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SYNTHESIS AND USES OF PHOSPHINES CONTAINING P-N BONDS

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INTRODUCTION

The study of ligands containing phosphorus atoms has been of great interest throughout inorganic and organic chemistry. These ligands have been studied for the last three decades and have been found to be of considerable interest due their wide range of applications in organometallic chemistry for the development of industrial processes involving a great number of catalytic reactions.

Among these compounds, tertiary mono and diphosphines,[1–4] the most widely studied, have been the bidentate phosphorus ligands such as $Ph_2PCH_2CH_2PPh_2$ [bis(diphenylphosphino)ethane (dppe)], $Ph_2PCH_2PPh_2$ [bis(diphenylphosphino)methane (dppm)] and their tetramethyl analogues $Me_2PCH_2CH_2PMe_2$ [bis(dimethylphosphino)ethane (dmpe)], $Me_2PCH_2PMe_2$ [bis(dimethylphosphino)methane (dmpm)], that were found to act as chelating or bridging ligands (Figure 1)[5–11] Further investigations revealed that some compounds analogous to dppm and dmpm could also behave as monodentate ligands, binding to the metal through one phosphorus atom and leaving the other one pendant or uncoordinated.[12–15]

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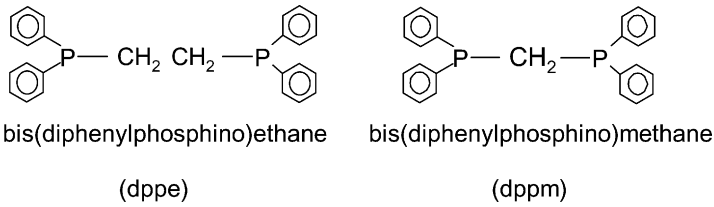


Figure 1. Tertiary diphosphines.

Ligands with longer alkyl chains in between the two phosphorus atoms have also been investigated. A few examples are $Ph_2PCH_2CH_2CH_2PPh_2$ [bis(diphenylphosphino)propane (dppp)],[16–18] $Ph_2PCH_2CH_2CH_2CH_2PPh_2$ [bis(diphenylphosphino)butane (dppb)][19–21] and $^tBu_2P(CH_2)_{5\text{-}8}P^tBu_2$. They act as bidentate ligands which, in some cases, can coordinate to mutually *trans* positions in square planar complexes (Figure 2).[22–23]

The alkyl chain backbone of these ligands has also been substituted by aromatic spacer groups between the two donor atoms, giving compounds such as $Ph_2PC_6H_4PPh_2$ [1,4-phenylenebis(diphenylphosphine)][24–26] and $Me_2PC_6H_4PMe_2$ [1,4-phenylenebis(dimethylphosphine)][27] among others (Figure 3).

Compared with the vast body of data accumulated on ligands where the phosphorus atom is linked by a carbon atom or chain, considerably less has appeared for those ligands where the backbone of the molecule comprises a heteroatom or group such as ligands containing P-N bonds. This is, perhaps, because it has been assumed that this bond will be very labile, although the phosphite ligands that contain a P-O bond have been extensively studied.[28] Surprisingly little advantage had been taken of the ease of preparation of the P-N bond containing compounds. Mono- and biphosphine ligands containing P-N bonds are becoming more important and are being studied, as their P-C analogues, for their potential properties in catalytic reactions as transition metal complexes.[29–35] For example, Rh and Pt complexes of aminophosphines have proved to be

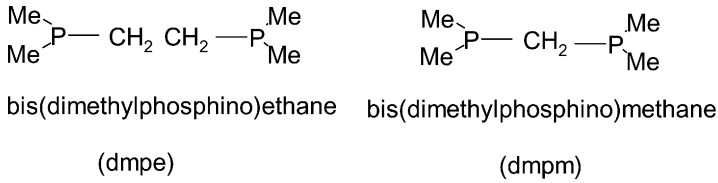
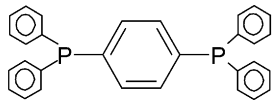
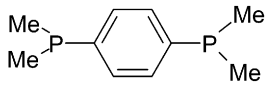


Figure 2. Tertiary diphosphines containing chains of-$(CH_2)_n$-(n > 2).



[1,4-phenylenebis(diphenylphosphine)]



[1,4-phenylenebis(dimethylphosphine)]

Figure 3. Tertiary diphosphines with aromatic spacer group between the two P atoms.

efficient catalysts for asymmetric hydrogenation and hydroformylation reactions.[36]

MONOAMINOPHOSPHINES: LIGANDS CONTAINING ONE P-N BOND, R_2N-Px

Studies of monophosphines containing one P-N bond started in the late 1960s with emphasis on the kinetic and NMR properties that these ligands exhibit.

In 1968, Imberly and Friebolin studied the kinetic properties of a large number of aminophosphines by NMR and it was shown that at room temperature the nitrogen-inversion was fast but the phosphorus-inversion was slow. At higher temperatures (+80°C) they found that, in aminophosphines of the type $(Me)_2N$-P(Ph)C1, there was a fast chlorine exchange so an inversion of configuration at the phosphorus took place. At low temperatures (−80°C) a dependence of the barrier of rotation upon the size of the substituents was observed and the rotation around the P-N bond was slow. Presumably the pπ-dπ bonding was in part responsible for the high barrier to rotation found when comparing ligands derived from hydrazine with the analogous derivatives of ethane[37] The same year Schmidpeter and Brecht investigated the ^{31}P-NMR properties of all members of the series $L_nPh_{3-n}PY$ and n-Bu_3PY (L = Me_2N, MeO; n = 0, 1, 2, 3; Y = O, S, Se) by converting them to the methylchalcogeno-phosphonium ions $[L_nPh_{3-n}PYMe]^+$ and $[n\text{-}Bu_3PYMe]^+$, respectively, and found both positive and negative ^{31}P chemical shift values. The shifts depend on Y and *n*, increasing approximately linearly with *n* and being the most negative for Y = O. It was suggested that Y on methylation decreases and L increases the shielding of P by altering their (p→d)π electron contributions. ^{1}H-NMR and IR techniques were also used to complete the study.[38] Continuing with the NMR studies, Yoder and co-workers investigated the ^{13}C-^{1}H coupling constants (Hz) as a probe of the nature of the bonding in group V amines (e.g Me_2PNMe_2 and

$P[NMe_2]_3$ and to elucidate the effect of various substituents on some group IV and V amines (e.g Ph_2PNMe_2 and Cl_2PNMe_2).[39] They concluded that the magnitude of methyl ^{13}C-H coupling constants in compounds of the type X-CH_3 depends on the effective electronegativity of X in a way that the greater the effective electronegativity of X, the greater the coupling constant. Two factors determine the effective electronegativity of nitrogen in amines of the type M-NMe_2; firstly it depends on the σ-electronegativity of M; and secondly it is subject to the extent of π interaction between N and M (the greater the extent of π interaction the greater the effective electronegativity of N). The effective electronegativity of nitrogen in group V amines suggests the π-acceptor order $P > N \geq As > Sb$. Although all electronegativity scales agree that nitrogen is considerably more electronegative than phosphorus, $P > N$ demonstrates a considerable π interaction between N and P. The authors also concluded that a small effect was produced by the substitution of a dimethylamino group for a methyl group due to the π-electron release to the central atom. A decade later, Buchanan and Preusser.[40] synthesized a series of related 4-alkyl- and 4-aryl-substituted-1-dimethylphosphonopiperazine derivatives, which are interesting compounds as potential insecticides, and recorded their ^{13}C and ^{15}N spectra, providing in this way a useful tool for future comparison with related molecules. They noticed that the carbon (C-2) shifts (C-C-N-P) are insensitive to remote substitution and that the magnitudes of $^2J(PNC)$ and $^3J(PNCC)$ were very similar, meaning a large degree of nitrogen lone-pair delocalization into the N-P bond. During the same period of time, Krannich and co-workers[41] investigated the multinuclear NMR spectral data for an homologous series of tertiary phosphines, $R_{3-n}P(NMe_2)_n$, aminophosphonium ions, $[R_3PNR'R'']^+$, and phosphonium ions, $[R_{4-n}PMe_n]^+$, where R = Me, Et, n-Pr and Ph, R′ and/or R″ = H, Me and n = 0 and 1. The authors found that the ^{31}P chemical shift increases ($\Delta\delta_p$ is positive) when quaternization by alkylation or when chloramination occurs. Other parameters appeared to be affected as well; the ^{13}C chemical shift decreases ($\Delta\delta_p$ is negative) for all carbons as well as does $^2J(PC)$, whilst $^1J(PC)$, $^3J(PC)$, $^3J(PNCH)$ and $^2J(PCH)$ all increase. When the Me_2N group was substituted for an alkyl on aryl group, the ^{31}P chemical shift and the magnitude of $^1J(PC)$ increased.

In 1970, A. H. Cowley and co-workers[42] used NMR techniques to investigate the stereochemistry of trivalent nitrogen attached to phosphorus; in particular, the study was centered in the identification of the

rate-determining stereochemical processes, assessment of the conformational preferences at low temperature (40 to -150°), and evaluation of the various factors that could affect the magnitudes of the rotational or inversional barriers. Due to the presence of a lone pair of electrons on both phosphorus and nitrogen atoms, the potential stereochemical processes include rotation around the phosphorus-nitrogen bond and pyramidal inversions at both nitrogen and phosphorus. Which process is the rate determining step in isomerization reactions is not obvious because barriers to nitrogen inversion can vary over a wide range and can be raised by the presence of a heteroatom that binds directly with the nitrogen or could be reduced when there is the possibility of a $p\pi$-$d\pi$ interaction. They concluded that the P-N bond torsion was the rate-controlling feature for acyclic, symmetrically substituted and other aminophosphines. Consistently, they could not find a nitrogen inversional barrier in 2,2-dimethyl-1-diphenylphosphinoaziridine down to -150°. The authors also attempted to assess the influence of steric effects, lone pair-lone pair repulsions and $p\pi$-$d\pi$ bonding in maintaining the preferred geometry determined by the torsion barriers. It was found that, even at -80°, the symmetrical aminophosphines (R_2NPX_2) were undergoing rapid P-N bond rotation and that the R groups became inequivalent below -120°, so they concluded that the *gauche*-type conformation is adopted at low temperatures.

Mathis and Lafaille[43] investigated the chemistry of some aminophosphines where the phosphorus was trivalent, using infrared spectroscopy, and they observed that the stretching frequency ν_{PN} varies considerably ($790–1010\,cm^{-1}$) and seems to manifest a relation with the possibility of conjugative resonance of the nitrogen lone pair with the vacant "d" orbitals of the phosphorus atoms. If the nitrogen atom is part of an unsaturated ring, low frequencies appeared and this effect was noticed to be more important than the possible substituents on the phosphorus atom. The effect of the substituents on the phosphorus depends on 1) the inductive effect so that electronegative substituents lower the energy of the phosphorus "d" orbital and help the π-bonding with the nitrogen, and on 2) the possibility of the conjugation of the substituents with the phosphorus atoms as well, which can make difficult the return of the nitrogen lone pair. They also correlated the IR results with the rotation barrier of the nitrogen-phosphorus bond determined using NMR studies. They explained the results by nitrogen-phosphorus orbital overlapping discussions. Eight years later, Mathis, Zenati, Ayed and Sanchez[44] used

IR spectroscopy to estimate the lone pair basicity of a nitrogen atom on aminophosphanes (> P-N-) and iminophosphanes ($P^{(v)} = N$-R). They deduced that the bascity of nitrogen in iminophosphanes was more important than in aminophosphanes when identical substituents were placed on the phosphorus atom. This study was carried out by measuring the decrease of $\Delta\nu_{X\text{-}H}$ between the $\nu_{X\text{-}H}$ (X = O or N) when the X-H was hydrogen bonded (P = N...H-X; P-N...H-X) and the free absorption $\nu_{X\text{-}H}$ of the same compound.

In 1974, Osokin, Safin and Nuretdinov[45] studied the electronic effects in amides of trivalent phosphorus acids such as $ClP[NMe_2]_2$, $PhOP[NMe_2]_3$, $PhP[NMe_2]_2$, $PhP[NMe_2]_2$, $MeP[NMe_2]_2$, Cl_2PNMe_2, $(MeO)_2PNMe_2$ and $(C_2H_5)_2PNMe_2$, by ^{14}N and ^{35}Cl NQR spectroscopy. They had previously concluded that electron donating substituents on a phosphorus atom, such as dialkylamino groups, decreased the ^{35}Cl NQR frequency in these types of compounds. They studied the changes in the electron density at the nitrogen atom by the local electrical field gradient at the ^{14}N nuclei, which depends on the contribution of the unshared pair of electrons of the nitrogen atom (polarity of the P-N bond).[45] They extended these studies to amides of P(III) acids. Because of the small change shown in the asymmetry parameter they concluded that the polarity of the P-N bond in this series depended little on the inductive effect of the substituents. Changing from tetrahedral to trigonal conformation should induce an increase in the p character of the N lone pair orbital and this should increase the QCC (quadrupole coupling constant) in amides compared to amines. Because the QCC results for amides did not show a considerable change with respect to the amine series, they concluded that the lone pair of the nitrogen in amides was taking part in the formation of a multiple bond with the phosphorus atom instead. ^{14}N NQR results suggested that the lone pair on N is not involved in any donor-acceptor interaction. The EN (electronegativity) studies demonstrated the polarity, so the population of the orbitals of C-N bond in the amides of P(III) acids are similar to those of the orbital of the N-H bond in aliphatic amines. The chlorine as a substituent on the phosphorus atom has a great influence on the population of the orbital of the N lone pair, manifesting an inductive effect because of the decrease in the population of the orbitals of the N-P σ bond.

Ishmaeva and co-workers[46] used dipole moments (DM) to study the polarity of the P-N bond in unsymmetrical phosphorus amides and observed that the polarity of the P-N bond depends on the valence state

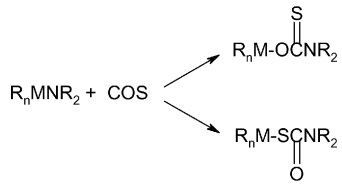


Figure 4. Direction of COS insertion in some organometallic amines.

of the phosphorus atoms and the nature of the substituents attached to both atoms (i.e. insertion of Cl increased the DM).

The insertion of different sulfur molecules such as SO_2[47] and CX_2[48,49] (X = O, S) into the P-N bond of a wide range of monoaminophosphines was studied by several researchers. Moore and Yoder[50] also investigated the insertion of carbon oxysulfide (COS) into some amides (R_nMNR_2, R = Me, Ph) of germanium, phosphorus and arsenic and determined the free energies of activation for rotation about the carbonyl-nitrogen bond (Figure 4). This study was of particular interest since the reaction of unsymmetrical molecules with these amides could yield possible structural isomerism. COS is an attractive molecule for these studies due to the presence of both hard and soft atoms of the same periodic group, which could insert with either oxygen or sulfur attached to the metalloid depending on the hard and soft characteristics of M. The authors attempted the insertion reaction with some monoaminophosphines $R_2PN(CH_3)$ (R = CH_3 (I), Cl (II), C_6H_5 (III)) among other amides. The insertion proceeded exothermically with I and did not occur with II, apparently because an increase in the hardness of the organometalloid group makes the production of the M-S isomer less favorable yet does not sufficiently enhance the production of M-O isomer to allow its isolation. They used IR technique to determine the direction of insertion and since the insertion products showed absorption in the carbonyl region, they concluded that the insertion gave M-S isomers. Using NMR techniques they demonstrated the apparent hindered rotation about the carbonyl-nitrogen bond, which produced magnetically non-equivalent N-alkyl groups.

The monoaminophosphines have also been used to perform different reactions with the aim of obtaining functionalized derivatives that might exhibit a wide range of properties and applications. Scherer and Schieder[51] carried out the oxidation of aminophosphines (as $[Me_3C]_2$P-NH-Me) by trimethylsilyl azide (Me_3SiN_3) and obtained

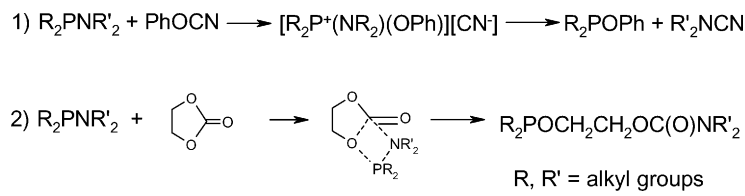


Figure 5. Reaction of P-N compounds with soft (1) and hard (2) acids.

