Review
The Backbone of Success of P,N-Hybrid Ligands: Some Recent Developments

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Abstract: Organophosphorus ligands are an invaluable family of compounds that continue to underpin important roles in disciplines such as coordination chemistry and catalysis. Their success can routinely be traced back to facile tuneability thus enabling a high degree of control over, for example, electronic and steric properties. Diphosphines, phosphorus compounds bearing two separated P\textsubscript{III} donor atoms, are also highly valued and impart their own unique features, for example excellent chelating properties upon metal complexation. In many classical ligands of this type, the backbone connectivity has been based on all carbon spacers only but there is growing interest in embedding other donor atoms such as additional nitrogen (–NH–, –NR–) sites. This review will collate some important examples of ligands in this field, illustrate their role as ligands in coordination chemistry and highlight some of their reactivities and applications. It will be shown that incorporation of a nitrogen-based group can impart unusual reactivities and important catalytic applications.

Keywords: amine groups; chelate effect; coordination chemistry; NMR spectroscopy; P ligands; synthesis

1. Introduction

Phosphorus compounds are of widespread fascination due to their importance in organic, coordination/organometallic chemistry, catalysis, and numerous other applications. Many such P-based compounds are derived from simple fundamental building blocks such as white phosphorus (P\textsubscript{4}) for example. Various industrial processes for accessing simple P-based compounds are well known and, nowadays, current challenges in generating such compounds more efficiently \cite{1} and sustainably are being actively pursued \cite{2}. Interest has spurred in converting P\textsubscript{4} into useful compounds directly \cite{3,4} and this area will no doubt continue to be a highly important area going forward.

The following review will provide a brief update, from the Author’s perspective, of selected examples of chelating diphosphines with a central nitrogen functional group in the backbone and illustrate the diverse behaviour(s) imparted by this additional donor atom. The focus will be on ligand design and synthesis protocols, \textsuperscript{31}P\textsubscript{1}H NMR spectroscopy as a useful tool for assessing purity and characterisation and an illustration of how such ligands are used, primarily in coordination chemistry and catalysis. This review is by no means exhaustive but will highlight the growing emergence of these ligands versus their all-carbon backbone counterparts which historically have been known for several decades. Depending on the diphosphine ligand, 4-, 5-, 6- (Figure 1) and larger chelate/macrocyclic rings with one (or more) –NH–/–NR– sites are formed upon complexation to a range of typical transition metals. The present review aims to embrace the Reader with a perspective of the importance of these ligands and their continuing prominence going forward. These ligands constitute important families to the already extensive number of known phosphorus compounds. As will be illustrated, the tuneability of phosphines thereby precisely controlling properties such as electronic effects, steric, asymmetry, solubility, chirality etc is applicable to the diphosphines discussed here.
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![Chemical structure](image)

**Figure 1.** Cartoon illustration of some known diphosphines bearing a N atom in the backbone (R, R’ = alkyl, aryl group).

Unlike general synthetic phosphorus methodologies widely used for constructing P–C bonds [5], the transformations shown in Scheme 1 are simple condensations and employ, typically, secondary chlorophosphines or secondary phosphines as key starting reagents. In many instances, especially the Phospha-Mannich based reactions [6,7], work-up and isolations are straightforward and target P(III) compounds can often be accessed in good to high yields. Furthermore, in an industrial context, these reactions are important in the industrial preparation of flame retardants for cotton based materials using [P(CH2OH)4]+ salts and condensation with urea [8]. The utility of this approach will be highlighted, using suitable examples, in the following sections.

Scheme 1. Key steps for relevant P-based ligand syntheses utilising R$_2$PCl and R$_2$PH.

