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Natural compounds in the synthesis of chiral organophosphorus ligands

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Abstract. Methods for the synthesis of chiral organophosphorus compounds based on natural optically active compounds (hydroxy acids, amino acids and their derivatives, mono- and disaccharides, mono- and diterpenoids, steroids) are discussed. Particular attention is given to the synthesis of bisphosphines and bisphosphinites. These compounds serve as ligands for transition metal complexes, which catalyse asymmetric hydrogenation. Data on the enantioselectivity of hydrogenation of unsaturated precursors of amino acids and unsaturated prochiral acids as well as on the enantioselectivity of hydrosilylation of ketones are surveyed. The bibliography includes 77 references.

I. Introduction

Chiral organophosphorus ligands are widely used in the synthesis of metal complex catalysts. It is these transition metal complexes with mono- and bidentate chiral phosphines and phosphinites that made it possible to perform important industrial reactions such as hydrogenation of prochiral unsaturated carbonyl compounds in preparative yield and with high enantioselectivity ($\geqslant 90\%$).

A large number of optically active phosphorus-containing ligands have been synthesised and used for the preparation of transition metal complexes exhibiting high catalytic activities resulting in high enantioselectivities.[1–5] Chiral organophosphorus ligands are prepared either by enantiospecific transformations of native optically pure compounds or by transformations of prochiral compounds followed by resolution of racemates. Among natural compounds, hydroxy and amino acids as well as carbohydrates are most commonly used for the synthesis of such ligands (more rarely, terpenoids and steroids, are employed).

Syntheses of chiral organophosphorus ligands with the use of natural compounds have not been systematically surveyed in the literature. The aim of the present review is to close this gap.

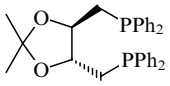
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II. Organophosphorus ligands based on hydroxy acids

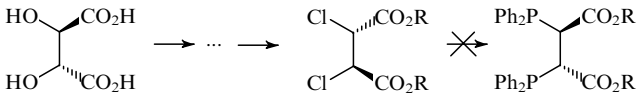
1. Synthesis of ligands

One of the first ligands used in asymmetric metal complex catalysis was DIOP, *viz*., (−)-*trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (**1**),



1

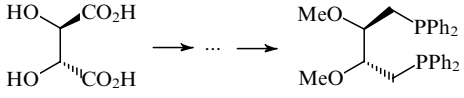
which was prepared by stereospecific transformations of (+)-(2*R*,3*R*)-tartaric acid (**2**).[6] The synthesis of **1** was preceded by unsuccessful attempts to prepare chiral bisphosphine **3** from intermediate dichloride **4** by the reaction of the latter with nucleophilic reagents, *viz*., diphenylphosphine or diphenylphosphides $MPPh_2$ (M = Li, Na, K). However, in all cases only optically inactive phosphine oxide was isolated from the reaction mixtures.



2 **4** **3**

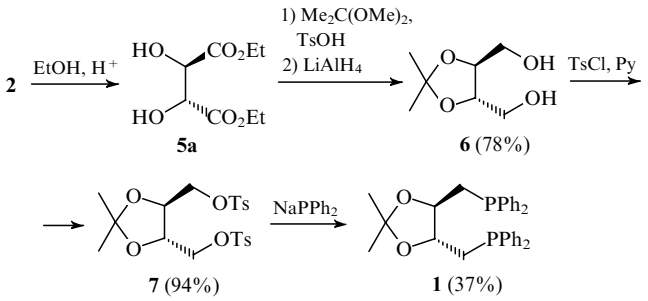
An approach based on transformations of diethyl L-tartrate (**5a**) first into acetonide, then into diol **6** and, finally, into ditosylate **7** appeared to be more efficient. Compound **7** was transformed into the target product (−)-DIOP (**1**) using sodium diphenylphosphide (Scheme 1).[7]

An analogous approach was used in the synthesis of dimethoxybisphosphine **8**.



2 **8**

Scheme 1

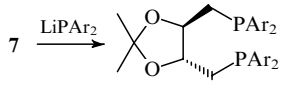


Unlike dimethoxy derivative **8**, DIOP is a crystalline compound due to which its isolation and additional purification can be substantially simplified. In addition, an essential advantage of ligand **1** over its acyclic analogue **8** is the conformational rigidity of the chelate ring formed upon its coordination to a transition metal atom due to the presence of *trans* substituents in the dioxolane ring. Metal complex catalysts thus prepared exhibit high stereoselectivity.[7]

In the syntheses of chiral phosphines from natural compounds, the phosphine group is introduced by nucleophilic displacement of the toluenesulfonyl (methanesulfonyl) group or the halogen atom with alkali metal phosphides. There are two main procedures for the preparation of the latter compounds. One procedure (*in situ* synthesis of phosphides) is based on the reactions of chlorophosphines R^1R^2PCl (R^1, R^2 = Ar, Alk) with alkali metals (Li, Na, K) in dioxane or tetrahydrofuran. Another widely used method involves the cleavage of the P–C(Ar) bond in tertiary phosphines by alkali metals followed by isolation of the resulting diarylphosphides.[8] To improve the efficiency of the synthesis, one or another modification of phosphinylation is often required. Thus, high yields were achieved in all steps of the above-considered procedure for the synthesis of DIOP (see Scheme 1) except for the step of phosphinylation, which decreased the total yield of the product to 27%.[7] Murrer *et al.*[8] suggested that phosphinylation of ditosylate **7** should be performed with the diphenylphosphide anion, which is formed *in situ* in the reaction of triphenylphosphine with an alloy of Na and K. The use of this expedient made it possible to increase the yield in the last step of the reaction to 72% (the total yield of the ligand was 49%).

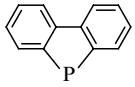
Other analogues of compound **1** were synthesised by the target replacement of substituents at the phosphorus atoms as well as by acetalisation of free hydroxy groups, which are generated upon hydrolysis of acetonide, with different carbonyl compounds.

For example, the reactions of ditosylate **7** with lithium diarylphosphides afforded symmetrical bisphosphines **9a**–**f**.[9–11]

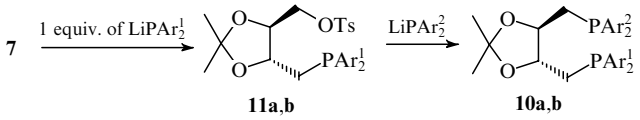


9a–**f**

Ar = 2-MeC_6H_4 (**a**), 4-MeC_6H_4 (**b**), 2,5-$Me_2C_6H_3$ (**c**), 4-MeO-3,5-$Me_2C_6H_2$ (**d**), 4-$Me_2NC_6H_4$ (**e**);

PAr_2 =  (**f**).

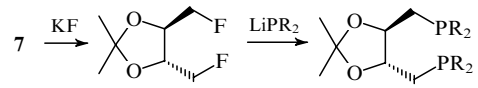
Unsymmetrical analogues of (–)-DIOP, *viz.*, compounds **10a**,**b** containing various aryl substituents at the phosphorus atoms, were synthesised in two steps. First, ditosylate **7** was treated with a particular lithium diarylphosphide (1 equiv.) and then the resulting monophosphines **11a**,**b** were treated with another diarylphosphide.[10]



11a,**b** **10a**,**b**

Compound	Ar^1	Ar^2	Yield (%)
11a	Ph	–	44
11b	3-MeC_6H_4	–	52
10a	Ph	4-$MeNC_6H_4$	51
10b	3-MeC_6H_4	4-$MeNC_6H_4$	52

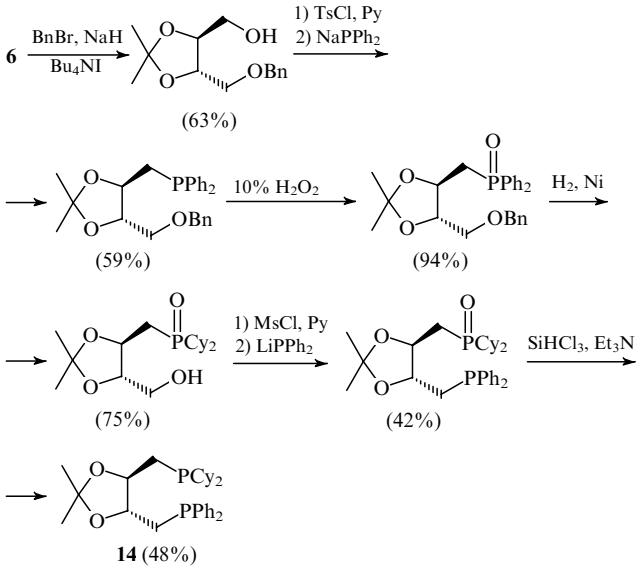
Alkyl derivatives of bisphosphine **1** were prepared from ditosylate **7** through intermediate difluoride **12**. The reactions of the latter with lithium dialkylphosphides afforded bisalkylbisphosphines, *viz.*, (–)-EtDIOP (**13a**), (–)-Pr^{i}DIOP (**13b**) and (–)-CyDIOP (**13c**).[12]



12 **13a**–**c**

R = Et (**a**, 83%), Pr^i (**b**, 34%), cyclo-C_6H_{11} (Cy) (**c**, 74%).

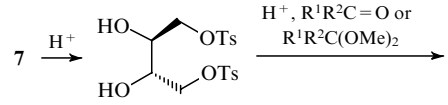
Unsymmetrical chiral bisphosphine (–)-DIOCP **14** containing cyclohexyl groups at one of the phosphorus atoms and bearing phenyl groups at another phosphorus atom was prepared from 2,3-*O*-isopropylidene-L-threitol (**6**) by the multistep synthesis.[13]



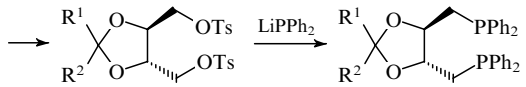
14 (48%)

Ms = $MeSO_2$.

The introduction of substituents containing highly polar functional groups, which can form salts, into bisphosphine molecules gives rise to water-soluble organophosphorus ligands.[14] Groups providing solubility of structural analogues of (–)-DIOP in water can be present not only in the aromatic fragments of the ligand (for example, quaternised compound **9e**) but also in the dioxolane ring. For example, among compounds **15a**–**e**, which were prepared from condensation products of diol **16** with various aldehydes or ketones,[9,15,16] polyoxadioxolanes **15d**,**e** are soluble in water.



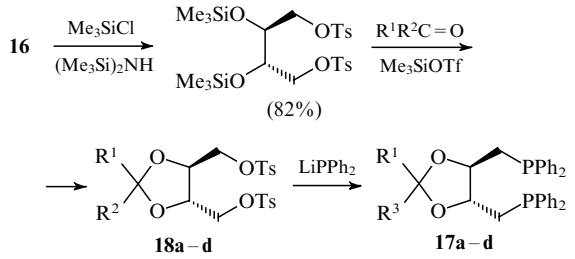
16



15a–e

$R^1–R^2$ = $(CH_2)_4$ (**a**), $(CH_2)_5$ (**b**); R^1 = H: R^2 = Ph (**c**), $CH_2O(CH_2CH_2O)_5Me$ (**d**), $CH_2O(CH_2CH_2O)_{16}Me$ (**e**).

Bisphosphines **17** synthesised in the study[17] are soluble in water due to the presence of hydroxy-containing substituents in the dioxolane ring.

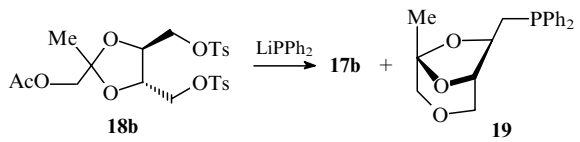


18a–d **17a–d**

Tf = CF_3SO_2.

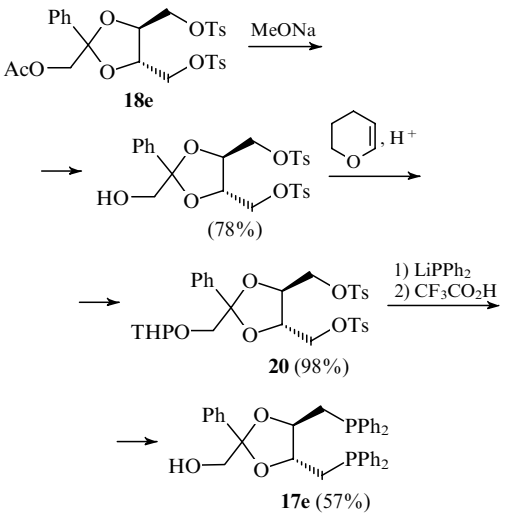
Compound **17**, **18**	R^1	R^2	R^3	Yield (%)	
				18	**17**
a	Ph	Me	Me	80	79
b	Me	CH_2OAc	CH_2OH	89	52
c	H	2-$AcOC_6H_4$	2-HOC_6H_4	70	76
d	H	4-$AcOC_6H_4$	4-HOC_6H_4	73	82

Ligands **17a–d** were prepared from the corresponding ditosylates **18a–d** by the reactions with lithium diphenylphosphide, which were accompanied by elimination of acetyl groups. Phosphinylation of ditosylate **18b** afforded bisphosphine **17b** in substantially lower yield compared to those achieved in all other cases because this reaction gave rise to phosphine **17b** along with bicyclic ether ketal **19** (43%).[17]



18b **19**

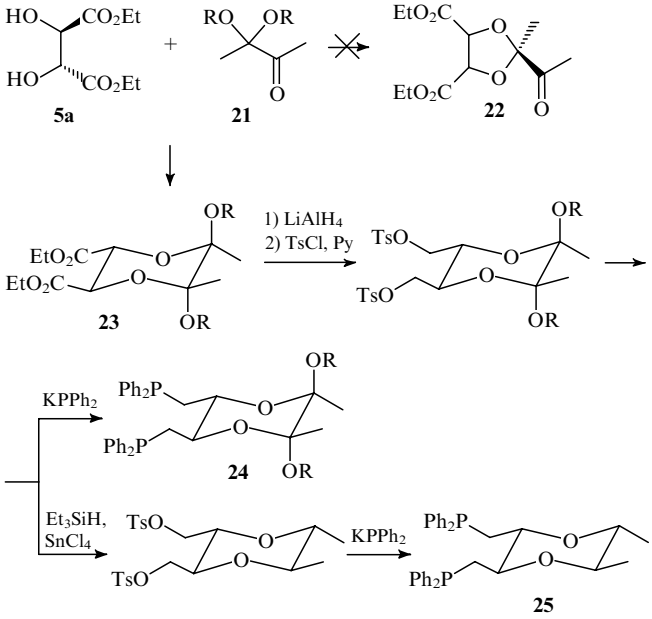
When performing analogous transformations of ditosylate **18e** (R^1 = Ph, R^2 = CH_2OAc), the acetyl group was replaced by the tetrahydropyranyl group to prevent undesired cyclisation in the final step of the synthesis. Subsequent transformations of ester **20** produced the target bisphosphine **17e**.[17]



18e **20** (98%) **17e** (57%)

THP is tetrahydropyranyl.

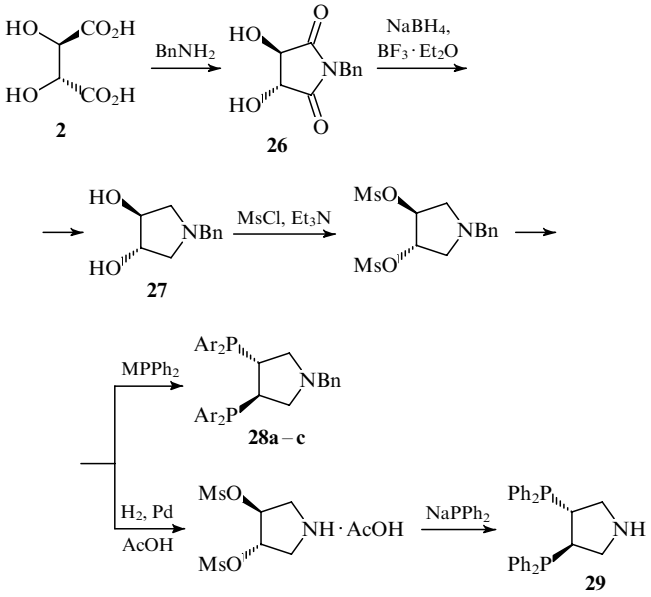
Attempts to subject diethyl tartrate **5a** to acetalisation with butane-2,3-dione monoketals **21** led to the formation of 1,4-dioxane **23** instead of the expected dioxolane **22**. Compound **23** served as the starting compound for the synthesis of chiral bisphosphines of new structural types **24** and **25**.[18, 19]



5a **21** **22** **23** **24** **25**

R = Me (**a**), Et (**b**).