N-silylated aminophosphinimines (as $[Me_3C]_2P(=NSiMe_3)(NHMe)$), which can be alcoholized (by reaction with MeOH), metalated (by reaction with Me_3MCl) and transformed into a wide range of substituted *N*- and *N*,*N*′-organometallic aminophosphinimines such as $[Me_3C]_2P[=N\text{-}MMe_3]$ (NHR) (R=H, Me), $[Me_3C]_2P[=N\text{-}MMe_3](NRM'Me_3)$ (R=H, Me) and $[Me_3C]_2P[=N\text{-}MMe_3](NMe_3)$(M=M′=Si, Ge, Sn). A year later Koketsu and co-workers[52] reacted P-N compounds (*N*,*N*-dialkyl-diphenylphosphinous amides as Ph_2PHMe_2 or diphenyl dialkylphosphoramidites as $(PhO)_2PNR_2$ where R = Me or Et) with alkylating reagents such as alkyl benzenesulfonates ($PhSO_2OR$ where R=Me or Et) and dialkyl sulfates ($SO_2(OR)_2$ where R=Me or Et) yielding phosphonium salts that gave phosphine oxide, benzenesulfonamides or polymeric materials when heated at 100°C for 5–10 hours. In these reactions, the P–N compound behaved as an ambident reagent because 1) the reaction could take place at the phosphorus center, the P being a base, when soft acids (electrophilic reagents) were used as reagent partners (which was the subject of the Koketsu et al.[52] work) or 2) as the nitrogen base and the phosphorus atom attack when hard acids such as estercarbonyl compounds are used as a reagents (see reference 52 and therein) (Figure 5).

The same authors studied the reaction of (diethylamino)dialkylphosphine with ethylene carbonate and performed kinetic studies using IR spectra, monitoring the decrease in the amount of ethylene carbonate (Figure 6).[53] They concluded that the rates varied according to the type

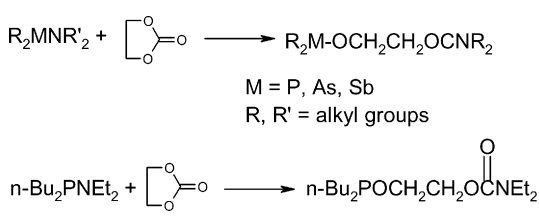


Figure 6. Reaction of aminophosphines with ethylene carbonate.

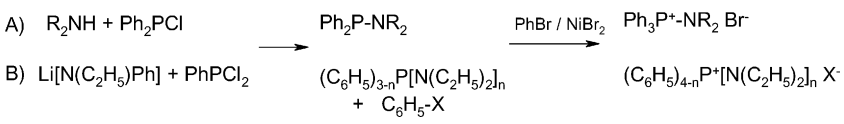


Figure 7. Two-step arylation of aminophosphines to obtain aminophosphonium salts.

of alkyl substituents on the phosphorus atom (secondary alkyl > primary alkyl > methyl), which acts as an electrophilic site accepting an electron pair from the ester atom of the ethylene carbonate. The electrophilicity is affected by the hyperconjugation effect of the substituents.

Cristau and co-workers[54] arylated aminophosphines to aminophosphonium salts (Figure 7) through a versatile two-step method, which avoided problems such as limitations in the choice of reagents or difficulties in the purification of the products, which are encountered using other methods.

The synthesis of compounds of the type $R_2P\text{-}NR'_2$ was first described in 1961, when Sisler and Smith[55] synthesized several new *N*-substituted aminodiphenylphosphines and their sulfur derivatives (Figure 8). Their synthetic work is of general interest of comparison with other compounds. They obtained IR data for all the new compounds with ν(P-N) in the 870–750 cm^{-1} region and all the sulfides showed an extra absorption band at approximately 715 cm^{-1} for ν(P-S). The new aminophosphines were prepared by one of two procedures: a) aminolization of Ph_2PCl with the aliphatic or aromatic amines or b) the amine was converted first to the corresponding sodium amide and then reacted with Ph_2PCl.

Ten years later, Atkinson and Smith[56] performed reaction of (dialkylamino)diphenylphosphines (R_2NPPh_2; R = Me, Et, Pr, Bu) with $[Mo(CO)_6]$ and $[(C_7H_8)Mo(CO)_4]$, aiming to study the possible dinuclear molybdenum complexes with both phosphorus and nitrogen as bridging ligand atoms, since there were relatively few reports of reactions between metal carbonyls and tri-covalent phosphorus derivatives containing a

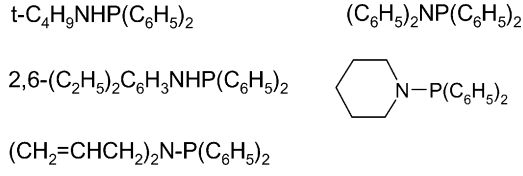


Figure 8. Aminodiphenylphosphines.

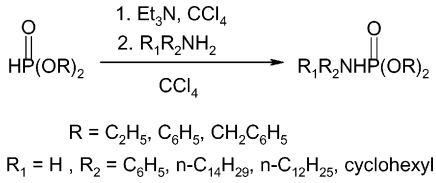


Figure 9. Synthetic path to *N*-dodecylphosphoramidate analogues.

P-N bond. However, the reactions yielded only phosphorus-bridged derivatives due to cleavage of the P-N bond at the high reaction temperatures. By IR spectroscopy they showed that the ability of phosphorus to accept electrons from the metal was not affected by bonding to nitrogen because no reduction of the carbonyl frequency (which is sensitive to π-bonding) in $[(R_2NPPh_2)_xMo(CO)_y]$ ($x = 1$, $y = 5$; $x = 2$, $y = 4$) compared to $[(Ph_3P)_xMo(CO)_y]$ derivatives due to p_π–d_π electron delocalization was observed. Warner and co-workers[57] studied the synthesis of diethyl *N*-dodecylphosphoramidate compounds (Figure 9) and their activity as a potential inhibitors of dental plaque. They found inactive compounds when lengthening the chain of the N substituent and when preparing diphenylesters.

Palladium(II) complexes of benzylphosphorus ligands were investigated by Verstuyft and co-workers[58] since there was considerable interest in complexes of sterically hindered phosphines because they undergo "internal-, cyclo-, or ortho-metallation" reactions. They are very good catalysts for homogeneous hydrogenations and isomerizations of unsaturated organic substrates at ambient temperature and pressure. A good metal candidate for this purpose was palladium because of the greater lability of the palladium (II) complexes compared to the platinum (II) complexes, as illustrated by the appearance of both *cis*- and *trans*- isomers in solution in the case of the palladium (II) complexes. Moreover, the palladium (II) complexes often spontaneously isomerize at measurable rates. The palladium and platinum complexes were studied in detail by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR and electronic spectroscopy, to elucidate their geometry in solution and in the solid state, and tested in catalysed isomerizations. The results were enhanced by conductivity studies and investigation of the photochemical behavior of the azide complexes. Most of the chloride complexes were *trans* in solution and probably *trans* in the solid state as well. Geometric isomerism did not occur and none of the

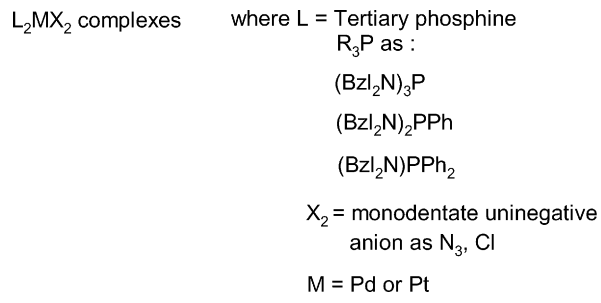


Figure 10. Palladium(II) and platinum (II) complexes of benzylphosphorus ligands.

chloride complexes were found to be photosensitive in solution (Figure 10).

Brunner and Hammers[59] investigated the BF_3-promoted stereospecific insertion of carbon monoxide into the metal-carbon σ bonds of optically active [CpFe(CO)(CH_3)L] = $PPh_2N(CH_2Ph)$-(S)-CHMePh (Figure 11). The overall stereochemistry demonstrated was: the acetyl group ended up where the carbonyl ligand was bonded and the incoming carbonyl ligand occupied the position of the former methyl group.

Some amides of phosphoric and thiophosphoric acid were synthesized (Figure 12) and their radioprotective properties[60] evaluated. Many nitrogen-containing compounds have shown good radio-protective properties. The radioprotective activity (RPA) depends on both the amide and the acid parts of the molecule and it was found to be very high for thiophosphoryl and butyryl derivatives of cyclohexylamine while the phosphoric acid cyclohexylamide was much less active. The amine itself and its salts did not display appreciable RPA. For the synthesis of the new amides they successfully used intermediate bis(silyl) ethers for the synthesis of difficult-to-obtain amides of phosphoric and thiophosphoric acids.

Nifantyev and co-workers[61] obtained pure salts of tetrafluoroboric acid with aminophosphines (Figure 13). It was concluded that the protonation occurred at the phosphorus atom by means by NMR and X-ray

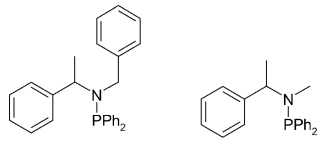


Figure 11. Ligands used in the carbon monoxide insertion.

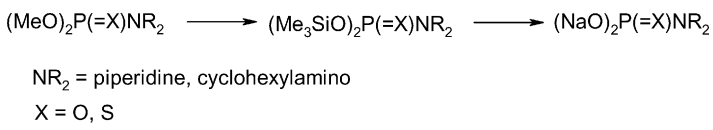


Figure 12. Synthesis of amides of phosphoric and thiophosphoric acids.

techniques. None of the aminophosphonium salts prepared could phosphorylate nucleophiles but the presence of some bases that turned the phosphonium salts into H-complexes facilitated the phosphorylation. The aminophosphine ligands were obtained by a) reaction of lithium diethylamine with di(t-butyl)chlorophosphine with potassium pyrrolide in toluene, in both cases, at 20°C for 12 h.

Pyridylaminophosphines have been investigated by different researchers (Figure 14) and their coordination behavior studied in detail through the years. Because of the presence of several potential coordination atoms, their coordination chemistry was found to be quite interesting, with some of the ligands acting as a bidentate and others even as a tridentate chelating ligands.[62,63,64]

More recent studies have been carried out on monoaminophosphines. The new ligands *o*-$Ph_2PN(H)C_6H_4X$ (X = C(O)Me, C(O)Ph) were successfully synthesized by reaction of Ph_2PCl and *o*-$H_2NC_6H_4X$.[65] A small $^2J(PH)$ coupling observed in the ^1H NMR suggested that the ligands were monosubstituted. The P(V) compound, *o*-$Ph_2PN(H)C_6H_4$-$C(O)CH_3$, was obtained by oxidation of *o*-$Ph_2PN(H)C_6H_4C(O)CH_3$, with 30% aqueous hydrogen peroxide. To achieve the orthometallation of the phosphinoamine ligands with late transition metals (Pt and Rh), the new ligands were reacted, in a first stage, with $[Pt(CH_3)_2(cod)]$ and $[\{RhCl_2(Cp^\star)\}_2]$ to give the precursor complexes, cis-$[Pt(CH_3)_2$ $\{o\text{-}Ph_2PN(H)C_6H_4C(O)CH_3\text{-}P\}_2]$ and $[RhCl_2(Cp^\star)\{o\text{-}Ph_2PN(H)C_6H_4$ $C(O)Ph\text{-}P\}]$. The orthometallated compounds $[Pt\{o\text{-}Ph_2PN(H)C_6H_3C(O)$ $CH_3\text{-}P,C\}_2]$ and $[RhCl(Cp^\star)\{o\text{-}Ph_2PN(H)C_6H_3C(O)Ph\text{-}P,C\}]$ were then formed by thermal activation of the C-H bond by refluxing in xylene for 24–48 h. The platinacycle appeared as a mixture of both *cis* and *trans*

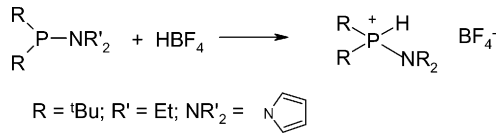


Figure 13. Protonation of aminophosphines.

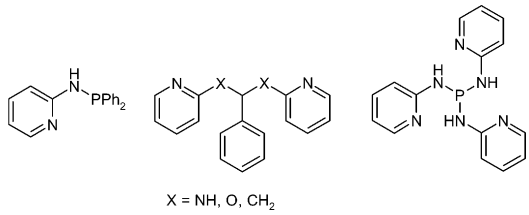


Figure 14. Pyridylaminophosphine ligands.

isomers as was demonstrated by ^{31}P and ^{1}H NMR spectroscopy. Furthermore, IR studies showed the absence of any carbonyl interaction with the platinum center. The platinum (II) center was approximately squre-planar with two chelating orthometallated ligands arranged in a *cis* geometry. The rhodium orthometallated complex had a classic three-legged piano stool geometry where the rhodium(III) center is coordinated to a η^5 Cp★, one chloride and a η^2 [*o*-$Ph_2PN(H)C_6H_3C(O)Ph$-*P*,*C*]-orthometallated ligand. By using phosphinoamine ligands, $R_2PN(H)R$ (R = aryl substituent), they achieved the first example of cyclometallated M-P-N-C-C compounds (Figure 15).

Braunstein and co-workers[66] studied the coordination properties of new acetamide-derived *P*,*O* phosphine ligands, $Ph_2PNHC(O)Me$ and $Ph_2PN(Me)C(O)Me$, which behaved as rigid and/or hemilabile *P*,*O* helates with Pd(II). The new ligand $Ph_2PNHC(O)Me$ was prepared by condensation of *N*-trimethylsilylacetamide with Ph_2PCl in toluene at 60°C. They isolated this compound which had been studied before by Wollins et al., who performed the *in situ* reaction of this compound with

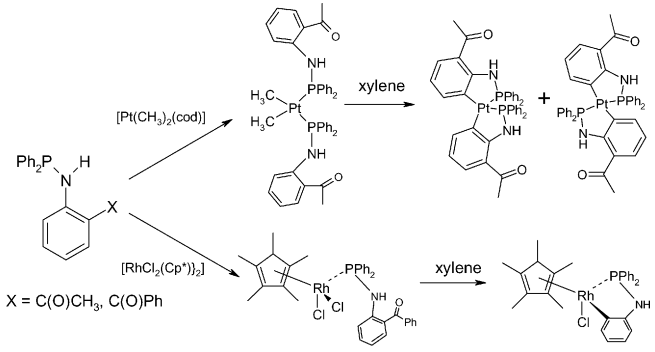


Figure 15. Orthometallation of funcionalized phosphinoamines.

sulfur. This approach is related to that described by Schmutzler et al.[57] for the preparation of urea and thiourea phosphine derivatives. A tautomeric equilibrium between the acetamido and the iminol forms was anifested by the appearance of two signals in the ^{31}P NMR spectroscopy. This did not occur for the corresponding *N*-methylderivative, which could be prepared from $Me_3SiN(Me)C(O)Me$ and Ph_2PCl in CH_2Cl_2 at room temperature. The complex [(dmba)PdCl{$PPh_2NHC(O)Me$}] was obtained by reaction of the corresponding ligand with [Pd(dmba)(μ-Cl)]$_2$ (dmba-H = *N*,*N*-dimethylbenzylamine). The broad ^{31}P NMR signal suggested dynamic behavior in solution. This was rationalized in terms of an equilibrium resulting from the hemilability of the corrdinated ligand. By addition of $Ag(O_3SCF_3)$ the equilibrium was shifted towards the cationic species, [{(dmba)Pd{$PPh_2NHC(O)Me$}[O_3SCF_3]]. When those reactions were attempted with the *N*-methyl derivative, the results were clearly different as the complex [(dmba)PdCl{$PPh_2N(Me)C(O)Me$}] did not manifest any equilibrium process and it became a cationic species only when $Ag(O_3SCF_3$ was added, yielding [(dmba)Pd{$PPh_2N(Me)C(O)$-Me}[O_3SCF_3] in which the amide oxygen atom is coordinated to the Pd centre. By reaction of the new ligands with [PdCl(Me)(cod)] (cod = 1,5-cyclootadiene) and T1[PF_6] in acetonitrile, the authors generated more cationic Pd(II) complexes where the ligands act as hemilabile ligands, binding the Pd centre through P and O atoms. These cationic complexex can react with $Ph_2PCH_2C(O)R$, e.g. [PdMe{$PPh_2NHC(O)Me$}{PPh_2-$CH_2C(O)R$}][PF_6]. The added *P*,*O* phosphine behaves as a monodenate ligand and $Ph_2PNHC(O)Me$ remains chelated to the Pd centre. The higher chelating ability of Ph_2PN{Me}$C(O)Me$ compared to $Ph_2PNHC(O)Me$ was thus comfirmed (Figure 16). when both acetamido derived phosphine ligands are present in the same complex, $Ph_2PN(Me)$-$C(O)Me$ is preferred over $Ph_2PNHC(O)Me$ as the chelate, but a ligand redistribution occurs in solution. Carbonylation of the cationic complexes afforded the corresponding acetyl complexes, in which the acyl ligand occupies a position *cis* to phosphorus, irrespective of the position of the alkyl ligand in the precursor complex.