2. P–N Chemistry

2.1. Synthesis of Selected Examples

The ligand 1a (Figure 2), bearing a phenyl substituent (X = Y = H), has been known for over 25 years [9] and related analogues have been described [10]. The pyridyl analogue, 1b, was first reported in 2000 by Woollins and co-workers and prepared from 2-aminopyridine, NEt$_3$, and ClPPh$_2$ at 0 °C and isolated as a white powder in 78% yield [11]. Reaction of an in situ generated lithiated amide, with 1 equiv. of Ph$_2$PCl, afforded air stable 1c as a white solid in 66% yield and showed a 31P signal at 38.5 ppm [12]. A single crystal X-ray structure analysis of 1c revealed a P–N distance of 1.702(13) Å. Ligand 1c could function in a P-monodentate fashion, but also through one of the phenyl rings on the benzhydryl group as a tethered $\eta^6$-arene when bound at a Ru(II) piano-stool centre. Pope and co-workers [13] prepared a range of fluorescent phosphinous amides 1d–f from a stoichiometric reaction of the appropriate primary amine:ClPPh$_2$ in CH$_2$Cl$_2$, and NEt$_3$, at 0 °C. It was found that 1d–f could be isolated as colourless, yellow oils or as a dark orange solid and showed 31P signals at 42.2, 42.1, and 26.1 ppm, respectively. These ligands were coordinated to gold(I) and displayed interesting photophysical properties. In 2022, unlike conventional pathways to phosphinoamines (Route A, Scheme 1) previously highlighted, an electrochemical pathways route has been reported as an alternative strategy for gen-
erating P–N bonds. For example, **1g** could be accessed through coupling of secondary amines/phosphines and concomitant H$_2$ evolution [14]. Utilising a single P–N bond forming step has successfully enabled the preparation of PN$_2$-tridentate ligands such as **1h** and **1i** [15,16] which have subsequently been widely studied in various catalytic transformations via metal ligand cooperative catalysis. The synthesis of **1h** was accomplished using NEt$_3$/tBuLi, tBu$_2$PCl, and 6-[diethylamino)methyl]pyridine-2-amine. The tridentate phosphinoamine, **1j**, was prepared from Cy$_2$PCl and BzNH$_2$ in C$_6$H$_6$, in the presence of excess NEt$_3$, and was isolated as a colourless solid in 69% yield [17]. The $^{31}$P NMR of **1j** showed one resonance for the PN atom at 32.6 ppm (as a dd) and $-12.6$ ppm (as a d for the -PCy$_2$ groups, Table 1). Other multidentate ligands, such as **1k** [18], were synthesised by reaction of (2-C$_5$H$_4$N)CH$_2$N(CH$_2$CH$_2$NH$_2$)$_2$ with 2 equiv. of $^1$Pr$_2$PCl in THF in the presence of excess NEt$_3$ to afford the desired product as a pale yellow oil in 88% yield and a $^{31}$P NMR at 63.9 ppm (in C$_6$D$_6$). P–N formation can be accomplished, through condensation, upon reaction of 2-aminopyridine and [ClP(NMe$_2$)$_2$, which upon subsequent deprotonation with excess NEt$_3$ to afford the desired product as a pale yellow oil in 88% yield and a $^{31}$P NMR at 63.9 ppm (in C$_6$D$_6$). The three NH sites could further be readily deprotonated, with tBuLi and quenched with GaCl$_3$, to form a corresponding Ga compound. The ligand **1n** (abbreviated as TPAP) was synthesised from reaction of tris[2-[N-(2-pyridinmethyl)]-aminopropyl]amine and ClP(NMe$_2$)$_2$, which upon subsequent deprotonation with excess tBuOK in THF gave **1n** as a white solid which displayed a $^{31}$P resonance at 126 ppm [22,23].

