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REVIEW

Catalytic Methods for Building up Phosphorus–Carbon Bond

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Abstract—The review deals with reactions leading to formation of phosphorus–carbon bonds in the presence of transition metal complexes.

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1. INTRODUCTION

Recent advances in the field of catalysis by metal complexes are determined to a considerable extent by the use of phosphine ligands. The most promising methods for preparation of the latter are based in turn on reactions involving formation of phosphorus–carbon bonds, which are catalyzed by transition metal complexes. Catalytic reactions leading to P–C bond formation turned out to be also useful for preparation of four-coordinate phosphorus derivatives, such as alkyl-, aryl-, alkenyl-, allyl-, α-hydroxy- and α-dialkylaminoalkylphosphonates, -phosphinates, -phosphine oxides, etc. These compounds are important for organic synthesis as building blocks in the preparation of efficient biologically active substrates and also as model compounds for studying mechanisms of biochemical processes.

The present review summarizes published data on catalytic reactions involving P–C bond formation in the presence of transition metal complexes.

2. SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS BY CROSS COUPLING OF ARYL OR VINYL HALIDES OR TRIFLUOROMETHANESULFONATES WITH P-CENTERED NUCLEOPHILES

2.1. Synthesis of Aryl(Vinyl)phosphonates

2.1.1. Reactions with trialkyl phosphites. The reaction of trialkyl phosphites with alkyl halides [1–3] (the famous Arbuzov reaction) leads to formation of phosphonates $RP(O)(OR')_2$. It became possible to involve aryl and alkenyl halides in this reaction under catalysis by transition metal complexes (Scheme 1).

Scheme 1.

$$Ar(Vin)Hlg + (RO)_3P \xrightarrow[-RHlg]{NiCl_2,\ NiBr_2,\ 150–200^\circ C} Ar(Vin)P(O)(OR)_2$$

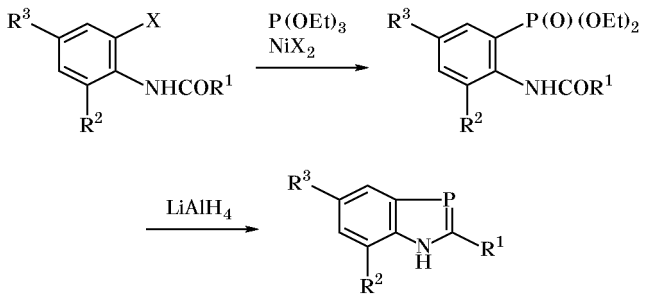
52–95% (Ar)
62–80% (Vin)

Ar = Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, 2-ClC_6H_4, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-$MeOCOC_6H_4$, 4-Et_2N-C_6H_4, 4-NCC_6H_4, 4-$MeCOC_6H_4$, 2-naphthyl, 2-$EtOCOC_6H_4$, 3-$EtOCOC_6H_4$, 4-$EtOCOC_6H_4$, 4-HO-3,5-$(t\text{-}Bu)_2C_6H_2$, 2-thienyl; Vin = $RC(=CH_2)$, R = Me, Et, *i*-Pr, CH_2CMe_2-CH_2; Vin = (*E*)-$R'CH=CH$, R′ = H, Ph, Cl, $P(O)(OEt)_2$.

Nickel [4–7] and palladium complexes [8, 9] are used as catalysts. The reaction requires severe conditions (150–200°C), but the yields of aryl- and alkenylphosphonates are high. Exceptions are reactions with *ortho*-substituted aryl halides, where the yield decreases to 15–40%. Even alkenyl chlorides, such as α- and β-chlorostyrenes and vinyl chloride, give rise to alkenylphosphonates in high yields under catalysis by $NiCl_2$ [6, 7].

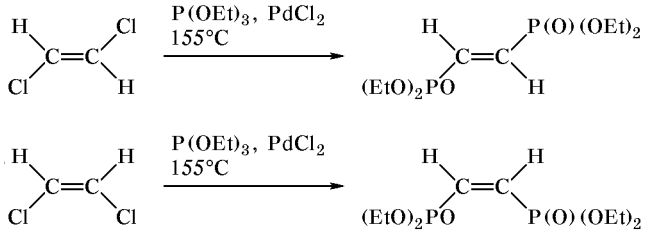
Heinicke *et al.* [10] recently reported on the reaction of triethyl phosphite with 2-haloanilides in the presence of NiX_2 complexes. The resulting *o*-acylaminophenylphosphonates are intermediates in the synthesis of 1*H*-1,3-benzazaphospholes (Scheme 2).

Scheme 2.



Reactions catalyzed by palladium(II) chloride or acetate also provide almost quantitative yields of the products. The process is highly stereospecific: the configuration of the initial alkene is retained in the product. Scheme 3 illustrates the reaction with isomeric 1,2-dichloroethenes as an example [8, 9].

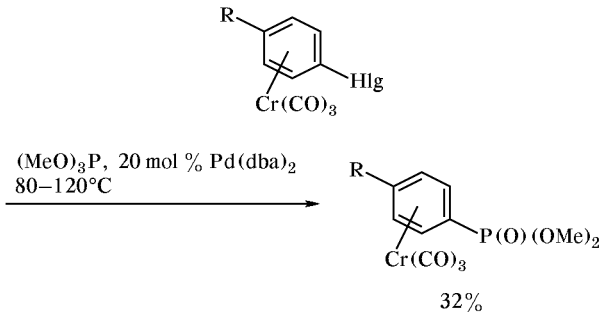
Scheme 3.



It should be noted that the above reactions were reported prior to the discovery of cross-coupling of aryl(vinyl) halides with organometallic compounds. However, they can be regarded as the first example of transition metal complex-catalyzed cross coupling leading to formation of carbon–element bonds (unless copper-catalyzed reactions are considered). The catalytic Arbuzov rearrangement requires very high temperature which is not necessary for common cross-coupling reactions. But the most important is that they involve no transmetalation stage typical of cross-coupling reactions. The reaction temperature can be

reduced via activation of aryl halide by converting it into a tricarbonylchromium complex and the use of trimethyl phosphite instead of commonly used triethyl phosphite. However, the yields were low even at high catalyst concentration [11] (Scheme 4).

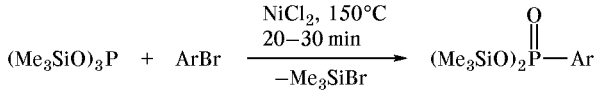
Scheme 4.



Hlg = Br, Cl.

The catalytic arylation of tris(trimethysilyl) phosphite occurs at a much higher rate [12, 13] (Scheme 5). Treatment of the resulting arylphosphonates with methanol at room temperature gives the corresponding phosphonic acids in quantitative yield [13].

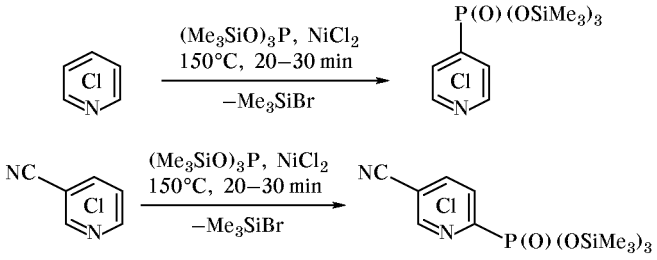
Scheme 5.



Ar = Ph, 4-ClC_6H_4, 4-BrC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 5-ethoxycarbonyl-2-furyl, 2-naphthyl.

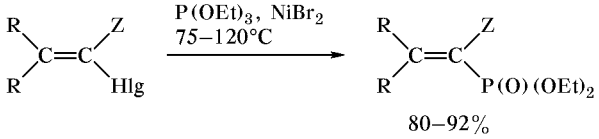
Pentafluoro(chloro)pyridines react with tris(trimethylsilyl) phosphite in a selective fashion, yielding γ-substituted products, while in the reaction with tetrachloro-3-cyanopyridine the α-chlorine atom is replaced (Scheme 6).

Scheme 6.



We succeeded in effecting under milder conditions reactions of triethyl phosphite with akenyl halides having an alkoxy or diethylamino group in position *1* [14, 15] (Scheme 7).

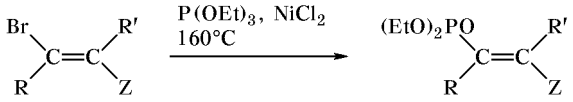
Scheme 7.



Hlg = Cl, Br; R = H, Me; Z = OR, NR_2.

Analogous reactions with 2-halovinyl ethers or 2-haloenamines occur at higher temperature, but the yields are also fairly high [14] (Scheme 8).

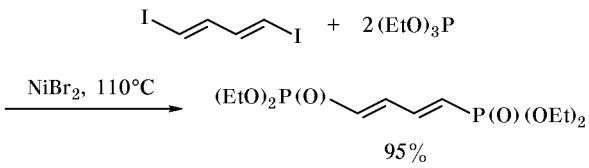
Scheme 8.



R = H, Me, Br; Z = OEt, morpholino, piperidino.

(*E*,*E*)-1,3-Diiodobutadiene was converted into bis-1,4-(diethoxyphosphinoyl)-1,3-butadiene in high yield [16] (Scheme 9).

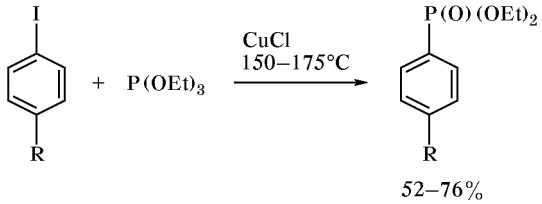
Scheme 9.



In the above reactions, triethyl phosphite acts as both phosphorylating and reducing agent.

Copper salts, e.g., CuCl, CuBr, CuI, and $Cu(OAc)_2$, also catalyze the Arbuzov rearrangement [17]. Some reactions were accomplished with a stoichiometric amount of copper [18, 19] (Scheme 10).

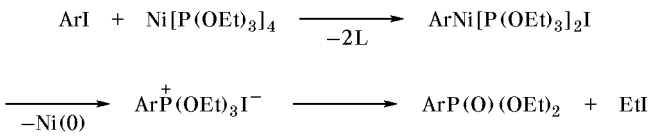
Scheme 10.



R = H, 4-Me, 4-Cl.

Balthazor [20] showed that the reaction involves formation of phosphite Ni(0) complex. The author also presumed that aryl(vinyl)phosphonates are formed as a result of fast oxidative addition of aryl-(vinyl) halide to the Ni(0) complex, followed by slow decomposition to give phosphonium salt which is transformed into phosphonate (Scheme 11).

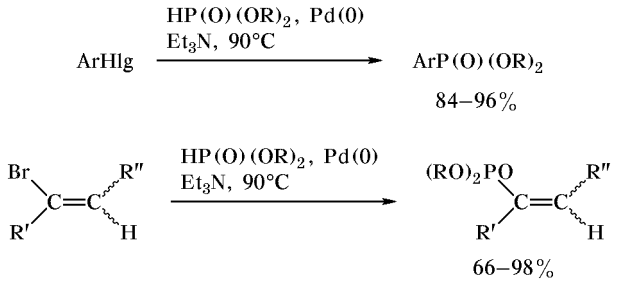
Scheme 11.



It is seen that the process lacks one of the key stages of the catalytic series, namely transmetalation, and that the reductive elimination stage is followed by a typical Arbuzov rearrangement.

2.1.2. Reactions with dialkyl hydrogen phosphites. The known Michaelis–Becker reaction of alkyl halides with dialkyl hydrogen phosphites, which occurs in the presence of bases, can also be effected in the presence of transition metal complexes, primarily in the presence of palladium complexes. This reaction was extensively studied by Hirao and co-workers in 1980s [21–23]. It may be regarded as a classical example of cross-coupling with formation of a C_{sp^2}–P bond. As in the cross-coupling with organometallic compounds, the reaction readily occurs with aryl halides having electron-acceptor substituents, while with those having strong electron-donor substituents, especially amino and hydroxy groups, it is difficult to occur [24]. Alkenyl halides react in a stereoselective manner, yielding 92–100% of the product [21, 23] (Scheme 12).

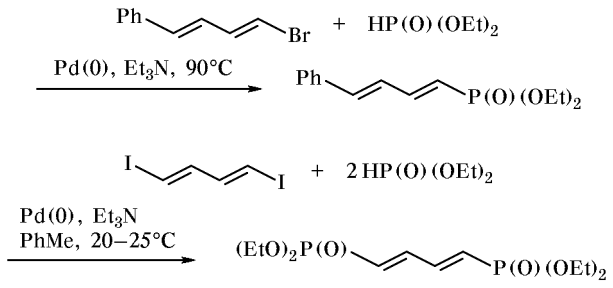
Scheme 12.



Ar = Ph, 4-MeC_6H_4, 2-$MeOC_6H_4$, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$, 4-$MeCOC_6H_4$, 4-$MeOCOC_6H_4$, 4-CNC_6H_4, 2-$MeOCOC_6H_4$, 2-$HOCH_2C_6H_4$, 4-BrC_6H_4, 2-BrC_6H_4, 1-naphthyl; R′ = Ph, R″ = H; R′ = H, R″ = Ph (*E*), Ph (*Z*); R′ = H, R″ = Me (*Z*).

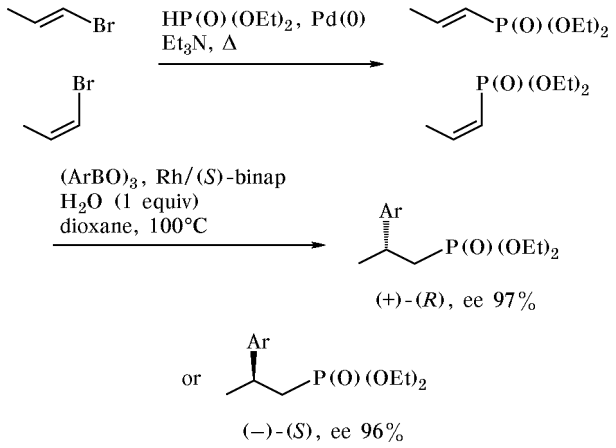
Likewise, mono- and disubstitution products are formed in reactions with 1,3-dienyl halides [21, 16] (Scheme 13).

Scheme 13.

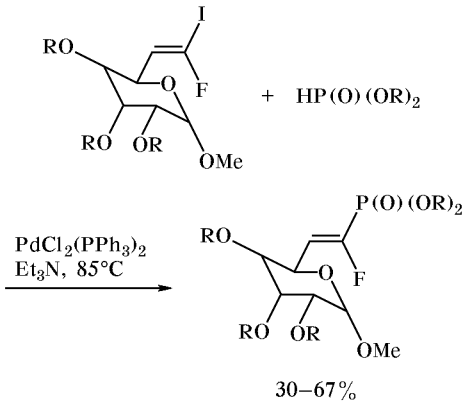


The resulting vinylphosphonates are then brought into various syntheses. For example, Heck-type asymmetric arylation of these compounds by the action of $(ArBO)_3$ in the presence of chiral rhodium complexes gave optically active phosphonic acids with high enantioselectivity [25] (Scheme 14).

Scheme 14.

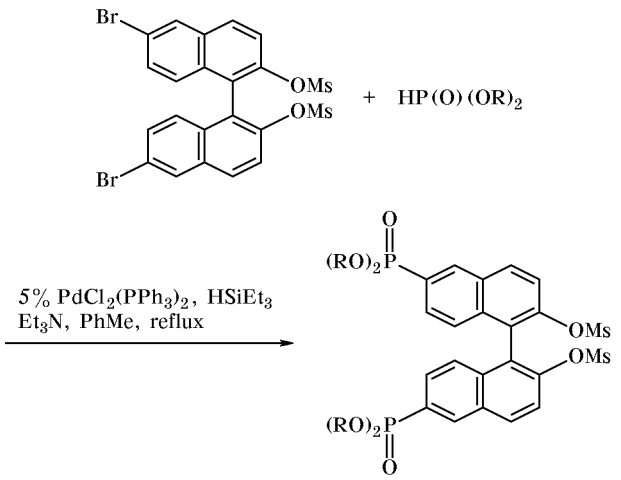


Scheme 15.



Gross *et al.* [26] reported on palladium-catalyzed stereoselective synthesis of (*E*)- and (*Z*)-α-fluorovinylphosphonic acids which are analogs of glucose 6-phosphates (Scheme 15). The reaction of 6,6′-dibromo-1,1′-binaphthalene-2,2′-diyl bis(methanesulfonate) with $(EtO)_2P(O)H$ gave products which found application in the synthesis of new hybrid organic and inorganic laminated materials [27] (Scheme 16). Triethylsilane was added to reduce $PdCl_2(PPh_3)_2$.

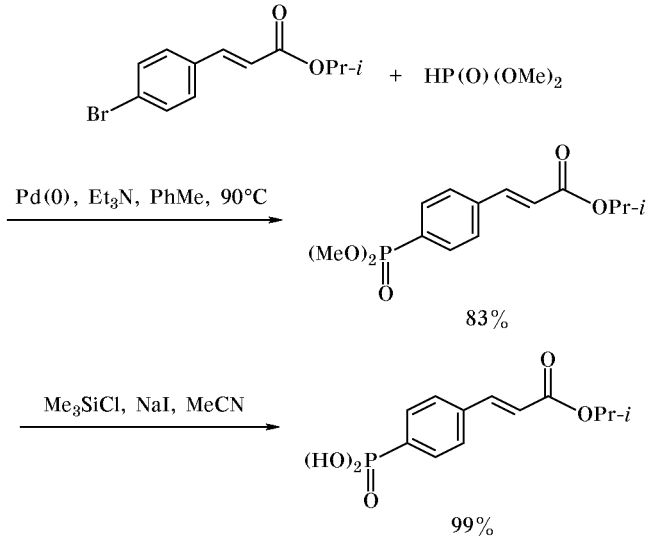
Scheme 16.



R = H, Et, *i*-Pr.

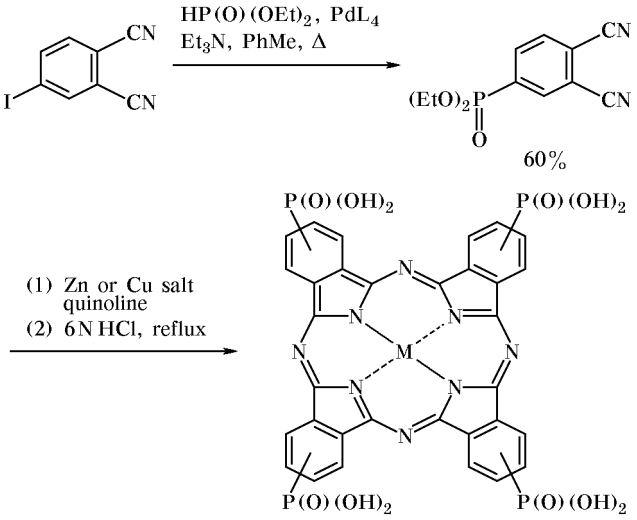
The reaction of isopropyl *p*-bromocinnamate with dimethyl hydrogen phosphite gives the corresponding phosphonate and phosphonic acid which can be grafted to proteins for creation of antibodies [28] (Scheme 17).

Scheme 17.



Bigge *et al.* [29] synthesized phthalocyanine zinc and copper complexes having phosphonate groups in the aromatic rings, starting from 4-iodophthalodinitrile which was converted into 4-diethoxyphosphinoylphthalodinitrile. Such water-soluble phthalocyanines attract interest as photosensitizers for photodynamic therapy [30].

Scheme 18.

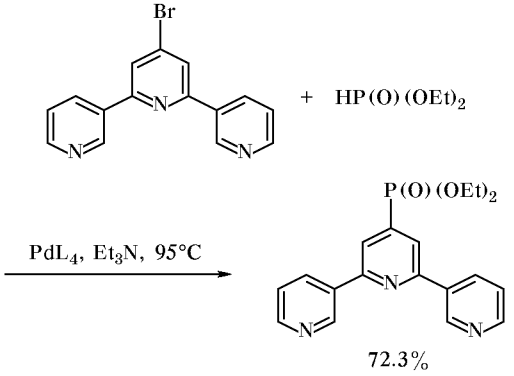


M = Zn, Cu.

A new phosphorylated terpyridine ligand was synthesized by reaction of the corresponding bromo derivative with diethyl phosphonate [31] (Scheme 19). Its ruthenium complexes, as well as ruthenium complex of the corresponding acid, are potential photosensitizers.

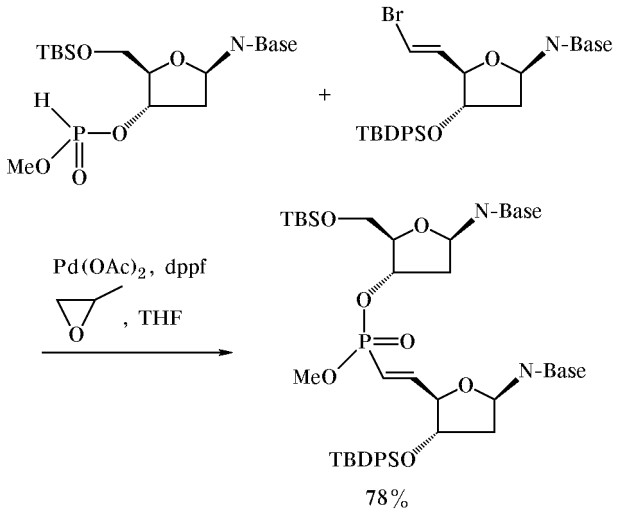
Several phoshorylated 5′-deoxy-5′-methylene thymidine dimers were synthesized using palladium-catalyzed cross-coupling as key stage [32, 33] (Scheme 20). Modified nucleic acid fragments thus obtained are of interest for creation of drugs. In these

Scheme 19.