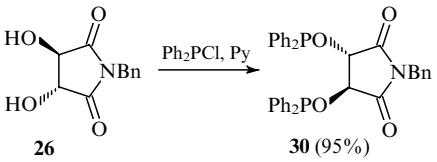
Yet another procedure for the preparation of C_2-symmetrical ligands involves structural transformations of (+)-(2*R*,3*R*)-tartaric acid (**2**) into pyrrolidine-type 1,2-bisphosphines. For example, heating of acid **2** with benzylamine afforded cyclic imide **26**, which was reduced by $NaBH_4$ to form dihydroxypyrrolidine **27**. The latter served as the starting compound for the synthesis of the DEGUPHOS ligand (**28a**), its derivatives (**28b**,**c**) and the PYRPHOS ligand (**29**). The presence of the amino group in these compounds substantially facilitates both their isolation from the reaction mixtures as hydrochlorides and subsequent purification.[20–22]



2 **26** **27** **28a–c** **29**

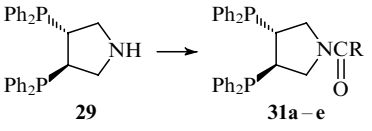
M = Na (for **28a**), Li (for **28b**,**c**);
Ar = Ph (**a**), 4-$Me_2NC_6H_4$ (**b**), 4-MeO-3,5-$Me_2C_6H_2$ (**c**).

Treatment of imide **26** with chlorodiphenylphosphine in pyridine produced bisphosphinite **30**.[23]

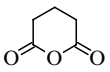


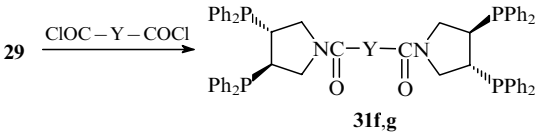
26 **30** (95%)

Acylation of the secondary amino group in bisphosphine **29** made it possible to prepare compounds **31a**–**g**, including C_2-symmetrical ligands **31f**,**g**, *viz*., oxalic and terephthalic acid diamides.[21]



29 **31a**–**e**

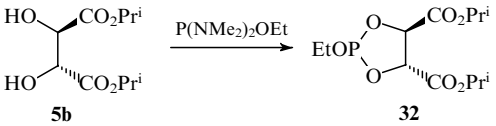
Reagent	Product	R	Yield (%)
PhCOCl	**a**	Ph	89
$(Boc)_2O$ (Boc = $Bu^tOC(O)$)	**b**	OBu^t	96
	**c**	$(CH_2)_3CO_2H$	100
$MeO(CH_2)_2OCH_2COCl$	**d**	$CH_2O(CH_2)_2OMe$	83
$MeO(CH_2CH_2O)_3CH_2COCl$	**e**	$CH_2(OCH_2CH_2)_3OMe$	80



31f,**g**

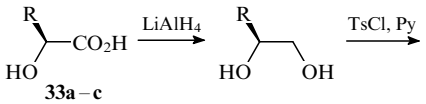
Y is a bond (**f**, 83%), C_6H_4-*p* (**g**, 88%).

Cyclic monophosphites were synthesised based on derivatives of tartaric acid. For example, the reaction of diisopropyl tartrate **5b** with ethyl bis(dimethylamino)phosphinite produced compound **32**.[24]

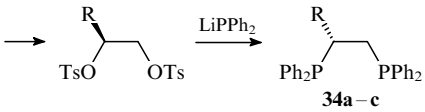


5b **32**

Bidentate organophosphorus ligands are derived also from natural α-hydroxycarboxylic acids. However, the general procedure for the preparation of chiral 1,2-bisphosphines based on these ligands involves the reaction of vicinal ditosylates with alkali metal organophosphides, which is difficult to reproduce. In this step of the synthesis, the S_N2 reaction is generally accompanied by competitive elimination giving rise to intermediate oxiranes. The latter are subjected to the repeated nucleophilic attack by the phosphide anion to produce a mixture of undesired hydroxymonophosphines. Under certain conditions, the latter reaction becomes the major process, which substantially decreases the yield of the target bisphosphines. Nevertheless, bisphosphines (*R*)-PROPHOS (**34a**) and (*R*)-PHENPHOS (**34b**) were prepared from (*S*)-(+)-lactic (**33a**) and (*S*)-(+)-mandelic (**33b**) acids in 10 and 20% yields, respectively. The reaction with (2*R*,3*R*)-butanediol (**35**) afforded C_2-symmetrical 1,2-bisphosphine (*S*,*S*)-CHIRAPHOS (**36**). The (*R*)-CYCPHOS ligand (**34c**) was synthesised from (*S*)-(+)-hexahydromandelic acid (**33c**), which was generated by hydrogenation of (*S*)-(+)-mandelic acid (5% Rh/Al_2O_3 as the catalyst). Unlike the (*R*)-PHENPHOS compound (**34b**) isolated in pure form, bisphosphines (*R*)-PROPHOS (**34a**), (*R*)-CYCPHOS (**34c**) and (*S*,*S*)-CHIRAPHOS (**36**) were contaminated with by-products. To purify the latter bisphosphines, they were transformed into insoluble complexes with $NiCl_2$ and then optically pure ligands were regenerated by treatment with sodium cyanide.[25–28]

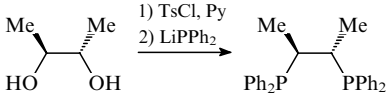


33a–**c**



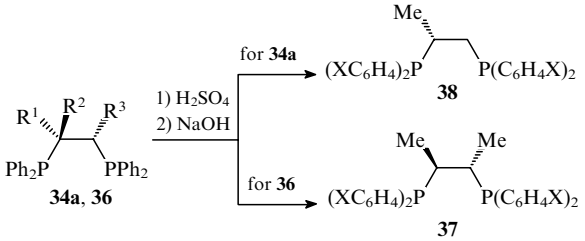
34a–**c**

R = Me (**a**), Ph (**b**), Cy (**c**).



35 **36** (14%)

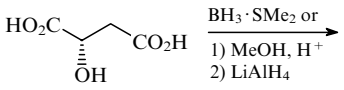
The introduction of highly polar substituents into the aromatic fragments of the (*R*)-PROPHOS (**34a**) and (*S*,*S*)-CHIRAPHOS (**36**) ligands gave rise to water-soluble derivatives. The reaction of chiral ligand **36** with oleum produced the tetrasulfonated analogue of (*S*,*S*)-CHIRAPHOS (**37**). Under the same conditions, sulfonation of bisphosphine **34a** proceeded much more slowly and with lower selectivity. The tetrasulfonated analogue of (*R*)-PROPHOS (**38**) was isolated only as a mixture with trisulfonated phosphine and phosphine oxide (in 55%, 35% and 10% yields, respectively).[29]



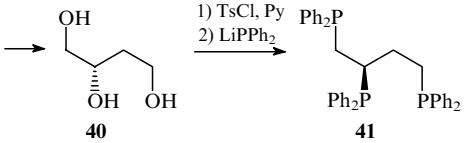
34a, **36** **38** **37**

34a: R^1 = Me, R^2 = R^3 = H; **36**: R^1 = H, R^2 = R^3 = Me; X = 3-SO_3Na.

Mono-, bi- and tridentate chiral phosphine ligands in which only one diphenylphosphine group is directly bound to the asymmetric centre were synthesised starting from L-malic acid (**39**). Reduction of acid **39** with the borane dimethyl sulfide complex followed by the two-step treatment of triol **40** with tosyl chloride and lithium diphenylphosphide afforded 1,2,4-trisphosphine **41**.[30]

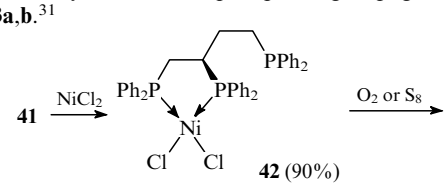


39

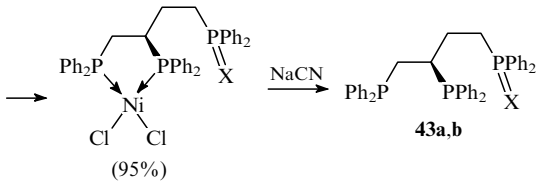


40 **41**

Trisphosphine **41** can selectively form nickel complex **42** involving only the vicinal phosphine groups. This made it possible to modify the remote phosphine group giving rise to ligands **43a**,**b**.[31]



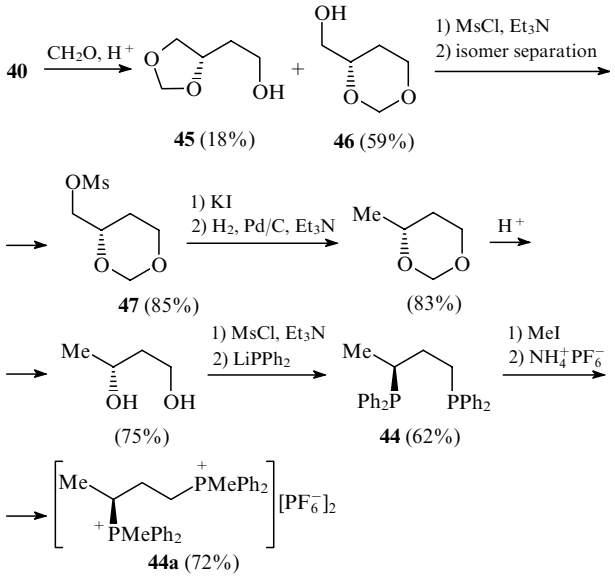
42 (90%)



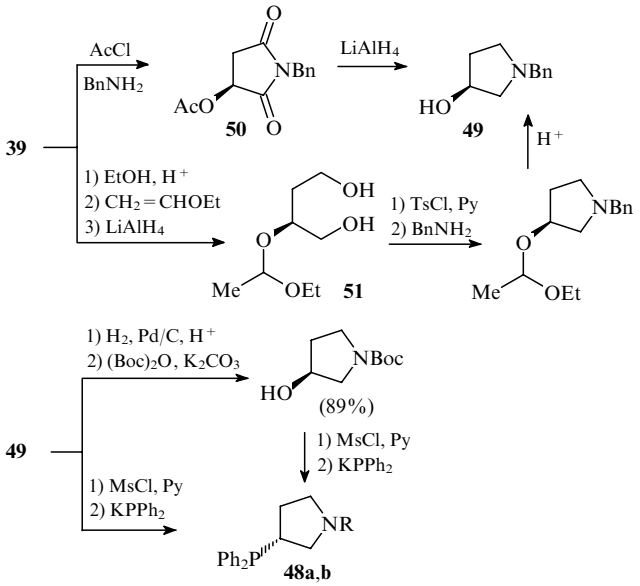
(95%) **43a**,**b**

X = O (**a**, 63%), S (**b**, 77%).

Chiral 1,3-bisphosphine **44** was synthesised starting from triol **40**, which was prepared by reduction of dimethyl L-malate.[32] The reaction of compound **40** with formaldehyde produced a mixture of cyclic acetals **45** and **46**. The latter was subjected to mesylation without separation. The major isomer **47**, which was isolated from the mixture of the resulting methanesulfonates, was transformed into the target bisphosphine **44** in five steps. The reaction product was characterised as the stable bisquaternary salt **44a**.



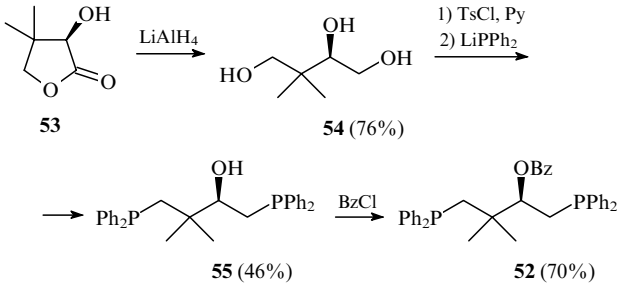
The synthesis of chiral monophosphines **48a**,**b** from L-malic acid (**39**) was based on transformations of intermediate hydroxypyrrolidine **49**. The latter was prepared without epimerisation of the chiral centre either by the two-step synthesis (heterocyclisation followed by reduction) through imide **50** or by the six-step



R = Bn (**a**, 75%), Boc (**b**, 70%).

synthesis (reduction followed by heterocyclisation) through protected triol **51**.[33]

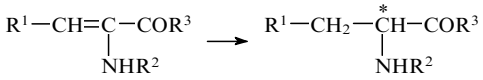
In the study,[30] bisphosphine **52** was synthesised starting from natural optically active pantolactone **53**. Tosylation of triol **54** followed by phosphinylation of the tosylates yielded bisphosphine **55** instead of the expected trisphosphine.



The phosphorus-containing ligands thus prepared were used for the synthesis of metal complex catalysts.

2. Use in asymmetric synthesis

The stereodifferentiating abilities of ligands and catalysts are most often estimated and compared using catalytic asymmetric hydrogenation, for example, asymmetric hydrogenation of unsaturated α-amino acids and their derivatives.



R^1 = Alk, Ar; R^2 = Alk, Ar, COAlk, COAr; R^3 = OH, OAlk, $NAlk_2$.

Metal complexes with DIOP exhibit high catalytic activities in hydrogenation with enantioselectivity varying from moderate to high depending on the structure of the substrate subjected to hydrogenation. It appeared that the enantiomeric purities of the hydrogenation products of free *N*-acylaminocinnamic acids are much higher (*ee* = 25% – 81%) than those of the hydrogenation products of their esters on the same catalysts (*ee* = 5% – 55%).[4]

The products were obtained with an enantiomeric excess of 90% – 92% by reduction of certain enamides using the cationic complex $[Rh(COD)(DIOP)]^+ClO_4^-$, where COD is cyclooctadiene.[3] The methyl substitution in the *meta* position of the aromatic ring of the ligand made it possible to achieve an enantiomeric purity of 88% in the asymmetric synthesis of 3-(3,4-dihydroxyphenyl)alanine derivatives.[9]

Analogues of DIOP containing electron-donating substituents at the phosphorus atom were also successfully used as catalysts for asymmetric hydrogenation of electron-deficient alkenes and carbonyl compounds. Thus, reduction of itaconic acid and its β-aryl derivatives catalysed by Rh(I) complexes with ligands **9d**,**e** afforded products with an enantiomeric purity of 91% – 96%, whereas the enantioselectivity of reduction of these substrates in the presence of the Rh(I) complex with unmodified DIOP was at most 58%.[11]

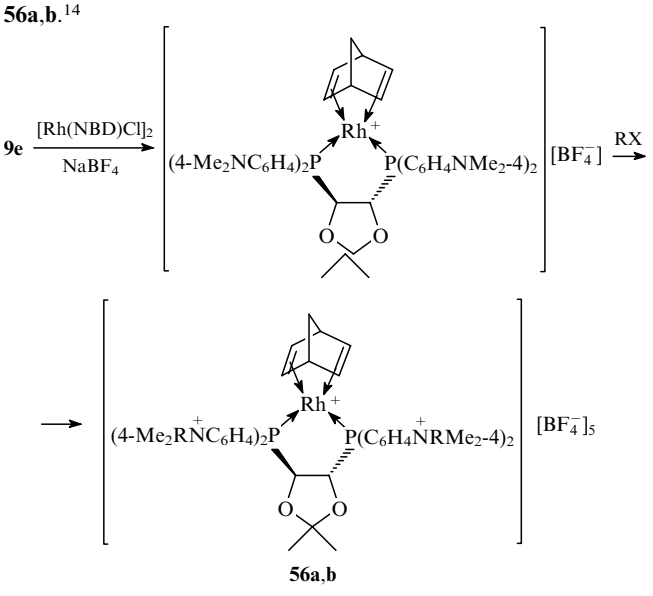
The Rh(I) complexes with chiral bisphosphines **13a** – **c** were successfully used in hydrogenation of α-oxo amides and *N*-oxoacylamino acid esters. It was demonstrated that the activity and enantioselectivity of the catalyst increases as the size of the alkyl substituent at the phosphorus atom in the ligand increases. The enantiomeric excess of up to 77% was achieved in hydrogenation of *N*-benzylphenylglyoxylamide catalysed by the Rh(I) complex with CyDIOP ligand **13c**.[12] The Rh(I) complex with DIOCP ligand **14** appeared to be a better stereodifferentiating catalyst for asymmetric hydrogenation of α-ketopantolactone than the Rh(I) complexes with the DIOP and CyDIOP ligands. The enantiomeric purities of the products prepared with the use of these catalysts were 72%, 52% and 45%, respectively.[13]