![Figure 2. Selected examples of phosphinoamines bearing one or more P–N bonds.](image-url)

A well-known transformation of tertiary phosphines is their oxidation and this reactivity is also the case for phosphinoamines which react with H$_2$O$_2$, elemental sulfur or selenium or even BH$_3$.SMe$_2$ to give the corresponding P(V) analogues. These aminophosphine chalcogenides display a rich and varied chemistry towards a range of alkali metal complexes, frequently involving deprotonation of the NH group [24].
2.2. Importance of –N(H)—Backbone Functionality in P–N Ligands

The impact of an –N(H)— group in catalysis can be nicely illustrated by the methyl substituted derivative Ph₂PN(Me)(2-C₅H₄N) 1o which could be prepared from 2-(methylamino)pyridine in Et₂O and nBuLi as base followed by quenching with ClPPh₂ [25]. After workup, 1o was isolated as a pale yellow crystalline solid in 65%. The palladium(II) catalysed methoxycarbonylation of olefins using 1b as ligand, bearing an –NH— spacer, was found to be an efficient catalyst system. In contrast, when using 1o instead, a significantly reduced catalytic activity was observed thereby demonstrating an important effect of the –NH— group. The free –NH— group in these singly substituted phosphinoamines also enables further P–N bond coupling reactions to occur leading to, for example, unsymmetrical P–N–P diphosphinoamines, as will be discussed further in Section 3.2.

Coordinated aminophosphines, bearing an –NH— group, often display excellent hydrogen bonding capabilities and are often investigated using single crystal X-ray crystallography. For example, cis-dichloroplatinum(II) complexes of ester functionalised analogues of 1a show intramolecular N–H⋯ClPt H-bonding [10]. With the inclusion of an additional acceptor, such as that in 1b, intermolecular N–H⋯N hydrogen bonding linking two molecules into a dimer pair was observed [11]. Other H-bonding motifs have also been observed but are not discussed here.

Deprotonation of the secondary amine group can also enable amido based ligands to be prepared as illustrated by the elegant work of Velian and co-workers [26]. This group showed that the coordinated Ph₂PN(H){C₆H₄(4-Me)} ligand in a cobalt selenide cluster could be deprotonated, using nBuLi and reacted with FeCl₂, to form a mixed Co/Fe cluster in which [Ph₂PN(C₆H₄(4-Me))]⁻ bridges an Fe and Co metal centre. Likewise, a copper complex of 1j, was found to undergo deprotonation with KH to form a binuclear amido complex in which 1j functions as a P₃N-tetradentate ligand [17]. Deprotonation of 1m with nBuLi was shown to afford trianionic trisamido ligands which could be used to form an interesting array of heterometallic complexes [18,19]. The –NH— group in complexes of pincer ligands (e.g., 1h, 1i) play an important catalytic role through metal-ligand cooperation involving dearomatisation/rearomatisation via deprotonation/reprotonation steps [16].

3. P–N–P Chemistry

3.1. Synthesis of Selected Examples

Small bite-angle diphosphines such as the ubiquitous dppe [bis(diphenylphosphino)ethane] have attracted much interest over the years as an excellent chelating or bridging ligand for mononuclear and polynuclear metal centres. Closely related to dppe, namely dppa [bis(diphenylphosphino)amine, Figure 3], has also been widely studied as an excellent coordinating ligand [27–30]. One further attractive advantage of dppa, over dppe, is the ease by which it is possible to further functionalise the central amine with a range of different substituents and some highlights to demonstrate this behaviour will be reviewed here. The diphosphine, dppa, can readily be synthesised from ClPPh₂ and (Me₃Si)₂NH and isolated as a white solid [31].

One of the most spectacular successes of bis(phosphino)amines in catalysis has focused on extensive studies of PNP ligands that have been reported, in relation to the formation of 1-octene via a Cr catalysed ethylene tetramerisation [32]. A typical PNP ligand is based on Ph₂PN(’Pr)PPh₂ (2a) and an extensive library of other –N(alkyl)— based systems have been reported [33,34]. Suntharalingam and co-workers [35] prepared a simple alkyl chain (diposphino)amine, Ph₂PN(C₆H₁₃)PPh₂ (2b) from n-hexylamine and 2 equiv. of ClPPh₂ in CH₂Cl₂ in the presence of NEt₃ and was isolated as a white solid in 81% yield. A diagnostic ³¹P resonance at δ 62.1 ppm (in CDCl₃) was observed (Table 1). Homoleptic Group 10 metal complexes were prepared, as their tetrafluoroborate salts, and the Pd/Pt complexes were shown to be extremely potent complexes for CSC mammosphere activity.