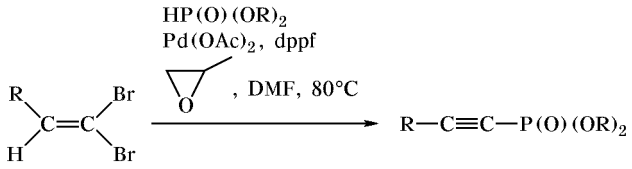
reactions, 1,2-epoxypropane was used as a base instead of triethylamine. In the 1,1-dibromoethenyl derivative of thymidine, one bromine atom is reduced, so that only monophosphorylated product is formed [34]. Such reaction is known for 1,1-dibromoalkenes as a method of synthesis of terminal alkenyl bromides from 1,1-dibromoalkenes [35, 36].

Scheme 20.

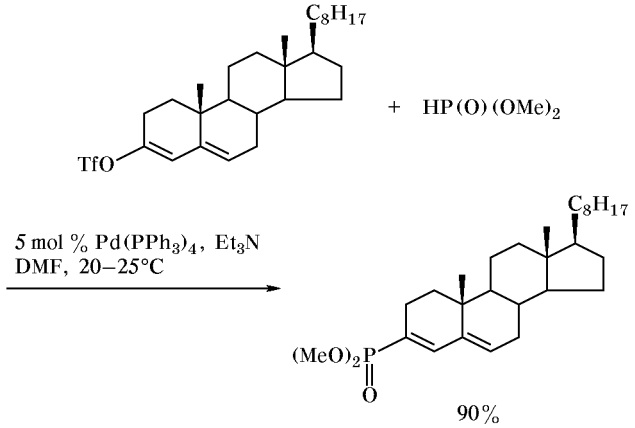


Another pathway of the reaction of 1,1-dibromoalkenes with dialkyl phosphonates includes successive substitution and elimination, leading to alkynylphosphonates [37] (Scheme 21).

Scheme 21.

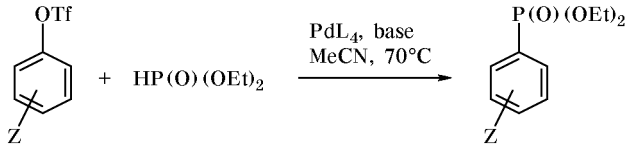


Scheme 22.



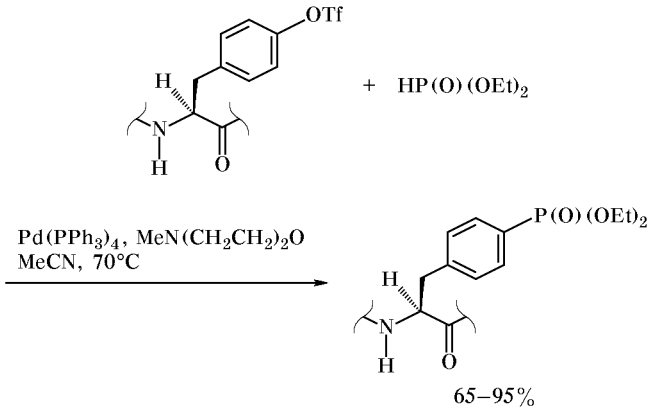
Apart from alkenyl halides, mono- and polycyclic alkenyl trifluoromethanesulfonates were involved in reactions with dialkyl hydrogen phosphites. In these cases, palladium-catalyzed cross-coupling occurs at room temperature [38] (Scheme 22). Aryl trifluoromethanesulfonates also react with $(EtO)_2P(O)H$ in the presence of palladium catalyst [39] (Scheme 23).

Scheme 23.

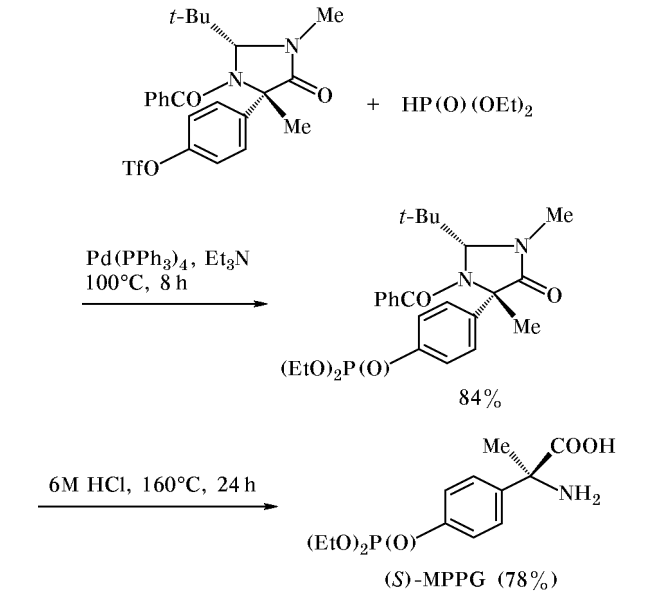


Z = 2-Me, 2-MeO, 2-Cl, 2-MeOC(O), 3-MeOC(O), 3-Br, 4-NO_2.

Scheme 24.

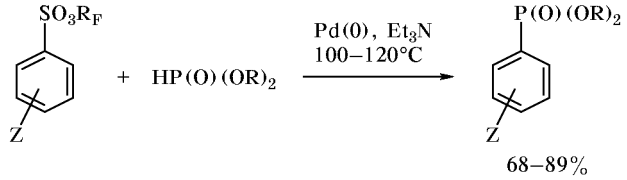


Scheme 25.



The reaction was used in stereoselective modification of thyrosyl peptides to obtain new phosphonate derivatives as models of enzyme inhibitors [40] (Scheme 24). New antagonists selective for metabotropic glutamate receptors, including (*S*)-α-methyl-4-phosphonophenylglycine [(*S*)-MPPG], were obtained on the basis of α-methyl-α-(*p*-trifluoromethylsulfonyloxyphenyl)glycine [41, 42] (Scheme 25). Other polyfluoroalkanesulfonates can also be brought into cross-coupling with dialkyl hydrogen phosphites [43, 44] (Scheme 26).

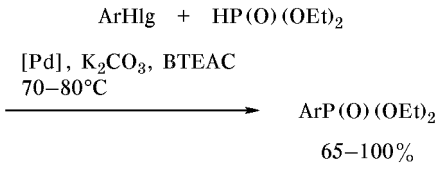
Scheme 26.



Z = H, 2-Cl, 4-OMe, 4-Cl.

Phosphorylation of aryl iodides in the presence of phosphine-free palladium was effected under conditions of phase-transfer catalysis. However, the presence of a phosphine ligand was necessary in the reaction with aryl bromides [45–47] (Scheme 27).

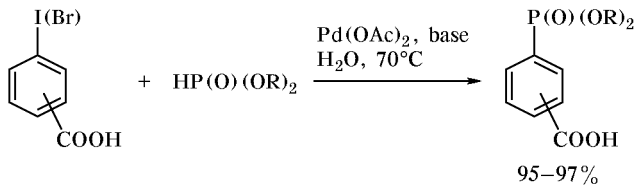
Scheme 27.



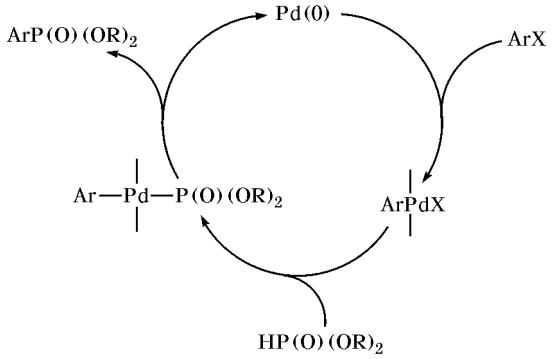
Hlg = I, Br; Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$, 4-NCC_6H_4, 4-ClC_6H_4, 4-$EtOCOC_6H_4$, 4-$HOCOC_6H_4$; [Pd] = $Pd(OAc)_2$ or $Pd(OAc)_2L$; L = PPh_3, PFu_3; BTEAC is benzyltriethylammonium chloride.

The reaction ensures high yields of the products but takes a long time. An analogous transformation occurs at a much higher rate in water or aqueous media. Here, aryl iodides also react in the presence of ligand-free palladium; however, a water-soluble phosphine ligand may be added [47] (Scheme 28).

Scheme 28.

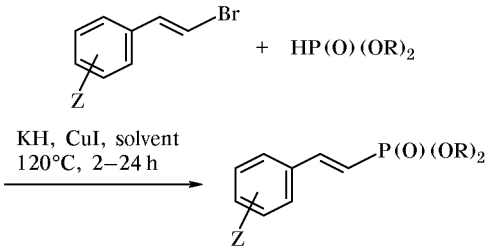


Scheme 29.

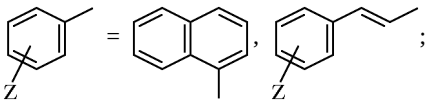


Scheme 29 illustrates the catalytic series. Apart from palladium and nickel complexes, the phosphorylation process may be promoted by copper complexes. In most cases, a stoichiometric amount of copper complex was necessary, e.g., in reactions of *o*-bromodiarylazo compounds with dialkyl and diphenyl hydrogen phosphites [48] or in reactions with β-bromostyrenes to obtain compounds possessing second harmonic generation (SHG) activity. Strongly polar solvents, KH as a base, and elevated temperature are necessary [49] (Scheme 30).

Scheme 30.



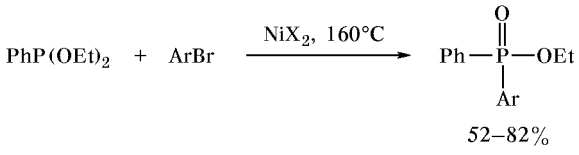
Z = 4-MeO, 2-MeO, 3-Cl, 3-MeS, 3-Me_2N, 3-Ph_2N, 3-Ph_2P;



2.2. Synthesis of Aryl(Vinyl)phosphinates

2.2.1. Reactions with alkyl(phenyl)phosphonous esters. As with trialkyl phosphites, nickel complexes

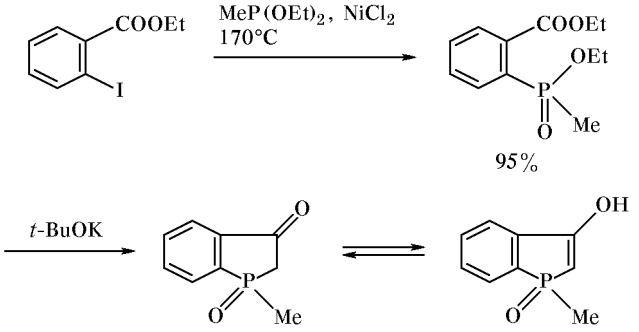
Scheme 31.



Ar = Ph, 1-naphthyl, 2-thienyl, 4-$MeOC_6H_4$, 3,5-Bu_2-4-HOC_6H_2.

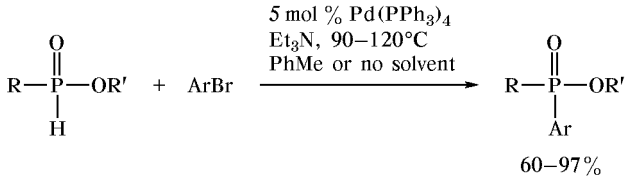
catalyze reactions of aryl(alkyl)phosphonous esters with aryl bromides [20, 21] (Scheme 31). These reactions were the key stages in the synthesis of iodinane (1-hydroxy-3-methyl-1,3-dihydro-1,2,3λ^5-benziodoxophosphole 3-oxide) [50] and phosphinindole [51] (Scheme 32).

Scheme 32.



2.2.2. Reactions with phosphinic esters. Arylphosphinates are synthesized in a way similar to the synthesis of arylphosphonates, starting from alkyl(phenyl)phosphinic esters. The reactions are catalyzed by palladium complexes in the presence of triethylamine, and the products are formed in high yields [52, 53] (Scheme 33).

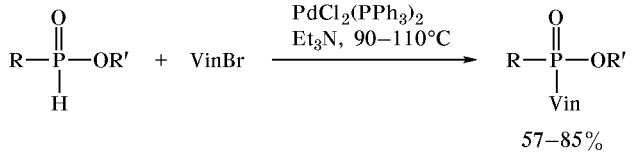
Scheme 33.



Ar = Ph, naphthyl, 2-MeC_6H_4, 2-thienyl, 4-R″C_6H_4 (R″ = Me, MeO, Cl, Ph, NO_2, Ac, AcNH, CN); R = Ph, Me, Bu; R′ = Et, Bu.

The vinylation process occurs under similar conditions, the configuration at the double bond remaining unchanged. According to [54], $PdCl_2(PPh_3)_2$ is more active than $Pd(PPh_3)_4$ (Scheme 34).

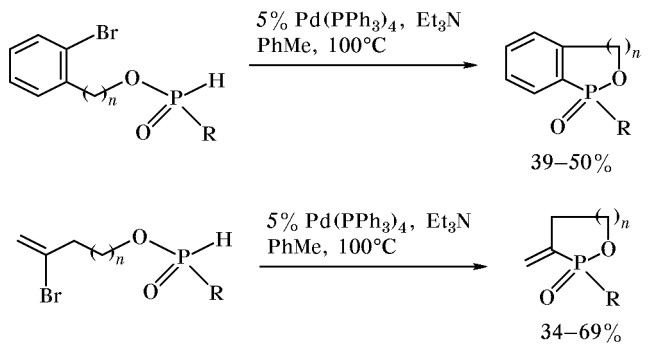
Scheme 34.



Vin = (*E*)- and (*Z*)-β-styryl, α-styryl, isobutenyl, (*Z*)-1-propenyl, (*Z*)-2-methyl-2-metoxycarbonylethenyl.

Intramolecular phosphorylation of ω-[*o*-bromophenyl(vinyl)]alkyl phenyl(or methyl)phosphinates leads to formation of benzoxaphosphacycloalkanes [55] or 3-methylene-1-oxa-2-phosphacycloalkane 2-oxides which can be regarded as phosphorus analogs of α-methylenelactones [56] (Scheme 35).

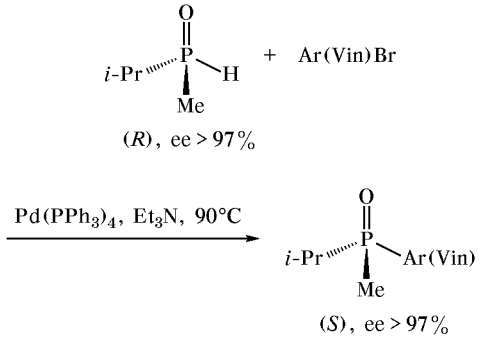
Scheme 35.



R = Me, Bu, Ph; *n* = 1–3.

Both arylation and vinylation of enantiomeric isopropyl (*S*)- and (*R*)- methylphosphinates in the presence of palladium(0) complex occur with retention of configuration at the phosphorus atom [57–60] (Scheme 36).

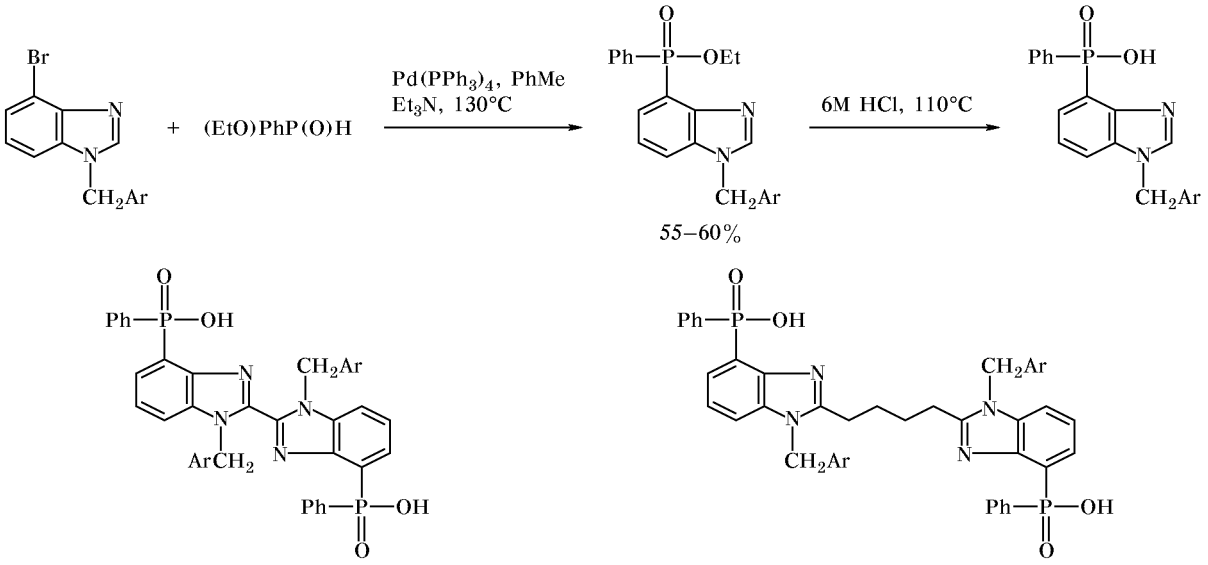
Scheme 36.



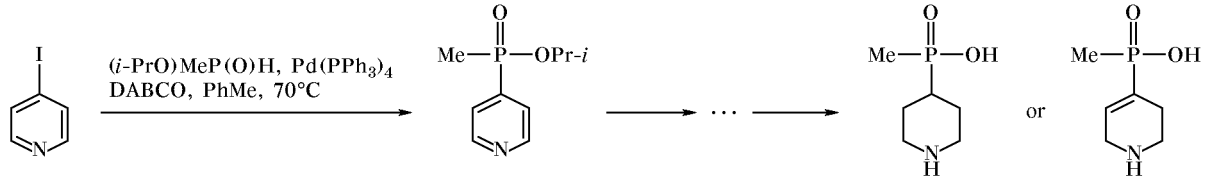
Edlin and Parker [61] obtained sterically hindered ligands for selective complex formation with zinc ion by cross-coupling of 4-bromobenzimidazole with ethyl phenylphosphinate (Scheme 37). Hetarylation of isopropyl methylphosphinate with 4-iodopyridine, followed by reduction and hydrolysis gave potential GABA (γ-aminobutyric acid) receptor antagonists, methyl(1,2,5,6-tetrahydropyridin-4-yl)phosphinic acid and its saturated analog, methyl(4-piperidinyl)phosphinic acid [62] (Scheme 38).

Monoarylation of H_2-phosphinates leads to arylphosphinates. To avoid further arylation, the reaction

Scheme 37.

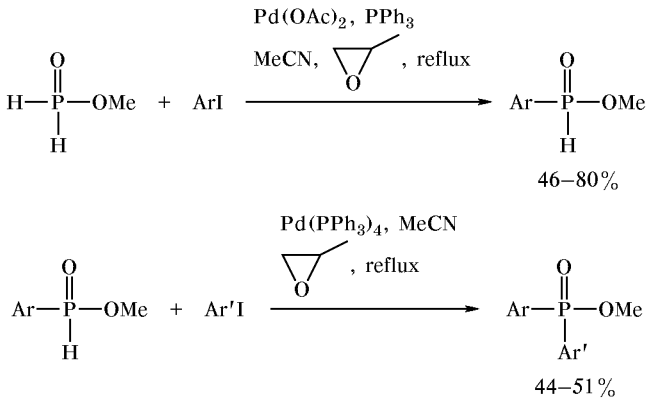


Scheme 38.



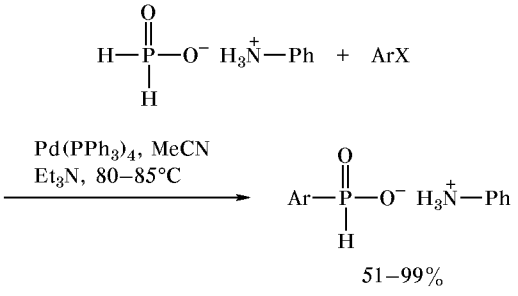
is carried out with excess H_2-phosphinate. The reaction also occurs in the absence of a base. In this case, 1,2-epoxypropane was used instead of amine to bind the liberated acid. Excess aryl iodide gives rise to double arylation; using two different aryl iodides, unsymmetrical diarylphosphinates can be obtained [63–67] (Scheme 39).

Scheme 39.