The same year Burrows and co-workers investigated the preparation of some amine-functionalized aminophosphines $Ph_2PN(R)CH_2CH_2NMe_2$ along with their reversible coordination to platinum and their use in heteronuclear dimer formation.[68] They prepared two new ligands, $Ph_2PN(H)CH_2CH_2NMe_2$, from reaction of PPh_2Cl with $NHRCH_2CH_2$ NMe_2 in the presence of the base n-butyllithium which afforded the

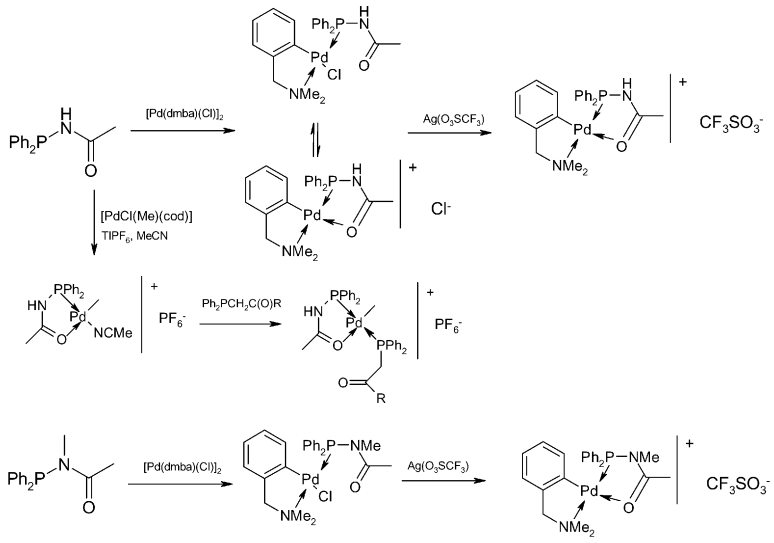


Figure 16. Coordination properties of hemilabile acetamide-derived *P,O* phosphine ligands.

ligand without contamination (whereas the use of Et_3N did not allow the isolation of the pure ligand) and the ligand $Ph_2PN(Me)CH_2CH_2NMe_2$, which was prepared in the same way but using Et_3N, that afforded the clean product. The reaction of 2 equivalents of $Ph_2PN(H)CH_2CH_2NMe_2$ with $[PtCl_2(cod)]$ in dichloromethane gave *cis*-$[PtCl_2L_2]$ (L = $Ph_2PN(H)CH_2CH_2NMe_2$), which was shown to be fluxional with one of the amine groups reversibly coordinating to displace a chloride, one ligand coordinated only through P whilst the other was bidentate with *P,N*-coordination. When those results are compared with the observations made previously for $Ph_2PNCH_2CH_2CH_2NMe_2$, which did not show fluxionality, and $Ph_2PNCH_2CH_2NMe_2$, which formed only *cis*-[PtCl(L-*P*)(L-*P,N*)]Cl, they concluded the differences were related to the relative stability of 6- and 5-membered chelate rings. This conclusion was supported by the species formed when reacting *cis*-$[PtCl_2L_2]$ with $Tl[PF_6]$, for the ligand $Ph_2PN(H)CH_2CH_2NMe_2$, where the removal of the chloride anion prevented the fluxional process. The reaction of 2 equivalents of $Ph_2PN(Me)CH_2CH_2NMe_2$ with $[PtCl_2(cod)]$ in dichloromethane gives the complex *cis*-$[PtCl_2(L\text{-}P,N)]$ (L = $Ph_2PN(Me)CH_2CH_2NMe_2$) in which $Ph_2PN(Me)CH_2CH_2NMe_2$ acts as a bidentate ligand suggesting the ease of formation of a 6-membered chelate ring in which the phosphorus atom is bonded to an sp^2 hybridized nitrogen atom as opposed to an sp^3 hybridized carbon

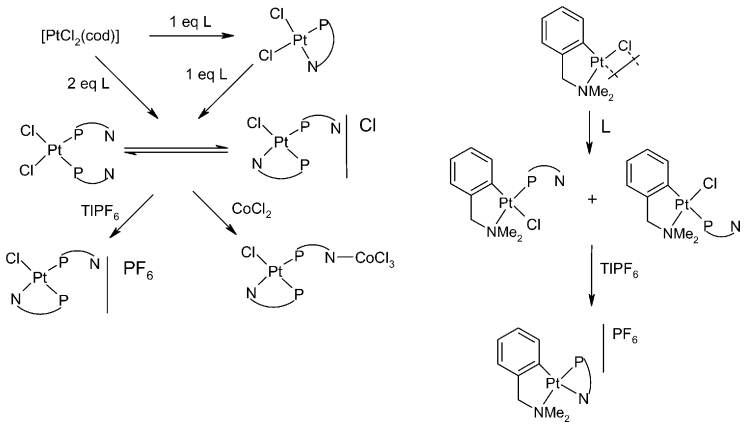


Figure 17. Coordination behavior of some amine-functionalized aminophosphines.

atom. $Ph_2PN(Me)CH_2CH_2NMe_2$ reacts with 1) $[\{Pt(dmba)(\mu\text{-}Cl)\}_2]$ to give [Pt(dmba)Cl(L)], which exists as a mixture of the two geometric isomers and which gives, when reacting with $Tl[PF_6]$, [Pt(dmba)(L-*P*,*N*)]-$[PF_6]$ as a single isomer in which the phosphorus atom is *trans* to the nitrogen atom of *N*,*N*-dimethylbenzylamine; and 2) $CoCl_2 \cdot 6H_2O$ and $ZnCl_2$ to give *cis*-$[(L\text{-}P,N)ClPt(\mu\text{-}L)MCl_3]$ (M = Co or Zn), which does not show metal-metal interactions between the platinum and cobalt centers when M = Co (Figure 17).

DIPHOSPHINES LIGANDS CONTAINING TWO *P-N* BONDS

Diphosphines of the general type $R_2PN(X)PR_2$ (diphosphinoamines)[69–77] and the less studied $R_2PN(X)N(X)PR_2$ (diphosphinohydrazines)[78–83] where X could be hydrogen, an alkyl or an aryl group have been prepared. These are interesting because of the variety of both phosphorus and nitrogen substituents that can be used (Figure 18).

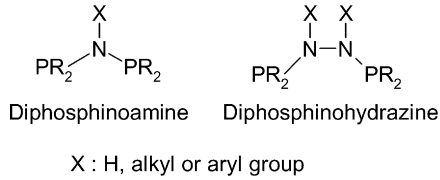


Figure 18. Diphosphinoamines and Diphosphinohydrazines.

Ligands Containing One *N* Atom and Two *P* Atoms, $R_2P\text{-}NX\text{-}PR_2$, $R_2PC_6H_4NPR_2$, $R_2P\text{-}O\text{-}NR\text{-}PR_2$

Bis(diphenylphosphino)amine, $Ph_2PNHPPh_2$ (dppa)[84] isoelectronic with dppm presents a similar coordinative versatility although there are differences in their reactivities in part due the presence of a nitrogen atom and its acidic amine proton (Figure 19). Dppa acts as a chelating ligand with transition metals. By sequential reaction, both phosphorus (III) nuclei can be oxidized (using i.e. hydrogen peroxide, sulfur or selenium) leading to its chalcogen derivatives, which can contain one or two phosphorus (V) atoms. The chalcogens can be the same or different, providing a wide set of possible ligands.[85–88]

Their co-ordination chemistry has been widely studied towards a great number of transition metals.[85,89] The monochalcogen ligands can act as monodentate ligands[90–92] with the subsequent possibility of deprotonation and formation of a new range of bidentate[93,94] complexes. Monochalcogen ligands, when containing a tertiary nitrogen, show bidentate behavior.[95] The dichalcogen ligands appear to act as bidentate ligands,[96–104] and their salts often display cross-co-ordination, producing interesting three dimensional structures[105–110] (Figure 20).

There are only a few examples of unsymmetrical di-tertiary phosphine ligands of the type of *o*-$R_2PC_6H_4(X)PR_2$ (Figure 21). Davis and Mann reported[111] the first P-C bond containing diphosphinoamine with this skeleton and were followed by Abicht[112] and Issleib. Later, Schmutzler et al.[113] prepared a series of P-C bond containing diphosphines with *o*-C_6H_4O spacer groups using various phosphorus halides. Pringle et al.[114,115] reported a chiral bidentate phosphine-phosphite together with a chiral phosphine-triphosphite that was found to act as a tetradentate ligand and Heinicke and co-workers[116] described the synthesis of a number of unsymmetrical phosphine-phosphinites. Finally, some examples have appeared where the phosphorus atom of the above type of compounds was linked to a nitrogen atom giving diphosphinoamine

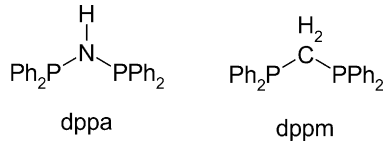


Figure 19. Dppa and dppm.

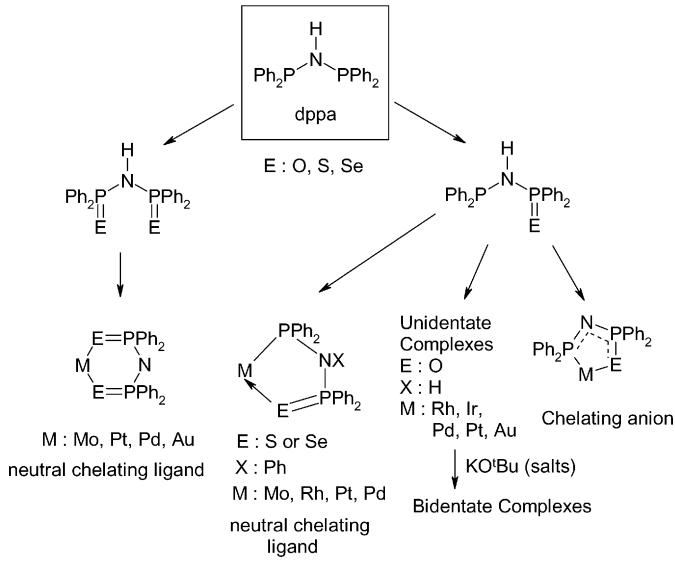


Figure 20. Oxidation and coordination chemistry of Dppa.

ligands. Two examples of this type with an *o*-$C_6H_4N(Me)$ backbone were synthesized by Heinicke and co-workers[117] by treatment of N-methyl-*o*-bromoaniline with n-butyllithium and subsequent addition of R_2PCl. The phosphine-triaminophosphine species was reported by Mazieres and Rauzy[118,119] as a reaction intermediate in the production of 1,2,3-benzazadiphosphole (Figure 21).

Aucott studied $R_2PN(X)PR_2$ compounds and their chalcogen derivatives, finding that this ligand presented three distinct modes of co-ordination, as a bidentate chelating ligand, a bidentate bridging ligand and a monodentate Ph_2PNH bound ligand using a variety of transition metals (Figure 22).[120,121]

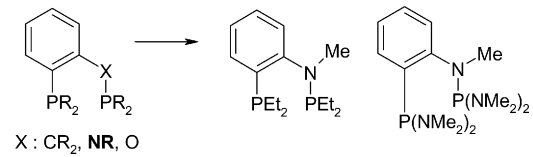


Figure 21. Di-tertiary phosphine ligands of the type of $R_2PC_6H_4(X)PR_2$ with an ortho substituent.

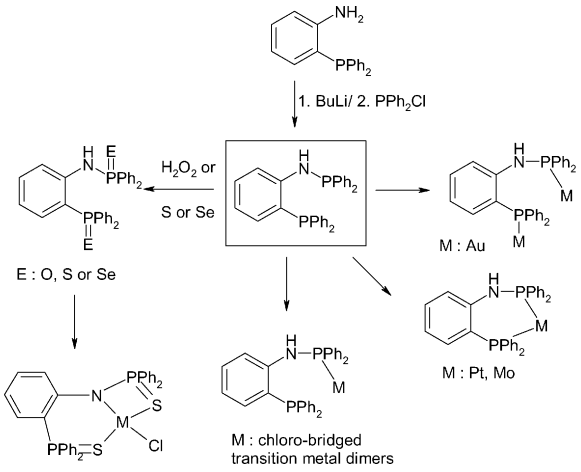


Figure 22. Oxidation and coordination chemistry of $Ph_2PNH(C_6H_4)PPh_2$.

Chiral amino-phosphinite and aminophosphine-phosphite type ligands were synthesised (Figure 23).[122] The greater nucleophilicity of the hydroxy over the amine or the amino functions allowed the selective synthesis of the so–called mixed aminophosphine-phosphinites where the two phosphorus nuclei have different R groups because different chlorophosphines could be used in two additional steps. The symmetrical amino-phosphosphinite was also isolated by the addition of two equivalents of the same chlorophosphine. Due to the wide variety of natural chiral amino-alcohols and precursors to chiral alcohols aminophosphine-phosphinites with very different electronic and steric properties have been obtained and their co-ordination chemistry well studied with a wide range of transition metals (nickel,[123–131,152] palladium,[132–135] platinum,[136–139] rhodium[140–151]. They show interesting catalytic applications.

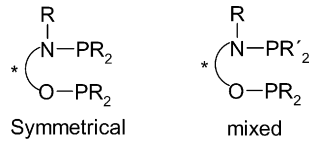


Figure 23. Amino-phosphinite and aminophosphine-phosphinite type ligands. ★ Denotes chirality.

LIGANDS CONTAINING TWO *N* ATOMS AND TWO *P* ATOMS

Urea, Thiourea and Hydrazine Diphosphine Derivatives, $R_2PN(X)N(X)PR_2$

Urea and thioureas have been used to synthesize compounds with the $R_2PN(X)N(X)PR_2$ skeleton. These ligands appear to be interesting as a result of their economically viable production and because, chemically, they offer a wide range of electronic and steric properties due the ease of variation of the substituents. Furthermore, they contain a sulfur or oxygen atom which can provide a site capable of further modification (Figure 1, 24). The first of these compounds was reported in the mid 1960s by condensation of isocyanates with diphenylphosphinic amide or *via* phosphorus-substituted carbodiimides.[154,155] Two decades later, the use of silylated starting materials as a new precursor for their synthesis was reported by Schmutzler. This new approach gave numerous diphosphine derivatives of urea.[156–160,67] Schmutzler and co-workers used another diphosphine derivatives, F_2PCl, for the synthesis of a new range of urea derivatives containing N,N′-dialkyl diphosphines.[160] Later, Woollins described the synthesis of $\{Ph_2PN(H)\}_2CO$ via the reaction of chlorodiphenylphosphine with N,N′-bis(trimethylsilyl)urea and their oxidation to chalcogen derivatives using hydrogen peroxide, sulfur or selenium.[161] Co-ordination studies of those ligands with a wide range of transition metals showed that When F_2PCl or Ph_2PCl are used, the ligands behaved in a bidentate chelating mode. [60-162,67] However, when different substituents (Ph and Bu) on P were used, the co-ordination behavior towards the transition metals was different, displaying a wider range of co-ordination modes, where not only phosphorus atoms participate in the chelation with the metal atom (Figure 24).[67] After the unsuccessful attempt of Schmutzler [163] to obtain the diphosphine substituted thiourea, Bhattacharyya et al.[161,164,165] succeeded in this aim by introducing small changes to the previous approach such as using room temperature and shortening the time of the reaction of thiourea with diphenylphosphinechloride in the presence of Et_3N. Unlike the urea compound, Schmutzler[166–168] was more successful in obtaining mono- and bis-substituted derivatives of thioureas with one or two equivalents of different chlorophosphines as well as some unsymmetrical derivatives. The coordination chemistry of these ligands has been studied and shows a preference for the chelation (P,P') or bis-chelation mode (P,P',O)[164,165] (Figure 24).