Additional functionalities have been incorporated into the –N(R)— backbone (2c, 2d) and, in these cases, no further donor atom participation was found in the resulting complexes that were studied [36,37]. Khan and co-workers have used some simple,
3.2. Importance of –N(R)– Backbone Functionality in P–N–P Ligands

The –NH– backbone functionality in P–N–P ligands is a good donor, for H-bonding, and has been shown to H-bond to various solvents (e.g., dioxane, MeOH, acetone) and anions (e.g., PF$_6^-$) [27–30].

Furthermore, like dpmm, it is possible to deprotonate the –NH– proton to give the corresponding diphenylphosphinoamido anion which could also coordinate to metal centres. To illustrate this point, Kemp and co-workers [43] prepared a five-co-ordinate indium(III) complex In(iPr$_2$PNPiPr$_2$)$_2$Cl by reaction of (iPr$_2$P)$_2$NLi and InCl$_3$ in Et$_2$O/THF.

Routes to increasing donor functionality in PNP ligand systems have been realised through the works of several groups. Balakrisna and co-workers [44] described a new terpyridine based diphosphinoamine 2i (Figure 4) prepared from reaction of the parent amine and CIPPh$_2$ in CH$_2$Cl$_2$ and the presence of NET$_3$. The phosphine 2i was isolated as a colourless solid in 48% yield and displayed a characteristic $^{31}$P resonance at δ 69.3 ppm (in CDCl$_3$). From a single crystal X-ray analysis, the two P–N bond distances are 1.713(2) and 1.721(2) Å with a P–N–P angle of 114.46(12)$^\circ$. The sum of the angles around the nitrogen centre is 359.77$^\circ$ indicating a planar geometry. Diphosphine 2i was shown to exhibit various ligating motifs (P,P-chelate, P,P-bridging, or as a multidentate system using all P donor atoms). Braunstein and co-workers [45,46] prepared a series of bis(phosphino)amines, including the thioether ligands 2j and 2k [R = PhCH$_2$, CH$_3$(CH$_2$)$_3$]. These were prepared from the corresponding primary amines and CIPPh$_2$, in the presence of NET$_3$, in Et$_2$O at 0 °C. Both 2j and 2k showed a single peak at δ 62.9 ppm in their $^{31}$P/$^1$H NMR spectra and both ligands could be used to afford heterodinuclear and trinuclear metal complexes.
through P2S-binding. Roodt and co-workers [47] developed new pathways to potentially water-soluble P–N–P ligands such as 2l. Hence, the N-Boc ligand was synthesised from the free primary amine and ClPPh2, in CH2Cl2, in the presence of NEt3. The product was isolated as a white solid in 81% yield and the 31P showed a signal at 63.8 ppm (in CD2Cl2). This ligand could be “protected” by coordination to an [Re(CO)3] fragment, whereupon the protecting group was removed with CF3CO2H followed by neutralisation to give a free pendant amine site.

![diagram](image)

Figure 4. Selected examples of functionalised bis(phosphino)amines.

Unsymmetrical R’2PN(R)PR’2 ligands [48–50] could also be synthesised through stoichiometric reaction of two different chlorophosphines and MeNH2 or PhobPN(H)Me (Phob = phobane) and Ar2PCI in the presence of NEt3. There was also a strong correlation with iminobisphosphine PPN products formed under certain experimental conditions [49–51]. On this theme, another intriguing reaction to note, for bis(phosphino)amines, is their rearrangement to iminobisphosphines, which is reversible and promoted by protonation/deprotonation [52]. The N=P–P group is isomeric to the P–N–P systems. The bis(phosphino)amine 2m reacts with HBF4 in CH2Cl2 to give 2n, as the tetrafluoroborate salt in quantitative yield. Deprotonation of 2n with NEt3 regenerated 2m. Agapie and co-workers have also shown the importance of aluminum induced isomerisation of PNP to PPN ligands and relevance to Cr based ethylene tetramerisation catalysis [53].