Anilinium phosphinate was proposed as a new phosphorylating agent to substitute for unstable alkyl phosphinates. Anilinium phosphinate selectively reacts with aryl halides and trifluoromethanesulfonates to give monoarylated products [68, 69] (Scheme 40).

Scheme 40.



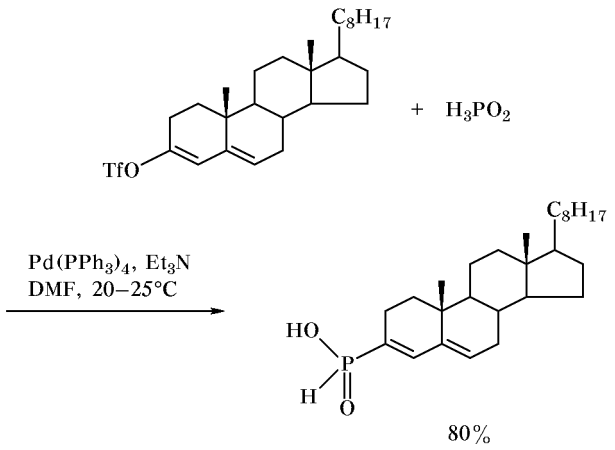
X = I, Br, OTf; Ar = Ph, 1-naphthyl, 2-naphthyl, ZC_6H_4 (Z = 2-Me, 4-Ac, 3-Me, 4-NO_2, 4-MeO, 2-Br, 3-Cl, 4-Cl, 4-HOCO, 4-MeOCO, $PhCH_2$, 4-CN).

These reactions are accompanied by side reduction of aryl halide to the corresponding arene [68].

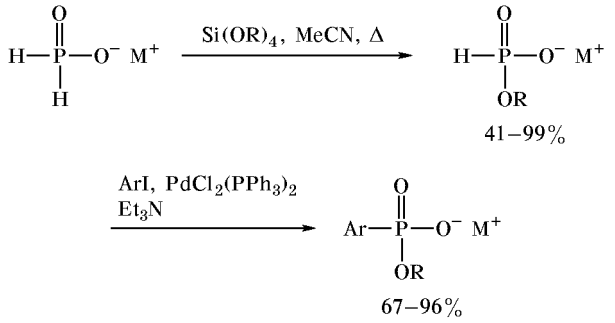
Holt and Erb [38] reported on the vinylation of phosphinic acid itself to obtain alkenylphosphinic acid of the steroid series (Scheme 41).

Another version of modification of $H_2P(O)OH$ or its salts is esterification with alkoxysilanes [70] or generation of phosphinic esters *in situ* by the action of ortho esters [66]. The corresponding esters and salts readily react with aryl iodides or bromides (Scheme 42). Schuman *et al.* [71] developed an efficient procedure for synthesizing 4-(4-carboxybutyl)-phenyl(2,4,6-trimethylphenyl)phosphinic acid, which was used to obtain a series of unsymmetrical diarylphosphinic acids (haptenes) with the goal of preparing catalytic antibodies for hydrolysis of peptides (Scheme 43).

Scheme 41.

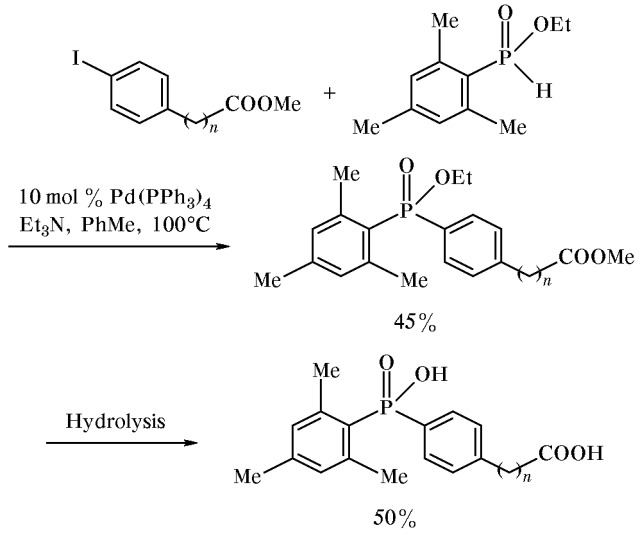


Scheme 42.



M = H, $PhNH_3$, NH_4; R = Me, Et, Bu, Ph, All.

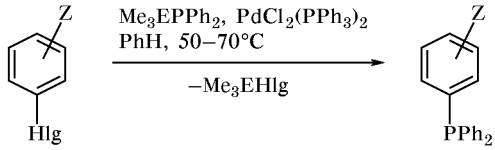
Scheme 43.



2.3. Synthesis of Aryl(Vinyl)phosphines and -phosphine Oxides

2.3.1. Reactions with phosphides Ph_2PM (M = $SiMe_3$, $SnMe_3$, ZnCl). Stille [72] was the first to apply cross-coupling approach to obtain diphenyl-(aryl)phosphines. Diphenyl(trimethylsilyl)phosphine and diphenyl(trimethylstannyl)phosphine were brought into reaction with aryl halides in the presence of $PdCl_2(PPh_3)_2$ or $PdCl_2(MeCN)_2$ as catalyst in benzene (Scheme 44). This reaction is analogous to the Migita–Kosugi reaction of ArBr with Me_3SiNR_2, reported in [73].

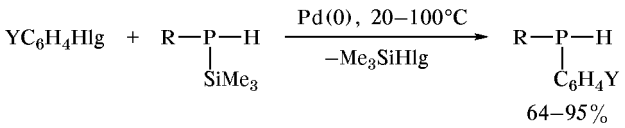
Scheme 44.



E = Si (yield 83%), Sn (74%); Z = 4-Me, 4-MeO, 4-AcNH, 4-$NCCH_2$, 4-MeOCO, Ac, 4-Cl, 2-Cl, 4-Br, 2-Br; Hlg = I, Br.

A similar procedure was used to obtain unsymmetrical secondary alkyl(aryl)phosphines [74, 75] (Scheme 45).

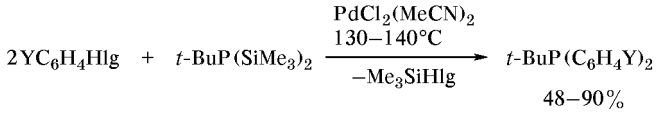
Scheme 45.



R = *t*-Bu, *i*-Pr; Y = H, Me, Cl, F, Br, I, CF_3, CN, COOR, MeO, Me_2N.

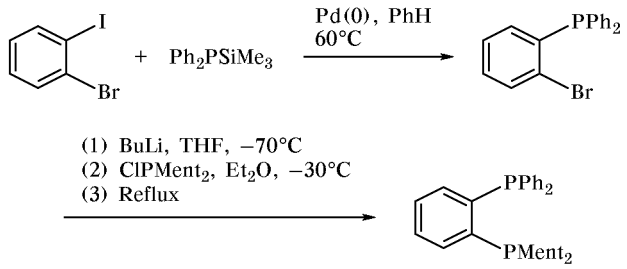
Tertiary alkyl(diaryl)phosphines were synthesized from *tert*-butylbis(trimethylsilyl)phosphine and aryl halides [75] (Scheme 46). Cross-coupling of *o*-bromoiodobenzene or 1,1′-diiodoferrocene with Ph_2PSiMe_3 was the initial stage in the synthesis of chiral menthylphosphine ligands [76] (Scheme 47).

Scheme 46.



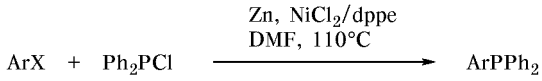
Y = 4-Br, 4-COOSiMe$_3$, 4-Me, 4-MeO, 3-CN, 3-COOSiMe$_3$.

Scheme 47.



An interesting version of cross-coupling with chloro(diphenyl)phosphine, catalyzed by nickel complex in the presence of zinc, was reported in [77] (Scheme 48).

Scheme 48.

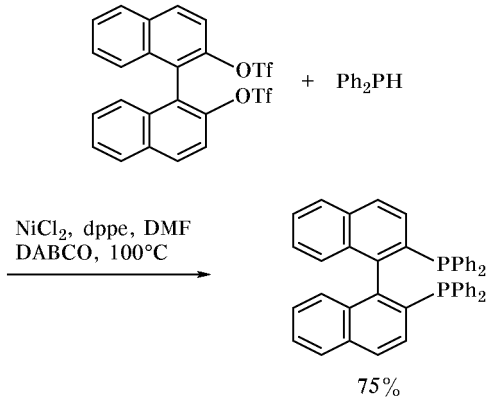


X = Br, OTf; Ar = 2-naphthyl, 1-MeOCOC$_{10}$H$_7$, 2-MeOCOC$_6$H$_4$, 2-BzlNHCOC$_6$H$_4$, 2-(*S*)-PhCH(Me)NHCOC$_6$H$_4$, 1,1′-binaphthalene-2,2′-diyl.

In this reaction, zinc performs two functions: it reduces Ni(II) to Ni(0) and gives rise to zinc phosphide Ph$_2$PZnCl which reacts with ArX. The yields of the products range from moderate to high. Aryl trifluoromethanesulfonates ensure greater yields than analogous bromides. As a result of double replacement in the corresponding trifluoromethanesulfonate, (*S*)-BINAP was obtained in 52% yield without racemization.

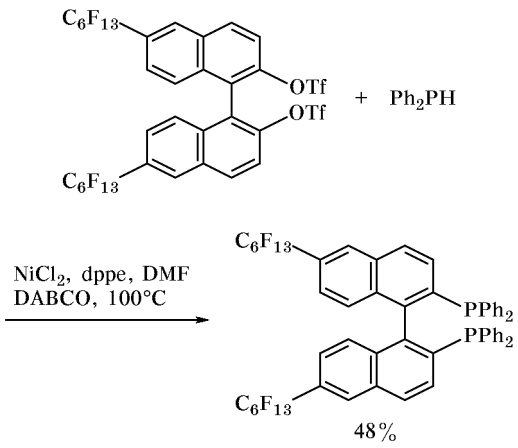
2.3.2. Arylation of secondary and primary phosphines. Free secondary or primary arylphosphines can be used instead of their silicon or tin derivatives in the arylation reactions. A new catalytic synthesis of BINAP was proposed by Merck. BINAP is one of the most efficient chiral ligands [78], which was synthesized for the first time by Noyori in early 1980s [79]. The best result (yield 75%) was obtained with diphenylphosphine and NiCl$_2$/dppe in DMF in the presence of DABCO as a base [80] (Scheme 49). Here, the main condition for successful synthesis was the use of free Ph$_2$PH instead of Ph$_2$P(O)H. The latter failed to provide formation of disubstituted product for steric reasons.

Scheme 49.



Perfluoroalkyl derivative of (*R*)-BINAP was obtained in 48% yield from the corresponding trifluoromethanesulfonate (Scheme 50). This ligand attract interest for reactions in two-phase systems and in supercritical CO$_2$ [81].

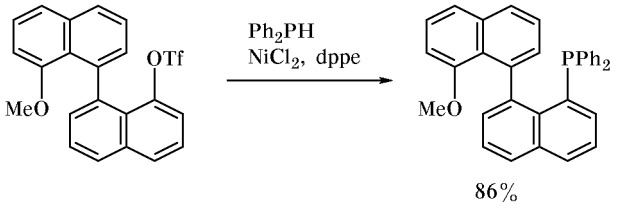
Scheme 50.



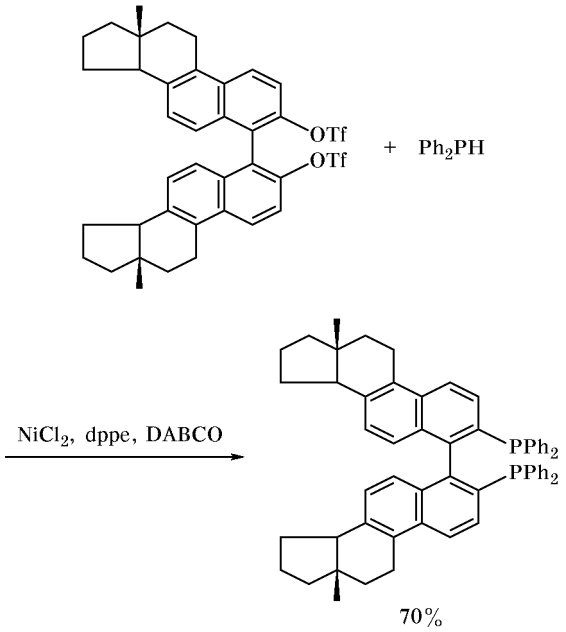
A new chiral unidentate ligand, 8-diphenylphosphino-8′-methoxy-1,1′-binaphthalene (8-MeO-MOP) was synthesized by cross-coupling of appropriate racemic trifluoromethanesulfonate and diphenylphosphine under the conditions developed by Merck [80] (Scheme 51). The isomeric products were separated via acylation with (1*S*)-camphenyl chloride [82]. An attempt to synthesize the same ligand according to the procedure proposed by Hayashi for the corresponding 2,2′-analogs (starting from phosphine oxide [83]) resulted in racemization at the phosphorylation stage [84]. Likewise, chiral bis-steroidal phosphine

was obtained from deoxyequilenin trifluoromethanesulfonate [85] (Scheme 52).

Scheme 51.

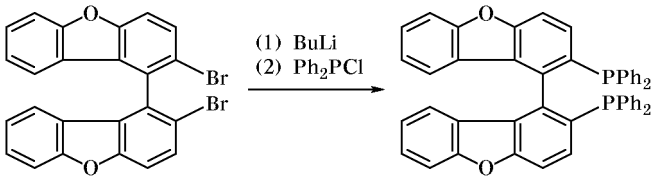


Scheme 52.



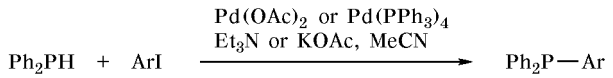
Owing to steric hindrance, 2,2′-bis(diphenylphosphino)-1,1′-bi(dibenzofuran) (BIFAP) cannot be obtained even with the use of diphenylphosphine, though monosubstitution successfully occurs in the presence of 10% $NiCl_2$/dppe in DMF at 100°C. Gelpke *et al.* [86] succeeded in synthesizing BIFAP according to a "Li-protocol," which is analogous to that developed by Noyori in the synthesis of BINAP [87]. The procedure includes halogen–lithium exchange and subsequent reaction with chloro(diphenyl)phosphine (Scheme 53).

Scheme 53.



Cross-coupling of phenyl- or diphenylphosphine with mono- and disubstituted aryl iodides afforded various tertiary phosphines, including those containing sulfo or carboxy group in the aromatic ring (water-soluble ligands) [88, 89] (Scheme 54).

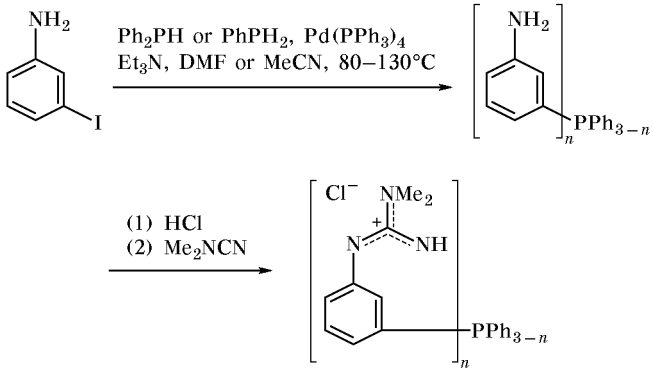
Scheme 54.



ArI: XC_6H_4I (X = 4-Me, 3-COOH, 4-COOH, 2-COOMe; 4-OH, 2-NH_2, 4-NH_2, 4-SO_3Na); XYC_6H_3I (X = Y = 3,5-Me_2, 3,5-$(COOH)_2$, 3,4-$(COOH)_2$; X = 4-OH, Y = 3-COOH; X = 2-OH, Y = 4-COOH; X = 3-COOH, Y = 4-NH_2.

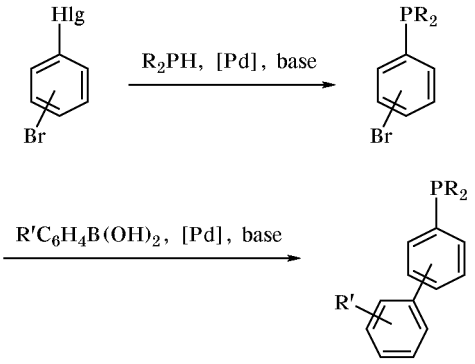
Water-soluble phosphines were also obtained by cross-coupling of phenyl- and diphenylphosphines with *m*-iodoaniline, followed by transformation of the amino group into guanidine moiety [90] (Scheme 55). Later on, a large series of polyfunctional and chiral phosphine ligands was synthesized via a combination

Scheme 55.



n = 1–3.

Scheme 56.

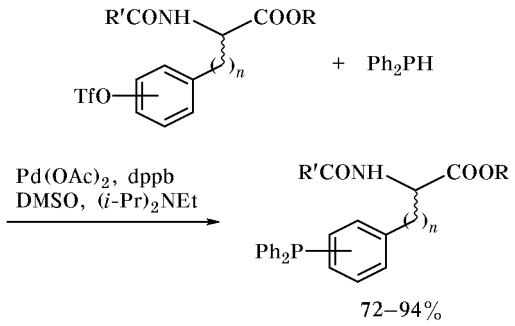


Hlg = I, Br; R = Ar, Alk; R′ = Me.

of palladium-catalyzed reactions involving formation of P–C and C–C bonds [91] (Scheme 56).

Phosphination of thyrosine and hydroxyphenylglycine derivatives, as well as of thyrosine-containing peptides [92] and D- and L-phenylalanine [93], was effected by cross-coupling of the corresponding trifluoromethanesulfonates with diphenylphosphine in DMSO (Scheme 57). The use of dimethyl sulfoxide (rather than DMF) is a necessary condition.

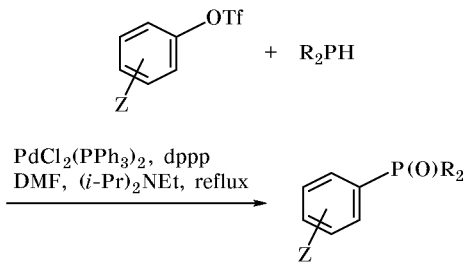
Scheme 57.



n = 0, 1.

Functionally substituted tertiary phosphine oxides, mainly those having a carboxy group, were prepared from aryl trifluoromethanesulfonates via palladium-catalyzed reaction with Ph_2PH [94] (Scheme 58).

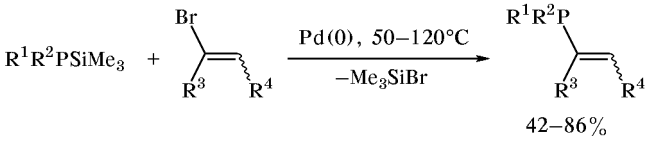
Scheme 58.



R = Et, Ph; Z = 3-COOMe; 4-COOMe; 3,5-$(COOMe)_2$; 2,6-$(COOMe)_2$, 4-MeO; 2-MeO-6-$MeOCH_2$.

2.3.3. Vinylation of phosphines and their derivatives. A catalytic procedure for the synthesis of alkenylphosphines was developed by Beletskaya and co-workers [95–98]. Vinylation of monosilyl derivatives of secondary and primary phosphines with alkenyl bromides leads to alkenylphosphines in moderate to high yields [95] (Scheme 59). Cross-coupling of alkyl(trimethylsilyl)phosphines with α-bromoalkenyl ethyl ethers afforded alkyl(α-ethoxyalkenyl)phosphines which were found to undergo

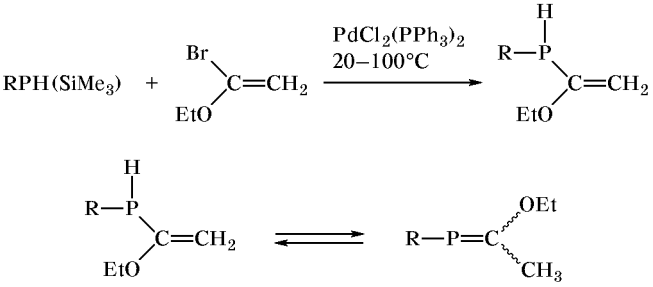
Scheme 59.



R^1 = R^2 = *i*-Pr, Ph; R^1 = H, R^2 = *i*-Pr; R^1 = H, R^2 = *t*-Bu; R^3 = H, *i*-Pr; R^4 = H, OEt, Ph.

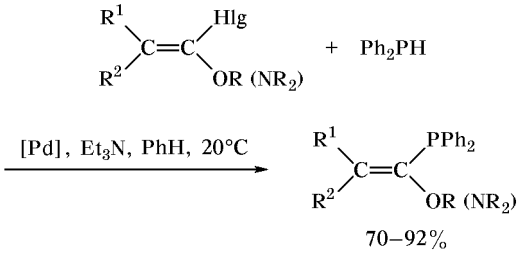
reversible 1,3-sigmatropic rearrangement to isomeric phosphaalkenes [96, 97] (Scheme 60).

Scheme 60.