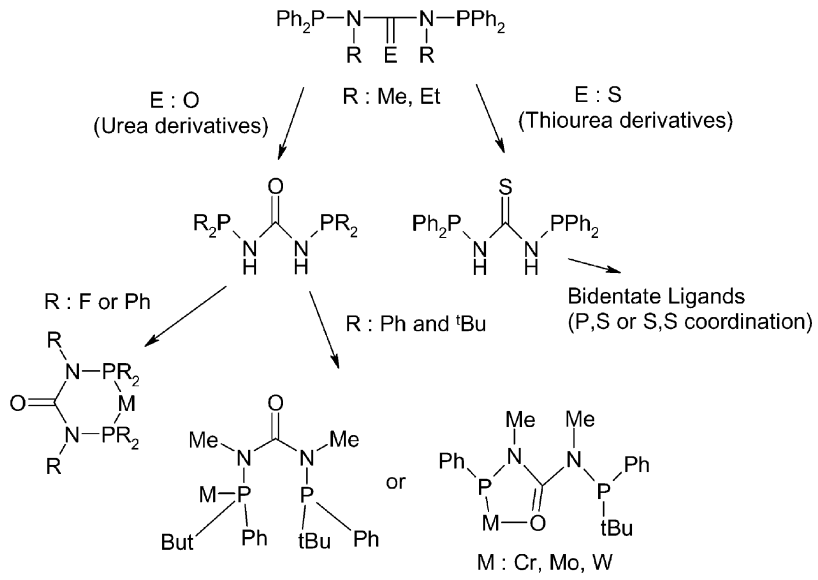


Figure 24. Urea and Thiourea Diphosphine derivatives, their oxidation and coordination chemistry.

More recently, Wainwright extended the work of Woollins and Schumutzler and studied the synthesis of diphosphine derivatives of dialkyl urea and thioureas, finding another possible pathway to this type of compounds by reacting N,N′-dimethylurea of N,N′-diethylthiourea with two equivalents of Ph_2 PCl in the presence of Et_3N.[170] They found that the derivatives of diaalkyl ureas act as *P*,*P*′ chelates and form six-membered rings when reacting with Pt (II), Pd (II), Mo(O) and Ph (I). They act as bridging ligands when reacted with Au (I). However, the reaction of the ligand $\{Ph_2PN(Me)\}_2CS$ with $[Ptcl_2(cod)]$ proceeds with P-N bond cleavage to give a novel five-membered heterocycle. They concluded that different substituents on the nitrogen atoms appear to have little influence on the chemical properties of the ligands and the complexes (Figure 25).

Compared to ligands of the general type $R_2PN(X)PR_2$, the chemistry of phosphorus-nitrogen compounds containing phosphorus-hydrazine backbones has been less well-studied. These ligands can be considered to be of particular significance because they have a similar chain length to dppe, which can form five-membered chelate rings. Furthermore, it is easier to manipulate the substituents on the backbone to give excellent

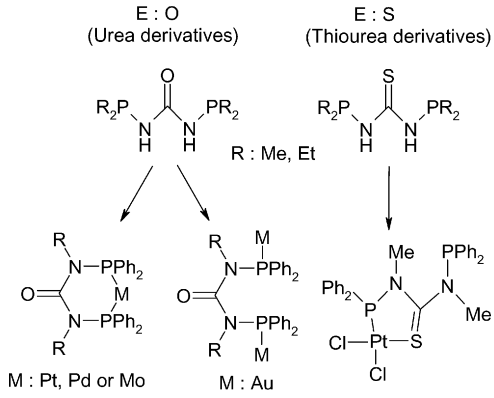


Figure 25. Coordination chemistry of some derivatives of Urea and Thiourea.

control of the steric and electronic properties of the ligands. This may be considerable importance in selective catalytic reactions (Figure 26).[170]

Gilje et al.[81] and North et al.[170] first reported, in the 1970s, The synthesis of phosphorus (III) hydrazines and Katti et al.[171,176] continued their studies of main group metal hydrazines reporting a one-step high-yield synthetic route to $Cl_2PN(Me)N(Me)PCl_2$ by treatment of PCL_3 with 1,2-dimethylhydrazine dihydrochloride.[177] The dichlorophosphine-hydrazine derivative can be used as a chloro precursor able to react easily with alkoxide and Grignard reagents to lead to an extensive range of alkoxy-, aryloxy- and aryl-substituted phosphine hydrazides.[178,179] Reddy et al.[180] reported the synthesis of cyclic phosphorus hydrazines $RP[N(Me)N(H)]_2PR$ by the condensation reaction of $RPCl_2$ with four equivalents of methylhydrazine and the potential use of this ligand for synthesizing, *via* reactions with phosphorus (III) halides[181] tetraphosphines containing both the phosphinoamine [P-N-P] and phosphorus (III) hydrazine [P-N-N-P] functionalities in the same molecule. Examples that were prepared include $[PhPN(Me)N(PPh_2)]_2$, $[PhPN(Me)N(P(OCH_2CF_3)_2)]_2$ (Figure 27).[180]

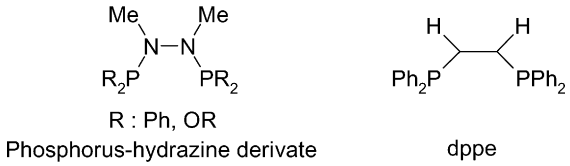


Figure 26. Hydrazine derivatives and dppe.

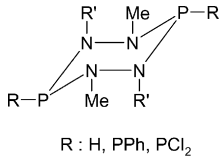


Figure 27. Cyclic Phosphorus Hydrazines.

A large number of transition metals was used to study the coordination chemistry of the phosphorus-hydrazine ligands such as Mo^0, W^0 (bidentate chelation complexes),[180,177] or Pt^{11} / Pd^{11} in which the ligands showed as cisbidentate chelation mode,[180,177,178] or Rh (obtaining dimers that could be cleaved to form compounds that could act as analogues of the Wilkinson catalyst $[RhCl(PPh_3)_3]$.[7,180] The cyclic phosphorus hydrazines were found to benave as binetate ligands[180] and the tetraphosphine ligands gave four-membered metallacyclic complexes when reacted with transition metals[181] (Figure 28).

Recently, Wainwrigh[170] studied bis(chlorophosphino)diethylhydrazine ($CL_2PN(Et)N(Et)PCl_2$) derivatives such as$(PhO)_2PN(Et)N(Et)P(OPh)_2$, $Ph_2PN(Et)N(Et)PPH_2$ and $[(PhCH_2)_2PN(Et)N(Et)P(CH_2Ph)_2]$ as well as a number of diphenyl derivatives of $Cl_2PN(Me)N(Me)PCl_2$ and ($Cl_2PN(Et)N(Et)PCl_2$) with substituents in the *ortho* position ($(o\text{-}C_6H_4OCH_3)_2$ $PN(Et)N(Et)P(o\text{-}C_6H_4OCH_3)_2$, $(o\text{-}C_6H_4OCH_3)_2PN(Me)N(Me)P(o\text{-}C_6H_4OCH_3)_2$ and $((o\text{-}C_6H_4CH_3)_2PN(Me)N(Me)P(o\text{-}C_6H_4CH_3)_2$ (Figure 29) to investigate the effect of the various aryl groups on the approach of reactants in catalytic processes.

The ligands $(PhO)_2PN(Et)N(Et)P(OPh)_2$, $Ph_2PN(Et)N(Et)PPh_2$, $(PhCH_2)_2PN(Et)N(Et)P(CH_2Ph)_2$, $(o\text{-}C_6H_4OCH_3)_2PN(Et)N(Et)P(o\text{-}C_6H_4OCH_3)_2$, $(o\text{-}C_6H_4OCH_3)_2PN(Me)N(Me)P(o\text{-}C_6H_4OCH_3)_2$ and $(o\text{-}C_6H_4CH_3)_2PN(Me)N(Me)P(o\text{-}C_6H_4CH_3)_2$) have a *cis*-bidentate chelation preference when reacted with Pt(II)/PD(II) and the methoxy substituents on the phenyl ring do occupy positions above and below the palladium atom, contrary to what they had hoped, which results in significant

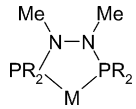


Figure 28. Coordination chemistry of some phosphine derivatives of hydrazines.

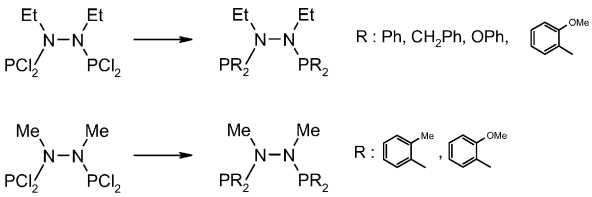


Figure 29. Derivatives of ($Cl_2PN(Et)N(Et)PCl_2$) and ($Cl_2PN(Me)N(Me)PCl_2$).

congestion above and below the coordination plane and this may limit the mechanistics pathways available during a catalytic process. they also concluded that a change in substituents on the nitrogen atom had little effects on the electronic properties of the ligands and complexes [169] (Figure 30).

Ligands of the Type PxN(CR_2)NPx, Where n = 2, R = alkyl or Aryl Groups and Px = P(III) or P(V)

There exists a very extensive data base of diaminophosphines containing a diamine where the two nitrogen atoms are separated by two carbon atoms. Considering the aim of this work, we only review aspects of this field more relevant to our study. Both secondary and tertiary diamines have been used to achieve new diaminophosphines with important features. Our overview will begin with an introduction to the investigations based on secondary diamines, will continue with pertinent studies of tertiary amines and will conclude with the recent publications on ($Ph_2PN(CH_2Ph)CH_2(CH_2Ph)N(CH_2Ph)PPh_2$.

In 1971, Edmundson[182] studied the reaction of diaminoalkanes with diphenyl phosphite and triethylamine in carbon tetrachloride or with diphenyl phosphorochloridothionate obtaining bis(diphenoxyphosphinylamino)alkanes and related compounds instead of the ω-aminoalkylphosphoramidic esters that had been reported before. Synthetically *m*-and

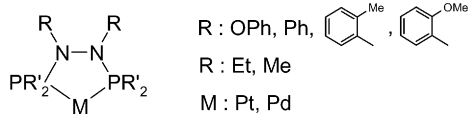


Figure 30. Coordination chemistry of some derivatives of ($Cl_2PN(Et)N(Et)PCl_2$) and ($Cl_2PN(Me)N(Me)PCl_2$).

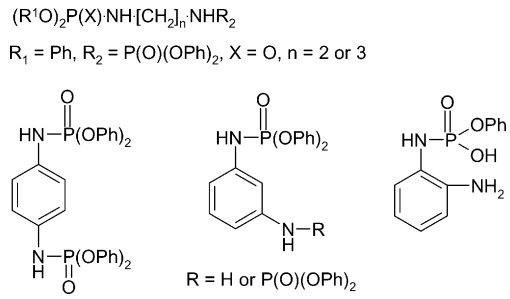


Figure 31. Phosphorylation of diamines.

p-phenylenediamines behaved similarly although *m*-phenylenediamine could also be monophosphorylated *o*-Phenulenediamine is anomalous yielding o-phenyl N-(2-amionophenyl)phosphoramidate (Figure 31).

The effect of triethylamine on the asymmetric hydrogenation of alkenes with cationic and neutral rhodium complexes of a chiral bisphosphine ligand ((IS,2S)-1,2-bis(diphenylphosphinoamino)cyclohexane and (2S,3S)-2,3-bis(diphenylphosphinamino)-butane) as a catalyst was investigated for differently substituted alkenes (Figure 32).[183] It was noted that the cationic catalyst gave better results for both reactiavity and stereoselectivity of the reaction than the neutral catalyst. Furthermore the presence of triethylamine affects the rate of the reaction and the optical yield in several different ways. 1) If the alkene had a free carboxyl but no β-carbonyl group, the conversion rate increased and the optical yield was low, 2) if the alkene had both groups, the conversion rate is not affected and the optical yield increased, and 3) if the alkene had a β-carbonyl group but lacked the free carboxyl group, the conversion rate decreased and the optical yield was not affected. The explanation of those results was based on the possibility of forming a rigid chelating substrate-rhodium complex.

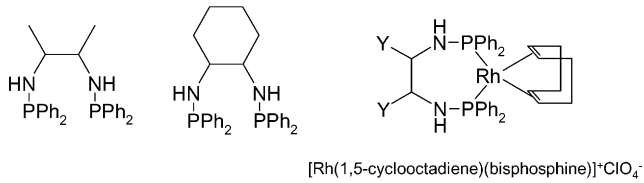


Figure 32. Diphenylphosphinoamines and Rh complexes.

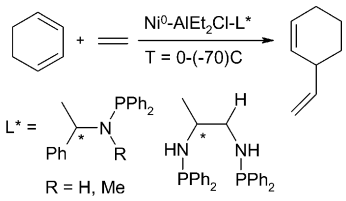


Figure 33. Chiral aminophosphines for the asymmetric codimerization of cyclohexa-1,3-diene.

Buono, Peiffer, Mortreux and Petit[184] found that chiral aminophosphine-nickel catalysts were effective in creating chirality in the cyclohexa-1,3-diene-ethene codimerization and that this reaction occurs almost without isomerization. The optical yields are greatly improved by carrying out the catalysis at low temperatures. They concluded that a) because of the limited isomerization, the optically active products were produced in nearly quantitative yields and could be used in further synthetic applications requiring chirality on a C_6 ring, and b) the most optically active aminophosphine ligands were easily prepared, in particular $Ph_2PNH(CH(Me)CH_2NHPPh_2$ from Ph_2PCl and (−)-(R)-1,2-diaminopropane. Because all the enantiomers of the aminophosphines were readily available, both enantiomers of 3-vinylcyclohexene were accessible (Figure 33).

Reactions of coordinated P-ligands provide an easy method for the preparation rare bimetallic complexes with unsymmetrical, bridging bis-(P-donor) ligands.[185] The dinuclear bis(aminophosphine) and aminophosphiene-aminophosphorinane complexes are prepared by reaction of $[Mo(CO)_5(R_2PNHCH_2CH_2NH_2)]$ with $[Mo(CO)_5(Ph_2PCl)]$ (Figure 34). The dinuclear complexes are relatively stable, although they can slowly decompose upon standing either in solution or in the solid state. When $[Mo(CO)_5(P(OCH_2CMe_2CH_2O)Br)]$ is used instead of $[Mo(CO)_5(Ph_2PCl)]$, the reaction does not go to completion, presum-

$$[Mo(CO)_5(R_2PNHCH_2CH_2NH_2)] + [Mo(CO)_5(Ph_2PCl)] \longrightarrow [(CO)_5Mo(R_2PNHCH_2CH_2NHPPh_2)Mo(CO)_5]$$

$R_2 = Ph_2$ or $OCH_2CMe_2CH_2O$

Figure 34. Preparation of dinuclear complexes of diaminophosphine ligands.

ably due to the slow rate of nucleophilic displacement of bromide from the complex. These reactions provide precise control over the coordination environment of the metals because the bridging, bidentate ligand is formed after the P-donor have been coordinated to the metal centres. The structural data suggests that the Ph_2P group is a better electron donor (poorer electron acceptor) than is the $P(OCH_2CMe_2CH_2O)$ group. This is as expected based upon the electronegativities of the P substituents.

More recently, Bochmann and co-workers [186] approached the synthesis of some selenium and tellurium diphosphinoamine (R_2PNH $CH_2CH_2NHPR_2$) derivatives. With divalent metals, the degree of association of the diphosphinoamine ligand depends on the steric requirements of the R substituent groups on the phosphorus atom. Monomeric complexes are obtained when using bulky R groups, whilst dimeric complexes are formed when using R groups such as Me, at least when the phosphinoamine ligands are of the type $R_2P(S)NR'$. Since high degrees of association were undesirable for potential applications in materials synthesis, the authors synthesised a series of *tert*-butyl -substituted compounds such as $^tBu_2P(E)NHCH_2CH_2NHP(E)^tBu_2$ (E = Se or Te) (Figure 35). The chalcogeno derivatives are accessible either from the reaction of the corresponding aminophosphine $^tBu_2PNHCH_2$ $CH_2NHP^tBu_2$ with selenium/tellurium or from $R_2P(E)Cl$ and primary amines. In this case they were prepared in a one–pot reaction by addition of $^tBu_2PCl$ to the lithium amides $LiNHCH_2CH_2NHLi$ yielding the aminophosphine $^tBu_2PNHCH_2CH_2NHP^tBu_2$. Subsequent refluxing of the reaction mixture in toluene with finely powdered selenium or tellurium gave the potentially tetradentate chalcogenophosphophinic amides.