The impact of an –N– substituent is clear with regard to the relationship between steric effects and 1-octene/1-hexene selectivities using PNP/Cr complexes. Roodt [54] introduced a steric parameter to describe the steric bulk at the N atom of a range of bis(phosphino)amine ligands, a parameter similar to the Tollman cone angle widely appreciated. Furthermore, simple –N(R)– group manipulation (R = H, Me, Et) of bis(diphenylphosphino)amines can afford a range of novel, unique, polynuclear gold(I) sulfido complexes as reported in 2020 by Yam and co-workers [28].

Finally, our group has shown [41] that the P–N bond undergoes room temperature methanolysis in which one bond is cleaved affording a phosphinoamine, bearing an –NH– group, and a cis MeOPPh2 phosphinite bound at a Pt(II) square planar metal. Furthermore, C–H activation of an ortho C–Harom was found to occur, within the coordination sphere, affording a five-membered metallacycle that was confirmed by single crystal X-ray crystallography.

4. Bicyclic P–N Chemistry

Radosevich and co-workers [55] reported the synthesis of two phosphorus triamides 3a/3b (R = Me, iPr, Figure 5) from the reaction of triamines and PCl3 and NEt3 in a mixed THF/Et2O solvent to give 3a in 80% yield as an off-white solid. The N-propyl analogue, 3b, was prepared in 83% yield. For 3a the observed 31P shift was at 159.8 ppm and the P–N distances were found to be 1.7014(14) Å and 1.7190(13) Å whereas the pseudoaxial nitrogen was longer [1.7610(12) Å]. The synthesis of an unusual 10-aza-9-phosphatriptycene, [56] was achieved by reaction of the brominated tertiary amine and iBuLi, followed by addition of (ArO)3P (1 equiv) to give 3c in 71% yield and whose 31P displayed a signal at −77.0 ppm.
1,10-phenanthroline [59]. The PN$^-$ was prepared from the parent amine, HPPh$_2$, CH$_2$O in THF at 60 °C as a colourless oil in 80% yield and showed a signal at $-16.7$ ppm (Table 1). Under dynamic vacuum, the reaction of aniline and Ph$_2$PCH$_2$OH gave the phenyl analogue, 4b, in 95% yield and showed a signal at $-19.4$ ppm (in C$_6$D$_6$).