Functionalized vinylphosphines were synthesized by reaction of diphenylphosphine or its trimethylsilyl derivative with the corresponding alkenyl bromides or chlorides under catalysis by palladium [98] or nickel complexes [99] (Scheme 61).

Scheme 61.

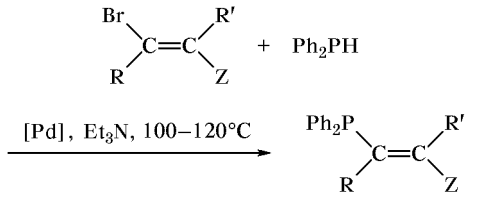


Hlg = Br, Cl; R^1 = H, Me; R^2 = H, Me, Me_3Si.

α-Haloalkenyl alkyl ethers and α-haloenamines react with diphenylphosphine at room temperature (even α-chloroenamines can be involved in the reaction), while analogous β-alkoxy- or β-dialkylaminoalkenyl bromides require more severe conditions (100–120°C) to complete the reaction (Scheme 62). Nickel complexes turned out to be more efficient than palladium complexes in reactions with less active alkenyl halides, such as 2-bromobutene and 1-bromovinylsilane. The latter almost do not react in the

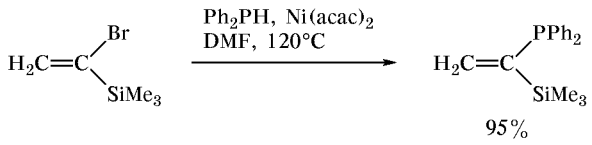
presence of palladium complexes. Here, the use of polar solvents is important [99] (Scheme 63).

Scheme 62.



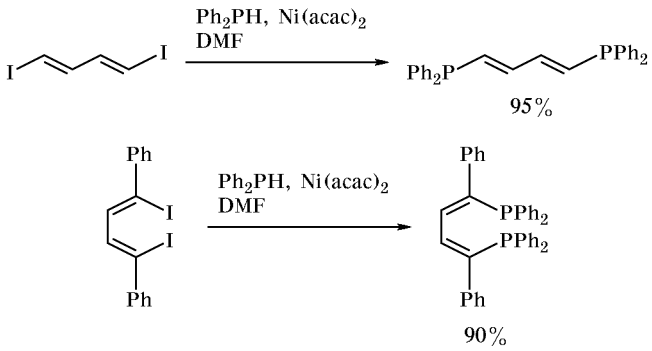
R = H, Br; R′ = H, Ph; Z = OR, NR_2, Me, Me_3Si.

Scheme 63.

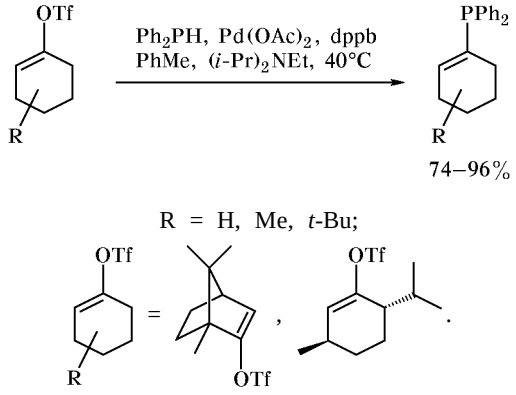


Likewise, two phosphino groups were introduced into positions *1* and *4* of butadienes [16] (Scheme 64).

Scheme 64.



Scheme 65.

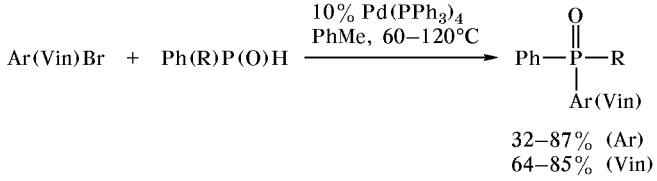


Vinyl trifluoromethanesulfonates derived from cyclic ketones react with diphenylphosphine in the presence of palladium complexes. The reaction occurs under mild conditions and is stereoselective [100] (Scheme 65). It should be noted that the above reactions are carried out with a large excess of phosphine which can also act as ligand. It seems surprising why excess phosphine does not hamper reactions involving formation of an unsaturated ML_2 intermediate.

2.3.4. Reactions with secondary phosphine oxides. Insofar as both initial and resulting phosphines readily undergo oxidation, cross-coupling reactions are often performed with phosphine oxides, and the product is reduced to tertiary phosphine with trichlorosilane. Many valuable ligands were obtained in such a way.

Cross-coupling of aryl and vinyl bromides with secondary phosphine oxides was reported for the first time by Xu *et al.* [101, 102] who performed stereospecific synthesis of unsymmetrical tertiary aryl- and alkenylphosphine oxides (Scheme 66).

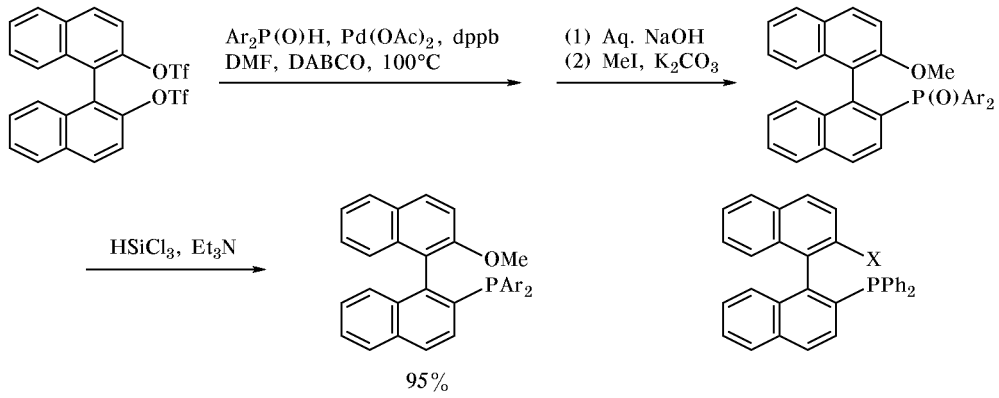
Scheme 66.



R = Bu, cyclohexyl, $PhCH_2$, Ph; Ar = Ph, 4-MeC_6H_4, 2-MeC_6H_4, 4-$MeCOC_6H_4$, 4-$MeCONHC_6H_4$, 4-$Me_2NC_6H_4$, 4-NCC_6H_4, 2-naphthyl, 4-biphenylyl; Vin = CH_2=CH, MeCH=CH, Me_2C=CH, (*Z*)- and (*E*)-PhCH=CH, MeOCOC(Me)=CH.

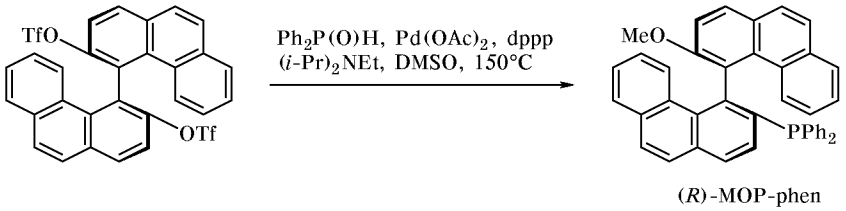
However, an attempt to obtain BINAP by the same reaction (starting from the corresponding bis-trifluoromethanesulfonate) was unsuccessful: only one CF_3SO_2O group was replaced [39]. The synthesis of a new class of optically active monophosphine ligands (MOPs), whose chirality originates from the presence of a binaphthalene skeleton, was reported in [27, 82, 103]. For this purpose, the procedure proposed in [39] was slightly modified (Scheme 67). Subsequent replacement of the trifluoromethylsulfonyl group in the phosphine oxide or final phosphine by other substituents gave a large series of monophosphine binaphthalene ligands with functional groups at C^2, which may be important for asymmetric induction in reactions catalyzed by transition metal complexes. This flexible synthetic procedure allows fine tuning of the phosphine ligands through variation of steric and electronic effects by introduction of various side chains into position *2′* and various substituents to the phosphorus atom [104].

Scheme 67.



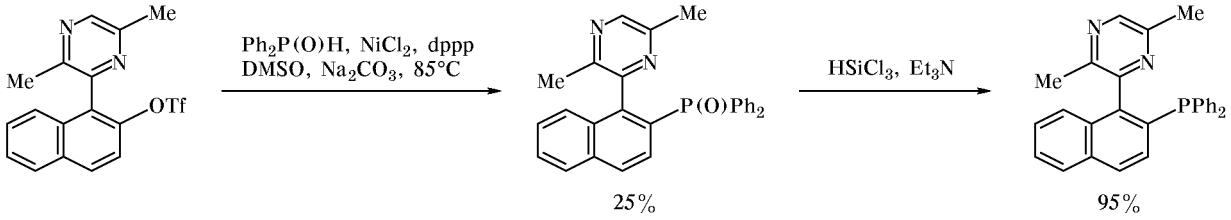
X = OH, OR, Et, $OSiMe_2Bu$-*t*, SEt, CN, CH_2NH_2, CH_2NMe_2, COOMe, COOH, CH_2OH, SH, H.

Scheme 68.

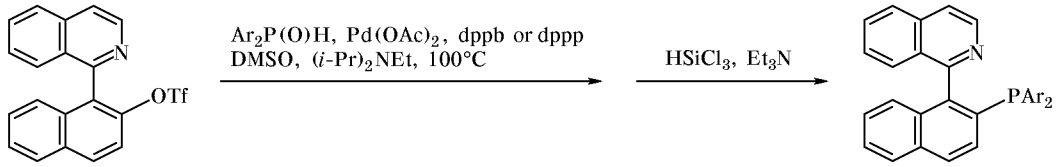


(*R*)-MOP-phen

Scheme 69.

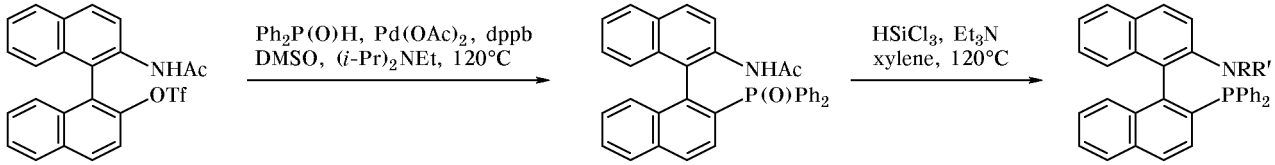


Scheme 70.



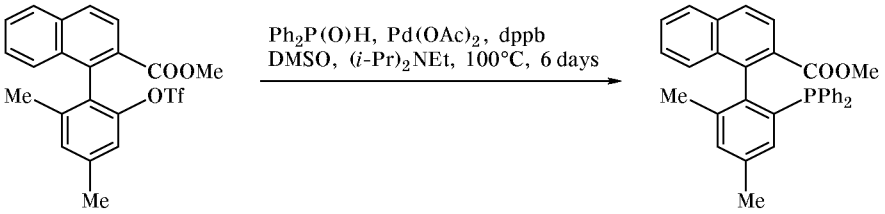
Ar = 3-MeC_6H_4, 3,5-$Me_2C_6H_3$, 2-furyl, 3-$CF_3C_6H_4$, 3,5-$(CF_3)_2C_6H_3$; Ar_2 = *o*,*o*′-biphenyldiyl.

Scheme 71.



R = Me, R′ = *i*-Pr, *cyclo*-C_6H_{11}; RR′ = $(CH_2)_5$.

Scheme 72.



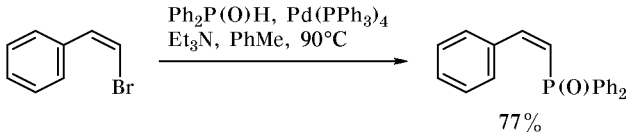
The same authors [105] developed a procedure for the synthesis of a phenanthrene analog of MOP, (*R*)-(+)-3-diphenylphosphino-3′-methoxy-4,4′-biphenanthrene (MOP-phen), by phosphination of the corresponding trifluoromethanesulfonate with diphenylphosphine oxide in the presence of the catalytic system $Pd(OAc)_2$/dppp/DMSO at 150°C (reaction time 10 h), subsequent replacement of the OTf group by OMe, and reduction with trichlorosilane in the presence of triethylamine (Scheme 68).

A series of aminophosphine ligands possessing axial and central chirality was synthesized from NOBIN and tartaric acid derivatives. The yield of Pd-catalyzed cross-coupling with $Ph_2P(O)H$ considerably increases when dppp is used as ligand instead of dppb [106, 107]. An axially chiral pyridazine-containing phosphine ligand was synthesized by Ni-catalyzed reaction of the corresponding trifluoromethanesulfonate with diphenylphosphine oxide in DMSO (Scheme 69). The optically pure ligand was obtained with the aid of *ortho*-palladated (*R*)-dimethyl[1-(1-naphthyl)ethyl]amine derivatives [108].

Brown and co-workers [109–111] prepared heterotropic P,N-ligands, 1-(2-diphenylphosphino-1-naphthyl)isoquinoline (QUINAP) and its analogs modified via variation of substituents on the phosphorus atoms, and also 6-(2-diphenylphosphino-1-naphthyl)phenanthridine (PHENAP) from the corresponding trifluoromethanesulfonates, diphenylphosphine oxide, and $Pd(OAc)_2$/dppp (or dppb) in DMSO (Scheme 70). A nitrogen analog of MOP [83], 2-dimethylamino-2′-diphenylphosphino-1,1′-binaphthalene (MAP), and a number of new N,N-disubstituted amino phosphines were obtained from trifluoromethylsulfonyloxy derivatives of NOBIN or its N-acyl analog via Pd-catalyzed reaction with diphenylphosphine oxide and subsequent reduction with trichlorosilane [112, 113] (Scheme 71). Sterically crowded *o*-methoxycarbonyl-*o′*-trifluoromethylsulfonyloxybiarene cannot be phosphorylated with diphenylphosphine oxide in the presence of palladium. However, the reaction was successful with its analog in which the methyl group is located *meta* (rather than *ortho*) relative to the trifluorosulfonyloxy group [114] (Scheme 72).

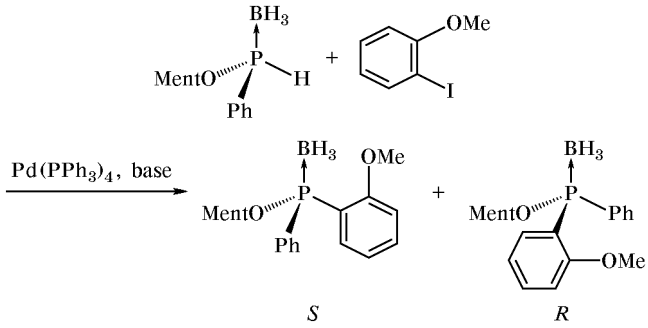
(*Z*)-ω-Bromostyrene stereoselectively reacts with diphenylphosphine oxide in the presence of palladium complex, yielding the corresponding (*Z*)-styryl(diphenyl)phosphine oxide [115] (Scheme 73). The product undergoes complete isomerization into the *E* isomer in the presence of a small amount of a base.

Scheme 73.



2.3.5. Reactions with phosphine–borane complexes. Phosphines form adducts with borane. The adducts are solid substances which are stable in air. The phosphorus atom in such a complex is protected from oxidation, but various transformations, including arylation or vinylation of secondary phosphines, are possible. The procedure is very convenient, though it requires additional efforts to obtain the initial complex and remove BH_3 from the resulting phosphine. Depending on the nature of the solvent and base, transformations of chiral phosphines can occur with conservation or inversion of configuration at the chiral phosphorus atom [116] (Scheme 74).

Scheme 74.

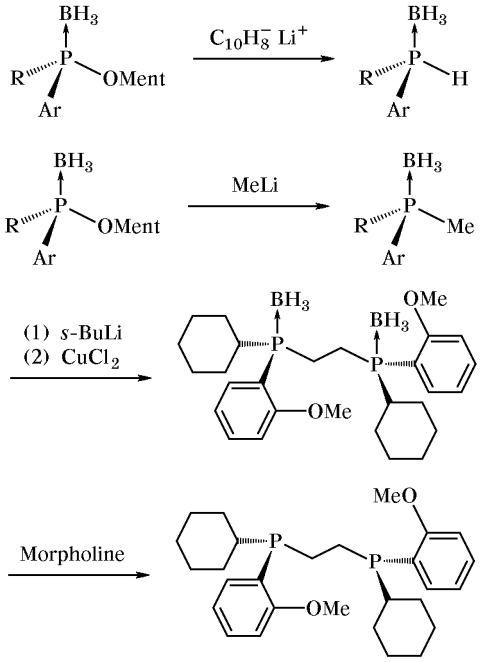


R:*S* = 100:0 (MeCN), 4:96 (THF).

Various optically pure phosphine–boranes were prepared following the above procedure [117, 118]

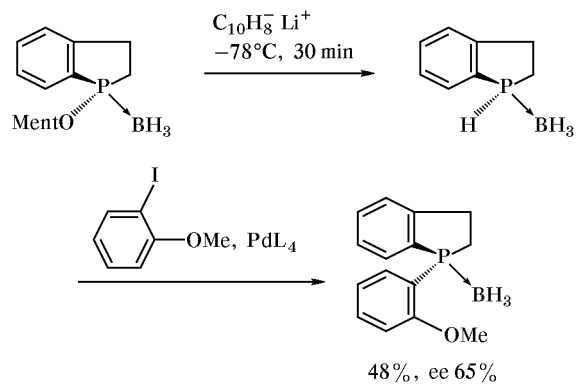
(Scheme 75). Among these, a chiral benzophosphole–borane complex shown in Scheme 76 [119].

Scheme 75.



R = cyclohexyl, *t*-Bu.

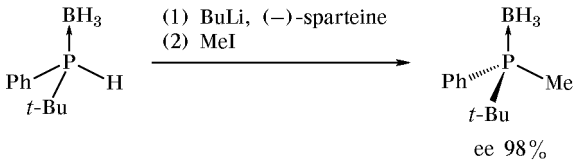
Scheme 76.



48%, ee 65%

Direct separation of P-chiral phosphine–boranes was effected through metalation in the presence of (–)-sparteine [120] (Scheme 77).

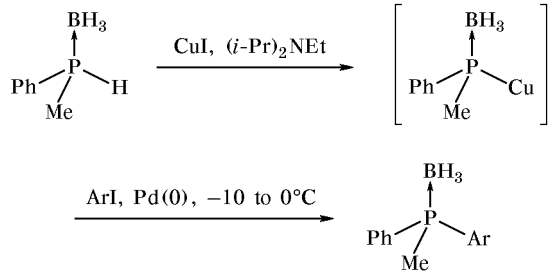
Scheme 77.



ee 98%

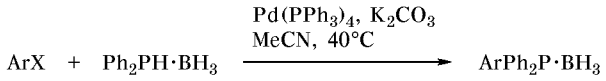
Apart from palladium catalyst, mild arylation of secondary phosphine–borane adducts is favored by addition of a catalytic amount of CuI. In this case, high yields are attained even at room temperature. It was presumed that the reaction involves intermediate formation of copper phosphide [121] (Scheme 78). Such mild conditions ensure arylation of a chiral phosphine with a high enantioselectivity (ee 94.5–99%) [122].

Scheme 78.



The arylation of Ph_2PH–BH_3 with aryl nonaflates and triflates was reported (Scheme 79).

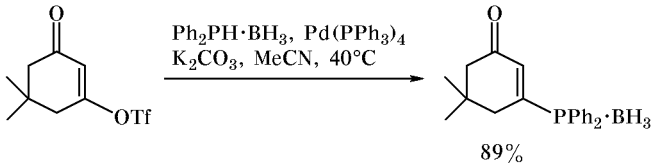
Scheme 79.



X = 2-$NfOC_{10}H_7$ (yield quantitative), 1-$NfOC_{10}H_7$ (87%); ArX = 2-MeO-7-$TfOC_{10}H_6$ (95%).

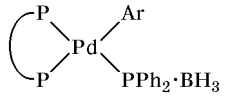
However, this procedure can be applied only to compounds having no nitrogen atoms: pyridyl nonaflate induces decomposition of the phosphine–borane complex. The reaction readily occurs with activated vinyl trifluoromethanesulfonates [123] (Scheme 80).

Scheme 80.



89%

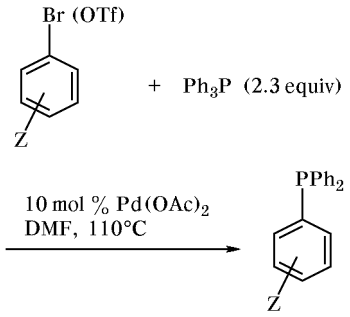
NMR study of the mechanism of arylation of Ph_2PH–BH_3 showed formation of the phosphide intermediate



If the reductive elimination is slow (Ar = C_6F_5), the corresponding intermediate can be isolated and characterized [124].