Rhodium catalysts containing DIOP derivatives with dibenzophosphole groups (compound **9f**) as ligands proved to be less

enantioselective in hydrogenation of α-acetamidocinnamic acid than Rh catalysts with unmodified bisphosphine ligands (*ee* decreased from 81% to 28%). At the same time, the use of ligand **9f** in a Pd(II) complex made it possible to increase the enantiomeric purity of the product of asymmetric hydroesterification of α-methylstyrene to 44% (in the case of DIOP, *ee* = 9%).[4]

Modifications of the acetal groups of DIOP (compounds **15a**–**c**) do not change the structure of the coordination centre of the catalyst and, consequently, have only a slight effect on the stereoselectivity of the reaction.[9,15] The enantioselectivity of hydrogenation of unsaturated acids catalysed by Rh(I) complexes with hydroxy-containing ligands **17b**–**e** is increased due, apparently, to additional interactions between the substrate and functional groups of the ligand remote from the coordination centre.[17] Hydrogenation of methyl (*Z*)-2-*N*-benzamidocinnamate on Rh(I) complexes with ligands **24** and **25** proceeded with moderate enantioselectivity. The highest enantiomeric excess (54%) was obtained in hydrogenation catalysed by the Rh(I) complex with ligand **24b**.[19]

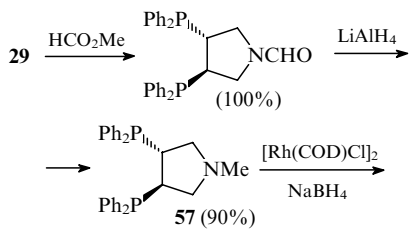
The synthesis of water-soluble chiral bisphosphine ligands enables one to solve some problems of homogeneous catalysis. In particular, the use of water-soluble rhodium phosphine catalysts for asymmetric hydrogenation in two-phase (aqueous–organic) systems substantially simplifies separation of the reaction products present in the organic phase from the catalyst. The rhodium phosphine complex that remains in the aqueous phase can be repeatedly used without substantial loss of efficiency. As mentioned above, water-soluble ligands are prepared by introducing highly polar functional groups into the bisphosphine structure. These groups can be present both in the phosphine and alkyl fragments of the molecule. For example, quaternisation at the nitrogen atoms of ligand **9e** [tetraamino analogue of (−)-DIOP] in the Rh complex afforded water-soluble chiral complexes **56a**,**b**.[14]

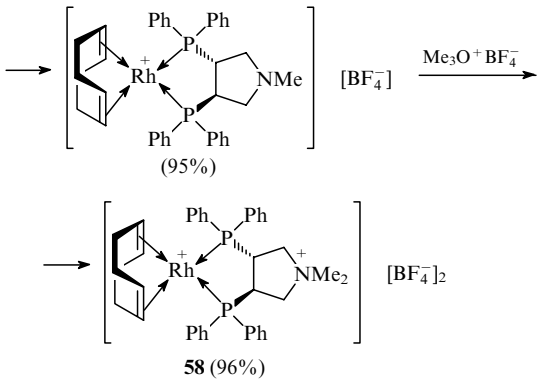


56a,**b**

NBD is norbornadiene; R = H (**a**), Me (**b**);
RX = HBF_4 (for **a**), $Me_3O^+BF_4^-$ (for **b**).

Quaternisation of the amino group of bisphosphine ligand **57** (prepared from PYRPHOS **29**) in the rhodium complex gave rise to water-soluble catalyst **58**.[20]





However, the enantioselectivity of hydrogenation in the presence of water-soluble Rh catalysts was found to be much lower than that of hydrogenation performed with Rh catalysts based on unmodified DIOP. Besides, the use of complexes **56a**,**b** led to a change in the sign of asymmetric induction. These results suggest that ammonium substituents in aromatic fragments of the DIOP ligand substantially influence the conformation of the chelate ring in the catalysts.[14]

The use of Rh(I) catalysts with water-soluble polyoxabisphosphines **15d**,**e** in hydrogenation of *N*-acylaminocinnamic acids in water led to a decrease in the enantiomeric purity of the product to 30% (hydrogenation on the same catalysts in ethanol gave *ee* = 75%).[16] The enantioselectivity of hydrogenation of *N*-acylaminocinnamic acids in water catalysed by the cationic Rh(I) complex with ligand **17a** was also no higher than 34%. However, the addition of sodium dodecyl sulfate as an amphiphilic agent to the reaction mixture made it possible to increase the enantioselectivity of the reaction to 77%.[34]

Hydrogenation of (*Z*)-α-acetamidocinnamic acids on Rh(I) complexes with bis(diphenylphosphino)pyrrolidine-type ligands proceeded with high enantioselectivity [92%, 94% and 96% for ligands **29** (PYRPHOS) and **28b**,**c**, respectively].[21,22] The use of catalyst **58** for hydrogenation of sodium α-acetamidocinnamate in water made it possible to prepare (*S*)-*N*-acetylphenylalanine with an enantiomeric purity of 90%.[20]

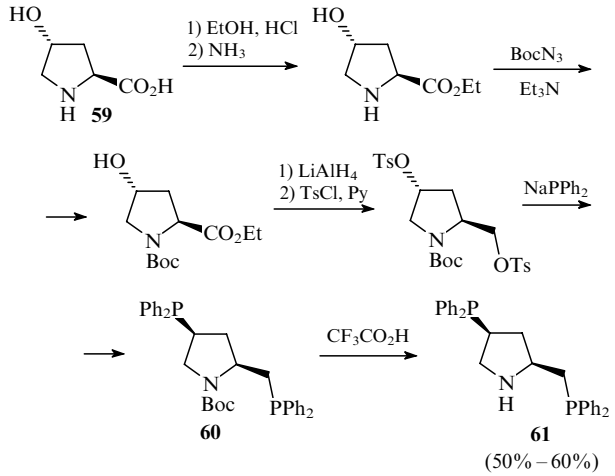
The Rh(I) complexes with the (*R*)-PROPHOS (**34a**), (*R*)-PHENPHOS (**34b**), (*R*)-CYCPHOS **34c** and (*S*,*S*)-CHIRAPHOS (**36**) ligands serve as highly efficient catalysts for enantioselective hydrogenation of unsaturated precursors of amino acids. The enantiomeric purities of the products prepared with the use of these catalysts were higher than 80%. The best result (*ee* = 100%) was achieved in hydrogenation of acetamidoisopropylacrylic acid catalysed by the Rh(I) complex with (*S*,*S*)-CHIRAPHOS.[25–28] The Rh(I) complex with ligand **37** [water-soluble analogue of the (*S*,*S*)-CHIRAPHOS ligand] also showed high enantioselectivity (*ee* up to 94%) in reduction of unsaturated amino acids both in water and a two-phase aqueous-organic system.[14,29]

The enantioselectivity of catalytic hydrogenation of precursors of amino acids catalysed by the Rh(I) complexes with ligands **41** and **44** appeared to be low. For example, reduction of (*Z*)-α-acetamidocinnamic acid using Rh(I) complexes with trisphosphine **41** afforded the target product with an enantiomeric excess of 25%.[31] The enantiomeric purity of the reduction product prepared with the use of the Rh(I) complex with ligand **44** was no higher than 20%.[32] The replacement of one phosphine group in ligand **44** by phosphine oxide or phosphine sulfide (compounds **43a**,**b**) led to a substantial enhancement of enantioselectivity of the catalyst. For example, the use of the Rh(I) complexes with ligands **43a**,**b** in the hydrogenation of (*Z*)-α-acetamidocinnamic acid made it possible to increase the enantiomeric purities of the products to 72%–74%.[31]

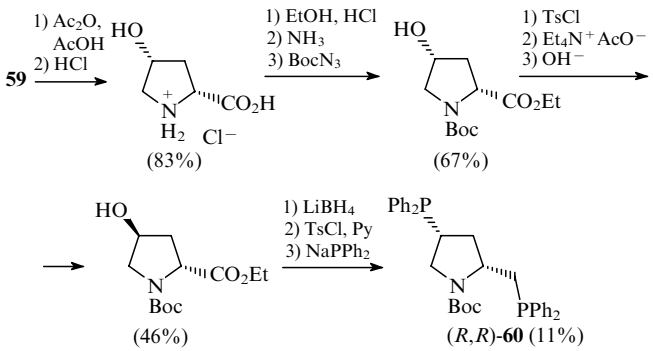
III. Organophosphorus ligands based on amino acids

1. Synthesis of ligands

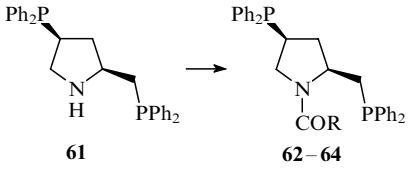
A large number of efficient chiral phosphorus-containing ligands were prepared starting from natural and synthetic amino acids. For instance, readily accessible 4-hydroxy-L-proline (**59**) can be used as the starting compound for the synthesis of the above-mentioned ligands. The first hydroxyproline derivatives to be prepared were 1,4-bisphosphines (2*S*,4*S*)-BPPM (**60**) and (2*S*,4*S*)-PPM (**61**).[35]



The synthesis of the optical antipode of bisphosphine **60**, *viz*., the chiral ligand (2*R*,4*R*)-BPPM, required successive epimerisation of two chiral centres of 4-hydroxy-L-proline (**59**).[36]



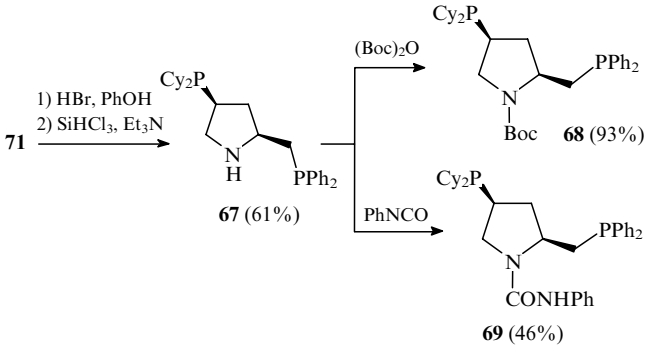
Later on, various derivatives of bisphosphinopyrrolidines **61**, *viz*., amides **62**, carbamides **63** and carbamates **64a**,**b**, were prepared.[37]



Reagent	Product	R	Yield (%)
HCO_2H, AcOH	**62a**	H	65
MeCOCl, Py (or Et_3N)	**62b**	Me	70
Bu^tCOCl, Py (or Et_3N)	**62c**	Bu^t	75
PhCOCl, Py (or Et_3N)	**62d**	Ph	91
MeNCO	**63a**	MeNH	95
Bu^tNCO	**63b**	Bu^tNH	73
PhNCO	**63c**	PhNH	76
MeOCOCl	**64a**	MeO	91
PhOCOCl	**64b**	PhO	99

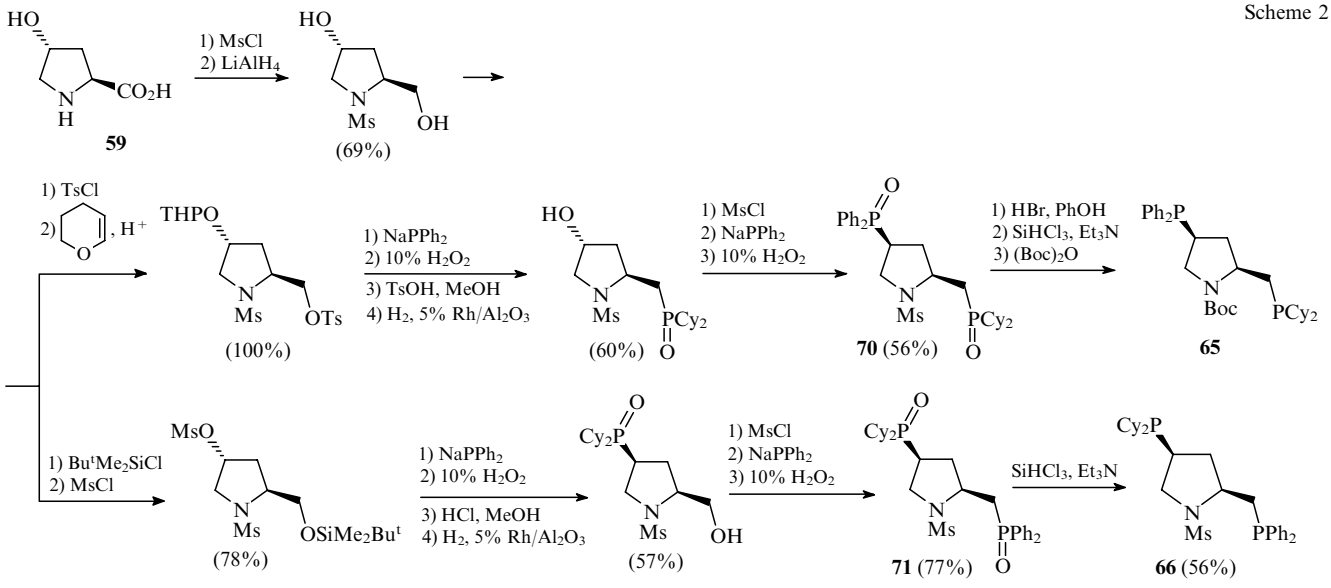
The synthesis of bisphosphines **65**–**69** containing various combinations of cyclohexyl and phenyl groups at the phosphorus atoms offers wide possibilities in the design of pyrrolidine-type ligands.[38,39] Multistep transformations of 4-hydroxy-L-proline (**59**) produced phosphine oxides **70** and **71**. Bisphosphine **65** was derived from compound **70** (Scheme 2).

Phosphine oxide **71** was used for the preparation of the target ligands **66**–**69.**

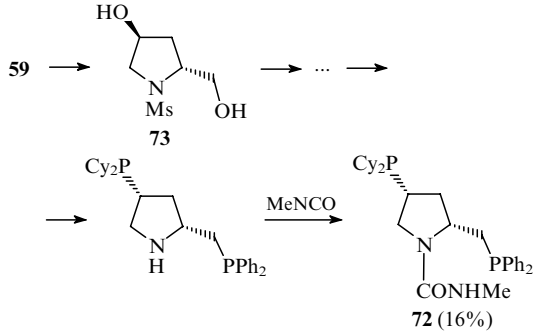


An analogous sequence of transformations was employed in the synthesis of ligand **72**, in which the stereocentres have configurations opposite to those in bisphosphine **65**. The ligand

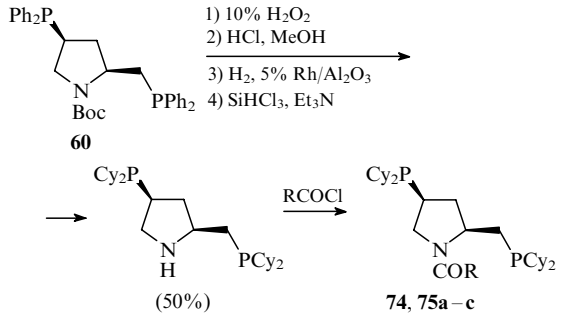
Scheme 2



72 was prepared starting from 4-hydroxy-*N*-(methylsulfonyl)-D-prolinol (**73**), which was generated by epimerisation of the chiral centres of 4-hydroxy-L-proline (**59**) according to the method used for the synthesis of the ligand (*R*,*R*)-**60**.[40]

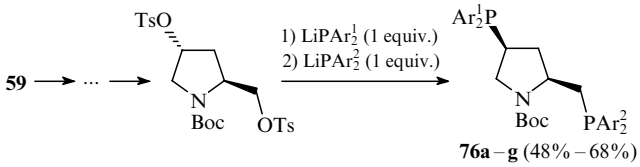


Chiral bisphosphines **74** and **75a–c** were generated from bisphosphine **60**.[12]



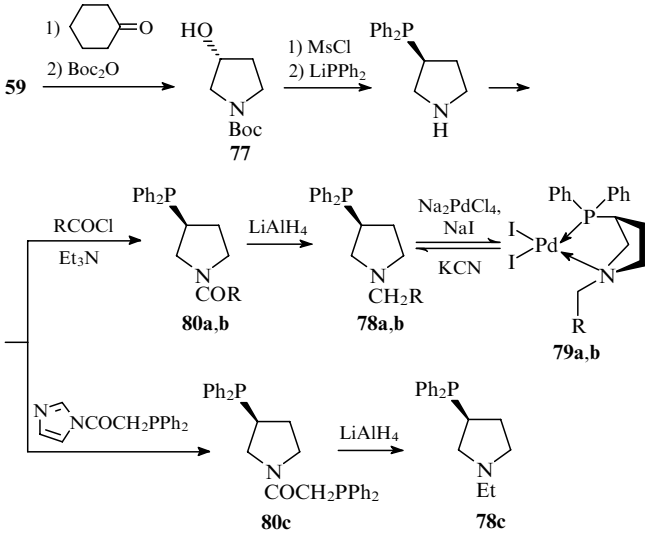
R = OBu^t (**74**, 54%), NHPh (**75a**, 78%), NHCy (**75b**, 75%), NHBu^t (**75c**, 89%).