Chiral phosphorus (V) reagents have been used as resolving agents, auxiliaries or ligands to promote various asymmetric reactions. Yang and Fang [187] combined the use of Lewis acid and bis-phosphoramidate reagents for the promotion of asymmetric cyanosilylation of benzaldehydes. They attempted to take advantage of the C2-symmetry and the

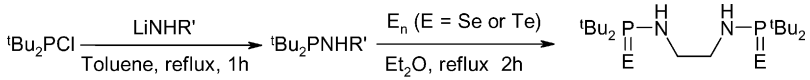


Figure 35. Selenium and tellurium diphosphinoamine derivatives.

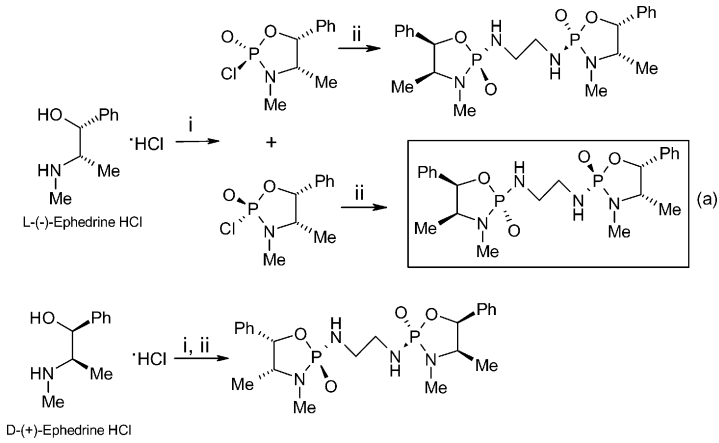


Figure 36. Preparation of chiral phosphorus(V) ligands.

better asymmetric induction of the ligand (2S, 2′S,4S,4′S,5R,5′R)-N,N′-bis(3,4-dimethyl-2-oxo-5-phenyl-1,3,2-oxazaphospholan-2-yl)-ethane-1,2-diamine expected because the phosphorus stereocenters that it contains are close to the reactive sites. The ligands were prepared from inexpensive ephedrines, $POCl_3$ and ethylenediamine (Figure 36). They observed a) the cyanosilylation occurred with reasonable enantioselectivity at room temperature, and b) the ligand could be recycled and used again, in minute amounts, by filtering it from the reaction mixture.

As a continuation of this study, they reported the preparation of some other chiral phosphorus(V) reagents and their use with borane/dimethylsulfide complex in the enantioselective reduction of aromatic, aliphatic and heterocyclic ketones.[188] The new ligands (Figure 37) were prepared from the reaction of ephedrine and $POCl_3$, followed by substi-

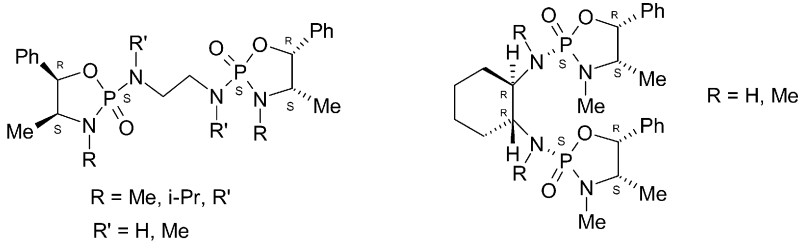


Figure 37. Some examples of chiral phosphorus(V) reagents.

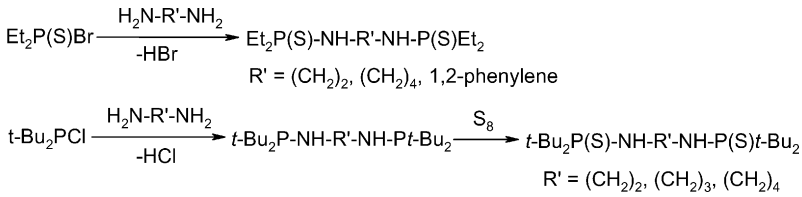


Figure 38. Synthesis of *N*, *N*-bis(*P*,*P*-dialkylthiophosphinyl)diamines.

tution with nucleophiles such as phenylmagnesium bromide, alcohols, amines, diamines and triamines. They observed retention of the configuration at the phosphorus center when they substitution reactions occurred in a stereospecific manner. The P(V) reagents acted as Lewis bases to react with borane, giving in *situ* zwitterionic species as the chiral reducing agents. The reactions carried out at 0°C in tetrahydrofuran afforded secondary alcohols with modest enantioselectivity.

Kuchen and co-workers[189] performed the synthesis of N,N′-bis (P,P-dialkylthiophosphinyl)diamines $R_2P(S)$-NH-R′-NH-$P(S)R_2$ from $Et_2P(S)Br$ and H_2N-R′-NH_2 with elimination of HBr in the case of R = Et, and from sulfuration of R_2P-NH-R′-NH-PR_2, which was generated without isolation form NH_2-R′-NH_2 and $^tBu_2PCl$, in the case of R = ^{t}Bu because of the relative inertness conferred by this group (Figure 38). The structural, spectroscopic and magnetic properties depend strongly on the organic substituents at P and N. when those ligands were reacted with Ni(II), monomeric complexes were obtained.

Fazylov and co-workers [190] described the synthesis of some diphosphino derivation of 2,3-diaminobutane, which exhibit interesting properties as antibacterial and herbicidal compounds. They performed a Todd-Atherton reaction of 2,3-diaminobutane with dialkyl hydrogen phosphites, observing that the diamine was phosphorylated independently

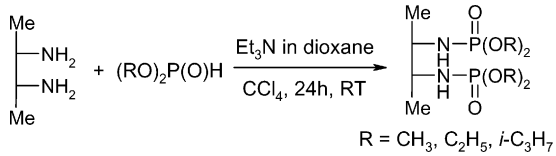


Figure 39. Reaction of 2,3-diaminobutane witgh dialkyl hydrogen phosphites.

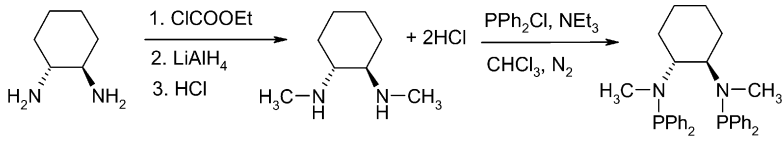


Figure 40. Synthesis of (1R,2R)-bis(*N*-diphenylphosphinomethylamino)cyclohexane.

of the reagent ratio (1:1 or 1:2 at two amino groups and gave bisphosphorylated compounds (Figure 39).

There have been several studies on (1R, 2R)-bis(N-diphenylphosphinomethylamino)cyclohexane. Firstly, Hanaki et al.[191] investigated the asymmetric hydrogenation of α-acylaminoacrylic acids catalysed by the rhodium(I) complex of (1R, 2R)-bis(N-diphenylphosphinomethylamino)-cyclohexane, which was easily prepared form (1R,2R)-bis(methylamino)-cyclohexane and chlorodiphenylphosphine (Figure 40). This reaction gave chiral N-acylated amino acids with high optical purity.

They found the ligand to be very effective in the above catalytic reaction and they speculated that was due to the conformationally stable seven-membered chelate structure of the ligand in the rhodium complex. On the basis of molecular modelling structures, they suggested that to reduce interactions between the methyl groups and the cyclohexane ring, the nitrogen atoms have to take an S configuration and the two phenyl rings on the phosphorus atoms were disposed axial and equatorial, with hindered rotation around the phosphorus-carbon bonds. This resulted in a very rigid and chiral environment around the phosphorus atom, which favored the asymmetric hydrogenation (Figure 41).

Around the same time, Onuma et al.[192,193] studied the same catalytic reaction and they extended the investigation to a correlation between the structure of the ligands and the chirality of the products. (R)-Amino acids were formed when using the rhodium complex of (R,R)-1 ((1R,2R)-bis(diphenylphosphinamino)cyclohexane), while (S)-amino acids were obtained when using rhodium-(S,S)-1 complex instead. However,

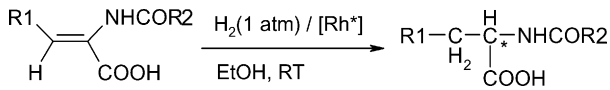


Figure 41. Asymmetric hydrogenation of α-acylaminoacrylic acids.

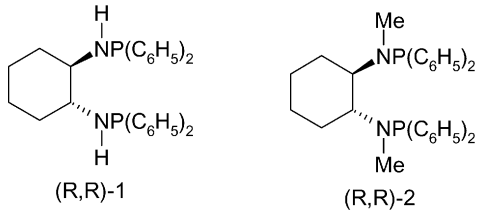


Figure 42. Chiral aminophosphines (R,R)-1 and (R,R)-2.

(S)-amino acids were obtained when rhodium complex of (R,R)-2 was used in contrast with the results of (R,R)-1 (Figure 42). Chiral reversion of the stereoselectivity by N-mythylation of the ligand occurred and they studied the stereochemistry of the complexes. They concluded that differences in the helical conformation of the complexes caused the inversion of stereoselectivity and that the complexes with left-handed helicity would give (R)-amino acids and the complexes with right-handed helicity would give (S)-amino acids.

Hanaki et al.[194] concluded their previous investigations[191] with the study of seven chiral diphosphines (Figure 43) along with their cationic 1,5-cyclooctadiene rhodium(I) complexes for the stereoselective hydrogenation of α-acylaminoacrylic acids.

The optical yields and absolute configurations of the products depend on the kind of diphosphine ligand. They confirmed the fact that aminophosphine complexes with methyl groups on the nitrogen atom always give (S)-amino acids and those with no methyl group give (R)-amino acids.

A new type of chiral aminophosphines, (3S)-[N,N′-bis(diphenylphosphino)]-3-aminopiperidine (**La**) and (3S)-N,N$^-$-bis(diphenylphosphino)]-3-(methylamino)piperidine (**Lb**) (Figure 44), were prepared by Osakada et al.[195] (Figure 45) and tested as potential ligands for the

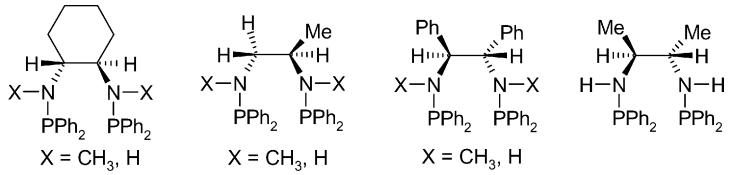


Figure 43. Chiral diphosphines.

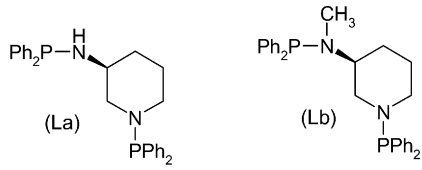


Figure 44. Aminophosphine derivatives of piperidine.

asymmetric hydrogenation of α-acylaminoacrylic acids with rhodium(I) to obtain optically active N-acyl-α-amino acids.

These ligands differ from the previously mentioned 1,2-diamino derivatives in not having C_2-symmetry, thus the two phosphorus atoms are inequivalent. Furthermore, the ligands could form a seven-membered chelate ring with a rigid conformation because two carbon atom and the nitrogen atom involved in the chelate are part of the piperidine ring. The products with (S)-configuration were obtained preferentially in all cases and N-methylation of the ligand did not affect the stereoselectivity of the reaction. This result is different from the results obtained when diphenylaminocyclohexane isomers were used, because the rhodium complexes of **La** and **Lb** presented similar stereoselectivity, there were no differences in the conformation of the ligand including the helical orientation of the phenyl groups.

In 1999, Shi and Sui[196] investigated the titanium(IV) alkoxide-promoted addition of diethylzinc to aldehydes (Figure 46) with C2-symmetric diphenylphosphoramides and diphenylthiophosphoramide derived from (1R,2R)-1,2-diaminocyclohexane as chiral ligands.

Diphenylphosphoramide and diphenylthiophosphoramide were prepared by reaction of diphenylphosphonic chloride and diphenylthiopho-

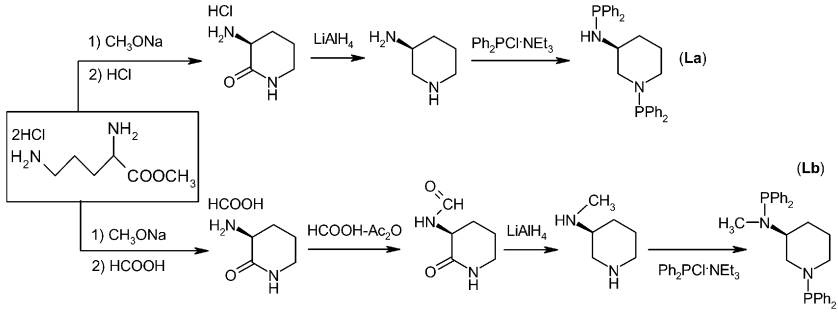


Figure 45. Synthetic pathway to prepare the chiral ligands La and Lb.

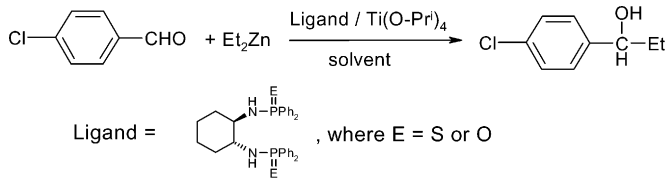


Figure 46. Titanium(IV) alkoxide-promoted addition of diethylzinc to aldehydes.

sphonic chloride with (1R,2R)-(−)-1,2-diaminocyclohexane in the presence of diisopropylethylamine in dichloromethane, respectively (Figure 47).

They found that the diphenylphosphoramide derived ligand had a so-called "ligand acceleration effect" because the reactivity of the active species bearing the chiral ligand was enhanced. It is quite an effective chiral ligand because the phosphoryl oxygen atoms can coordinate to the titanium center whilst the ligand maintains a rigid chiral C_2-symmetric environment and thus achieves a high enantioselectivity. However, no X-ray data were available to support this hypothesis. The diphenylthiophosphoramide–derived ligand showed an interesting behavior by preferentially yielding *sec*-alcohol with the S-configuration in the asymmetric reaction. This is the reverse enantioselectivity compared with that observed when the diphenylphosphoramide–derived ligand was used, maybe because of the different electron withdrawing ability of the P = S and P = O bonds. An interesting feature of those ligands was the fact that they could be recovered from the reaction mixture and could be used again in asymmetric reaction without loss of enantioselectivity. The solvent and the temperature were found to affect drastically the ee of the reaction products. It was concluded that these chiral ligands were effective for the asymmetric reaction but not as effective as ditriflamide ($C_6H_8(NH(SO_2CF_3))_2$). Again, Shi and Inoue,[197] two years later, investigated the enantiodifferentiating photoisomerization

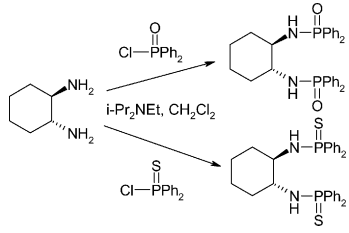


Figure 47. Preparation of diphenylphosphoramide and diphenylthiophosphoramide derived ligands.

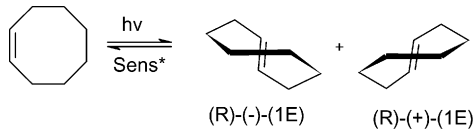


Figure 48. Enantiodifferentiating photoisomerization of (Z)-cyclooctene.

of (Z)-cyclooctene sensitized by the above-mentioned chiral C_2-symmetric phosphoramide (chiral sensitizer, Sens*)(Figure 48).

The major photochemical reaction observed was the E-to-Z isomerization of cyclooctene. Phosphoramides possessing structures isoelectronic with the phosphoryl esters were shown to function as effective sensitizers for the geometrical photoisomerization of simple alkenes, although the E-to-Z ratios obtained were smaller in general than those obtained with the phosphoryl esters.

Continuing with the study of the phosphoramide chiral ligands, Shi and Sui[198] investigated the silver(I)-promoted enantioselective allylation of aldehydes (Figure 49).