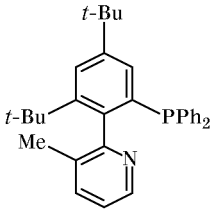
2.3.6. Reactions with triphenylphosphine. A simple and efficient procedure was recently proposed [125, 126] for preparation of tertiary arylphosphines having electron-donor and electron-acceptor substituents in the aromatic ring by Pd-catalyzed reaction of aryl halides or aryl trifluoromethanesulfonates with triphenylphosphine (Scheme 81).

Scheme 81.

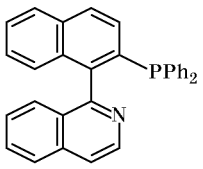


Z = 4-OCH, 4-Ac, 4-MeOCO, 4-NC, 4-MeO, 3-MeO, 4-Cl, 4-Me, 4-Bu-*t*, 3,5-Me_2.

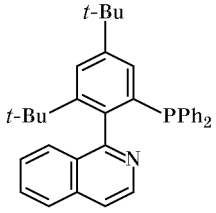
Other triarylphosphines Ar_3P can also be involved in this reaction to obtain $ArPAr_2$. Despite moderate yields of the resulting tertiary phosphines (27–58%), the procedure is very promising due to its simplicity and convenience. It was applied to preparation of biarene P,N-ligands, including QUINAP, from the corresponding trifluoromethanesulfonates [127]:



Pyphos, 68%



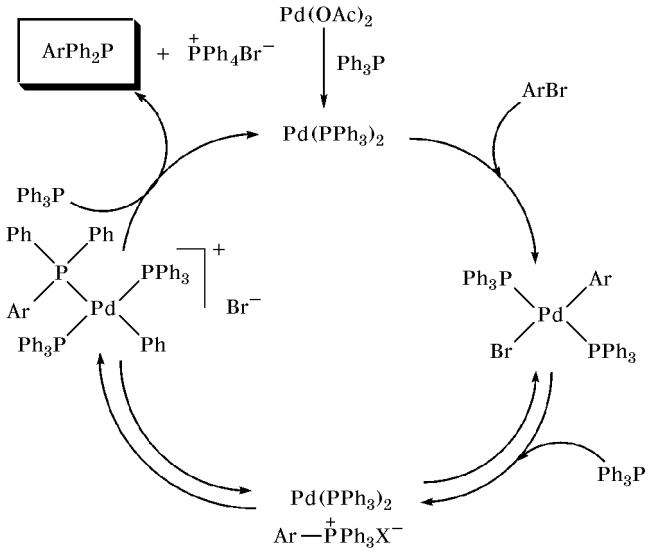
QUINAP, 53%



58%

According to the authors, the ArX-to-PPh_3 ratio is the most important factor. The reaction slows down or even terminates in the presence of excess phosphine (more than 2.5 equiv), as well as when its amount is insufficient. The proposed mechanism includes intermediate reversible formation of phosphonium salt and aryl group migration from palladium to phosphorus [127] (Scheme 82).

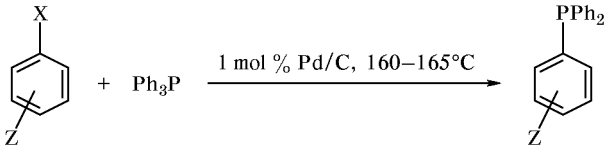
Scheme 82.



The known aryl–aryl interchange in the product of oxidative addition of aryl halide (or trifluoromethanesulfonate) [128] is readily explained by equilibrium formation of phosphonium salts and their subsequent addition to M(0) [129, 130]. The ability of phosphonium salts to form organopalladium derivatives like ArPdX is utilized in various reactions [131, 132].

Lai *et al.* [133] succeeded in effecting phosphination with Ph_3P as a source of the Ph_2P group. The reaction was carried out at 160–165°C in the presence of Pd/C as catalyst (Scheme 83).

Scheme 83.



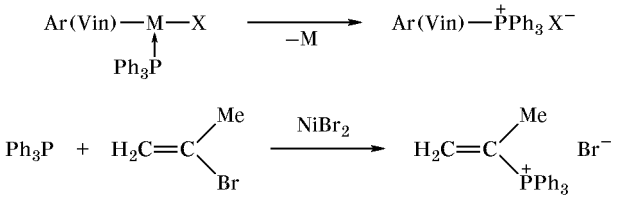
Z = 4-Ac, 4-MeOCO, 4-NC, 4-MeO, 4-OCH, 3-MeO; ArX = 8-X-quinoline; X = Br, TfO, NfO.

2.4. Synthesis of Phosphonium Salts

Reactions of aryl and vinyl halides with $(RO)_3P$ in the presence of transition metal complexes are known to involve intermediate formation of phosphonium

salts like $Ar(Vin)\overset{+}{P}(OR)_3\ X^-$. Likewise, reactions of ArX and VinX with tertiary phosphines give rise to phosphonium salts $Ar(Vin)\overset{+}{P}R_3\ X^-$. Unlike the former, quaternary salts derived from tertiary phosphines do not undergo further transformations [134–137] (Scheme 84).

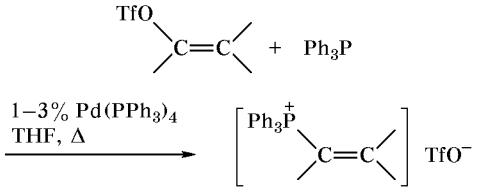
Scheme 84.



Such reactions have long been known, for phosphonium salts are useful synthetic products. However, Pd-catalyzed reactions have been reported much later than those catalyzed by Ni and Cu, and their extensive studies have started relatively recently.

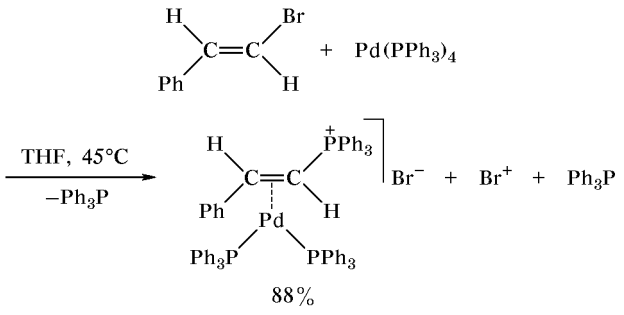
Various triarylphosphonium salts $Ar'Ar_3PX$ were obtained by reactions of Ar_3P with aryl iodides in benzene or toluene at 100–120°C (in a sealed ampule), using $Pd(PPh_3)_4$ or $Pd(OAc)_2$ as catalyst [138, 139]. An analogous reaction of Ph_3P with vinyl trifluoromethanesulfonates gives the corresponding vinylphosphonium salts in high yields (62–89%) and with high stereoselectivity [140–142] (Scheme 85).

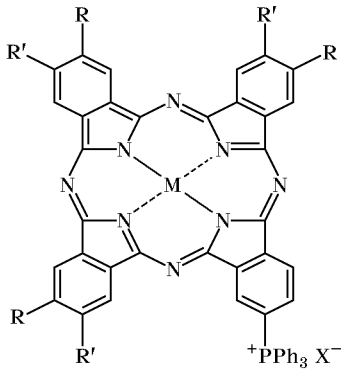
Scheme 85.



Phosphonium salt was formed in the reaction of $Pd(PPh_3)_4$ with an equimolar amount of *trans*-styryl bromide; its complex with zero-valent palladium was isolated [143] (Scheme 86). Phosphonium salts having a phthalocyanine fragment were synthesized by reaction of the corresponding bromides and iodides with triphenylphosphine using $PdCl_2(PPh_3)_2$ as catalytic precursor [144]. The products attract interest as hybrid materials possessing magnetic and nonlinear optical properties:

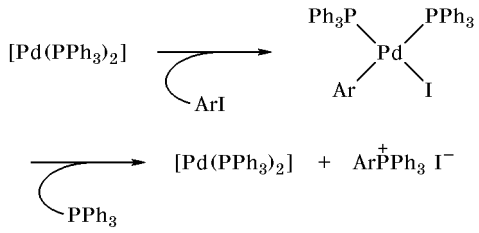
Scheme 86.





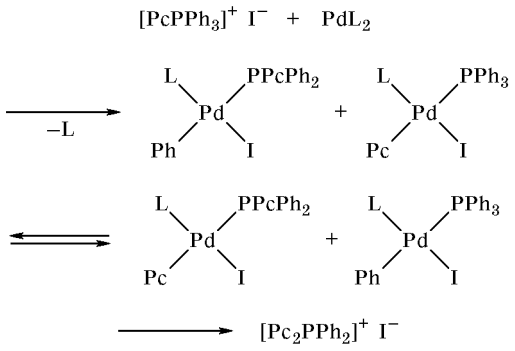
Insofar as the quatenization process is reversible, ligand scrambling at the palladium atom gives rise to formation of bis-phthalocyanine-substituted phosphonium salt $Pc_2\overset{+}{P}Ph_2\ I^-$ and even traces of the trisubstituted derivative. However, with a stoichiometric amount of the palladium complex, only monophthalocyanine phosphonium salt is formed [144]. The proposed mechanism includes oxidative addition of aryl halide to zero-valent palladium and subsequent reductive elimination of phosphonium salt (Scheme 87).

Scheme 87.



It is believed that ligand exchange at the phosphorus atom occurs within the palladium complex at the stage of oxidative addition of the initially formed phosphonium salt; both phosphorus–phthalocyanine and phosphorus–phenyl bonds are cleaved therein. The subsequent fast ligand exchange and reductive elimination give new phosphonium salt. The occurrence of ligand exchange at the phosphorus atom indicates that the oxidative addition of phosphonium salt to Pd(0) is reversible (Scheme 88).

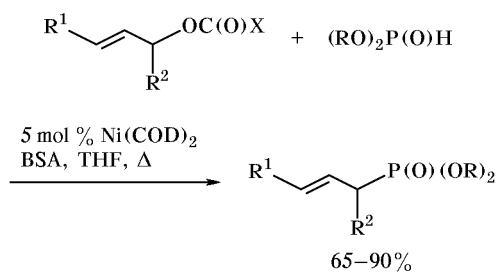
Scheme 88.



2.5. Synthesis of Allylphosphonates and Allylphosphine Sulfides

Reactions of allyl acetates and allyl carbonates with dialkyl hydrogen phosphites were effected under catalysis by nickel complexes in the presence of bis(trimethylsilyl)acetamide (BSA) as a base [145] (Scheme 89).

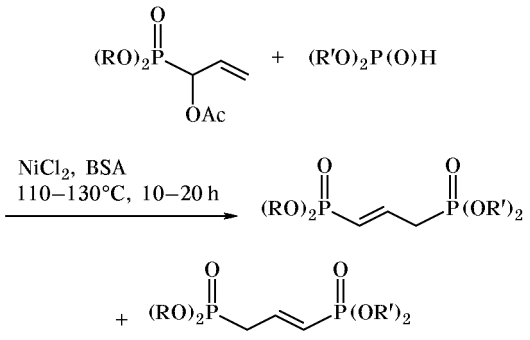
Scheme 89.



X = Me, OEt; R^1 or R^2 = H, Ph; R = Et, Bu.

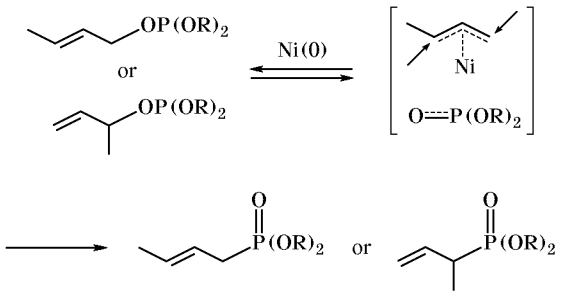
An analogous reaction between 1-acetoxyallylphosphonates [146] or -phosphinates with dialkyl hydrogen phosphites or phenylphosphonous esters in the presence of $NiCl_2$ gives a mixture of the corresponding allyl- and vinylphosphonates (Scheme 90).

Scheme 90.



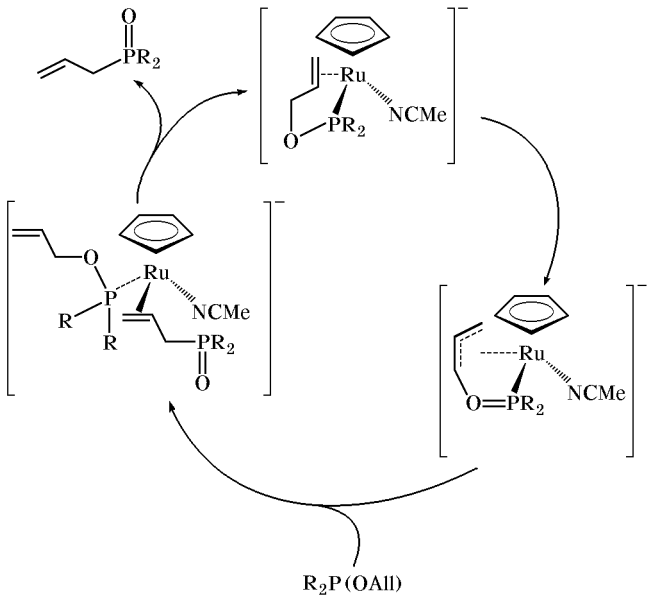
Nickel-catalyzed Arbuzov rearrangement of dialkyl allyl phosphites leads to allylphosphonates. Like those described above (phosphorylation and phosphination), the reaction involves formation of π-allyl nickel intermediate which undergoes attack by ambident phosphite ion on one of the π-allyl carbon atoms. The process can be accompanied by both allyl isomerization and change from the attack by oxygen to phosphorus [147] (Scheme 91).

Scheme 91.



The ruthenium complex $CpRu(MeCN)_3PF_6$ turned out to effectively catalyze allyl (Arbuzov) rearrangement [148]. Its possible mechanism is outlined in Scheme 92.

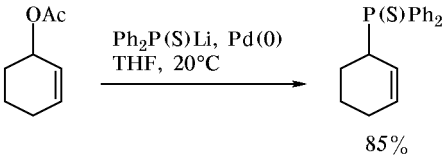
Scheme 92.



Lithium derivative of diphenylphosphine sulfide reacts with allyl carboxylates at room temperature to afford in high yield phosphine sulfides (Scheme 93) which can readily be reduced to the corresponding phosphines by a conventional procedure (with sodium

in toluene [149]). It should be noted that lithium phenylphosphide does not react with allyl acetate even on prolonged heating in boiling THF [150].

Scheme 93.



3. SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS BY ADDITION OF P–H AND P–E (E = S, Se) DERIVATIVES TO UNSATURATED COMPOUNDS

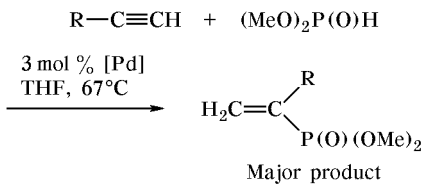
Addition of P–H-containing compounds, such as dialkyl phosphonates, diphenylphosphine oxide, diphenylphosphine sulfide, and diphenylphosphine, to unsaturated compounds (alkenes, alkynes, carbonyl compounds, and Schiff bases) is a well known method for preparation of various organophosphorus compounds (Pudovik reaction). These reactions usually follow either a radical mechanism or (with activated substrates in the presence of bases) a ionic mechanism analogous to Michael addition to activated alkenes. The reactivity of organophosphorus reagents changes in the series $Ph_2PH > Ph_2P(S)H > Ph_2P(O)H > (RO)_2P(O)H$. Naturally, each process has its own limitations concerning its regio- and stereoselectivity.

In the recent years, studies were reported in which the above reactions were catalyzed by metal complexes. Here, the following two points are important. First, reactions of P–H and P–E compounds with alkynes in the presence of transition metal complexes occur preferentially as *syn*-addition. Second, addition of P–H-containing compounds at a carbonyl or C=N bond, catalyzed by Lewis acids with chiral ligands, could yield chiral amino- or hydroxyalkylphosphorus derivatives, including amino- and hydroxyalkylphosphonic acids as phosphorus analogs of amino and hydroxy carboxylic acids.

3.1. Synthesis of Alkyl- and Alkenylphosphonates

3.1.1. Addition of dialkyl hydrogen phosphites to alkynes. The addition of P–H-containing compounds to alkynes in the presence of transition metal complexes was reported for the first time in [151]. The reactions were carried out under severe conditions, the product yields were moderate to low, and the selectivity was also low. Detailed studies on the catalytic hydrophosphorylation of multiple C–C bonds were performed by Tanaka and co-workers [152]. The authors showed that the reaction with alkynes, catalyzed by palladium complexes, occurs under fairly mild conditions and that the corresponding vinylphosphonates are formed in high yields and with high (or sometimes excellent) α-regioselectivity. An exception is trimethylsilylacetylene which gives rise to *trans*-β-trimethylsilylvinylphosphonate in a moderate yield for steric reasons. Using *cis*-$PdMe_2(PPh_2Me)_2$ as catalyst precursor, terminal alkynes were converted into various α-substituted vinylphosphonates in 80–95% yield and with 92–96% regioselectivity (Scheme 94).

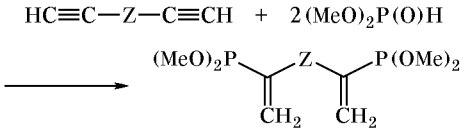
Scheme 94.



R = C_6H_{13}, Ph, 4-MeC_6H_4, $NC(CH_2)_3$, 1-cyclohexenyl.

If a substrate contains two triple bonds, the corresponding bis-phosphorylated product is obtained. When both double and triple bonds are present, only the latter is involved (Scheme 95).

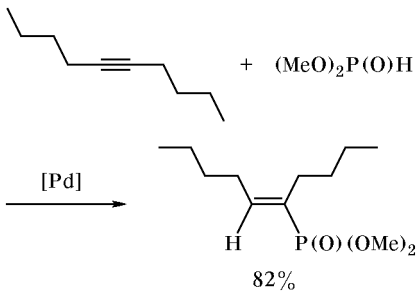
Scheme 95.



Z = $(CH_2)_5$, *m*-phenylene.

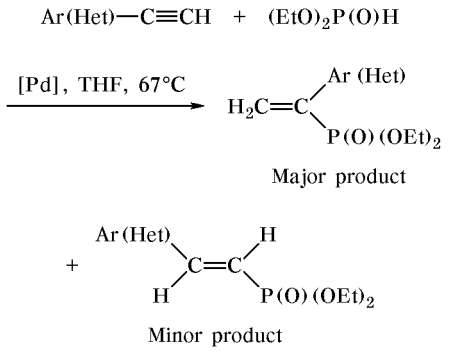
Analogous reactions with internal alkynes are very difficult to occur; they take more than 60 h against 15–20 h for terminal alkynes. However, the products are formed in high yield, and the process clearly follows the *syn*-addition pattern [152] (Scheme 96).

Scheme 96.



Numerous diethyl α-arylvinylphosphonates, including heterocyclic derivatives, were synthesized in the presence of a simple catalytic system, $Pd_2(dba)_3$–$CHCl_3$–$4Ph_3P$. In all cases, the yield of the α-isomer was greater than 90% [153, 154] (Scheme 97).

Scheme 97.

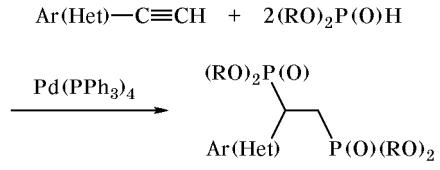


Ar = Ph, 4-$MeOC_6H_4$, 6-methoxy-2-naphthyl, pyridyl.

Vinylphosphonates were reduced with the system $HCOONH_4$–Pd/C to obtain α-arylethylphosphonates which can be regarded as phosphorus analogs of α-arylpropionic acids (including Naproxen and Ibuprofen). These compounds exhibit an interesting spectrum of biological activity [155]. Asymmetric hydrogenation of both vinylphosphonic acids and their esters was effected with molecular hydrogen in the presence of ruthenium complexes with chiral ligands [153, 155], as well as of chiral iridium complex [156].

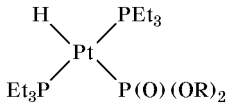
If the aryl (hetaryl) group is electron-acceptor, addition of the second phosphoryl fragment at the β-position is possible with the use of excess P–H reagent [157]. The reaction is likely to follow the catalytic Michael addition scheme (Scheme 98).

Scheme 98.



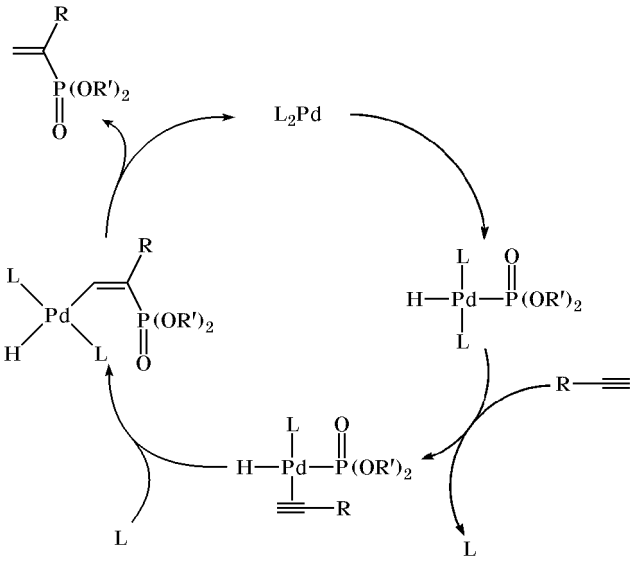
Ar = 4-$O_2NC_6H_4$, 4-NCC_6H_4; Het = 2-pyridyl, 4-pyridyl, 2-thiazolyl; R = Et, *i*-Pr.