Various ligands **76a–g** containing functional substituents in aromatic rings of the bisphosphine fragments were synthesised from other analogues of (2*S*,4*S*)-BPPM.[41–43]



Ar^1 = Ar^2 = 2-$MeOC_6H_4$ (**a**), 3-$MeOC_6H_4$ (**b**), 4-$MeOC_6H_4$ (**c**), 4-MeO-3,5-$Me_2C_6H_2$ (**d**), 4-$Me_2NC_6H_4$ (**e**);
Ar^1 = Ph, Ar^2 = 4-$Me_2NC_6H_4$ (**f**); Ar^1 = 4-$Me_2NC_6H_4$, Ar^2 = Ph (**g**).

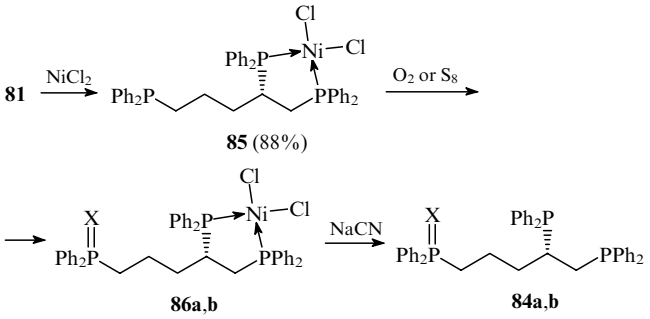
Alcohol **77**, which was prepared by decarboxylation of 4-hydroxy-L-proline (**59**), was transformed into chiral monophosphines **78a–c**. The optically pure ligands **78a**,**b** were isolated in the individual form after treatment of palladium complexes **79a**,**b** with potassium cyanide. It should be noted that reduction of phosphine amides **80a**,**b** with lithium aluminium hydride giving rise to phosphine amines **78a**,**b** proceeded smoothly without elimination of the diphenylphosphine group at the chiral centre. By contrast, analogous reduction of bisphosphine **80c** was accompanied by elimination of the activated phosphine group to form monophosphine **78c** instead of the expected tridentate P,N,P ligand.[33]



R = Ph (**a**), 4-MeC_6H_4 (**b**).

Chiral trisphosphine **81** and bisphosphine **82** were derived from L-glutamic acid **83** (Scheme 3).[30]

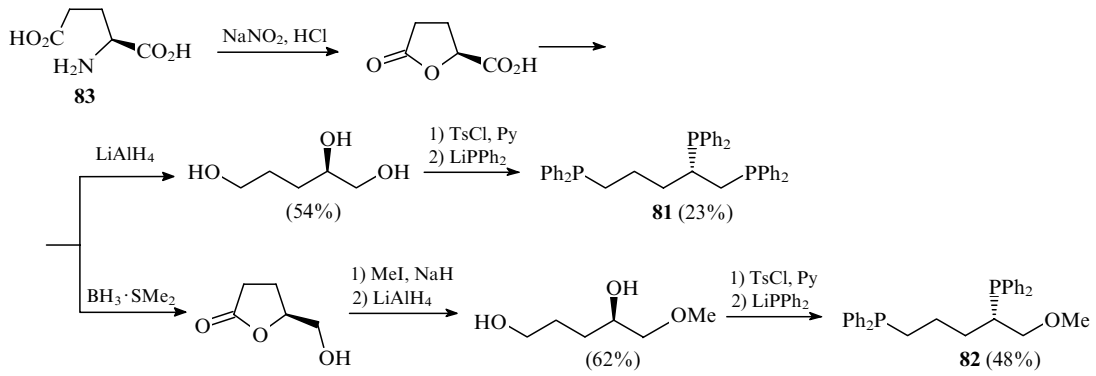
Phosphine oxide **84a** and phosphine sulfide **84b** were synthesised using a known procedure, which required the additional preparation of intermediate Ni complex **85** from trisphosphine **81**. Oxidation or sulfonation of the free phosphine group in compound **85** produced complexes **86a**,**b**, respectively. Regeneration with sodium cyanide completed the synthesis of the target ligands.[30,31]



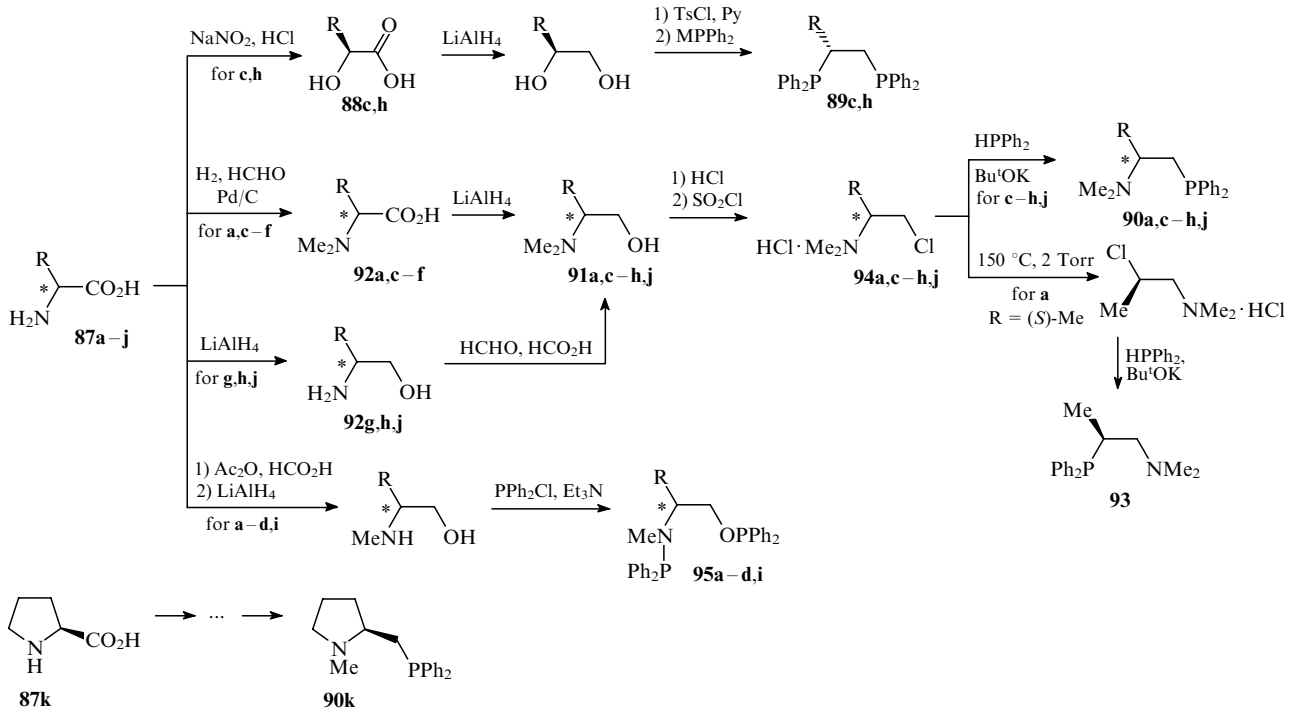
X = O (**a**, 63%), S (**b**, 31%).

Enantiospecific transformations of natural and synthetic amino acids were employed for the preparation of chiral 1,2-

Scheme 3



Scheme 4



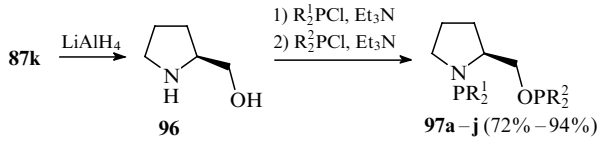
R = (*S*)-Me (**a**), (*S*)-Et (**b**), (*S*)-Pr^i (**c**), (*S*)-Bu^i (**d**), (*R*)-Bu^s (**e**), (*R*)-Bu^t (**f**), (*R*)-Cy (**g**), (*S*)-Bn (**h**), (*R*)-Bn (**i**), (*R*)-Ph (**j**); M = Li, Na, K.

bisphosphines, aminophosphines and phosphinoaminophosphinites (Scheme 4). The synthesis of bisphosphines was preceded by the transformation of the amino group in the starting amino acid into the hydroxy group under the action of HNO_2. For example, hydroxy acids **88c**,**h** derived from (*S*)-valine (**87c**) and (*S*)-phenylalanine (**87h**), respectively, were transformed into chiral bisphosphines **89c**,**h** according to a conventional procedure.[44]

Chiral ligands **90a**,**c**–**h**,**j**,**k** were synthesised starting from (*S*)-alanine (**87a**), (*S*)-valine (**87c**), (*S*)-leucine (**87d**), (*S*)-isoleucine (**87e**), (*R*)-*tert*-leucine (**87f**), (*R*)-cyclohexylglycine (**87g**), (*S*)-phenylalanine (**87h**), (*R*)-phenylglycine (**87j**) and (*S*)-proline (**87k**), respectively, by successive transformations involving *N*,*N*-dimethylation, reduction and chlorination in different orders. It should be noted that the key β-dimethylamino alcohols **91g**,**h**,**j** were synthesised in higher yields by *N*,*N*-dimethylation of amino alcohols **92g**,**h**,**j** prepared by reduction of the corresponding amino acids. Aminophosphine **93** was produced by the thermal rearrangement of chloro derivative **94a** followed by phosphinylation in the presence of potassium *tert*-butoxide.[23,45,46]

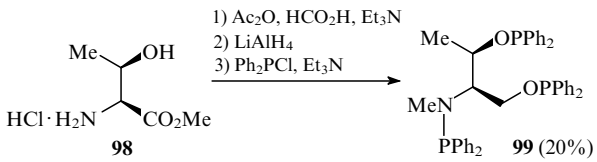
After *N*-formylation and reduction with $LiAlH_4$, amino acids **87a**–**d**,**i** were transformed into *N*,*O*-bisphosphinylaminoethanols **95a**–**d**,**i** (see Scheme 4).[47–49]

(*S*)-Prolinol (**96**) produced by reduction of (*S*)-proline (**87k**) was used as the starting compound for the synthesis of phosphinoaminophosphinites containing identical (**97a**–**d**) or different (**97e**–**j**) substituents at the phosphorus atoms.[50,51]



$R^1 = R^2 = Pr^i$ (**a**), cyclo-C_5H_9 (Cp) (**b**), Cy (**c**), Ph (**d**); $R^1 = Pr^i$, R^2 = Cp (**e**); R^1 = Cp: $R^2 = Pr^i$ (**f**), Cy (**g**), Ph (**h**); R^1 = Cy, R^2 = Cp (**i**); R^1 = Ph, R^2 = Cp (**j**).

Tridentate phosphinoaminobisphosphinite **99** was derived from (2*S*,3*R*)-threonine (**98**).[52]



The sequence of transformations of this compound is analogous to that used for transformations of amino acids **87a**–**d**,**i** into phosphinoaminophosphinites **95a**–**d**,**i** (see Scheme 4).

2. Use in asymmetric synthesis

Catalysts based on pyrrolidine-type bisphosphines BPPM (**60**) (proline derivatives) were used in hydrogenation of various substrates. Generally, such reactions proceed at 50 atm. For hydrogenation products of α-acetamidoacrylic acids, good results were obtained (enantiomeric purity up to 91%) in the presence of Rh(I) complexes with the unmodified (2*S*,4*S*)-BPPM ligand and its optical antipode, *viz*., (2*R*,4*R*)-BPPM.[35,36] The enantioselectivity of hydrogenation of (*Z*)-2-acetylamidocinnamic acid was increased to 98% by introducing the methoxy group in the *ortho* position of the benzene rings of this ligand (compound **76a**). The use of the Rh(I) complex with ligand **76c** containing the methoxy groups in the *para* positions of the benzene rings made it possible to increase the [substrate]:[catalyst] ratio from 10^3 to 10^4.[41] Hydrogenation of derivatives of (*Z*)-2-acetamidoacrylic acids on the Rh catalyst with ligand **76d** afforded products with *ee* = 99% (p_{H2} = 20 atm, [substrate]:[catalyst] = 10^4).[42] These results are consistent with the assumption[41,42] that an increase in the enantioselectivity of the catalyst results from the steric effect of the *o*-MeO substituents in the aromatic fragments of the ligand. The electron-donating substituents in the benzene ring also substantially influence the reaction rate, the best result being achieved for compounds containing the *p*-MeO groups.[41,42]

Hydrogenation of ketopantolactone catalysed by the Rh(I) complexes with the BPPM ligand proceeded with an enantioselectivity of 87% (50 °C, p_{H2} = 50 atm).[4] Of Rh(I) complexes with cyclohexyl analogues of the BPPM ligand, the metal complex with ligand **68** containing both the cyclohexyl and phenyl substituents

at the phosphorus atom provided the highest enantiomeric yield (*ee* up to 91%) in this reaction. The Rh(I) complexes with this bisphosphine and its analogue containing only the dicyclohexylphosphine groups (compound **74**) exhibited much higher catalytic activities in this reaction as compared to the catalyst prepared based on the unmodified BPPM ligand (the [substrate] : [catalyst] ratio increased from 10^2 to 10^4; see Refs 38 and 39). Hydrogenation of ketopantolactone in the presence of the Rh(I) complex with bisphosphine ligand **75c** containing the carbamoyl substituent proceeded under substantially milder conditions, *viz*., at room temperature and under normal H_2 pressure. However, the enantioselectivity of this reaction was at most 66%.[12]

Of the three types of rhodium catalysts with *N*-substituted pyrrolidinebisphosphines **62**–**64**, the Rh(I) complexes with *N*-carbamoyl ligands **63a**–**c** proved to be most efficient in the hydrogenation of 2-methylidenesuccinamic acid. The use of these catalysts led to an increase in the enantioselectivity to 77% at normal H_2 pressure, whereas hydrogenation catalysed by the Rh(I) complexes with ligands **62a**–**e** and **64a**,**b** proceeded only under an H_2 pressure of 30 atm, the enantiomeric purities being 43%–64% and 53%–66%, respectively.[37]

The introduction of the *p*-Me_2N group into the benzene ring of the BPPM ligand (compounds **76e**–**g**) led to an increase in the activity and stereoselectivity of the Rh catalyst for the hydrogenation of dimethyl itaconate. The best results (*ee* = 93%, the conversion was 100%) were achieved in the presence of the Rh(I) complex with ligand **76f** (for comparison, hydrogenation catalysed by the complex with unmodified BPPM afforded the product with an *ee* of 5% and a conversion of 36%).[43]