They had chosen sulfur derivatives as chiral ligands because sulfur can easily coordinate to different metals, giving stable chiral metal complexes. They prepared three different sulfur derivatives of bis-aminophosphine ligands, $\mathbf{L^1}$ and $\mathbf{L^2}$ from the reaction of diphenylthiophosphinic chloride with (1R,2R)-(−)-1,2-diaminocyclohexane and 1S,2S)-(−)-1,2-diphenylethylenediamine, respectively, in the presence of diisopropylethylamine in dichloromethane, and $\mathbf{L^4}$ from the two step reaction of (R)-(+)-1,1′-binaphthyl-2,2′-diamine and butyllithium to form the corresponding lithium amide followed by the reaction of the latter with diphenylthiophosphinic chloride. When they attempted the synthesis of $\mathbf{L^4}$ in the presence of diisopropylethylamine or triethylamine as a base, no reaction took place. The preparation of $\mathbf{L^4}$ is interesting because only one diphenylthiophosphinyl group could be introduced into the 1,1′-binaphthyl-2,2′-diamine, maybe due to the steric hindrance of the diphenylthiophosphinyl group (Figure 50). The chiral ligands, $\mathbf{L^1}$ and $\mathbf{L^2}$, provided a very low ee of *sec*-alcohol in thf or dichloromethane

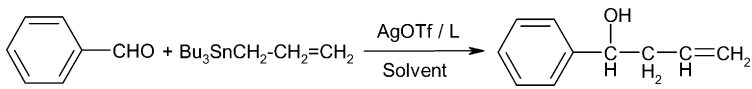


Figure 49. Silver(I)-promoted enantioselective allylation of aldehydes.

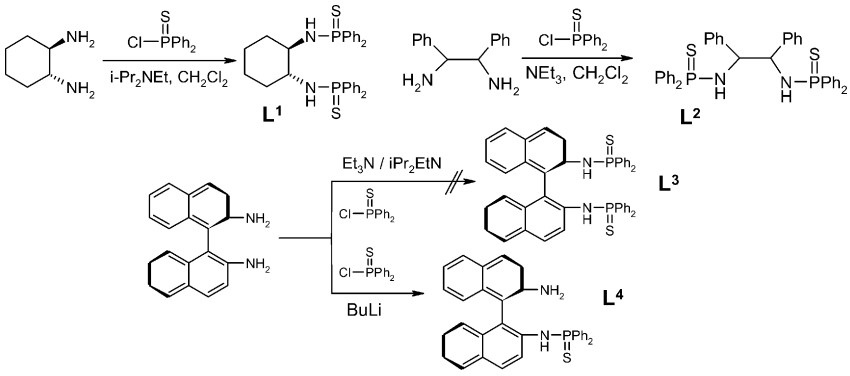


Figure 50. Synthesis of novel chiral ligands L^1, L^2, L^3 and L^4.

and L^4 gave ee's that reached 52% in thf and 50% in dichloromethane et $-20^{\circ}C$. The three ligands could be recovered from the reaction mixture and used again in the catalytic reaction without loss of enantioselectivity, showing their stability. The asymmetric reaction only takes place when there is a sulfur atom as a substituent on the phosphorus and no oxygen or selenium. Ligand L^4 could act as a bidentate ligand by coordination of the nitrogen and phosphoryl sulfur atoms to the silver(I) metal, affording a chiral silver(I) Lewis acid, but no supporting X-ray evidence was obtained. Finally, ligand L^4 was found to be an effective chiral ligand for the asymmetric reaction but no as good as the BINAP-silver(I) complex.

Compounds of the type $R(NHPPh_2)_2$, where R is an aryl group, were prepared by Ly.[199] They formed seven-membered chelate rings when complexed with different transition metals. The ligands were synthesized by a condensation reaction between chlorodiphenylphosphine and the appropriate deprotonated amine with different backbones in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine (DMAP), which significantly enhanced the reaction rate. Four compounds were synthesized, there of them containing an aromatic group attached to the diamine backbone ($[Ph(NHPPh_2)_2]$, $[(MeC_6H_3)(NHPPh_2)_2]$ and $[(C_{10}H_6)(NHPPh_2)_2]$) and the fourth containing an alkyl group connecting the two nitrogen groups that constitue the diamine backbone ($(C_2H_4(NHPPh_2)_2)$). Only two compounds were isolated, $[(C_6H_4)(NHPPh_2)_2]$ and $[(CH_3C_6H_3)NHPPh_2)_2]$, and they were found to have similar δp value to $Ph_2PNHPPh_2$. The compounds $[(C_{10}H_6(NHPPh_2)_2]$

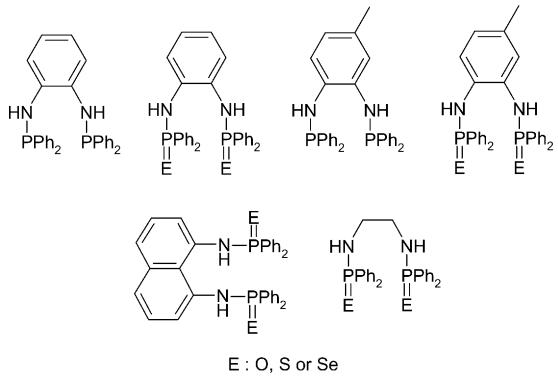


Figure 51. Ligands of the type $R(NHPPh_2)_2$ where R is an aryl or an alkyl group.

and $(C_2H_4(NHPPh_2)_2$ were only isolated as the chalcogen derivatives (Figure 51).[199]

Complexes of 3,4-$C_7H_6(NHPPh_2)_2$ were prepared using a number of different transition metals such as Mo (o) that gave a *cis*-octahedral seven-membered ring metal complex, Pt(II)/Pd(II) that gave *cis*-square planar seven-membered ring metal complexes and Au (I) giving a linear metal complex.[199] (Figure 52).

In 1973, Burgada and co-workers[200] investigated the mechanism of formation and transformation of a type of spirophosphoranes (Figure 53).

An evaluation of the steric effects of the rhodium (I) complexes of several chiral amino and diamino phosphines ligands in asymmetric hydrogenation of aminoacids was carried out by Pracejus.[201] The ligands contained two chiral α-phenylethyl groups with different degrees for conformational flexibility (Figure 54). In particular, they studied the

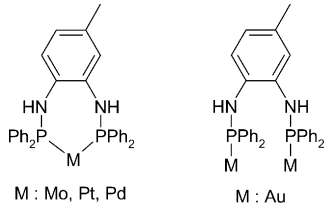


Figure 52. Coordination chemistry of ligands of the type of $R(NHPPh_2)_2$ where R is an aryl group.

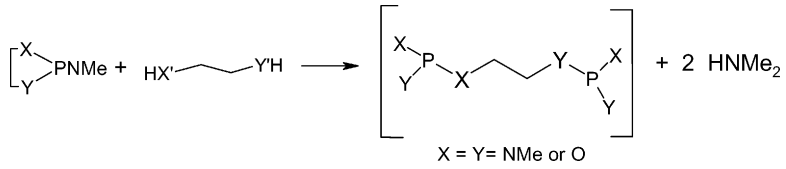


Figure 53. Spirophosphoranes.

diphosphinoamine ligand **P-NN-P** (Figure 54) that had been synthesized from the reaction of Ph_2PCl and N,N′-bis[(s)-α-phenylethyl]ethylenediamine in Et_2O.

This particular ligand, in MeOH (because the reaction had shown solvent dependence), strongly enhanced the rate and stereospecificity of the asymmetric reaction.

A series of new sterically hindered phosphoramidates was prepared[202] by the reaction of several secondary amines with bis(2,6-dimethylphenyl)chlorophosphate, the latter being obtained by treatment of phosphorus oxychloride with two equivalents of 2,6-dimethylphenol in the presence of magnesium chloride (Figure 55).

Suisse et al.[203] achieved the highest chemoselective synthesis of 4-vinylcyclohexane (VCH) known at that time, by butadiene cyclodimerization on nickel complexes with aminophosphinephosphinite and bis (aminophosphine) chiral ligands (selectivity up to 99%). The ligands were prepared according to procedures already described, by diphosphinylation of different amines (Figure 56).

It was reported that monodentate phosphine and aminophosphine ligands are less effective than bidentate ones in the selective synthesis of VCH. BisAMP was the ligand that demonstrated the highest selectivity to VCH among the bis(aminophosphine) ligands studied in this work. (S)-ProNNP performed quite well and although one equivalent was

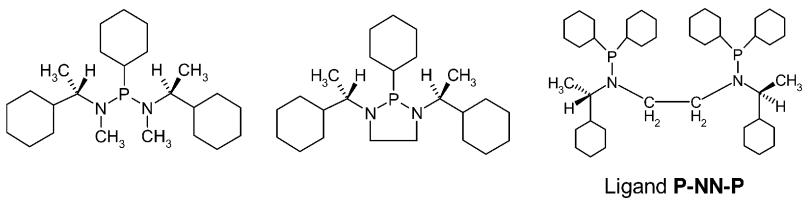


Figure 54. Chiral amino and diamino phosphine ligands.

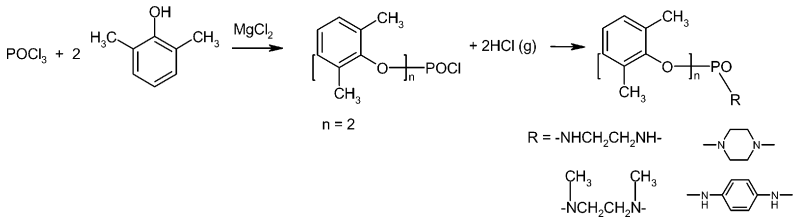


Figure 55. Preparation of phosphoramidates.

enough to induce a high chemoselectivity, with two equivalents this selectivity was enhanced to 98% without loss of enantioselectivity and activity.

Based on the same skeleton as (S)-ProNNP, a new series of ligands was prepared and their rhodium complexes were tested in asymmetric hydrogenation of activated ketones,[204] leading to high enantiometric excesses (up to 87% and 75% depending on the substrate) and in enantiomeric rhodium catalyzed hydroboration of olefins with catecholborane[205] giving enantioselectivities up to 77%.

In catalytic hydroformylation of alkenes to aldehydes, platinum(II) complexes of chiral diphosphines give high stereo- and regioselectivity and this type of reaction is controlled by the geometric properties of the transition metal complexes.[206] With this in mind, chiral diphosphines with the substructure of the aminoacid l-proline were prepared. Among these, (S,S′)-1,1′-bis(diphenylphosphino)-2,2′-bipyrrolidine (S-bipyrphos) (Figure 57) was prepared in three steps: 1) coupling of pyrrole and 2-pyrrolidone[206] 2) hydrogenation of the unsaturated bipyrrolidine product to give a mixture of R,R′-, S,S′-, and meso-bipyrrolidine, from which the S,S′-isomer was separated by recrystallization with D-tartaric acid, and 3) the reaction of (S,S′)-2,2′- bipyrrolidine with N,N'-dimethylaminodiphenylphosphine. [Pt(cod)Cl_2] was used to prepare the platinum complex of the resulting ligand, which contained a seven-membered chelate with a

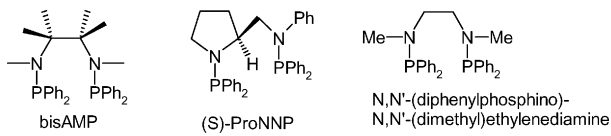


Figure 56. Bis(aminophosphine) chiral ligands.

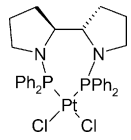


Figure 57. Structure of (S,S′-bis(diphenylphosphino)-2,2′bipyrrolidine (S-bipyrphos)complexed with Pt(II).

boat form. Its conformation was found to be fixed by the square planar platinum environment and the fused L-proline molecules and the phenyl groups occupying isoclinical (same inclination) positions rather than alternating axial/edge and equatorial/face arrangements.

De Vries et al.[207] and later on Mandoli et al.[208] studied a series of new bidentate chiral phosphoramidites based on TADDOL and BINOL phosphites (Figure 58). The latter authors investigated the effect of these ligands in copper-catalyzed asymmetric 1,4-addition of diethylzinc to cyclic α,β-enones (enantioselective tandem 1,4-addition-aldol reactions with 2-cyclopentenone). The new ligands were obtained from the reaction of α, α, α', α'-tetraphenyl-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol (TADDOL) or 1,1-bi-2-naphthol (BINOL) and either 1,2-ethylene- or 1,3-propylenediamine N,N'-disubstituted with chiral or achiral groups in toluene in the presence of Et_3N. They afforded products with e.e.s of up to 89 and 83%, respectively. They conclude that although TADDOL–derived ligands did not result in any advantage compared to the previous results, BINOL–derived ligands gave very promising results.

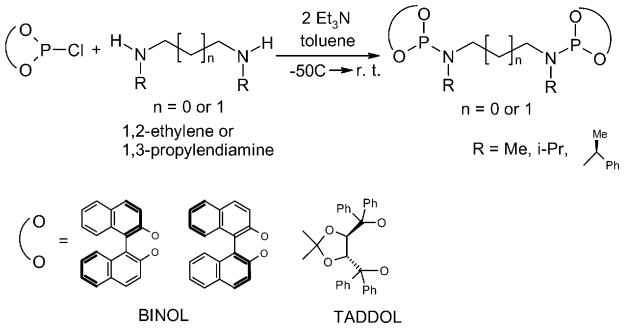


Figure 58. Preparation of bidentate phosphoramidites.

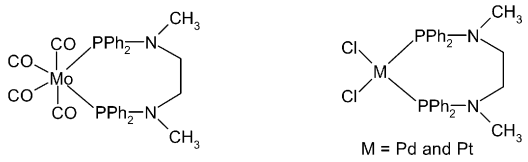
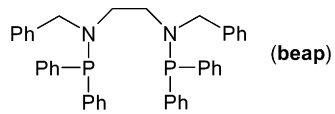


Figure 59. Transition metal chemistry of bis(phosphine) $Ph_2PN(Me)$-$CH_2CH_2N(Me)PPh_2$.

Bis(phosphine) ligands are becoming more and more important because of their potential applications in organic synthesis. By studying their transition metal chemistry, the mechanism of action of the often used in situ generation of a metal catalyst by reacting a ligand with a suitable metal precursor could be elucidated. The reactivity, stability and the steric and electronic situation around the metal center could be understood. The study of bis(phosphines) with two phosphorus centers separated by more than one type of atom in the spacer is not very extensive and the different electronegativities of the spacer groups is interesting because it has a great influence in the donor-acceptor properties of the phosphorus centers. With this in mind, Maravanji et al.[209] investigated the transition metal chemistry of the bis(phosphine) $Ph_2PN(Me)$-$CH_2CH_2N(Me)PPh_2$ (Figure 59). The ligand was prepared from the dropwise addition reaction of Ph_2PCl to N,N′-dimethylethylenediamine in the presence of Et_3N at $-10^{\circ}C$. The ligand reacts with group 6 tetracarbonyl derivatives of the type $[M(CO)_4L_2]$ ($M = Mo$, $L_2 =$ norbornadiene), giving seven-membered *cis*-chelated tetracarbonyl derivatives. Furthermore, treatment of $[MCl_2(cod)]$ ($M = Pd$ or Pt) with 1:1 molar proportions of the ligand in dichloromethane also afforded the seven-membered *cis*-chelated derivatives. This is very interesting because, since seven-membered chelates are less stable than five- or six-membered chelates, one of the metal-phosphorus bonds could become decoordinated for further reactions and for catalytic purposes.

The compound $Ph_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NPPh_2$ (**beap**) (Figure 60) was prepared by Payne and Stephan[210] from the reaction



(**beap**)

Figure 60. $Ph_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NPPh_2$ (beap) ligand.

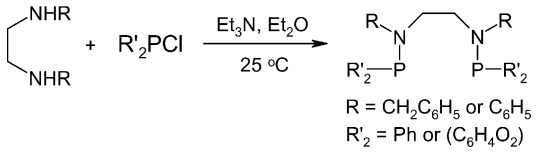


Figure 61. Preparation of bis(phosphines) of the type $X_2PN(R)CH_2CH_2(R)NPX_2$.

of N,N′-dibenzylethylenediamine with the dropwise addition of Ph_2PCl at room temperature in benzene in the presence of Et_3N.

[Pt(chelate)CH_3Cl] was prepared by reaction of [Pt(cod)(CH_3)Cl] with **beap**, subsequent reaction of these platinum halide complex with Ag[ClO_4] in acetone gave the acetone containing cation with perchlorate as the non-coordinating anion [Pt(**beap**)CH_3(acetone)][ClO_4] and a precipitate of silver chloride. Afterwards, group V donor molecules (X) displaced acetone from the cationic complex because they are better σ-donors giving [Pt(chelate)(Me)(X)][ClO_4].