Platinum complexes do not catalyze this reaction; however, *trans*-platinum complexes were obtained by reaction of $Pt(PEt_3)_3$ with dialkyl hydrogen phosphites. It was shown that such complexes (R = Et) are capable of reacting with phenylacetylene under fairly severe conditions (100°C) to give 63% of the corresponding α-isomeric product with more than 99% regioselectivity [152].



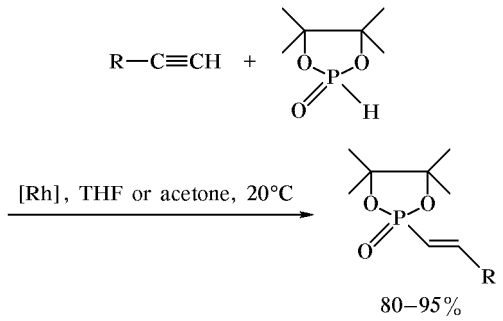
A mechanism was proposed, which includes oxidative addition of dialkyl hydrogen phosphite to zero-valence metal complex, coordination of acetylene, and its subsequent insertion into the palladium–phosphorus bond (Scheme 99).

Scheme 99.



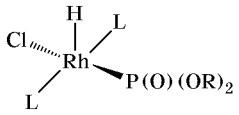
Tanaka *et al.* [158] studied reactions with alkynes of a five-membered cyclic phosphonate (4,4,5,5-tetramethyl-1,3,2λ^5-dioxaphospholane 2-oxide), which is the most reactive in the addition to multiple bonds. The reaction catalyzed by rhodium complexes was

Scheme 100.



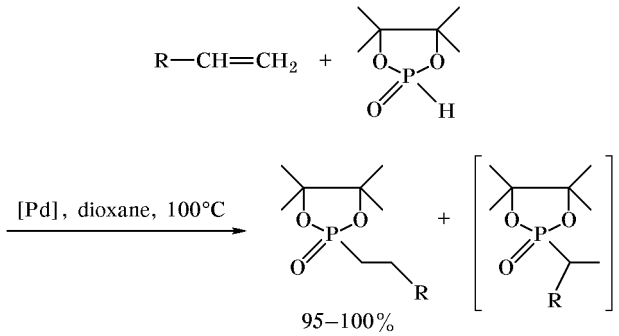
R = H, Ph, C_6H_{13}, *t*-Bu.

shown to be complementary to that catalyzed by palladium: as a result, the corresponding β-isomers with *E* configuration of the double bond were obtained at room temperature in high yields (Scheme 100). The cyclic phosphonate readily adds to Wilkinson's complex even at room temperature to give the following rhodium complex:



3.1.2. Addition of dialkyl hydrogen phosphites to alkenes. 4,4,5,5-Tetramethyl-1,3,2λ^5-dioxaphospholane 2-oxide was the only reagent which ensured successful hydrophosphorylation of nonactivated alkenes in the presence of *cis*-$Me_2Pd(PPh_2Me)_2$. Its six-membered analog, as well as linear dialkyl hydrogen phosphites, turned out to be inactive in the same process [159] (Scheme 101).

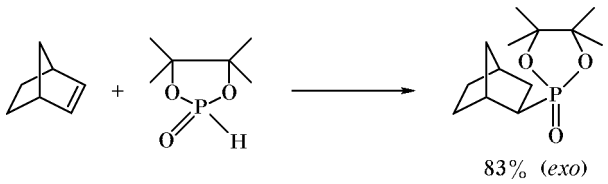
Scheme 101.



R = H, Me, Bu, C_6H_{13} (β-isomer); Ph (α : β = 1 : 1).

In contrast to alkynes, aliphatic alkenes give rise exclucively to β-phosphorylated products (except for styrene from which a 1 : 1 mixture of α- and β-isomers was obtained). With cyclohexyl(diphenyl)phosphine as ligand, the α-isomer was obtained as the major product in the reaction with styrene. No phosphorylation occurred with internal alkenes, except for cyclic strained alkenes, such as cyclopentene and norbornene (Scheme 102).

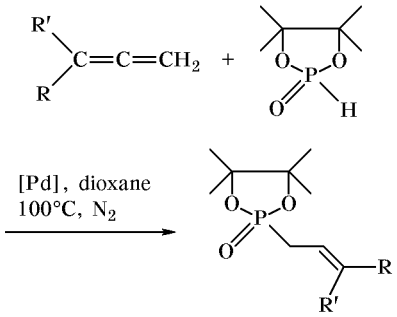
Scheme 102.



Nickel and rhodium complexes are considerably less effective than palladium complexes.

3.1.3. Addition of dialkyl hydrogen phosphites to 1,2- and 1,3-dienes. 4,4,5,5-Tetramethyl-1,3,2λ^5-dioxaphospholane 2-oxide was successfully applied to hydrophosphorylation of various allenes [160]. In the presence of $PdMe_2$(dppf) as catalyst, the corresponding *E* isomers were formed in high yield and with high regio- and stereoselectivity (Scheme 103).

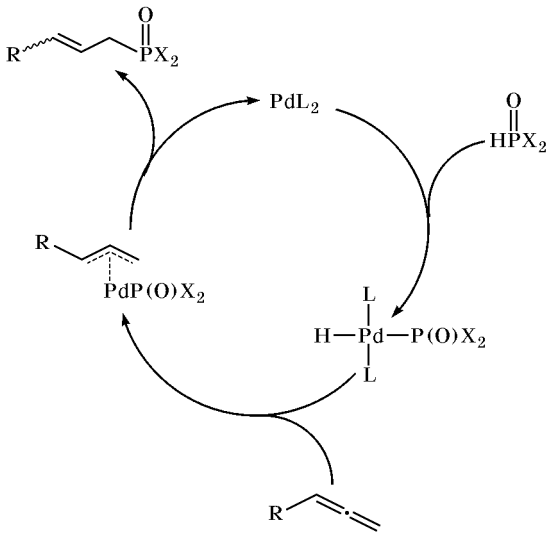
Scheme 103.



R = Bu, cyclohexyl, *t*-Bu, Ph; R′ = H; R = R′ = Me, Ph; RR′C = cyclohexylidene.

This reaction provides a convenient route to allylphosphonates. The formation of a π-allyl palladium complex is assumed, which is typical of the addition to allenes. The product structure is consistent with the hydropalladation mechanism shown in Scheme 104.

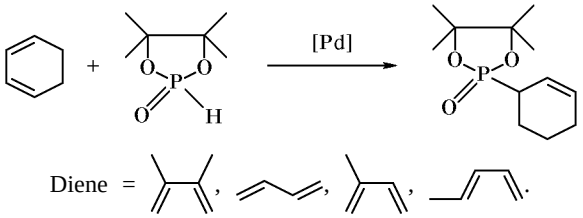
Scheme 104.



Tetrasubstituted allene, 2,4-dimethyl-2,3-pentadiene, is also capable of reacting with one phosphonate molecule. The reaction is accompanied by isomeriza-

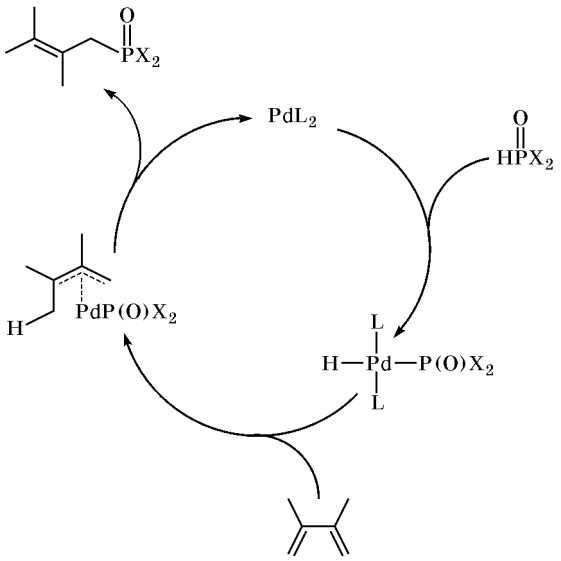
tion to give a mixture of allyl and vinylphosphonates. The reaction of the above five-membered phosphonate with conjugated dienes was accomplished in a similar way [161]. Dimethylpalladium with bidentate ligands, such as dppb, dppf, and BINAP, was used as catalytic precursor. Depending on the diene structure, the reaction temperature ranged from 60 to 100°C. The corresponding allylphosphonates were formed in high yields and with a good *E*-stereoselectivity (Scheme 105). The reaction was not stereoselective in the presence of palladium complexes with triphenylphosphine.

Scheme 105.



Here, like with allenes, double bond insertion at the Pd–H bond to form π-allyl palladium complex is presumed [161] (Scheme 106).

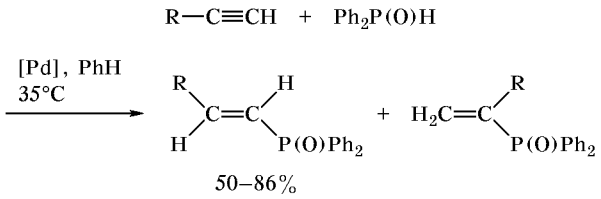
Scheme 106.



3.2. Synthesis of Alkenyldiphenylphosphine Oxides

Alkenyldiphenylphosphine oxides can be obtained by addition of diphenylphosphine oxide to alkynes. Triphenylphosphine palladium complex $Pd(PPh_3)_4$ is the best catalyst for the reaction of alkynes with diphenylphosphine oxide. It ensures fairly high yields and stereoselectivity (*syn*-addition), but, unlike the reaction with H-phosphonates, the corresponding β-phosphorylated products are mainly formed (>95%) [162] (Scheme 107).

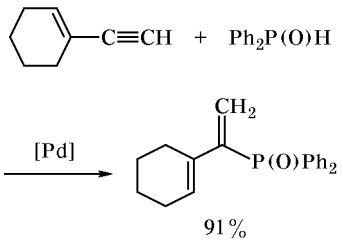
Scheme 107.



R = H, C_6H_{13}, Ph, 4-MeC_6H_4, $NC(CH_2)_3$, $HO(CH_2)_2$.

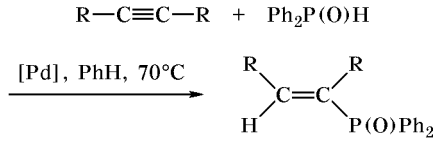
Hydrophosphorylation of diynes yields bis-β-phosphinoyl derivatives, and the reaction with 1-ethynylcyclohexene occurs exclusively at the triple bond (Scheme 108). However, only the α-isomer is formed (Markownikoff adduct). Presumably, the addition is directed by the double bond.

Scheme 108.



Internal alkynes also react with diphenylphosphine oxide, though at higher temperature. As a result, the *E*-adduct is formed exclusively, i.e., the reaction follows the usual *syn*-addition pattern (Scheme 109).

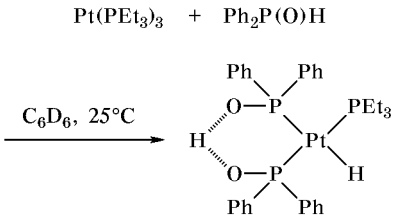
Scheme 109.



R = Pr (yield 61%), Ph (85%).

In the ^{31}P NMR spectra of the products obtained by oxidative addition of diphenylphosphine oxide to $M(PEt_3)_3$ complexes (M = Pt, Pd) three phosphorus signals were observed. According to the X-ray diffraction data, the isolated product contained two $Ph_2P(O)H$ molecules and the $P(O)Ph_2$ fragments were located *cis* [162] (Scheme 110).

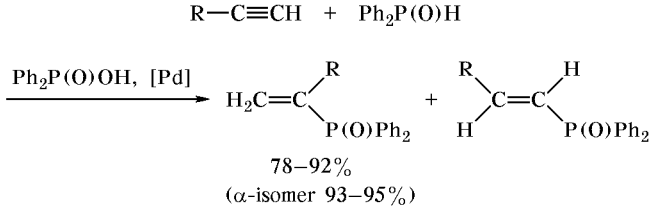
Scheme 110.



A mixture of α- and β-phosphorylated products in an overall yield of 65% was obtained in the reaction of 1-octyne with a stoichiometric amount of palladium complex which, according to the NMR data, had a similar structure. The isomer ratio differed from that found in the catalytic reaction; however, this may be due to change of the reaction conditions (temperature and the structure of palladium complex). It was presumed that the reaction occurs as alkyne insertion into the H–Pd bond, i.e., like hydropalladation [162].

Tanaka and co-workers [163] succeeded in altering the regioselectivity of the above reaction by performing it in the presence of a catalytic amount of diphenylphosphinic acid [$Ph_2P(O)OH$, 1 mol %]. The latter also enhances the activity of the catalyst. Even the $PdMe_2$(dmpe) complex, which is inactive in the absence of $Ph_2P(O)OH$, catalyzes the reaction at 100°C, and the product yield attains 93% (the ratio α:β is 92:8; Scheme 111). It should be noted that 1 mol % of $Ph_2P(O)OH$ against 5 mol % of the catalyst is sufficient to considerably change the regioselectivity. These data indicate that palladium complex formed with participation of diphenylphosphinic acid exhibits much higher catalytic activity than the complex formed by addition of $Ph_2P(O)H$ alone.

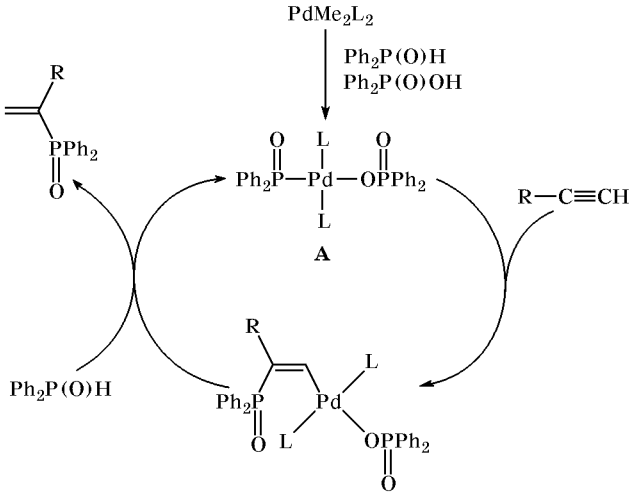
Scheme 111.



R = H (54%), C_6H_{13}, Ph, 4-$Me_2NC_6H_4$, $NC(CH_2)_3$, $HO(CH_2)_2$; [Pd] = *cis*-[$PdMe_2(PPhMe_2)_2$].

As in the addition of dialkyl hydrogen phosphites, trimethylsilylacetylene is an exception. The catalytic system $Ph_2P(O)H$–$Ph_2P(O)OH$ also accelerates addition to internal alkynes, though the reaction takes a longer time than with terminal alkynes [163]. The authors proposed a mechanism shown in Scheme 112,

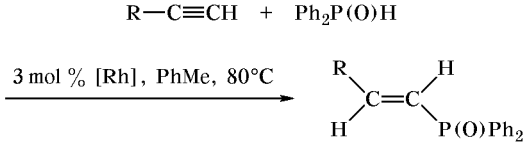
Scheme 112.



which involves alkyne insertion into the Pd–P bond of palladium complex. However, some questions arise. First, complex **A** could be formed only as a result of Me–Pd bond cleavage, i.e., other Pd(0) complexes should be inactive. Second, it is hardly probable that the C–Pd bond is protonated by phosphine oxide rather than by the acid, even if their different concentrations are taken into account. Nevertheless, the fact is that the regioselectivity changes almost completely on addition of $Ph_2P(O)OH$.

Rhodium complexes are also effective catalysts of the addition of diphenylphosphine oxide, but the reaction direction does not change [164] (Scheme 113).

Scheme 113.

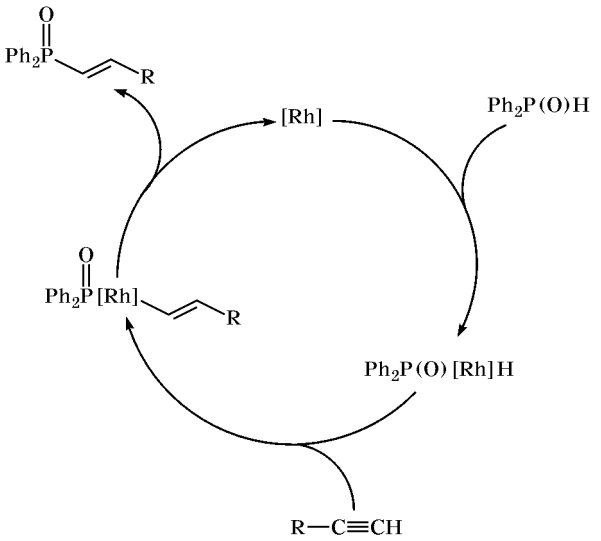


R = C_6H_{13}, *t*-Bu, Ph, $Cl(CH_2)_3$, $NC(CH_2)_3$, Bu_2NCH_2; [Rh] = $RhX(PPh_3)_3$: X = Cl, Br, I (Br and I are better).

High yields were obtained from various alkynes having both electron-donor and electron-acceptor substituents, aromatic, aliphatic, and heteroaromatic radicals, and conjugated bonds, regardless of the triple bond position (terminal or internal). Some acetylene derivatives react even at room temperature. The addition product is obtained in a high yield even under catalysis by Rh/C but at 110°C. The RhCl(cod) complex is also active, i.e., the presence of a phosphine ligand is not necessary. Scheme 114 illustrates the catalytic cycle for reactions catalyzed by palladium

and rhodium complexes. In the two cases, alkyne insertion into the metal–hydrogen bond occurs.

Scheme 114.



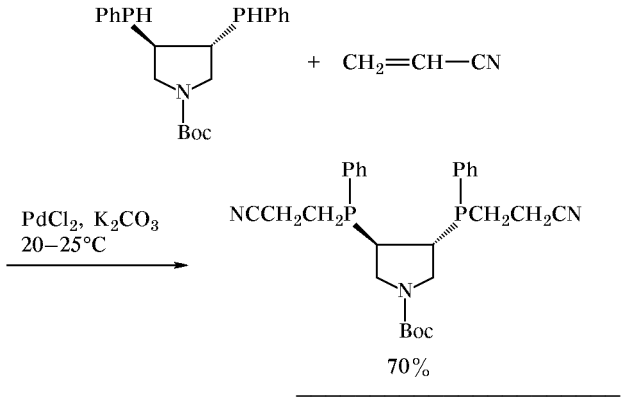
Thus the above reaction can be regarded as a method of synthesis of *E*-alkenylphosphine oxides.

Here, we should note the study performed by Tanaka and co-workers [165] on the addition of diphenylphosphinic acid to terminal alkynes, catalyzed by the ruthenium complex $Ru_3(CO)_{12}$. Formally, this reaction is irrelevant to the present review, for it gives no carbon–phosphorus bond (the products are alkenyl diphenylphosphinates).

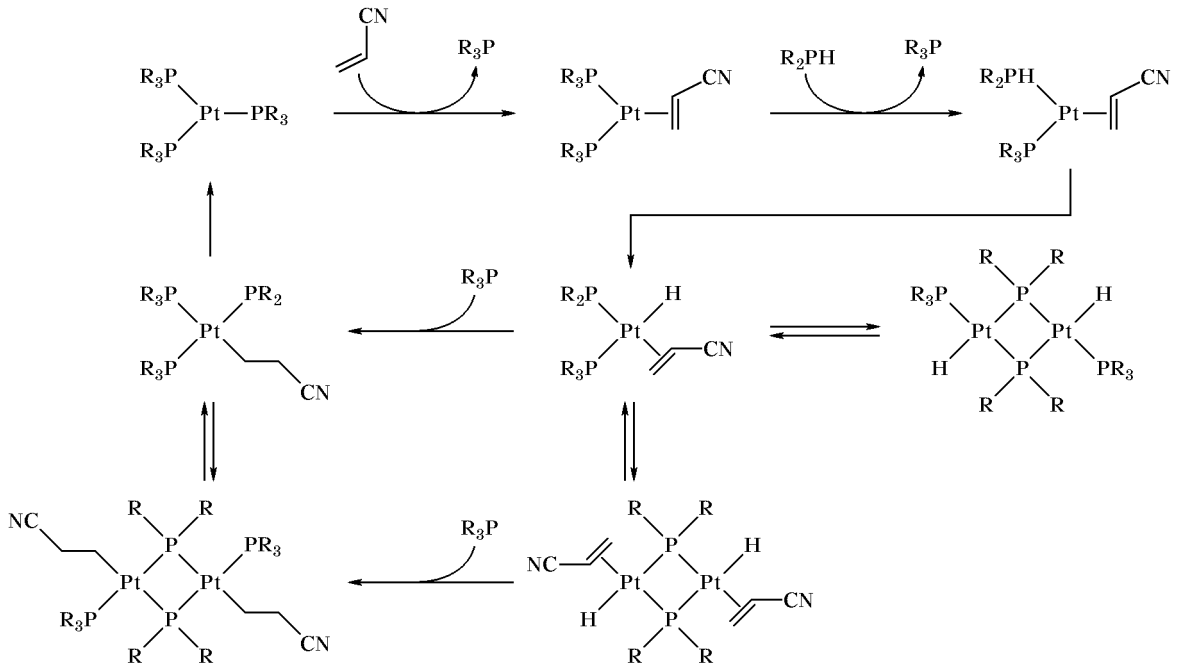
3.3. Synthesis of Alkyl- and Alkenylphosphines

3.3.1. Addition of primary and secondary phosphines to alkenes. Phosphines of the general formula $R_{3-n}PH_n$ (n = 1–3) usually add to activated olefins in the presence of acids or bases or radical initiators [166–168]. Nagel *et al.* [169] were the first to demonstrate the possibility for hydrophosphorylation of alkenes to be catalyzed by transition metal complexes: the authors effected addition of 3,4-bis(phenylphosphino)pyrrolidine to acrylonitrile and methyl acrylate in the presence of 2% $PdCl_2$ (Scheme 115).