The Rh(I) complexes with tris- (**81**) and bisphosphines (**82**) exhibited moderate enantioselectivity in hydrogenation of (*Z*)-α-acetylaminocinnamic acid (*ee* = 31%–36% and 54%–58%, respectively). The transformation of one of the phosphine groups into phosphine oxide (compound **84a**) or phosphine sulfide (compound **84b**) led to an increase in the enantioselectivity of the catalyst for hydrogenation of (*Z*)-α-acetylaminocinnamic acid. Thus, the enantiomeric purities of the hydrogenation product prepared in the presence of the Rh(I) complexes with ligands **84b** and **84a** were 54%–58% and 85%–89%, respectively.[31,32]

Rhodium complexes with bisphosphines **89c**,**h** were successfully used in enantioselective hydrogenation of (*Z*)-α-acylaminoacrylic acids to form the corresponding α-acylamino acids (*ee* = 85%–99%).[44] Unlike Ni(0) complexes with β-dimethylaminomethylphosphines **90a**,**c**–**h**,**j**, Ni(0) complexes with ligands of this type proved to be less efficient in catalytic asymmetric cross-coupling. The highest enantiomeric purity (*ee* up to 80%) of the products of this reaction was achieved with the use of Rh(I) complexes prepared based on ligands **90c**,**e**,**h**,**j**. It was demonstrated that an increase in the stereoselectivity of hydrogenation in the presence of catalysts containing aminophosphines of the structural type **90** as ligands is favoured by an increase in the volume of the substituent at the chiral β-carbon atom directly bound to the dimethylamino group. For example, *ee* of 25% and 38% were achieved in hydrogenation catalysed by the Ni(0) complexes with ligands **93** and **90e**, respectively.[45,46] In asymmetric hydrosilylation of acetophenone, Rh(I) complexes with phosphinoaminophosphinites **95a**,**c** showed low enantioselectivity (*ee* = 10%–26%), which depended on the structure of the silane used.[48] Hydrogenation of *N*-acetylaminocinnamic acid in the presence of the Rh(I) complex with phosphinoaminophosphinite **95i** afforded products with *ee* = 60%.[49]

Cationic Rh(I) complexes based on ligands **97** were used as catalysts for asymmetric hydrogenation of activated ketones, the best results (*ee* = 85%) being achieved with the complex based on phosphinite **97j**.[50,51]

Asymmetric hydrovinylation of 1,3-cyclohexadiene catalysed by Ni(0) complexes with ligand **99** afforded products with *ee* = 93%, whereas the enantioselectivity of the same reaction in the presence of Ni(0) complexes with phosphinoaminophosphinites **95a**,**c** was no higher than 50%.[52]

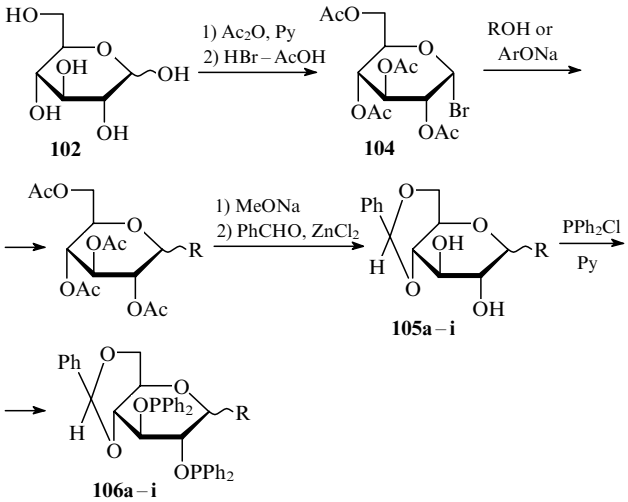
Therefore, the above-considered examples demonstrate that metal complexes with chiral organophosphorus ligands based on both natural and synthetic amino acids show promise as catalysts.

IV. Organophosphorus ligands based on carbohydrates

1. Synthesis of ligands

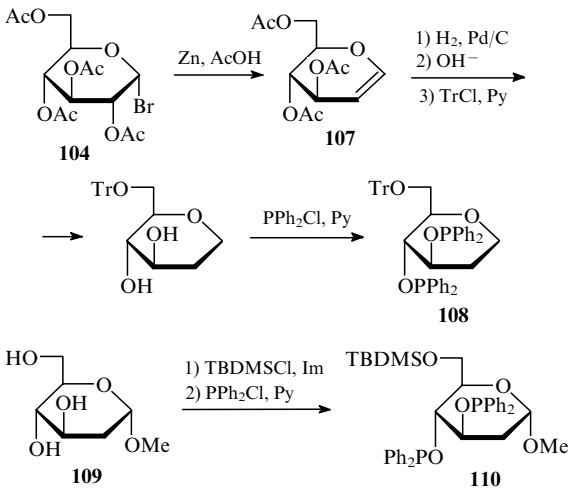
Carbohydrates and their derivatives are readily accessible, optically pure and contain several functional groups at the asymmetric centres with different configurations, which can be readily transformed. Hence, these compounds are attractive for the synthesis of chiral heteroorganic ligands. The synthesis of diastereomeric bisphosphines **100a**,**b** and bisphosphinites **101a**,**b** from α-D-glucose **102** was described in the study.[53] In this synthesis, 3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose **103** (Scheme 5) was generated as an intermediate.

D-Glucopyranoside **102** was transformed into glucosyl bromide **104**, from which aryl- and alkyl-*O*-glucosides **105a**–**i** were generated. The latter compounds were used in the synthesis of chiral 2,3-bis(diphenylphosphinites) **106a**–**i**.



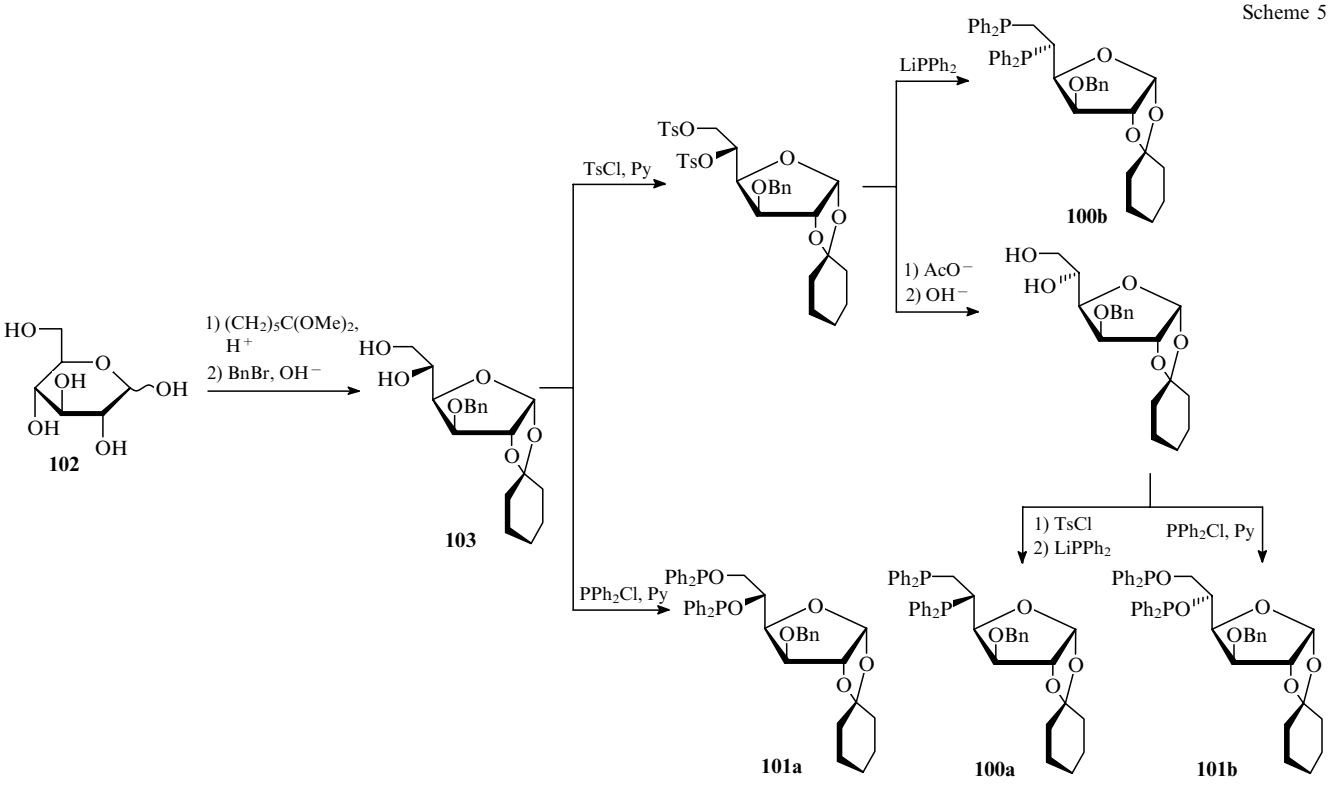
R = α-OMe (**a**), α-OPh (**b**), β-OBn (**c**), β-OPh (**d**), β-OC_6H_4Me-2 (**e**), β-OC_6H_4Me-4 (**f**), β-$OC_6H_4NO_2$-2 (**g**), β-$OC_6H_4NO_2$-4) (**h**), β-$OC_{10}H_7$-2 (**i**).

Treatment of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide **104** with zinc in acetic acid afforded tri-*O*-acetyl-D-glucal **107**, which was used for the synthesis of 3,4-bisphosphinite **108**.



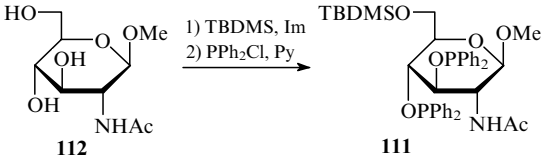
Tr is trityl, TBDMS is *tert*-butyldimethylsilyl, Im is imidazole.

Scheme 5

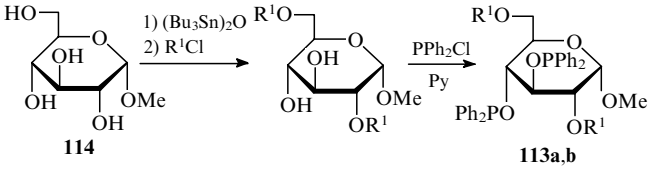


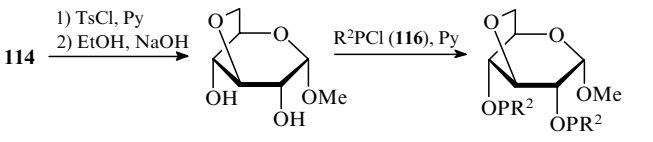
Phosphinite **110** was derived from methyl-2-deoxy-α-D-glucopyranoside **109**.[54]

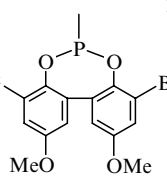
Analogous bisphosphinite **111** was generated from 2-acetylamino-β-methyl-2-deoxy-D-glucopyranoside **112**.[54]



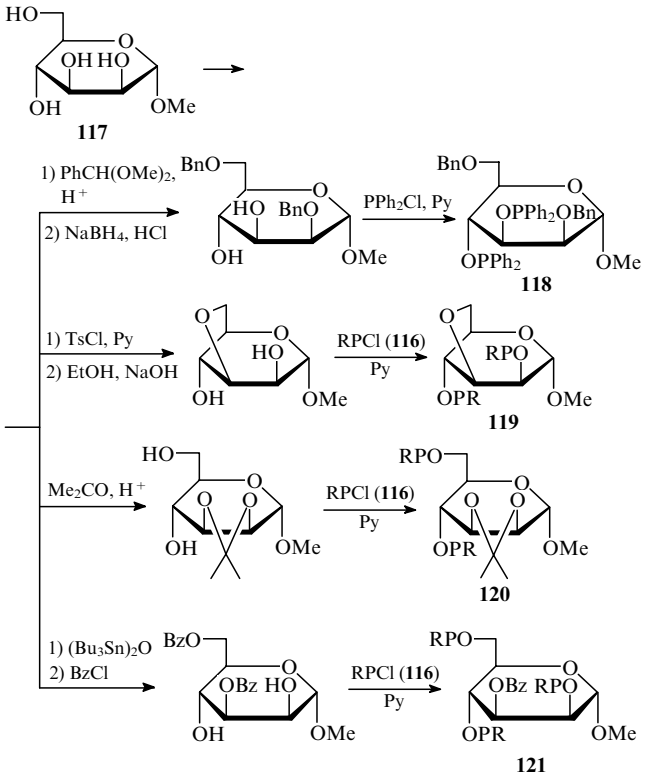
3,4-Bis(diphenylphosphinites) **113a**,**b** were prepared by selective acylation of methyl-α-D-glucopyranoside (**114**) followed by phosphinylation.[54] The same glycoside **114** was used for the synthesis of the 2,4-bisphosphite of 3,6-anhydroglucopyranoside **115** containing bulky substituents, *viz*., derivatives of *o*,*o*′-biphenylene **116**.[55]





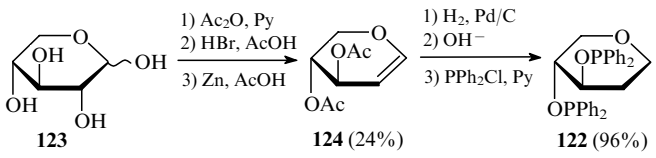
R^1 = $COBu^t$ (**a**), COPh (**b**); R^2P =  (BMOPP).

Methyl-α-D-mannopyranoside **117** was transformed into 3,4-bisphosphinite **118**, 2,4- (**119**) and 4,6-bisphosphites **120** and **121** employing different procedures for the protection of the hydroxy groups.[54, 55]

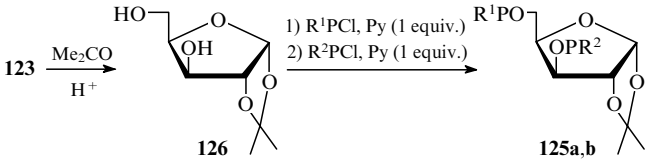


RP = BMOPP.

Bisphosphinite **122**, which was isolated as a complex with Cu(I) and then purified,[56] was synthesised from D-xylopyranose **123** through di-*O*-acetyl-D-xylal **124**.

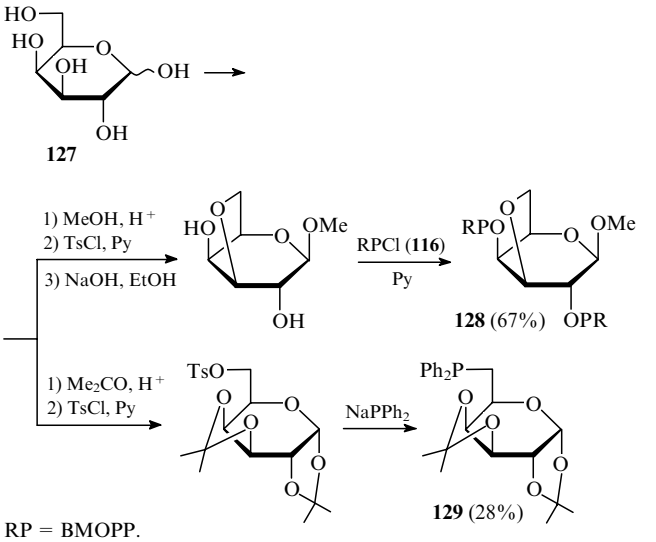


Ligands **125a**,**b** containing the bulky *o*,*o*′-biphenylene substituents were prepared by the reactions of 1,2-*O*-isopropylidene-D-xylofuranose **126** with phosphorochloridites.[55]



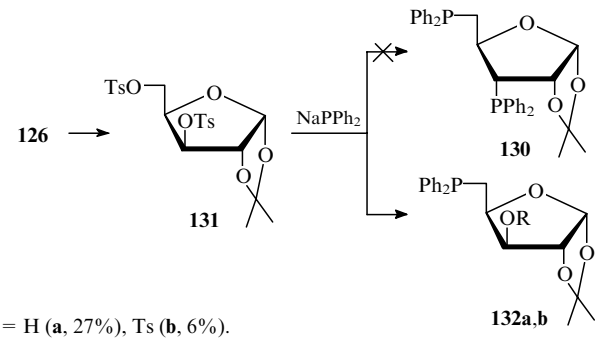
R^1P = BMOPP: R^2P = R^1P (**a**, 53%), P(2-Bu^t-6-Me$C_6H_3O)_2$ (**b**, 27%).

