been synthesized. Many transition metal complexes display good catalytic properties when they are coordinated to some phosphine ligands. Certainly, the best example of a chiral economic method is enantioselective catalysis by using catalyst derived from transition metal complexes bearing the required chiral information in asymmetric ligands.[144]

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