Scheme 115.



Scheme 116.

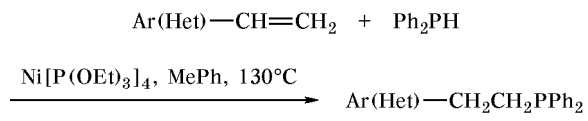


Pringle and co-workers [170] reported on the hydrophosphination of acrylonitrile, catalyzed by Pt(0) complexes, as the first example of hydrophosphination of alkenes in the presence of transition metal complexes. Tris(cyanoethyl)phosphine platinum complex catalyzes the addition of $PH(CH_2CH_2CN)_2$ to acrylonitrile, which is complete in 6 h at room temperature (in acetonitrile). On the basis of the results of kinetic and NMR studies, two concurrent mechanisms were proposed (Scheme 116). The formation of mono- and dinuclear intermediates is likely to explain a complex dependence of the reaction rate on the concentration of tris(cyanoethyl)phosphine [171, 172].

Metal complex-catalyzed hydrophosphination of activated alkenes was shown to be more advantageous than the addition promoted by radical initiators [173, 174]. Ethyl acrylate reacts with PH_3 in the presence of Pt(0) complexes to give the corresponding tris-adduct with a selectivity higher than 90%; in the AIBN-catalyzed reaction, an equimolar mixture of mono-, bis-, and tris-adducts was obtained [175]. Glueck *et al.* [176–178] showed that Pt-catalyzed hydrophosphination of acrylonitrile involves oxidative addition of phosphine to the metal, olefin insertion into the Pt–P bond, and reductive elimination.

The reactions studied by Pringle and Glueck were performed exclusively with activated alkenes (Michael acceptors). We were the first to effect hydrophosphination of weakly activated olefins and their heteroelement-containing analogs in the presence of phosphite Ni(0) complexes [179] (Scheme 117).

Scheme 117.

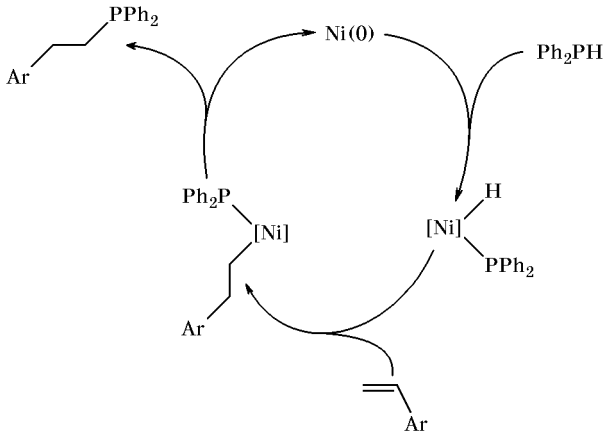


Ar = Ph, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 4-MeC_6H_4, 4-ClC_6H_4; Het = 4-pyridyl, 5-methyl-2-pyridyl, 2-pyridyl.

The reaction is regioselective: the corresponding β-phosphorylated adduct is the only product. The fact that no α-adduct is formed in the addition of Ph_2PH to styrenes and vinylpyridines allows us to rule out formation of π-allyl intermediates, which is typical of Pd-catalyzed hydroamination of styrene [180]. A probable catalytic cycle includes oxidative addition of phosphine to Ni(0) with formation of hydride phosphide complex, alkene insertion into the Ni–H bond, and subsequent reductive elimination (Scheme 118).

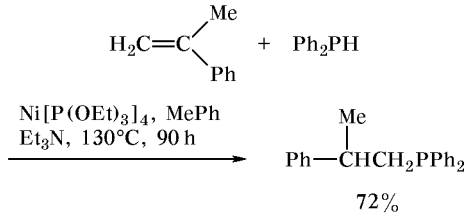
Hydrophosphination of α-methylstyrene attracts specific interest, for this reaction leads to appearance

Scheme 118.



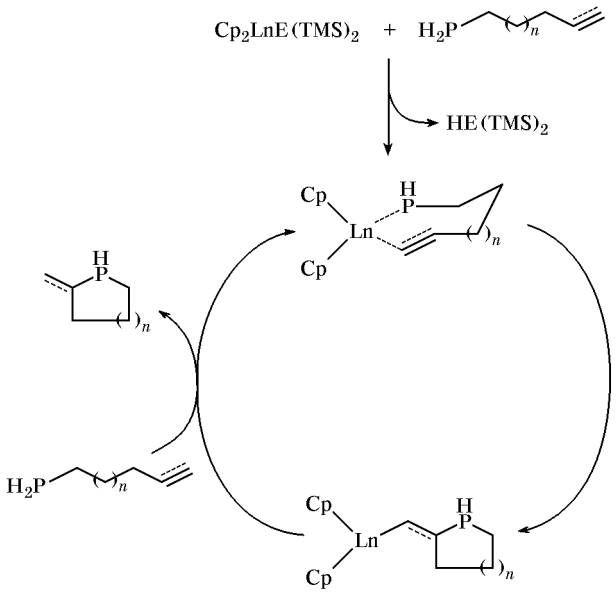
of an asymmetric center and hence makes it possible to perform an asymmetric synthesis (Scheme 119).

Scheme 119.



Cyclopentadienyl lanthanide complexes of the general formula $Cp_2LnE(TMS)_2$ (Ln = La, Sm, Y, Lu;

Scheme 120.

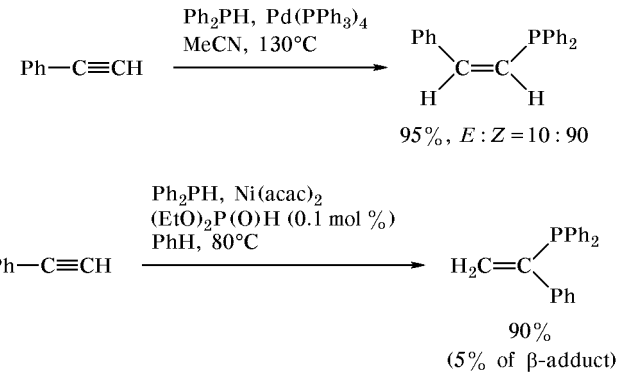


E = CH, N.

E = CH, N; TMS = $SiMe_3$) catalyze intramolecular hydrophosphination of alkenyl- and alkynylphosphines. The reaction is based on the ability of phosphine to split the Ln–Alk bond with formation of a phosphide complex, followed by insertion of the unsaturated fragment into the Ln–P bond. Subsequent cleavage of the C–Ln bond with phosphine results in formation of a phosphorus-containing heterocycle having two chiral centers and regeneration of the catalytic species [181–184] (Scheme 120). Insertion into the Ln–P bond is the rate-determining stage in this process [183].

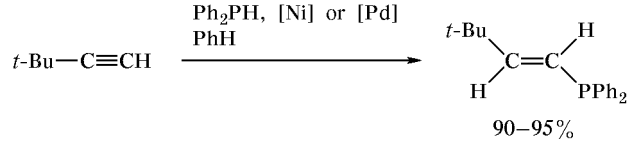
3.3.2. Addition of diphenylphosphine to alkynes. The first example of hydrophosphination of terminal and internal alkynes, catalyzed by palladium and nickel complexes, was reported in [185]. The reaction regioselectivity depends on the catalytic system and alkyne nature. Hydrophosphination of phenylacetylene in acetonitrile in the presence of Pd(0) complex leads exclusively to the β-adduct, while the reaction with $Ni(acac)_2$ in the presence of diethyl phosphonate gives almost pure α-adduct (α : β = 95 : 5) (Scheme 121).

Scheme 121.



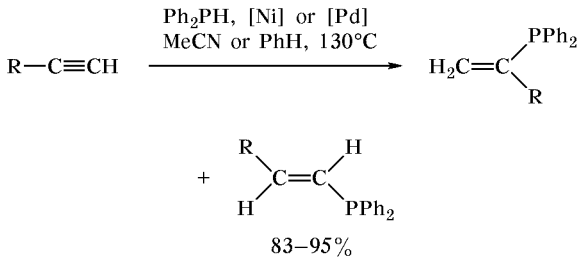
In the reaction of diphenylphosphine with *tert*-butylacetylene, the corresponding β-adduct is formed as the only product for steric reasons (Scheme 122).

Scheme 122.



The addition of diphenylphosphine to other alkylacetylenes is characterized by lower selectivity, and both regio- and stereoselectivity strongly depend on the reaction conditions (Scheme 123).

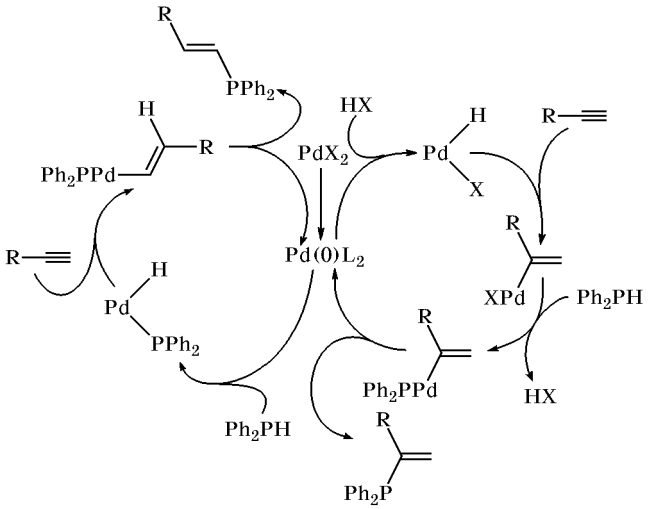
Scheme 123.



R = Pr, C_5H_{11}, $MeOCH_2$, Me_2NCH_2.

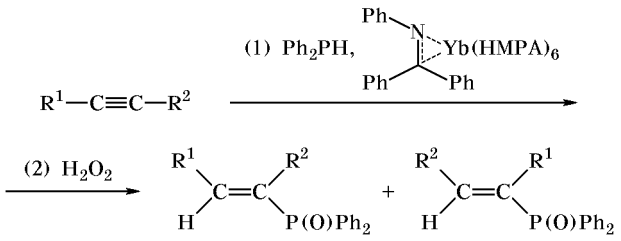
The different selectivities in the reactions catalyzed by Pd(0) and Ni(0) complexes or $Pd(Ni)X_2$ are explained by formation of catalytic amounts of HX (HOAc or HBr) *in situ*, which initiate the second catalytic cycle shown in Scheme 124.

Scheme 124.



Takaki *et al.* [186] recently showed that hydrophosphination of alkynes may be catalyzed by ytterbium complex with Schiff base, $[Yb(\eta^2\text{-}Ph_2CNPh)\cdot(HMPA)_6]$ (Scheme 125).

Scheme 125.



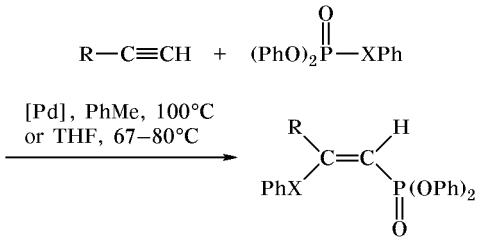
R^1 = Ph, Pr, C_5H_{11}, *t*-Bu, C_6H_{13}; R^2 = Ph, $SiMe_3$, H, Pr, Me.

The yields range from 52% to quantitative. The reaction with internal alkynes is regio- and stereoselective, while from terminal alkynes mixtures of the corresponding α- and β-adducts are formed, the latter prevailing.

3.4. Synthesis of Phenylthio- and Phenylselenoalkenylphosphonates

Addition to alkynes of compounds having heteroelement E–E′ bonds leads to alkenes possessing two carbon–heteroelement bonds (C–E and C–E′) which are characterized by different reactivities [187, 188]. Such reactions are known for phosphorus–selenium and phosphorus–sulfur compounds, which occur in the presence of *O*,*O*,*S*(*Se*)-triphenyl thio(seleno)phosphate [189, 190]. The corresponding products are formed in high yield and with high regioselectivity: the phenylthio or phenylseleno group in the product occupies the β-position. The reaction usually follows the *syn*-addition pattern, leading to (*Z*)-1-diphenoxyphosphinoyl-2-phenylthio(seleno)alkenes. A small amount of the *E* isomer was formed only from arylacetylenes at elevated temperature, and it disappeared when the temperature was reduced. Triphenylphosphine palladium complex, $Pd(PPh_3)_4$, was used as catalyst, though some other complexes were also active. On the other hand, many palladium complexes, as well as platinum compounds, exhibited no catalytic activity, although the possibility for oxidative addition leading to *trans*-PhSe(H)M$(PEt_3)_2 \cdot P(O)(OR)_2$ was demonstrated in [189] (Scheme 126; the corresponding palladium complex was characterized by the X-ray diffraction data).

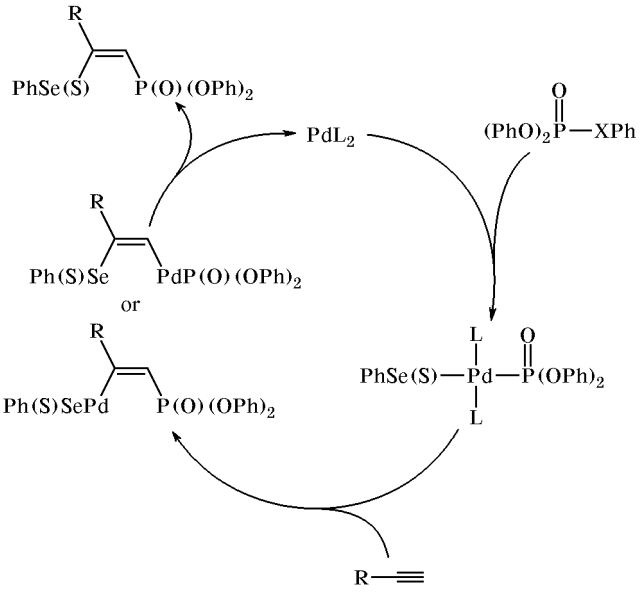
Scheme 126.



X = S, Se; R = C_6H_{13}, *t*-Bu, $NC(CH_2)_3$, $HO(CH_2)_2$, $Cl(CH_2)_3$, *t*-$BuOCO(CH_2)_2$, $MeOCH_2$, Bu_2NCH_2, 4-ZC_6H_4 (Z = H, Cl, F, Me), Me_3Si; R–C≡CH = CH≡C–$(CH_2)_5$–C≡CH, 1-cyclohexenylacetylene.

Neither alkenes nor internal alkynes can be involved in this reaction. No mechanism was proposed for alkyne insertion into the palladium complex Se(S)–Pd–P; i.e., it remains unclear whether palladophosphorylation or palladoselenation (thionation) occurs. We believe that the latter version is more probable, especially if the failure of reaction with internal alkynes is taken into account (Scheme 127).

Scheme 127.

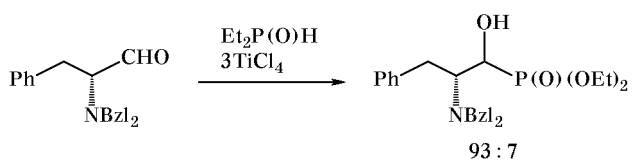


3.5. Synthesis of α-Hydroxy- and α-Aminoalkylphosphonates, -phosphinates, and -phosphine Oxides

3.5.1. Addition of dialkyl hydrogen phosphites to aldehydes. Thermal addition of dialkyl hydrogen phosphites to aldehydes and Schiff bases, catalyzed by metal complexes, underlies important methods for preparation of the corresponding α-hydroxy and α-amino phosphonates which are phosphorus analogs of α-hydroxy and α-amino carboxylic acids. The use of chiral catalysts allows synthesis of compounds enriched in a certain enantiomer. Such products exhibit a wide spectrum of biological activity [191–201], and study of the relations between their biological activity and absolute configuration is an important problem [202–215].

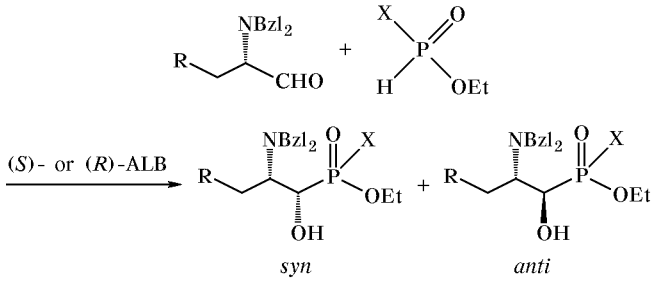
Yokomatsu *et al.* showed that the $TiCl_4$-catalyzed reaction of chiral 2-dibenzylamino-3-phenylpropionaldehyde with diethyl hydrogen phosphite is characterized by a high stereoselectivity [216] (Scheme 128).

Scheme 128.



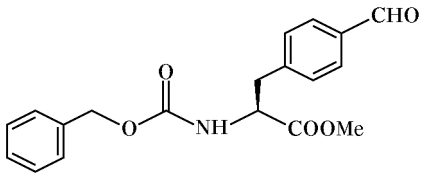
High diastereoselectivity was observed in the phosphination of optically active α-amino aldehyde in the presence of ALB as catalyst (20 mol %). In this case, the *syn*/*anti*-isomer ratio can be controlled by the chirality of ALB (chiral Al/Li/BINOL, Shibasaki's catalyst [217]; Scheme 129).

Scheme 129.



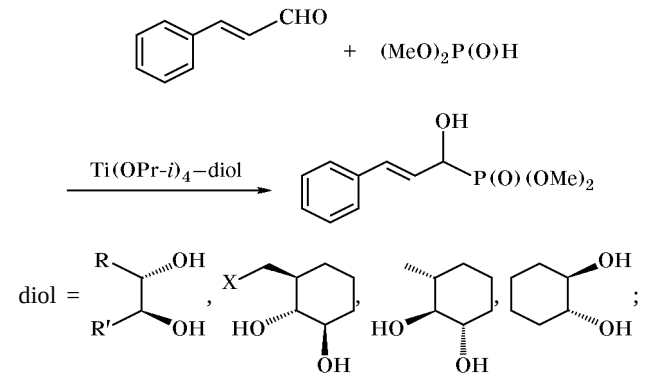
X = H, Et; R = Bzl, (*R*)-ALB, *syn*:*anti* = 87:13; R = Bzl, (*S*)-ALB, *syn*:*anti* = 6:94; R = *t*-Bu, (*R*)-ALB, *syn*:*anti* = 94:6; R = *t*-Bu, (*S*)-ALB, *syn*:*anti* = 2:98.

The chiral aldehyde



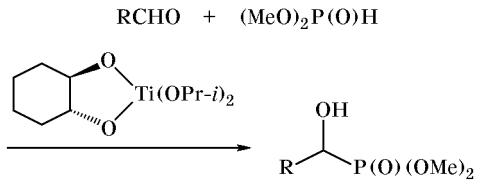
reacts with diethyl hydrogen phosphite in the presence of LLB (Ln/Li/BINOL) with a diastereoselectivity of 75:25; in the presence of ALB, the ratio of diastereoisomers is 80:20 [218]. The resulting β-amino-α-hydroxyphosphinic acids are key intermediates in the synthesis of potential inhibitors of human renin and HIV-protease. The effect of titanium complexes with various chiral diols was studied using the reaction of cinnamaldehyde with dimethyl hydrogen phosphite as an example [219] (Scheme 130). The best results (ee ~70%) were obtained with the 1,2-cyclohexanediol complex. Enantiomeric excess of about 50–65% was obtained with the same catalyst in the reactions with aromatic aldehydes (Scheme 131).

Scheme 130.



R = R′ = *i*-PrOCO; $PhCH_2OCO$; R = $PhCH_2OCO$, R′ = Ph; R = R′ = Ph; X = ArCOO (Ar = Ph, 4-$MeOC_6H_4$, 1-naphthyl, 2-naphthyl), X = *t*-$BuMe_2Si$, Ph_3CO.