Chiral 2,4-bisphosphite **128** was synthesised in several steps from D-galactose **127**.[55] The same compound was used for the preparation of monophosphine **129**.[15]



RP = BMOPP.

Unlike pyranosides, the synthesis of 3,5-bisphosphines based on furanosides presented difficulties. Thus, an attempt to synthesise bisphosphine **130** from 1,2-*O*-isopropylidene-D-xylofuranose **126** through ditosylate **131** led to the formation of a mixture of monophosphines **132a**,**b**.[57]



R = H (**a**, 27%), Ts (**b**, 6%).

It was hypothesised [60] that attempts to synthesise compound **130** failed due primarily to steric overcrowding of the 1,2-*O*-isopropylidene-3,5-di-*O*-tosyl-D-xylofuranose molecule (**131**). The α-attack of the diphenylphosphide anion on the C(3) atom of the furanoside ring of compound **131** is hindered by steric effects, and the S_N2 reaction with sodium diphenylphosphide does not proceed. To relieve steric hindrances, attempts were made to synthesise bisphosphine ligands **136** from monotosylate **134** through alkene intermediates **135a**,**b**. The latter were prepared by the reaction of 3-oxofuranose **133** with α-cyanomethylidenetriphenylphosphorane. The reactions of isomeric nitriles **135a**,**b** with sodium diphenylphosphide afforded the same bicyclic product **137** instead of the corresponding bisphosphines **136**. Reduction of compound **137** with $LiAlH_4$ gave rise to phosphinoamine **138** (Scheme 6).[57]

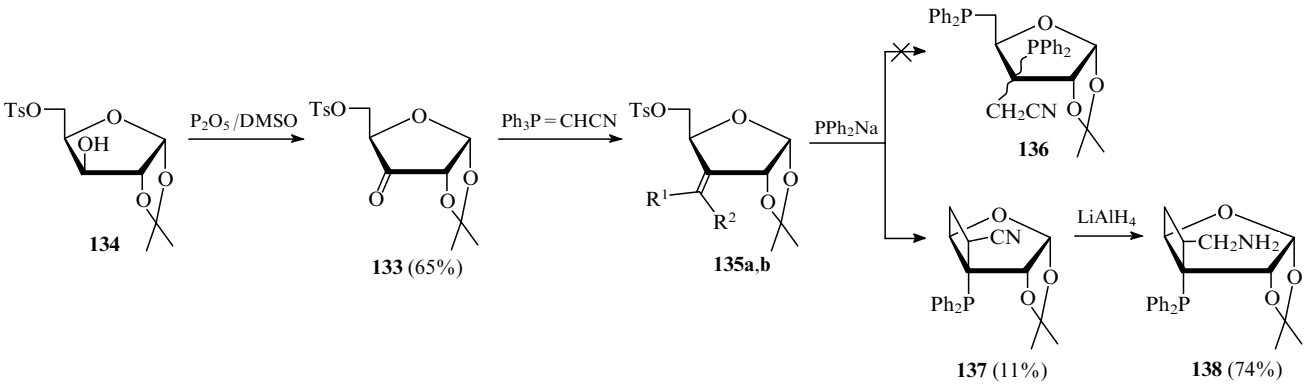
Chiral polyoxabisphosphines of the general formula **139** were synthesised from D-mannitol (**140**). Intermediate polyoxadioxolanes **141** were prepared according to two procedures, *viz*., by the reactions of chlorides with isopropylideneglycerol **142** under conditions of phase transfer catalysis or by the reactions of chloro ethers **143** with the corresponding alkoxides. Sodium alkoxide of *N*,*N*-diethylaminoethanol was used for the synthesis of dioxolane **144**, which was transformed into the target bisphosphine **145** (Scheme 7).[58]

Acetonide **146** derived from D-mannitol (**140**) was used as the starting compound in the synthesis of diastereomeric epoxides **147a**,**b**, which were reduced to the key diols **148a**,**b** (Scheme 8). The latter served as the starting compounds in the synthesis of chiral organophosphorus ligands.

Examples of the use of diol **148a** in the synthesis of chiral bisphosphinites **149a**,**b**, bisphosphine **150** and phospholanes **151** and **152** were gived in the study.[59] Diastereomers of these compounds were prepared from diol **148b** according to an analogous scheme (Scheme 9).

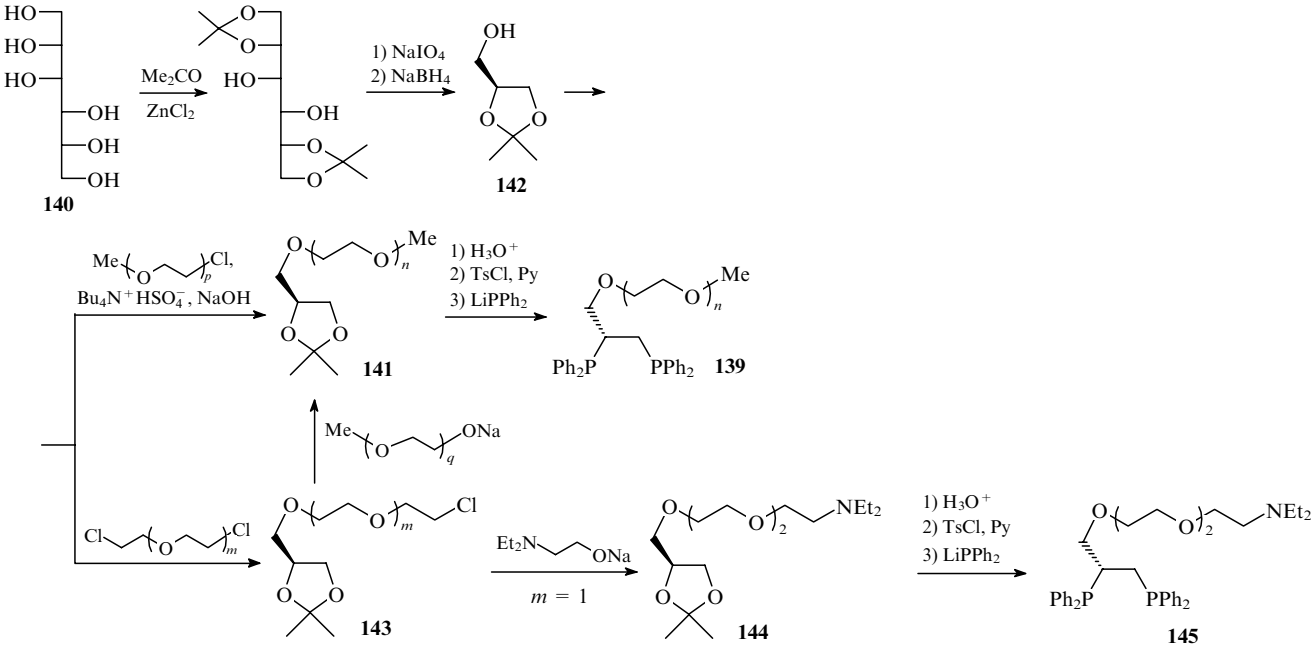
Examples of the use of oligosaccharides as the starting chiral compounds for the synthesis of organophosphorus ligands are much fewer in number as compared to monosaccharides. For

Scheme 6



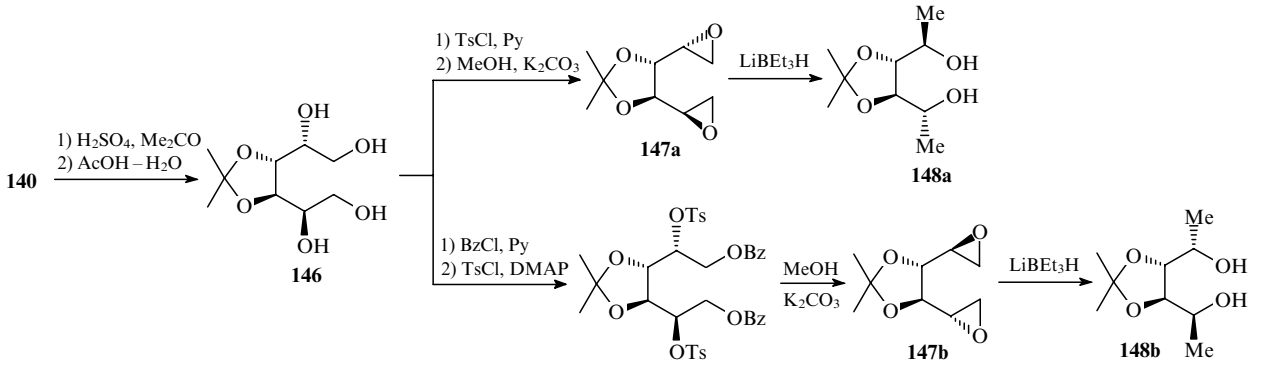
R^1 = CN, R^2 = H (**a**, 67%); R^1 = H, R^2 = CN (**b**, 24%)

Scheme 7

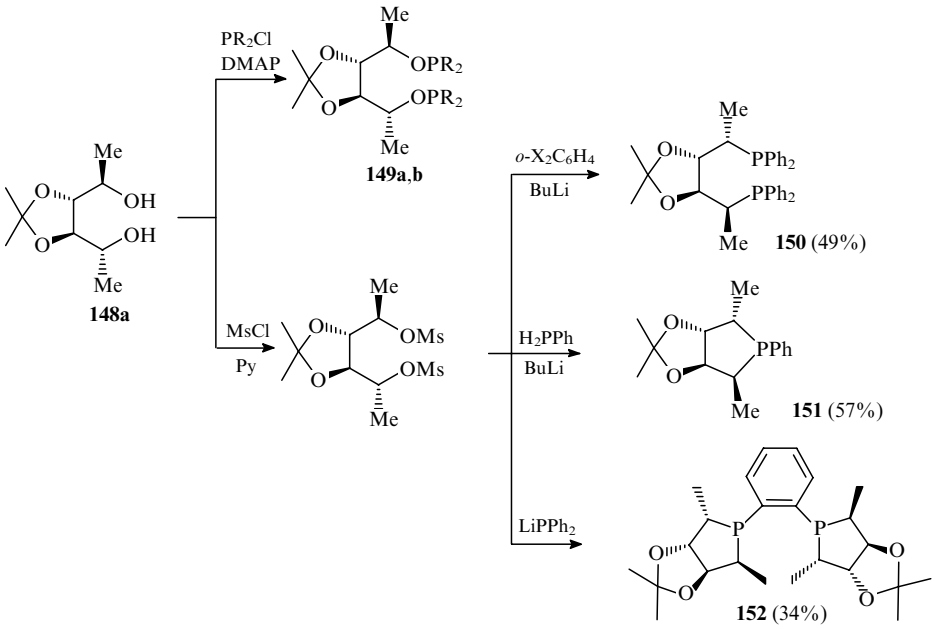


$p = 1-3$, $n = 1-5$, $m = 1, 2$, $q = 0-2$.

Scheme 8

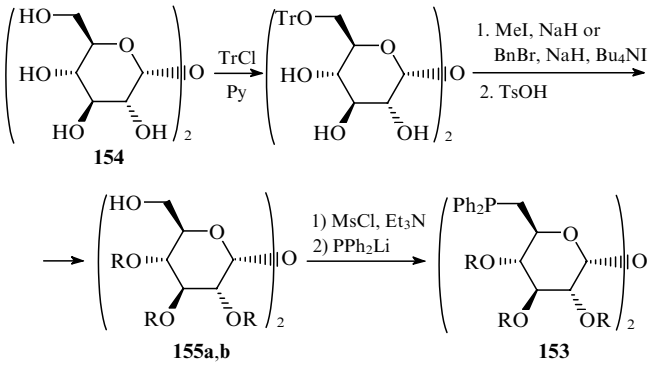


Scheme 9



R = Ph (**a**, 66%), 3,5-$Me_2C_6H_3$ (**b**, 42%); X = PH_2; DMAP is 4-dimethylaminopyridine.

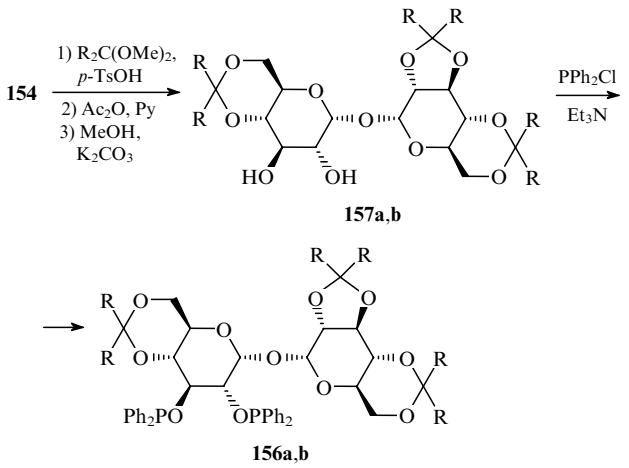
instance, phosphines **153a**,**b** were prepared from disaccharide α,α-trehalose (**154**) according to the standard sequence of reactions employed in carbohydrate chemistry. This procedure made it possible to synthesise the key intermediates **155a** (or **155b**), which were then transformed into the target ligands **153**.[60]



154 **155a**,**b** **153**

R = Me (**a**), Bn (**b**).

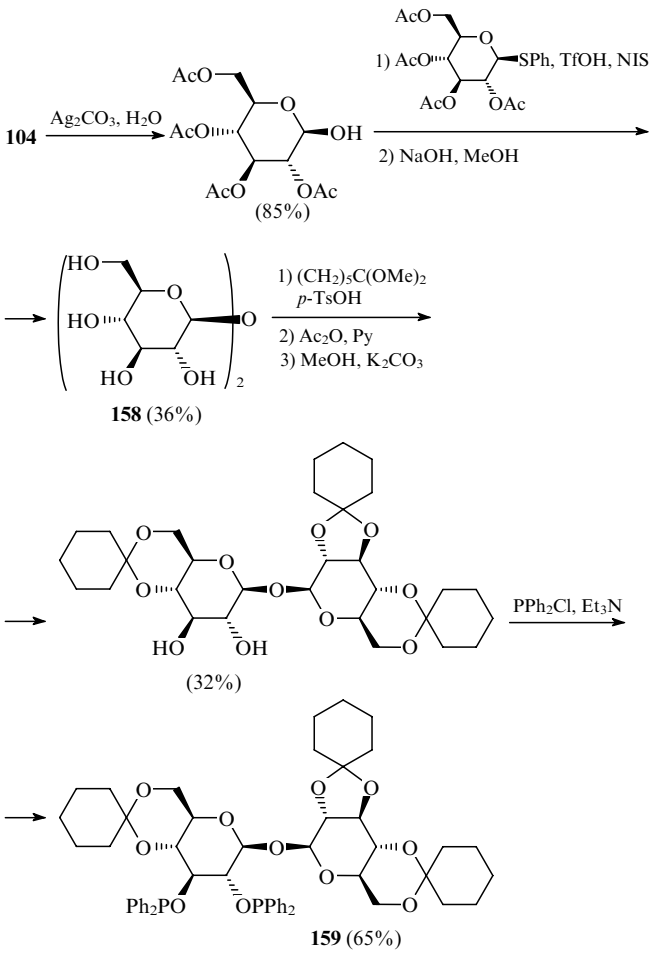
Bisphosphinites **156a**,**b** were prepared from α,α-trehalose (**154**) through the formation of alkylidene derivatives **157a**,**b** whose isolation involved successive acetylation–deacetylation steps.[61]



154 **157a**,**b** **156a**,**b**

R = Me (**157a**, 14%; **156a**, 63%),
R–R = $(CH_2)_5$ (**157b**, 63%; **156b**, 65%).