Balakrishna and co-workers[211] reinvestigated bis(phosphines) of the type $X_2PN(R)Ch_2CH_2(R)NPX_2$ (R = Ph or CH_2Ph, X = Ph, R = CH_2Ph_2, $X_2 = O_2C_6H_4$) because of their potential use as stabilizers of transition metal chelates in low valent states in a variety of metal-mediated organic transformations and for complexation studies (phosphorus-phosphorus coupling through the metal in its chelate complexes), catalytic (alkylation of various allylic acetates) and medicinal applications. The ligands were prepared from reaction of N,N′-substituted ethylenediamine derivatives with two moles of chlorodiphenylphosphine or $(C_6H_4O_2)PCl$ in the presence of trietylamine in Et_2O at 0°C (Figure 61).

Their coordinative properties were studied by treating the bidentate ligands with different Group 6 metal carbonyl and platinum metal derivatives containing one or two labile ligands (Figure 62) forming *cis*-seven-membered metallacycles.

Ligands of the Type $P_xN(CR_2)_nNP_x$, Where n = 3, 4, 5, R = alkyl or Aryl Groups and P_x = P(III) or P(V)

In this section, bis(aminophosphines) ligands where the two nitrogen centers are separated by three, four of five carbon atoms will be discussed. Detailed mention will go to those ligands where the backbone of the diamine contains four spacer carbon atoms, especially 2,2′-bis(diphenylphosphinoamino)-1,1′-binaphthyl ligand (BDPAB).

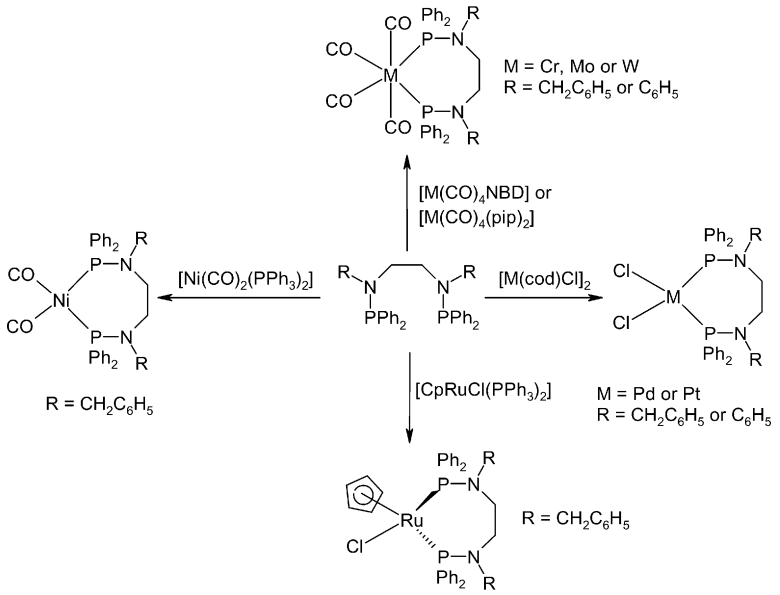


Figure 62. Preparation of $X_2PN(R)CH_2CH_2(R)NPX_2$ complexes.

There are few examples of ligands of the type $P_xN(CR_2)_nNP_x$, where n = 3 and the carbon atom are part of an alkyl structure. van Leeuwen et al.[212] have described phosphoramidites as novel modifying ligands in rhodium catalysed hydroformylation of 1-octene and styrene using $[Rh(CO)_2(acac)]$ as catalyst precursor. They decided to trisubstitute the nitrogen to introduce more bulk in the proximity of the phosphorus atoms and thus, have a more crowded rhodium center, which could influence the regioselectivity of the reaction. When 1-octene was used as a substrate, the diphosphoramidites showed reaction rates about

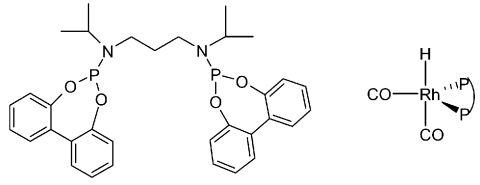


Figure 63. Bis(biphenyl-2,2′-diylphosphorochloridite)-N,N′diisopropylpropane-1,3-diamine (Ligand O-P-N), and its bis-equatorial coordination to rhodium.

three times slower, less isomerization and higher linear selectivity (up to 91% for ligand **O-P-N**, Figure 63) than the monophosphoramidites. When styrene was used as a substrate, it was shown that the diphosphoramidites were again slower than the monophosphoramidites. By catalyst characterization studies they proved the formation of a hydrido rhodium complex and the fact that both phosphorus atoms of the diphosphoramidites coordinated in a bis-equatorial manner to the rhodium center in $[RhH(CO)_2L]$. Diequatorial coordination promotes preferential formation of linear aldehydes. It is important to notice that they observed predominantly decomposed ligand in the case of ligand **O-P-N** when the preparation of the rhodium hydrido complex was attempted.

Ligands of the type $P_xN(CR_2)_nNP_x$ where $n = 3$ and the carbon atoms are part of an aromatic structure are unsual. Ly et al.[199] prepared some bis(aminophosphines). They prepared $[(C_{10}H_6)(NHP(E)PPh_2)_2]$ where E = S, Se, from the reaction of Ph_2PCl with 1,8-diaminonaphthalene in the presence of thriethylamine and DMAP in thf followed by the addition of sublimed sulfur, grey selenium or both to yield the chalogen derivatives $\mathbf{L^x}$, $\mathbf{L^y}$ or $\mathbf{L^z}$ respectively (Figure 64).

X-ray studies revealed that there is a symmetric arrangement with the phosphorus atoms being on opposite sides of the naphthalene plane. The pyramidalization at nitrogen leads to these structures being chiral. The ligand $[(C_{10}H_6)(NHPPPh_2)_2]$ was not isolated and no metal complexes of this ligand were prepared.

Ligands of the type $P_xN(CR_2)_nNP_x$, where $n = 4$, R = aryl groups and P_x = P(III) or P(V) have been studied.

For the stabilization of polymers such as rubber against aging, organic tervalent phosphorus derivatives were prepared and cyclic alkyl o-phenylene phosphites were found to be good stabilizers because they react with free radicals as tervalent phosphorus derivatives and as amine.[213] They were prepared from the reaction of o-phenylene phosphor-

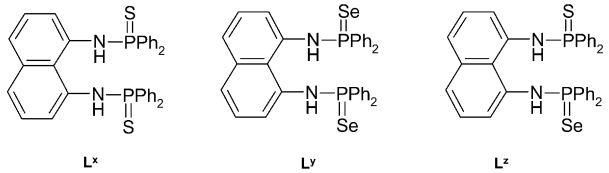


Figure 64. Chalcogen derivatives of $[(C_{10}H_6)(NHPPPh_2)_2]$.

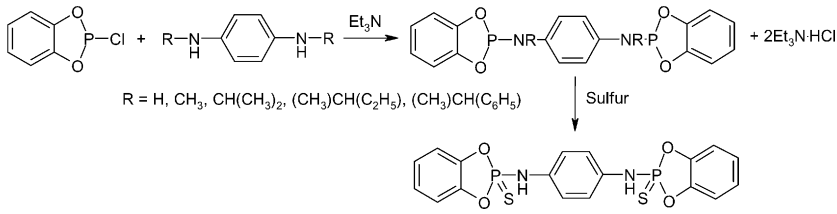


Figure 65. Synthesis of cyclic o-phenylene phosphoramidites and its chalcogen derivative.

ochloridite with primary and secondary amines in the presence of triethylamine with moderate heating in benzene. The phosphoramidite reacted with sulfur to obtain the chalcogen derivative, which was isolated and characterized (Figure 65).

A. Mustafa and co-workers[214] prepared p-phenylene-bis(diphenylphosphonamide) from the reaction of p-phenylenediamine with diphenylphosphorylchloride in pyridine (Figure 66).

Uehara and co-workers[215] prepared a very air-stable atropisomeric chiral bisphosphine, (S)-6,6′-dimethyl-2,2′-bis(diphenylphosphinamino)-biphenyl (MABP). Its rhodium(I) complex was found to be highly effective for the asymmetric hydrogenation of 2-acetamidoacrylic acid even at low temperatures (below 0°C) and low atmospheric pressure. Their synthesis is shown in Figure 67.

More recently, Saady and co-workers[216] achieved the first synthesis of fully deprotected diimidotriphosphoric acid and derivatives designed for the synthesis of PNPNP nucleotides and dinucleotides using a diaminophosphine compound as starting material (Figure 68). The synthetic pathway gave access to differently functionalized PNPNP sequences on which regioselective monodeprotection could be performed. Because benzyl esters can be removed under mild hydrogenolysis conditions, they were chosen as substituent groups. The diaminophosphine starting material used, {2-{[[bis(benzyloxy)phosphoryl]amino]methyl]benzyl} phosphoramidic acid dibenzyl ester, was prepared from o-xylylenedia-

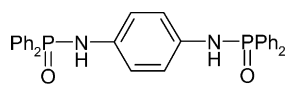


Figure 66. p-Phenylene-bis(diphenylphosphonamide).

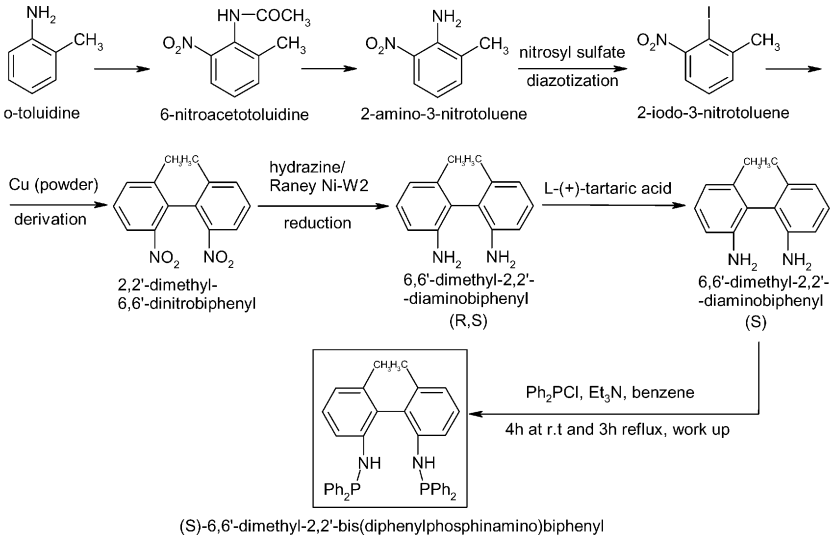


Figure 67. Synthesis of MABP.

mine and dibenzyl chlorophosphate in THF in the presence of anhydrous triethylamine at 0°C.

In 1980, Miyano and co-workers[217] reported a facile preparation of 2,2′-bis(diphenylphosphiamino)-1,1′-binaphthyl (BDPAB) (Figure 69), suggesting that it was a very interesting ligand for the rhodium catalyzed asymmetric hydrogenation of α-acylaminoacrylic acids and esters because of its structural rigidity and simplicity, resistance to racemization and effectiveness of chiral recognition. When using BDPAB in the asymmetric

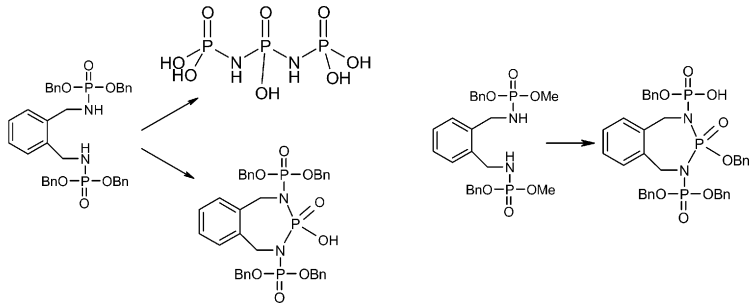


Figure 68. Synthesis of PNPNP nucleotides and dinucleotides.

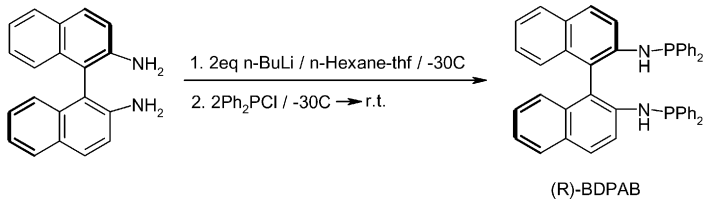


Figure 69. Synthesis of BDPAB.

reaction, the corresponding amino acids of up to 95% optical purity were obtained.

The same authors, four years later, reported the synthesis of Me-BDPAB (Figure 70) and along with BDPAB, MABP and BINAP they studied their effectiveness as chiral ligands in the same rhodium(I) catalyzed asymmetric hydrogenation of α-acylaminoacrylic acids and esters.[218] Both Me-BDPAB and BDPAB were found to produce high optical yields (80–95%) and to form nine-membered chelate ring rhodium(I) complexes with a square planar rhodium(I) center. Although (S)-BDPAB always gave (S)-α-amino acids and (R)-BDPAB the preferred (R)-counterparts, MABP (Figure 69), which seems to form closely related Rh(I)-complexes to BDPAB, gave opposite enantioselection in the hydrogenation of (Z)-α-acetamidoacrylic acid to N-acetylalanine.

Attempts to synthesize the ethyl-analogue of Me-BDPAB, (Et-BDPAB), were unsuccessful, presumably because the N-ethyl substituent

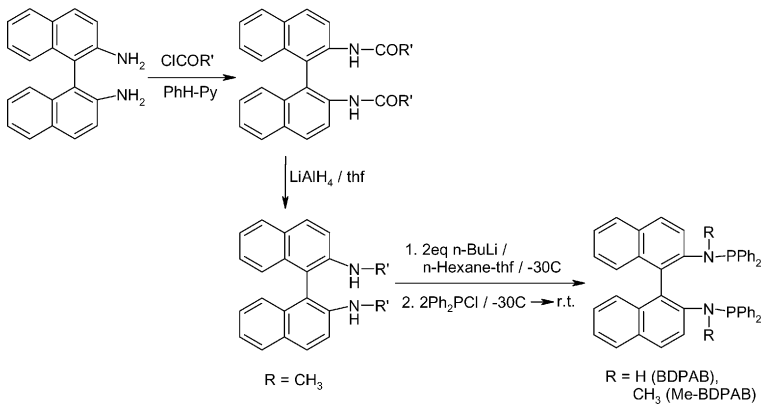


Figure 70. Synthesis of BDPAB and Me-BDPAB.

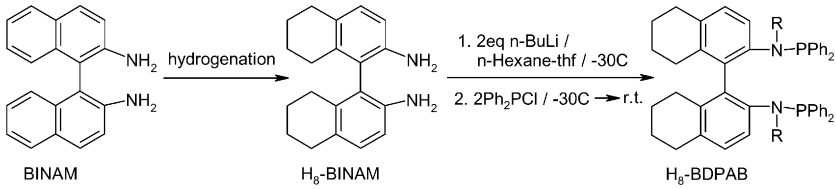


Figure 71. Synthesis of H_8-BDPAB (2,2′-bis(disphenylphosphinoamino-5,5′,6,6′,7,7′,8,8′-octahydro- 1,1′-binaphthyl).

imposes severe steric hindrance on the amide anion due to steric repulsion by the naphthalene nucleus and thus inhibits the nucleophilic attack at the phosphorus center.

More recently, Zhang and co-workers[219] achieved the preparation of a new bis(phosphinoamine) ligand with a similar amine backbone to BDPAB but without the aromatic environment on the rings remote from the nitrogen atoms, H_8-BDPAB (2,2′-bis(diphenylphosphinoamino-5,5′,6,6′,7,7′,8,8′-octahydro- **1**,1′-binaphthyl). It was prepared via partial hydrogenation of BINAM followed by reaction with Ph_2PCl (Figure 71).

They found consistently higher enantioselectivities in the enantioselective hydrogenation of chiral amine derivatives with rhodium(I)-(R)-H_8-BDPAB than when BDPAB was used. They concluded that the reason for the increase in the enantioselectivity of the catalyst was related to the increased steric interactions caused by the partial hydrogenation of the binaphthyl backbone.

Ligands $P_xN(CR_2)_nNP_x$, where n = 5 and R = alkyl or aryl groups and $P_xNCH_2CH_2$-O-$CH_2CH_2NP_x$, where P_x = P(III) or P(V), have also been prepared and studied.