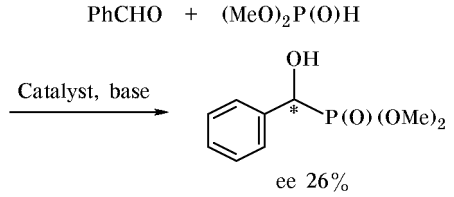
Scheme 131.



R = 4-XC_6H_4, (*E*)-PhCH=CH, 2-cyclohexenyl.

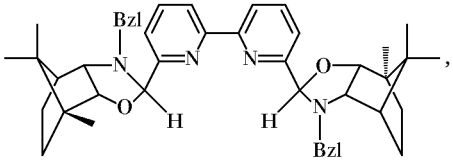
The addition of dimethyl hydrogen phosphite to benzaldehyde, catalyzed by zinc salts with N,O-chiral ligands or other chiral amino alcohols, is characterized by a poor enantioselectivity [220] (Scheme 132).

Scheme 132.

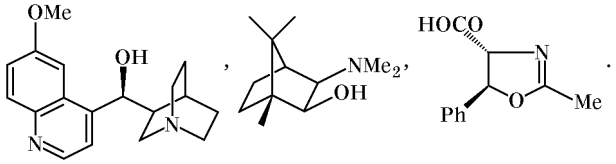


ee 26%

Catalyst = $Zn(OTf)_2$ +

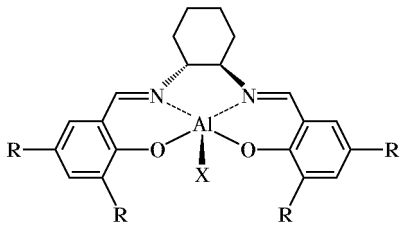


,



.

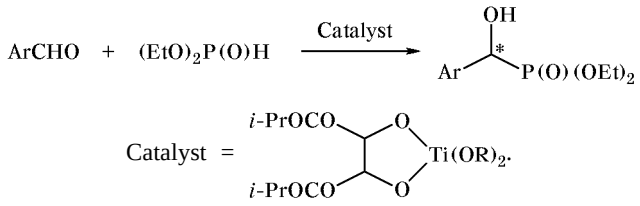
Chiral aluminum complexes with SALEN ligands (see structure below), depending on the X substituent in the ligand and that in the *para* position of benzaldehyde, ensure enantiomeric excess from 10 to 54% [221]. A moderate enantioselectivity (ee ~30%) was observed in the reaction of cinnamaldehyde with dimethyl hydrogen phosphite in the presence of La-binaphthol (La/Li/BINOL) [221].



R = H, *t*-Bu; X = Me, Cl, CF_3SO_2O.

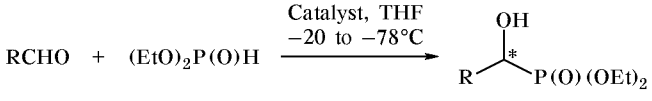
The maximal enantiomeric excess in the reaction with aromatic aldehydes (ee 53%) was attained with the use of Sharpless' catalyst (titanium tartrate) in ether (Scheme 133). The enantioselectivity strongly depended on the solvent [222].

Scheme 133.



With a catalytic system including La/Na/BINOL (LSB), it was shown that the aldehyde nature (aromatic or α,β-unsaturated), substituent in the benzene ring, solvent, temperature, and substituent in the binaphthol strongly affect the enantioselectivity. Introduction of phenyl groups into the 6,6′-positions increases ee, as compared to unsubstituted binaphthol, while it decreases when ethoxymethyl groups are present in positions *3,3′*. Scheme 134 shows the results obtained at –40°C in THF in the presence of 20 mol % of 6,6′-diphenyl-BINOL [223].

Scheme 134.



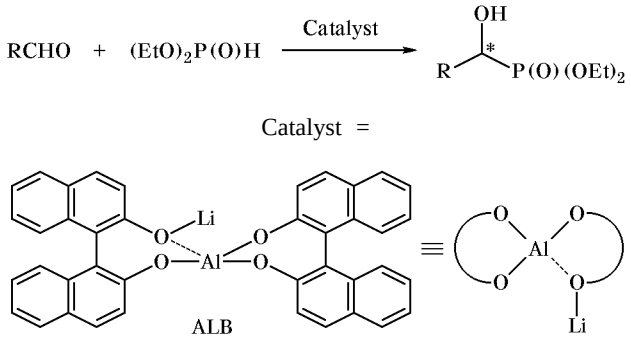
Catalyst = La/Na/6,6′-diphenyl-BINOL.

RCHO	ee, %	RCHO	ee, %
PhCHO	39	PhCH=CHCHO	4
4-MeC_6H_4CHO	69	1-$C_{10}H_7CHO$	35
4-$MeOC_6H_4CHO$	74	$PhCH_2CH_2CHO$	0
4-ClC_6H_4CHO	52		

It was very advantageous to use specially prepared heterobimetallic catalysts (Shibasaki) in which both metals are nontransition elements. It should be noted that the complex BINOL–lanthane is formed in the presence of lithium or sodium, but a required structure is likely to be obtained only under certain conditions.

Hydrophosphorylation of aldehydes catalyzed by LnL(S,P)B complexes (where Ln = La, Pr, Sm, Gd, Dy, Yb; L = Li, S = Na, P = K; B = BINOL) gave the corresponding α-hydroxy phosphonates with ee of 55 to 90% (Scheme 135).

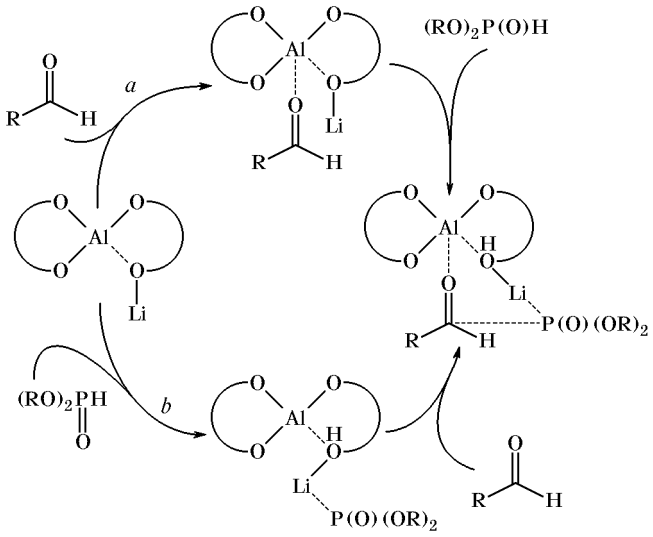
Scheme 135.



R = Me, 4-ZC_6H_4 (Z = H, Cl, Me, MeCOO, NO_2), (*E*)-PhCH=CH, Me_2C=CH, cyclopentenyl, cyclohexenyl, etc.

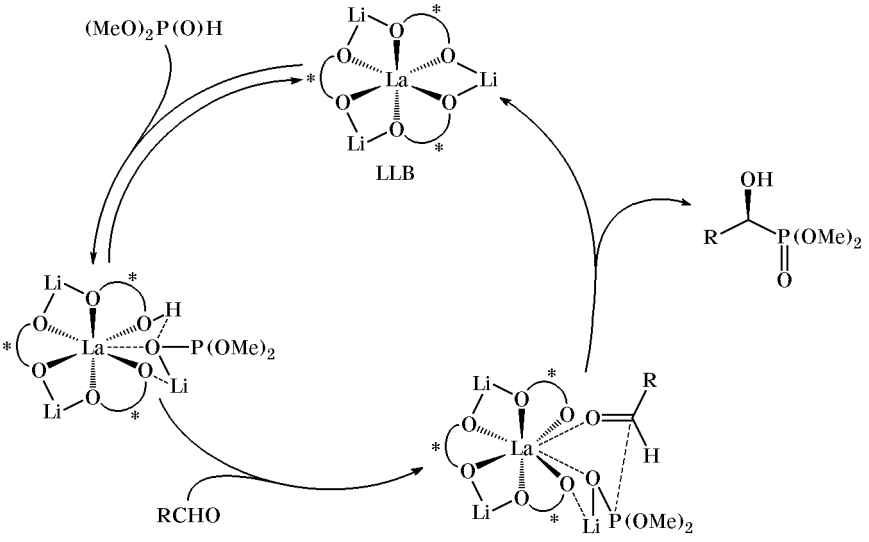
It was presumed that lithium alkoxide acts as Brønsted base, while aluminum alkoxide, as Lewis acid. The result is that both electrophile and nucleophile are activated in a single complex [224, 225] (Scheme 136).

Scheme 136.



Remarkable results were obtained by Shibasaki and co-workers [226] with the use of a lanthane complex, LLB = La/Li/BINOL, which was synthesized by

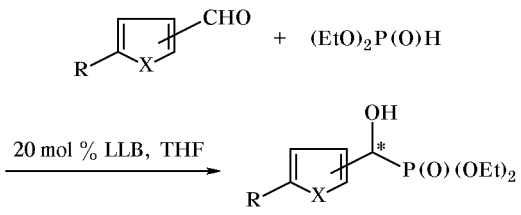
Scheme 137.



an improved procedure from $LaCl_3 \cdot 7H_2O$ and BINOL dilithium salt in the presence of *t*-BuONa in THF at 50°C. In the reaction of dimethyl hydrogen phosphite with aldehydes, enantiomeric excess of up to 95% was obtained (for *p*-dimethylaminobenzaldehyde). With aliphatic aldehydes, the results were also better than in the presence of ALB as catalyst. The proposed mechanism involves simultaneous activation of the aldehyde and phosphite with participation of lanthane and lithium (Scheme 137).

However, dramatic increase in enantiomeric excess in the presence of LLB instead of ALB was not observed for all aldehydes. With benzaldehyde and its *p*-nitro and *p*-chloro derivatives, the situation was the reverse. The values of ee obtained with the use of ALB were considerably greater than with LLB. For example, in the case of benzaldehyde ee was 90% in the presence of ALB against 79% with LLB [226, 224]. The strong effect of substituent in the aldehyde indicates that coordination of oxygen to metal is important. The nature of the metal (La, Eu, Sm) also affects ee [227]. Using LLB as catalyst, reactions of heteroaromatic aldehydes with diethyl hydrogen phosphite were accomplished [222] (Scheme 138). The maximal ee (73%) was obtained for 5-methyl-2-thiophenecarbaldehyde (cf. ee 41% for unsubstituted 2-thiophenecarbaldehyde).

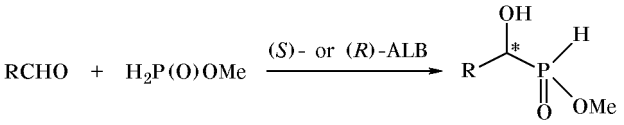
Scheme 138.



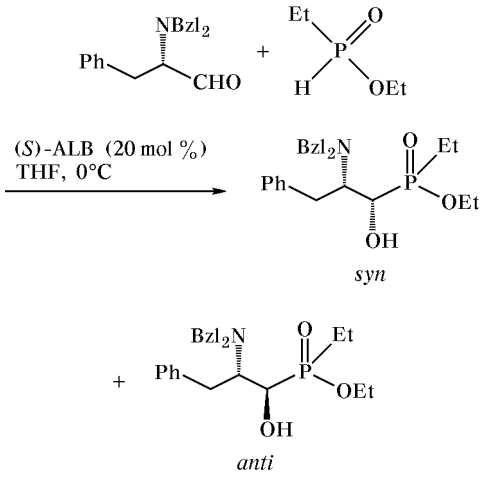
X = O, S; R = H, Me.

3.5.2. Addition of alkyl phosphinates to aldehydes. Shibuya and co-workesr [228] reported on the reaction of aldehydes with methyl phosphinate in the presence of ALB (Scheme 139).

Scheme 139.



Scheme 140.

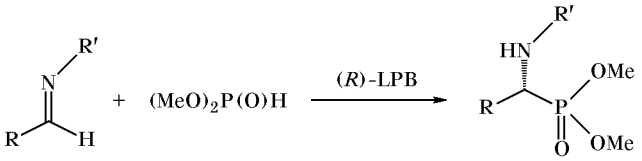


syn:*anti* = 11:89.

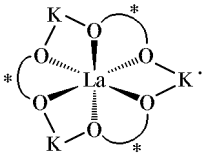
It should be noted that LLB failed to catalyze the reaction with benzaldehyde and that poor stereochemical results were obtained with LPB as catalyst. The reaction catalyzed by ALB gave 62% of the product with ee 85%. With excess aldehyde, double phosphorylation occurred. The arylated product was obtained with ee 61–82%. This reaction was used in diastereoselective synthesis of β-amino-α-hydroxyalkylphosphinates from *N*,*N*-dibenzyl-α-amino aldehydes and ethyl ethylphosphinate, catalyzed by (*S*)-ALB [229] (Scheme 140).

3.5.3. Addition of dialkyl hydrogen phosphites to Schiff bases. Asymmetric hydrophosphorylation of Schiff bases, performed by Shibasaki with the use of heterobimetallic catalysts, gave remarkable results [230]. Althouth the yield and enantiomeric excess depended on the nature of Schiff base and solvent, temperature, and catalyst, an ee value of 96% was attained. The most effective was catalyst containing potassium cations [230] (Scheme 141).

Scheme 141.



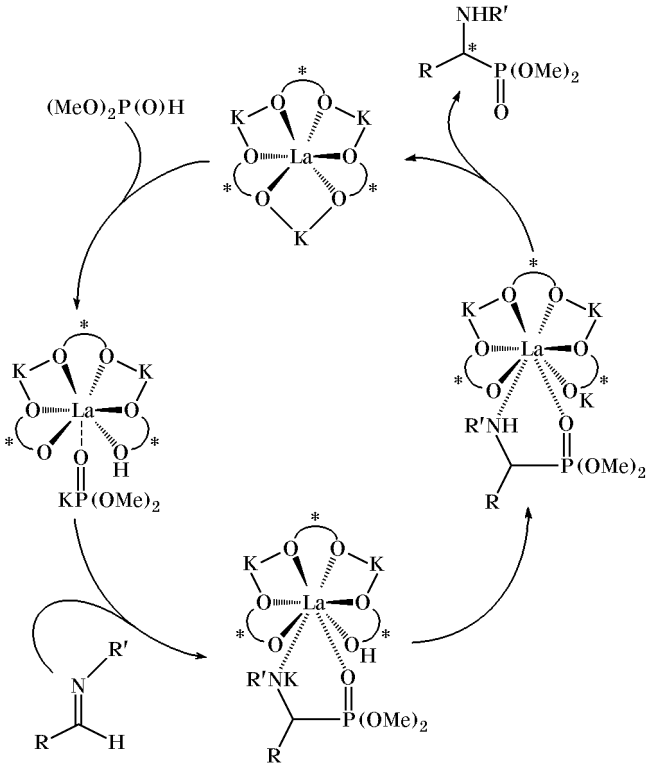
(*R*)-LPB =



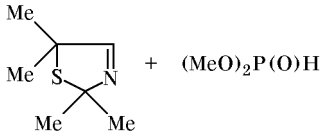
Schiff base	Yield, %	ee, %
R = *i*-Pr, R′ = $CH(C_6H_4OMe\text{-}4)_2$	70	96
R = Et, R′ = $PhCH_2$	80	91
R = C_5H_{11}, R′ = $PhCH_2$	87	85

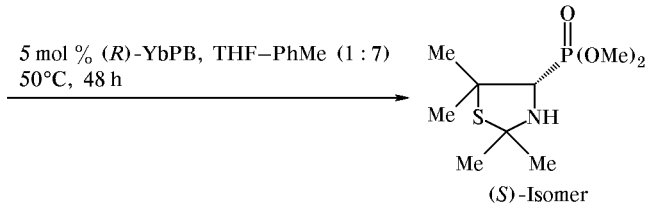
This procedure have found large-scale application in the synthesis of chiral α-amino phosphonic acids [231]. A probable mechanism shown in Scheme 142 includes deprotonation of dimethyl hydrogen phosphite, its coordination to the metal through the oxygen atom, and subsequent protonation which gives the final product and regenerates the catalyst [230]. Analogous reaction with participation of both titanium and lanthanide complexes was reported for cyclic Schiff bases (Scheme 143). Extensive studies of the reaction conditions showed that the optimal relation between the yield and the selectivity is as follows: yield 86%, ee 98%. This result was obtained with

Scheme 142.

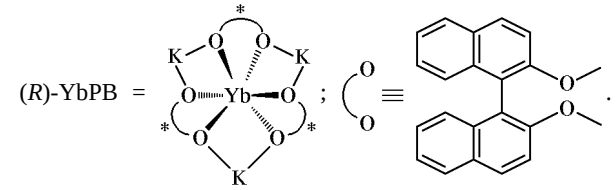


Scheme 143.





(*R*)-YbPB =

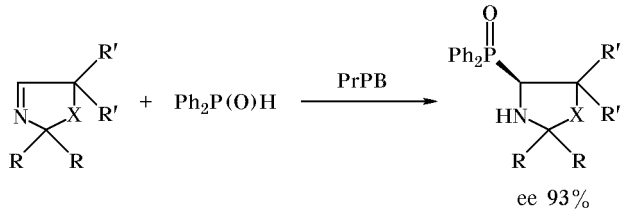


ytterbium complex (YbPB, 5 mol%) at 50°C in 48 h in a 1 : 7 tetrahydrofuran–toluene mixture [232].

3.5.4. Addition of phosphine oxides to Schiff bases. Diphenylphosphine oxide adds to cyclic Schiff bases in a similar way. The reaction was reported by Shibasaki and co-workers [233] to occur with high

yield (50–98%) and ee (75–93%), the best catalyst being praseodymium complex PrPB (Scheme 144).

Scheme 144.

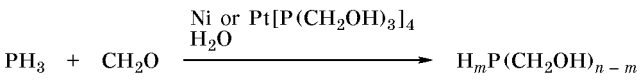


X = S, R = Me, R′ = H, Et, Me, R′R′ = $(CH_2)_5$; RR = $(CH_2)_5$, R′ = Me, Et; X = CH_2, R = Me, R′ = H.

3.6. Synthesis of α-Hydroxy- and α-Aminoalkylphosphines

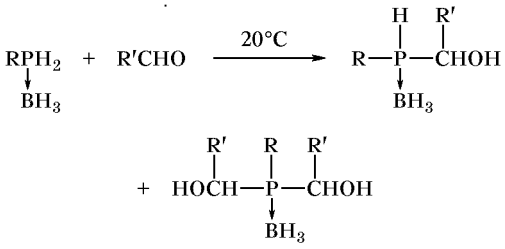
Transition metal complexes are capable of catalyzing addition of phosphine to aldehydes. For example, the reaction of phosphine with formaldehyde in the presence of Pt(II) complex gives water-soluble tris(hydroxymethyl)phosphine $P(CH_2OH)_3$. Appropriate Pt, Pd, and Ni complexes, $M[P(CH_2CH_2OH)_3]_4$, also catalyze analogous reactions in aqueous medium [234–236] (Scheme 145).

Scheme 145.

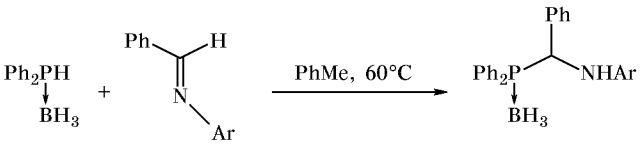


n = 1–3; *m* = 0, 1, 2.

Scheme 146.



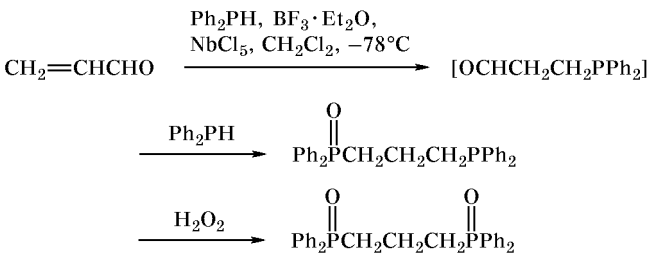
R = Ph, Me, R′ = Ph, Et.



Ar = Ph, $PhCH_2$, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$EtOCOC_6H_4$, 4-BuC_6H_4.

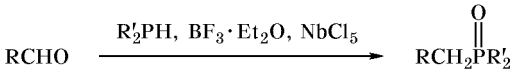
Phosphines are also capable of adding to aldehydes (and even to ketones) or Schiff bases in the absence of transition metal complexes provided that they are activated by complex formation with borane [237, 238] (Scheme 146). α,β-Unsaturated carbonyl compounds take up two Ph_2PH molecules in the presence of a stoichiometric amount of niobium(V) chloride $NbCl_5$–$BF_3 \cdot Et_2O$ [239] (Scheme 147). Depending on the enone, the yield of the product was 71–80%.

Scheme 147.



The addition of Ph_2PH to aldehydes can also be effected by a catalytic amount of $NbCl_5$; the reaction can be regarded as redox process [239] (Scheme 148).

Scheme 148.



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