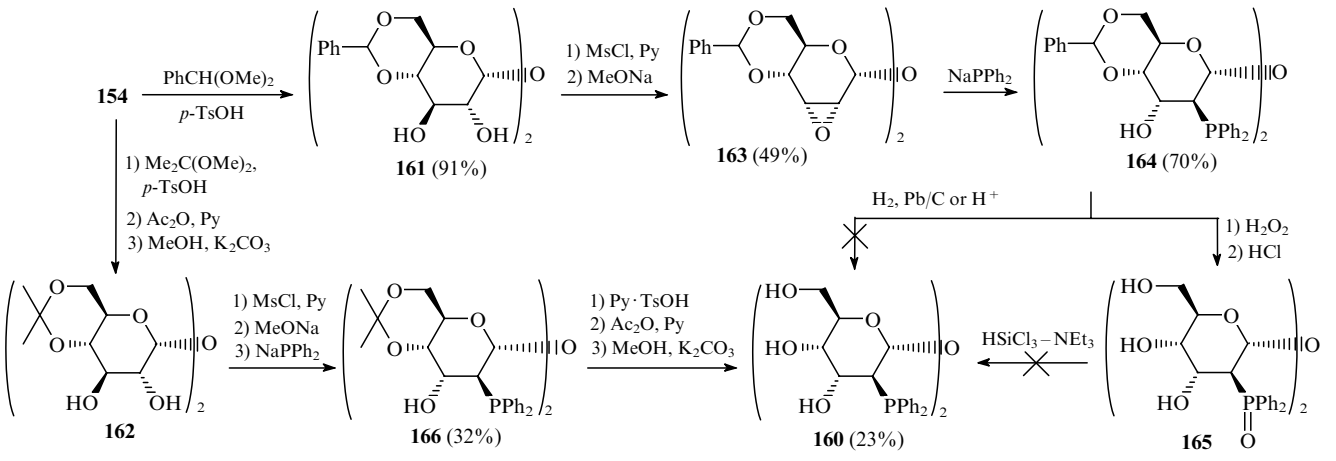
Unnatural carbohydrate β,β-tetrahalose (**158**) was produced from 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**104**) and used in subsequent transformations into bisphosphinite **159**.[61]



NIS is *N*-iodosuccinimide.

Several procedures were developed for the synthesis of 2,2′-bisphosphine **160**. These procedures are associated with the choice of protective groups, which can selectively protect hydroxy groups in the starting carbohydrate, *viz*., α,α-trehalose (**154**) (Scheme 10). Two derivatives of this disaccharide, *viz*., benzylidene (**161**) and diisopropylidene (**162**) derivatives, were prepared. Compound **161** was transformed into bis(epoxide) **163** in two steps. Treatment of the latter with sodium diphenylphosphide afforded phosphine **164**. Attempts to prepare 2,2′-bisphosphine **160** by direct hydrogenolysis of compound **164** on the Pd/C catalyst failed. An attempt to reduce intermediate phosphine oxide **165** with trichlorosilane was also inefficient. The procedure for the preparation of polyhydroxybisphosphine **160** through acetonide **162**

Scheme 10



154 **161** (91%) **163** (49%) **164** (70%)
162 **166** (32%) **160** (23%) **165**

proved to be more successful. Hydrolysis of phosphinylated compound **166** with pyridinium *p*-toluenesulfonate produced the target ligand **160** (see Scheme 10).[62]

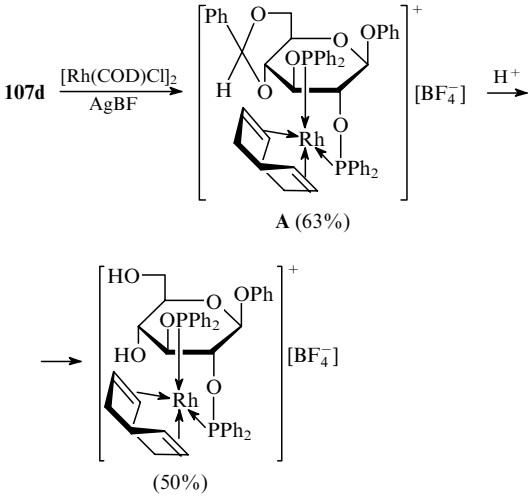
The above-considered examples demonstrate that a broad spectrum of chiral organophosphorus compounds can be synthesised based on carbohydrates. The compounds thus prepared were used for the synthesis of metal complex catalysts.

2. Use in asymmetric synthesis

Hydrogenation of a series of unsaturated acids and their esters in the presence of Rh(I) complexes with bisphosphines **100a**,**b** and bisphosphinites **101a**,**b** afforded the corresponding saturated products with an enantiomeric excess of 67%. Hydrogenation catalysed by the Rh(I) complexes with ligands **100a** and **101a** produced compounds having the (*R*) configuration, whereas hydrogenation in the presence of the Rh(I) complexes with their diastereomers **100b** and **101** yielded products with the (*S*) configuration.[53]

Study of the behaviour of the Rh(I) complexes with chiral organophosphorus ligands **106a**–**i** in hydrogenation reactions demonstrated that the presence of equatorial substituents in the glucopyranoside ring of the ligand leads to a decrease in the enantioselectivity of the catalyst. For example, hydrogenation of methyl (*Z*)-2-acetamidocinnamate catalysed by the Rh(I) complexes with β-anomeric ligands **106c**–**i** afforded products in enantiomeric yields of 91%–92%, whereas the enantioselectivity of analogous transformations on the Rh(I) complexes with α-anomers **106a**,**b** was no higher than 71%. Asymmetric hydrogenation of *N*-acylaminoacrylic acids in the presence of the Rh(I) complex with ligand **106d** proceeded with *ee* = 96%–99%. Hydrogenation of esters of these acids catalysed by the same complex proceeded with somewhat lower enantioselectivity (*ee* = 91%).

With the aim of studying the effect of intramolecular hydrogen bonds on the structure of a complex catalyst and its behaviour in enantioselective hydrogenation, the protective benzylidene group of ligand **107d** in rhodium complex **A** was subjected to hydrolysis.[63–65]

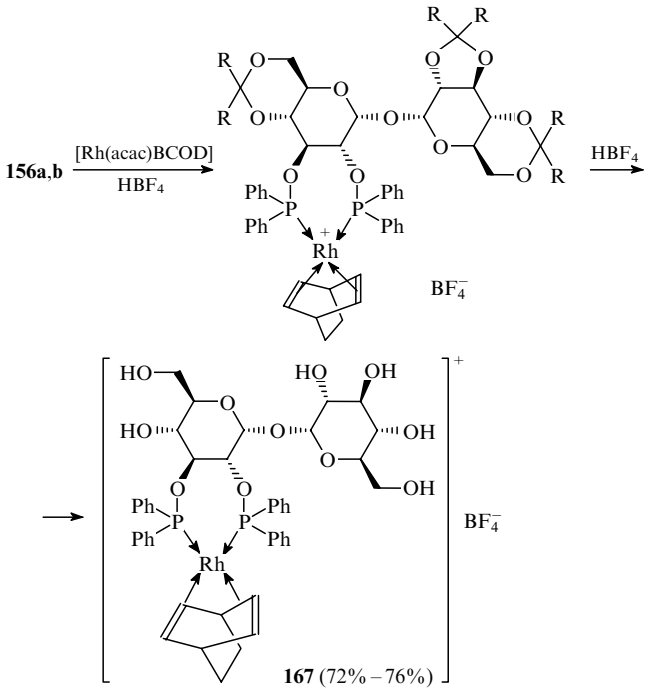


The use of Rh catalysts with ligands **106a**–**j** made it possible to carry out the successful synthesis of (*S*)-amino acids. By contrast, hydrogenation in the presence of complexes with 3,4-bisphosphinites **108**, **110**, **111**, **113**, **118** and **122**, in which the configurations of the carbon atoms [C(3) and C(4)] in the chelate ring of the catalysts are opposite to the configurations of the chiral centres [C(2) and C(3)] of the chelate ring of the catalysts with ligands **106a**–**j**, gave rise to (*R*)-amino acids. As in the case of ligands **106a**–**i**, the presence of equatorial substituents in the pyranose ring leads to a substantial decrease in the enantioselectivity of the catalyst. The best results (*ee* = 93%–98%) were achieved in the presence of the complex with ligand **111** containing only axial substituents.[56–56]

The Rh(I) complex with monophosphine ligand **129** exhibits moderate enantioselectivity (*ee* = 54%) in the hydrogenation of α-acetylaminoacrylic acids.[15] Asymmetric hydrogenation of α-acetamidocinnamic acid proceeded with good enantioselectivity (92%) on the Rh(I) complex with monophosphine **137**, whereas hydrogenation in the presence of the Rh(I) complex with reduced ligand **138** afforded the reaction products with an enantiomeric purity of 39%.[57] Hydrogenation of dehydroamino acids on the Rh(I) complexes with ligands **139** and **145** proceeded with enantioselectivity of no higher than 86%.[55]

When performing hydroformylation of styrene on Rh(I) complexes with bisphosphite ligands (compounds **115**, **119**, **120**, **121**, **125a**,**b** and **128**), the best stereochemical result (*ee* = 64%) was achieved in the presence of the Rh(I) complex with ligand **121**.[58]

The Rh(I) complexes with disaccharide bisphosphines **153a**,**b** were used as catalysts for the hydrogenation of α-(*N*-acetylamino)acrylates. The enantioselectivity of hydrogenation catalysed by the Rh(I) complex with ligand **153b** containing benzyl groups appeared to be much higher (*ee* = 82%) than that of hydrogenation on the Rh(I) complexes with methylated analogue **153a** (*ee* = 10%).[60] Water-soluble cationic Rh(I) complex **167** was synthesised from bisphosphinites **156a**,**b** based on trehalose.



R = Me (**a**), R–R = $(CH_2)_5$ (**b**); BCOD is bicyclooctadiene.

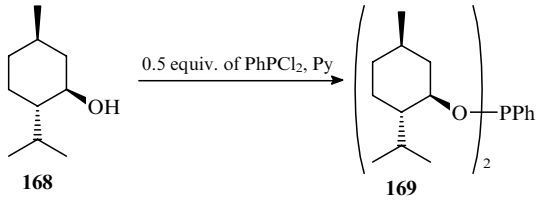
The Rh(I) complex with structurally similar ligand **159** was produced analogously. These catalysts prepared *in situ* showed high enantioselectivity (99%) in the hydrogenation of *N*-acetylaminocinnamic acids and their esters both in water and a two-phase aqueous-organic system.[61]

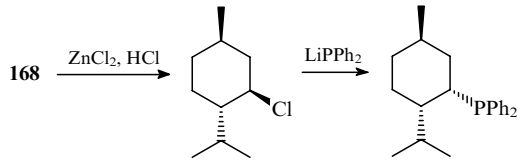
Analogous water-soluble transition metal complexes suitable for catalytic asymmetric reactions in organic and aqueous media can be prepared based also on other chiral organophosphorus ligands containing free or protected hydroxy groups, *viz*., bisphosphinites **149**, bisphosphine **150**, phospholanes **151** and **152**, their diastereomers and polyhydroxy-2,2′-bisphosphine **160**.[59,62] Investigations of the enantioselectivity of hydrogenation catalysed by metal complexes with organophosphorus ligands based on carbohydrates are being continued.

V. Organophosphorus ligands based on terpenoids and steroids

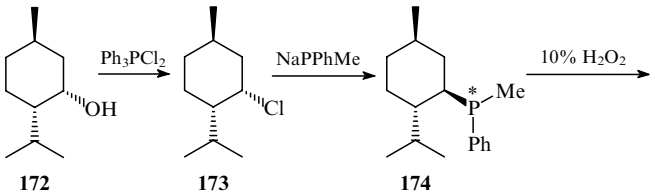
Syntheses of chiral ligands based on terpenoids are remarkable in that they use secondary metabolites of the plant origin (L-menthol, α-pinene, Δ^3-carene, levopimaric and dehydroabietic acids) as the starting compounds. These compounds are comparable to the above-considered hydroxy acids, amino acids and carbohydrates (L-tartaric acid, D-glucose, D-xylose, L-arabinose, L-phenylalanine, *etc.*) in accessibility, optical purity and structural diversity.

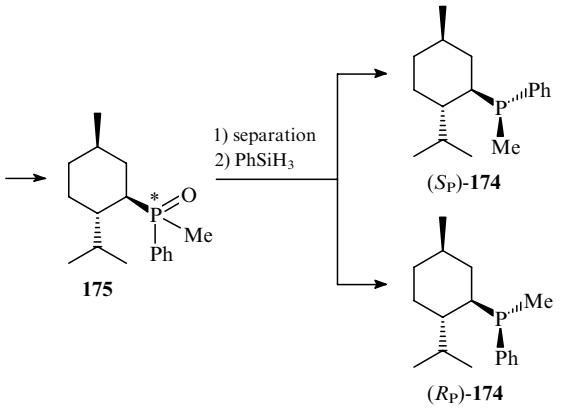
Chiral phosphonite **169** [15] and phosphine **170** [66] were prepared from L-menthol (**168**) according to rather simple procedures. Phosphine **170** was also generated by phosphinylation of L-menthyl chloride (**171**).



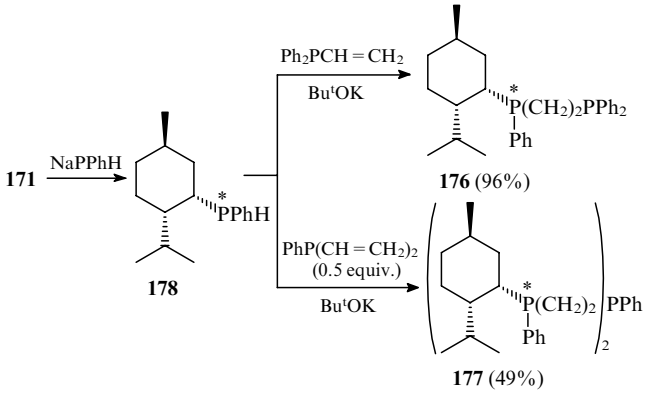


Neomenthol **172** was also used as the starting compound in the synthesis of chiral organophosphorus ligands. For example, treatment of L-neomenthyl chloride **173** with sodium phosphide containing different substituents afforded a mixture of diastereomers **174** possessing an additional asymmetric centre at the phosphorus atom. These diastereomers were purified and separated through chromatographically stable phosphine oxides **175**. After separation, all individual stereoisomers were reduced with phenylsilane to the corresponding menthylmethylphenylphosphines (S_P)-**174** and (R_P)-**174**. It was noted that, unlike the stable (S_P) isomer, the (R_P) isomer underwent partial epimerisation at the phosphorus atom (~13%–25%) under the reaction conditions.[67]

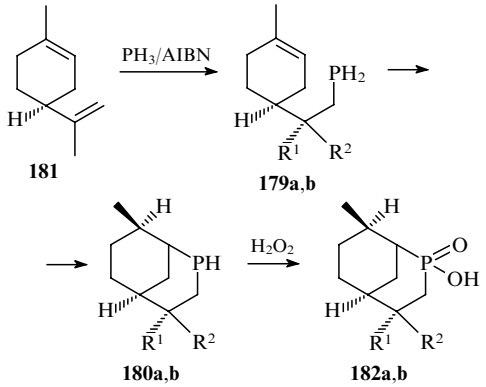




Ligands **176** and **177** were synthesised from L-menthyl chloride (**171**) by nucleophilic hydrophosphinylation. The reaction of chloride **171** with sodium phenylphosphide afforded a mixture of diastereomeric secondary phosphines **178**, whose coupling with phenylvinylphosphines gave rise to the desired ligands **176** and **177**. Individual stereoisomers of these compounds were isolated by recrystallisation.[68]

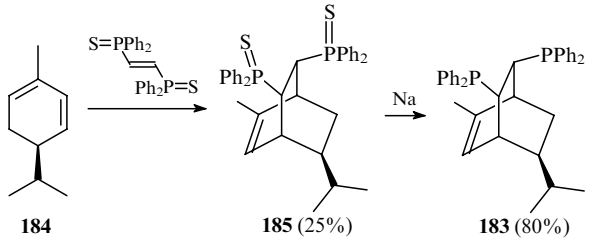


Mono- (**179a**,**b**) and bicyclic (**180a**,**b**) phosphines were prepared by radical hydrophosphinylation of limonene (**181**) with phosphine PH_3. Bicyclic phosphines **180a**,**b** were oxidised to stereoisomeric phosphinic acids **182a**,**b**.[69]

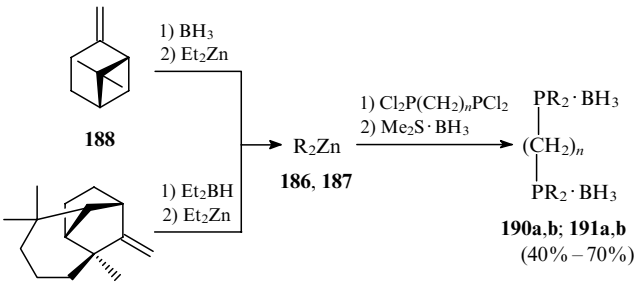


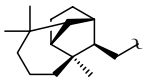
R^1 = H, R^2 = Me (**a**); R^1 = Me, R^2 = H (**b**);
AIBN is azobis(isobutyronitrile).