Schirmer and co-workers[220] prepared a series of group 6 complexes $[M(CO)_4(PNP{=}O)]$ and $[M(CO)_5(NMe_3)]$ (M = Cr, Mo, W) with N,N′-bis(diphenylphosphino)-2,6-diaminopyridine and trimethylamine oxide characterizing the products crystallographically. The same authors[221] published the X-ray crystal structure, preparation and properties of rigid tridentate chelate complexes of the mentioned bis(aminophosphine) ligand with M(II) and M(O) transition metals (M(II) = Ni, Pd, Pt; M(O) = Cr, Mo, W) (Figure 72). Those complexes appeared to show a nearly planar tridentate chelate ring system where a π electron delocalization effect is manifested. Some of those complexes have shown a relative activity in hydrogenation reactions as catalysts.

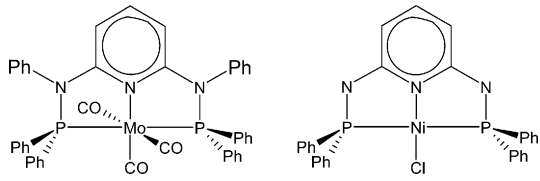


Figure 72. N,N′-bis(diphenylphosphino)-2,6-diaminopyridine-complexes.

The synthesis of macrocyclic phosphoramidites and thiophosphoramiditates with potential polydenate properties was performed by Bengourina and co-workers.[222] The cited compounds were obtained from the reaction of the chosen diamine with a bicyclic 1,3,2-oxazoniaphospholane salt and subsequent reaction with elemental sulfur (Figure 73).

Very recently, a four–step synthesis of 1,3-dihydrobenzodiazaphospholes, which contains two N-acyl diazaphospholine moieties, has been described (Figure 74, e.g R = H, X = CH_2OCH_2).[223]

Phosphinoamine Ligands from Cyclic Amines; Piperazine, Homopiperazine and Cyclam Phosphine Derivatives

This thesis concerns compounds where the diamine used to obtain the bis(aminophosphines) or bis(aminophosphites) is part of the piperazine or homopiperazine ring. Because of the close structural similarity, we

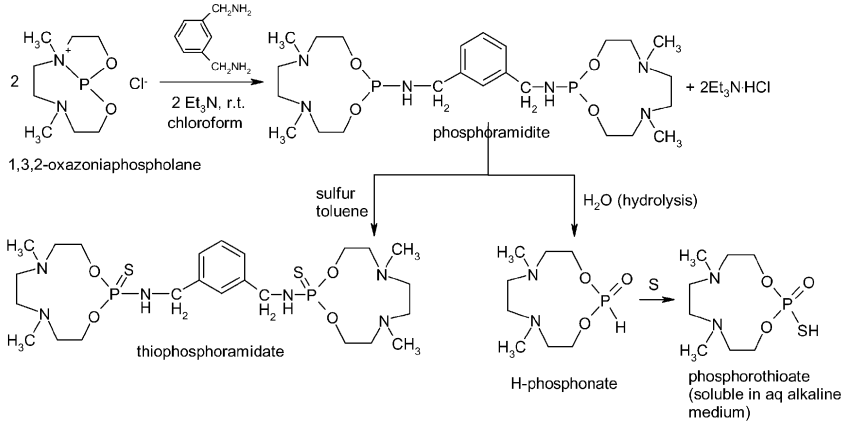


Figure 73. Synthesis of macrocyclic phosphoramidites and thiophosphoramiditates.

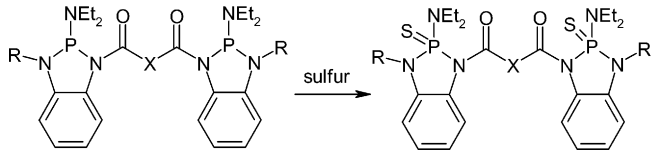


Figure 74. Synthesis of 1,3-Dihydrobenzodiazaphospholes.

now extend our overview to those bis(aminophosphines/phosphites) where the diamine was part of the analogue six-, seven- or eight-membered ring.

Zikolova and co-workers[224] synthesized a series of piperazine derivative compounds (Figure 75) because of their potential antitumoral activity. The compounds were prepared by reaction of piperazine with 2-chlorotetrahydro-2-H-1,3,2-oxazaphosphorine-P-oxide.

Kropacheva et al.[225] described the preparation of N,N′-di(ethylene) triamides of phosphoric and thiophosphoric acids, where the R group is unsubstituted piperazine (Figure 76).

Dipine is also of interest because of its potential antitumoral activity and to understand its pharmacokinetics, there have been studies on the synthesis of the ^{14}C labeled Dipine in different sites, such as in the tetraethylenimide carbons or phosphorus centers[226] and in the piperazine[227] ring. The same research group studied the mass spectra of Dipine and thiodipine to elucidate the metabolism of antitumor preparations.[228–230]

With similar skeletons but slightly different cyclic substituents on the phosphorus atoms, Cremlyn and Akhtar prepared some heterocyclic phosphorochloridates and other heterocyclic organophosphorus compounds,[231] which are of special interest as potential pesticides (Figure 77).

The same research group[232] synthesised some phosphorylated derivates of piperazine by reaction of piperazine with phosphoryl or thiophosphoryl chloride to obtain the dichloridate (I) or dichloridothioate (II). The reaction of (I) with primary amines in a molar ratio 1:4 gave the corresponding amidic chlorides (III). These were characterized as the derivates (IV, V, VI). The compound (II) reacted similarly with

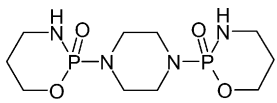


Figure 75. Cyclic phosphoramide piperazine derivatives.

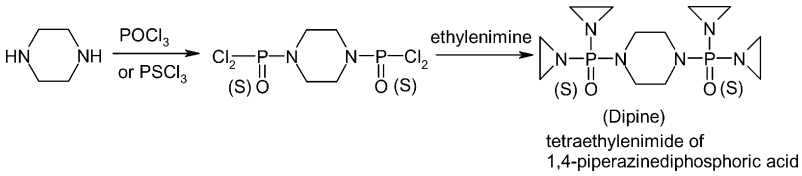


Figure 76. Bisphosphorus derivatives of piperazine.

isopropylamine to give the chloridothioate (VII). When (I) and (II) reacted with phenylhydrazine in molar ratio 1:8, the corresponding derivates (VIII and IX) were produced (Figure 78).

Piperazine and phenyl phosphorodichloridothionate react to give N,N′-bis(phenoxyphosphinothioyl)piperazine or 7-phenoxy- 1,4-diaza-7-phosphabicyclo[2,2,1]heptane-7-thione, depending on the reaction medium.[182]

The chiral phosphoramide, 1,4-bis[(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine (Figure 79), was synthesized from the reaction of 1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo (3.3.0)octane with piperazine and was successfully used as a catalyst in the borane-mediated asymmetric reduction of prochiral α-haloketones, giving the corresponding α-halo alcohols with 90-95% enantiomeric purities.[233]

The reaction of piperazine with Ph_2PCl to give the bis(aminophosphine) compound has been poorly investigated prior to our work. In a Japanese patent,[234] the reaction of piperazine with Ph_2PCl in benzene was described and the product obtained was reported to be the mono-substituted derivative, $Ph_2PN(C_2H_4)_2NH$. When Thomas et al.[235] repeated the reaction, they produced the bi-substituted product, $Ph_2PN(C_2H_4)_2NPPh_2$, and not the previously reported mono-substituted derivative. No coordination chemistry was described for the bis-substituted product.

The only similar example that we have found in the literature where the two nitrogen atoms belong to an eight-membered ring with three

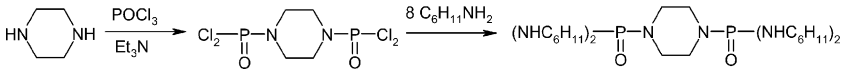


Figure 77. Preparation of some heterocyclic piperazine derivatives.

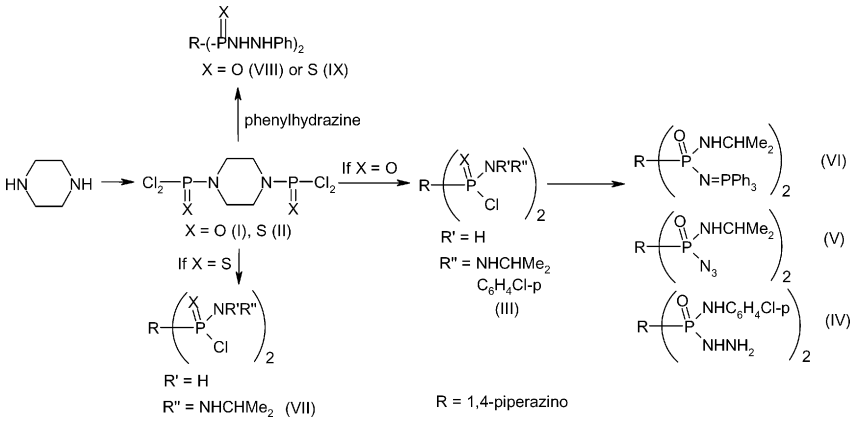


Figure 78. Synthesis of phosphorylated derivatives of piperazine.

carbons bridging the nitrogen atoms was by Huttenloch and co-workers,[236] who studied chiral bicyclic phosphoramidites for their applications in catalytic asymmetric C-C bond formation by Cu-catalyzed addition of different dialkylzinc reagents to cyclic and acyclic enones (enantiomeric ratio found was up to 91:9) and Rh-catalyzed hydrogenations of α,β-unsaturated esters, giving enantiomeric ratios up to 95:5. The best results were obtained when using 1,5-dimethyl-3,7-bis[(R)-1, 1′-binaphythyl-2,2′-dioxaphosphepinyl]-3,7-diazabicyclo-[3.3.0]octane.**(A)** (Figure 80).

To the best of our knowledge there is no record in the literature of any type of bis(phosphinoamine) where the two nitrogen atoms are contained in a homopiperazine ring apart from our own work.[240,242] Because of our study of cyclic amine containing bis(aminophosphines), it is important to mention those investigations where cyclam or closely related diamines have been used to prepare diphosphinoamine ligands.

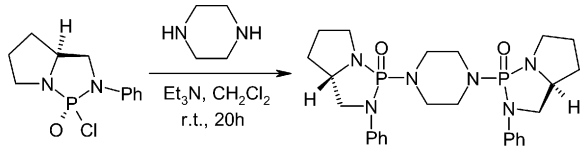


Figure 79. Preparation of 1,4-bis[(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0) octan-2-yl]piperazine.

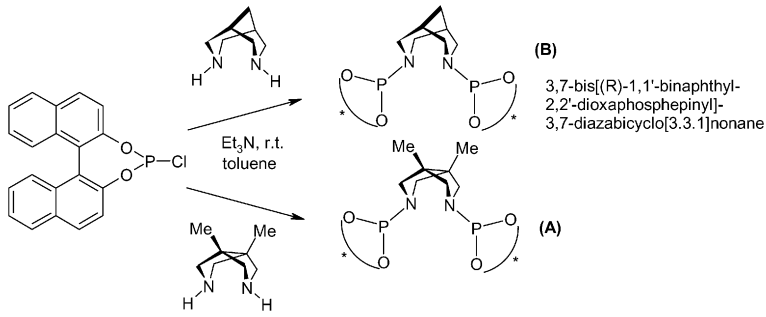


Figure 80. Synthesis of chiral phosphoramidite ligands (A) and (B).

In 1992, Khasnis and co-workers[237] investigated a metallic compound where cyclen was involved. They reported the first anionic η^2-cyclenPM(M = transition metal) derivative, Li[(η^2-cyclenP)Mo(CO)$_4$], by treatment of HcyclenPMo(CO)$_5$ (synthesized form cyclenPH and molybdenum hexacarbonyl) with butyllithium, and its reactivity with Ph_2PCl or alkyne dimethylacetylenedicarboxylate (DMAD) (Figure 81).

With the aim of finding an effective chemotherapeutic treatment for human immunodeficiency virus (HIV) infection, Bridger et al.[238] studied agents that targeted specific and critical events in the HIV replicative cycle. To achieve the synthesis of the desired phenylenebis(methylene)-linked bistetraazamacrocycles, they performed first the macrocyclization of some bissulfonates with toluene-sulfonamides, which yielded some macrocyclic bis(aminophosphites), as can be seen in Figure 82.

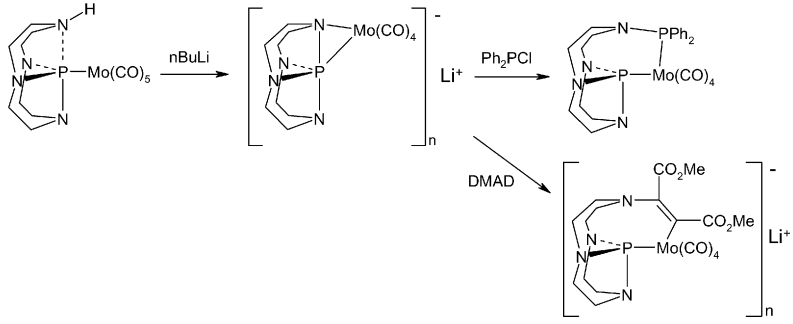


Figure 81. Insertion of a phosphenium ion and an activated alkyne into the metal-nitrogen bond of Li[(η^2-cyclenP)Mo(CO)$_4$].

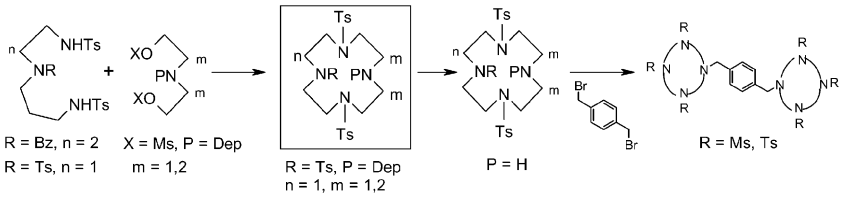
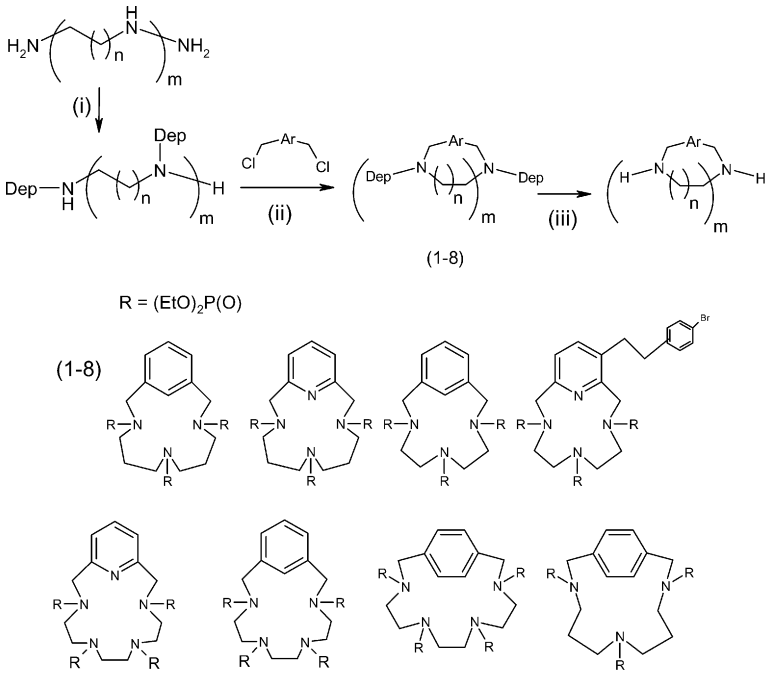


Figure 82. Synthesis of phenylenebis(methylene)-linked bis-tetraazamacrocycles (Dep = $(EtO)_2PO$).

Chellini and co-workers prepared a series of polyazacyclophanes[239] By reaction of the corresponding polyamines with diethyl phosphonate and CCl_4 in a solid base/organic liquid two-phase system in the presence of Bu_4NBr (as a phase transfer catalyst), they achieved fully



(i) $(EtO)_2P(O)H$, CCl_4, $NaHCO_3$, Bu_4NBr, r.t.; (ii) 50% NaOH/PhMe, $Bu_4N(HSO_4)$; (iii) HCl(g) in dioxane, r.t., NaOH.

Figure 83. Preparation of polyazacyclophanes.

diethoxyphosphoryl(Dep)-protected polyamines. The second step consisted of phase catalyzed alkylation of phosphoramidates with bis(chloromethyl)arenes in the presence of $Bu_4N(HSO_4)$, followed by the deprotection to give the polyazacyclophanes (Figure 83).

CONCLUSION

Phosphines containing P-N bonds represent a major class of molecules. The area is likely to continue to grow as the demand for carefully designed phosphines continues unabated. The ease of P-N bond forming reactions and the massive range of amines makes this an attractive area where careful control of molecular shape is important.

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