In the study,[70] the PHELLANOPHOS ligand (**183**) was derived from (−)-α-phellandrene (**184**) and used as a chiral diene in the Diels–Alder reaction with *trans*-vinylenebis(diphenylphosphine sulfide). Adduct **185**, which formed stereospecifically, was reduced to the target bisphosphine **183** by refluxing with sodium metal in toluene.

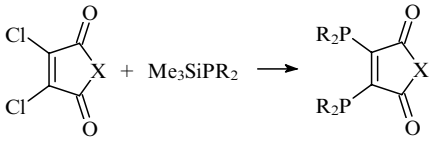


Chiral zinc organometallics **186** and **187**, which were prepared from β-pinene (**188**) and (+)-longifolene (**189**), respectively, by successive hydroboration and transmetallation, served as the starting compounds for the synthesis of the corresponding bidentate phosphines **190a**,**b** and **191a**,**b**. The latter were characterised as complexes with BH_3. These phosphines were used for preparing ruthenium complexes. The latter catalyse hydrogenation of 2-methyl-3-phenylpropenol with moderate enantioselectivity (*ee* = 45%).[71, 72]



R =  (**186**, **190**);  (**187**, **191**); n = 2 (**a**), 4 (**b**).

1,3-Bis(dimenthylphosphino)maleic anhydride **192** and substituted maleimides **193a**,**b** were synthesised by the reactions of dimenthyl(trimethylsilyl)phosphine with 2,3-dichloromaleic anhydride or 2,3-dichloromaleimides, respectively.[73]

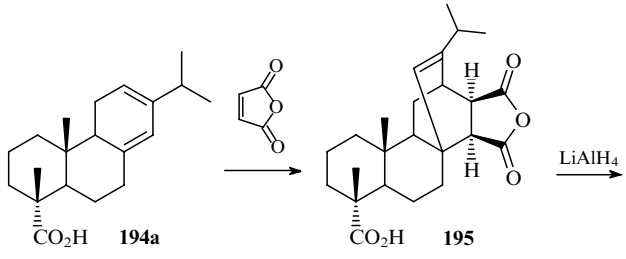


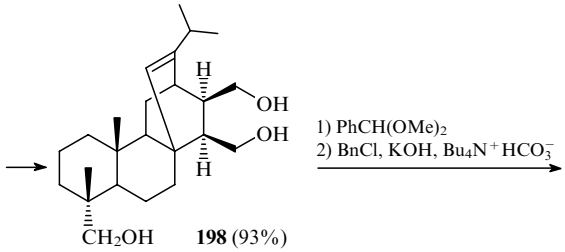
192; **193a**,**b**

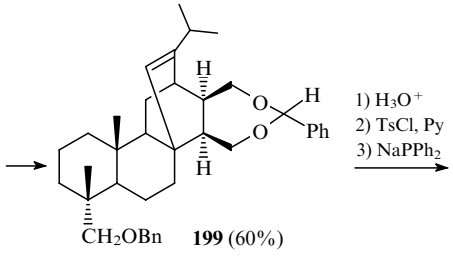
R is L-menthyl; X = O (**192**), NMe (**193a**), NPh (**193b**).

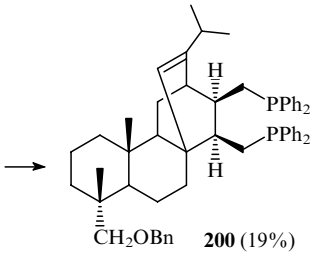
First syntheses of chiral organophosphorus ligands from diterpenoids were described in the studies.[74,75] The authors of the cited studies used the known adducts of levopimaric acid (**194a**) with maleic anhydride (compound **195**) and diethyl fumarate (compound **196**) as well as the adduct of the benzyl ether of levopimarol (**194b**) with diethyl fumarate (compound **197**).

Reduction of adduct **195** produced triol **198**. Protection of all hydroxy groups in compound **198** gave rise to compound **199**, from which the target bisphosphine **200** was prepared according to standard procedures.

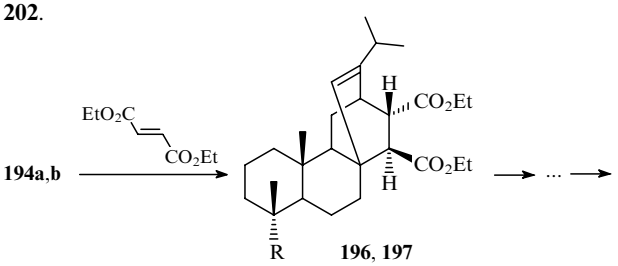


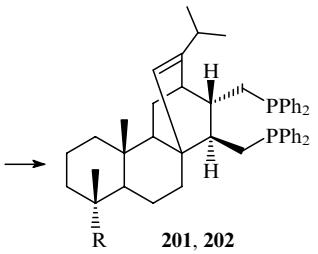






Adduct **196** was transformed into aminodiol through the formation of the morpholine derivative. Successive tosylation and phosphinylation of the aminodiol afforded bisphosphine **201**. Reduction of benzyl ether **197** with $LiAlH_4$ followed by standard transformations gave rise to analogous bisphosphine **202**.





R = CO_2H (**194a**, **196**), CH_2OBn (**194b**, **197**, **202**), $CH_2N(CH_2CH_2)_2O$ (**201**).

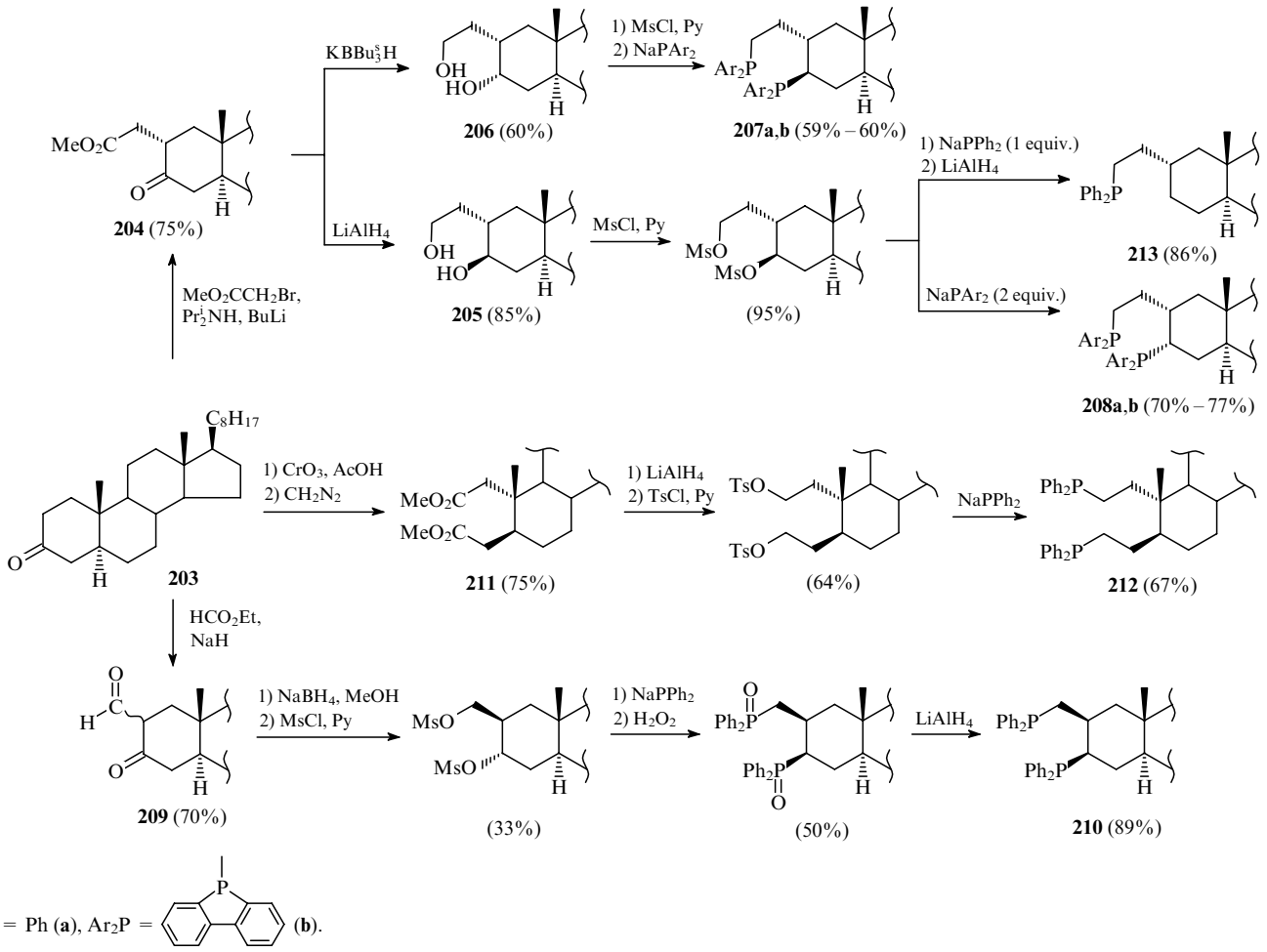
The reactions of bisphosphines **200**–**202** with di-μ-chlorobis(1,5-cyclooctadiene)dirhodium and $NaBF_4$ produced complexes of the $[Rh(COD)L]^+BF_4^-$ type. Rhodium complexes with phosphine **200** catalyse hydrogenation of (*Z*)-*N*-acetylaminocinnamic acid to give *N*-acetylphenylalanine in quantitative yield with *ee* = 37%. The optical purity of 3-(3,4-dihydroxyphenyl)-alanine prepared by hydrogenation of the corresponding precursor on this complex was 27%.

The Rh(I) complexes with phosphines **201** and **202** substantially accelerated hydrogenation of the above-mentioned unsaturated amino acids; however, these reactions gave rise to optically inactive products.

In the study,[76] chiral steroidal organophosphorus ligands were synthesised from cholestan-3-one (**203**). Alkylation of the latter compound with methyl bromoacetate afforded keto ester **204**, which was reduced to isomeric diols **205** and **206**. Then dimesylates were produced and used in the final step of the synthesis for the preparation of bisphosphines **207** and **208** using sodium diarylphosphides. 2-Formylcholestanone **209** was transformed into 1,4-bisphosphine **210** in several steps. 1,6-Bisphosphine **212** is rather readily generated from the oxidation product of cholestanone, *viz*., seco acid ester **211**. The synthesis of monophosphine derivative **213** from diol **205** was also described in the study [76] (Scheme 11).

Phosphorus-containing derivatives of monoterpenes were used as chiral ligands in the hydrogenation of a series of prochiral substrates catalysed by Rh(I) complexes. Hydrogenation of (*E*)-β-methylcinnamic acid in the presence of the Rh(I) complex with ligand **170** produced (*S*)-(+)-3-phenylbutyric acid with an enantiomeric purity of 61%.[66] The rhodium catalysts with ligands (S_P)-

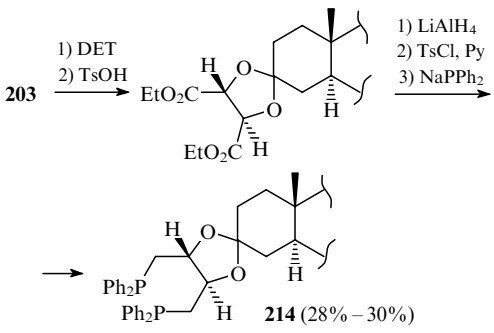
Scheme 11



174a and (*R*$_P$)-**174b** showed higher enantioselectivity (*ee* was 71% and 67%, respectively) in reduction of the same substrate. It should be noted that the use of these diastereomeric ligands made it possible to prepare both enantiomers of 3-phenylbutyric acid.[67] The Rh(I) complexes with diastereomeric bisphosphine ligands **176** catalysed the asymmetric hydrogenation of α-acylaminocinnamic acids. The enantioselectivity of hydrogenation of the latter acids in the presence of these catalysts appeared to be higher (*ee* = 85%) than that of hydrogenation of their esters (*ee* = 31%).[68] The Rh(I) complex with the PHELLANOPHOS ligand (**183**) exhibits high efficiency in the hydrogenation of unsaturated precursors of α-amino acids. The optical purities of the products prepared with the use of this catalyst were 94% – 95%.[70]

The catalytic activities and enantioselectivities of Rh(I) complexes with steroidal ligands derived from cholestan-3-one in the hydrogenation of (*Z*)-α-acetamidocinnamic acid were estimated. The Rh(I) complexes with 1,4- and 1,3-bisphosphines **207a**, **208a** and **210** (*ee* = 75% – 86%) appeared to be most efficient. Hydrogenation catalysed by the Rh(I) complexes with ligands **207a** and **210** afforded (*R*)-*N*-acetylphenylalanine, whereas hydrogenation on the complex with ligand **208a** gave rise to the product with the (*S*) configuration. The replacement of the diphenylphosphine groups in the ligands by the benzophosphindole groups leads to a substantial decrease both in the reaction rate and enantioselectivity of hydrogenation catalysed by the corresponding Rh complexes. The enantioselectivity achieved in the presence of Rh catalysts with such ligands (**207b** and **208b**) was 12% – 22%. Low enantiomeric yields of the products (*ee* = 44%) were observed in hydrogenation of (*Z*)-α-acetamidocinnamic acid on the Rh catalyst with 1,6-bisphosphine **212** as the ligand, whereas the Rh(I) complex with monophosphine **213** has no catalytic effect at all.[76]

The Rh(I) complex with bisphosphine **214** of the mixed type, which was prepared from cholestanone and diethyl tartrate, exhibited high enantioselectivity (*ee* = 90%) in the hydrogenation of (*Z*)-*N*-acetylaminophenylpropenoic acid.[77]

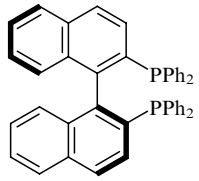


DET is diethyl tartrate.

Therefore, natural terpenes and steroids can be used as the starting compounds in the synthesis of chiral organophosphorus ligands for the preparation of metal complex catalysts for asymmetric homogeneous hydrogenation.

VI. Conclusion

The data surveyed in the present review raise the question of whether ligands prepared by transformations of natural molecules can compete with binaphthyl phosphorus-containing ligands of the BINAP type, which are by far the most efficient ligands for enantioselective catalysts.



In this competition, the advantage of the latter ligands is that they have been studied in much more detail as components of highly efficient catalytic systems. The best ligands serve as reference compounds and are used in fine organic synthesis. These ligands are widely advertised (which is also of importance) by manufacturing companies.

However, the most substantial drawback of binaphthyl ligands is their high price, which remains virtually unchanged over a long period of time. Hence, such ligands will find use in industrially promising processes only after the development of supercatalysts based on these compounds such that they can withstand tens and hundreds of thousands of catalytic cycles. As an example we refer to Rh(I) complexes with bidentate binaphthyl phosphines catalysing the enantiospecific shift of the double bond in the synthesis of L-menthol (Takasago process).

The main hopes, which stimulate investigations on the synthesis of chiral organophosphorus ligands based on available natural compounds, are pinned on the development of technological procedures for the preparation of inexpensive ligands, which can serve as components of catalysts for practically important reactions. These studies are in their infancy and, undoubtedly, will be continued.

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