The pyrimidine ligand 4s was prepared from Ph$_2$PH, (CH$_2$)$_3$O, and 2-aminopyrimidine, in C$_7$H$_8$ and isolated in 93% as a white solid [58]. The $^{31}$P chemical shift was indicative of single substitution. The 1,10-phenanthroline functionise ligand, 4d, could be isolated in 63% yield as a yellow solid, from the in situ reaction of HPPPh$_2$, (CH$_2$)$_3$O, and 2-amino-1,10-phenanthroline [59]. The PN$_2$-tridentate behaviour could be demonstrated through coordination to Co$^{2+}$ and Ni$^{2+}$ affording octahedral complexes with two ligands per metal. Here, the ligands are either PN$_2$- or N$_2$-coordinated. In 2021, Ren and co-workers showed that 4d could afford a trinuclear Au$_2$Ag complex through PN$_2$-coordination [60]. An alternative entry route to Ph$_2$PCH$_2$OH could be achieved through base (NEt$_3$) treatment of [PPh$_2$(CH$_2$OH)$_2$]Cl [61]. Accordingly, this was used to access 4e in 95% yield and which displayed a typical $^{31}$P resonance at $-35.9$ ppm. The corresponding oxide was obtained through reaction with aq. H$_2$O$_2$ in CHCl$_3$. The phosphino-aza crown 4f could be prepared from the parent amine, HPPPh$_2$, CH$_2$O in THF at 60 °C as a colourless oil in 80% isolated yield and showed a $^{31}$P chemical shift at $-26.3$ ppm [62]. Using a Re(I) complex of 4f incorporating the macrocyclic ring promoted binding of Group 2 metal ions. In 2021, our group recently described an unusual approach for obtaining coordinated P–C–N ligands from a bridging P–C–N–C–P ligand that was promoted by internal acid protonation from an arene group located on the central N atom [63]. This was shown to be a remarkably clean reaction affording 4g [and only RuCl$_2$(p-cym)(Ph$_2$PH), cym = cymene] and the progress of the reaction could be carefully monitored, in solution, by NMR spectroscopy. In the absence of a metal, this reaction did not proceed cleanly. It should also be added that P–C–N ligands can also undergo P–C cleavage affording a secondary phosphine complex. Reaction of tris(2-aminophenyl)amine in CH$_2$Cl$_2$ with Ph$_2$PCH$_2$OH (3 equiv.) in the presence of CaH$_2$ to remove H$_2$O, gave the phenyl 4h compound as a pale white solid in 82% yield and with a $^{31}$P of $-19.6$ ppm (in C$_6$D$_6$) [64]. A similar approach could be employed, for the isopropyl analogue of 4h, using $^{3}$Pr$_2$PCH$_2$OH affording a white powder in 90% yield [65(P) 3.1 ppm, C$_6$D$_6$] [65]. Finally, the success of Phospha-Mannich condensations, with Ph$_2$PCH$_2$OH, could be realised for the synthesis of highly decorated dendrimers with multiple terminal N–C–PPh$_2$ functionalities [66].
The synthesis of tripodal aminomethylphosphines, 4i [67], 4j [68–73] and 4k [74] have successfully been achieved through threefold condensation using P(CH$_2$OH)$_3$ and three equiv. of the appropriate amine, either in dynamic vacuum or using toluene as solvent in an azeotropic distillation to remove water. For 4k, the use of [P(CH$_2$OH)$_4$]Cl as a P(V) precursor and reaction with 4 equiv. of amine afforded the corresponding tetraaminoalkylphosphonium salts, followed by reduction with $^3$BuOK, gave the tripodal ligands in >85% isolated yields.

5.2. Importance of –N(H)– Backbone Functionality in P–C–N Ligands

The –N(H)– functionality can undergo intermolecular N–H ⋯ O H-bonding to solvent molecules such as MeOH and EtOH. In tripodal ligands such as 4f intramolecular N–H ⋯ N H-bonding persists between adjacent arms of the aminomethyl groups on P [74].

The –NH– group was shown to promote protonolysis of Ln$^{nacnac}$LnR$_2$(THF) (Ln = Y and Lu) with 2 equiv. of Ph$_2$PCH$_2$N(H)Ph yielding phosphinoamido complexes. Further reaction with Ni(COD)$_2$ (COD = cycloocta-1,5-diene) resulted in an unusual heterobimetallic species in which one of the P–C bonds was cleaved and the imine group is present within the coordination sphere. Cui et al. [75] showed how [Ph$_2$PCH$_2$NPh]$^{-}$ chelating amido ligands could be obtained upon deprotonation of the secondary amine, Ph$_2$PCH$_2$N(H)Ph. Furthermore, unusual heterobimetallic complexes could be obtained in which P–C bond cleavage of one [Ph$_2$PCH$_2$NPh]$^{-}$ ligand with both the PhN=CH$_2$ and PPh$_2$ fragments present in the coordination sphere. These findings demonstrate, under these conditions, the instability of the [Ph$_2$PCH$_2$NPh]$^{-}$ ligand. Johnson and co-workers [68–73] used tripodal ligands, based on three amido and one P donor sites, for constructing novel heterometallic complexes. The synthesis of 4j was accomplished using the water-soluble trialkylphosphine, P(CH$_2$OH)$_3$ and the desired aniline under neat conditions and with use of dynamic vacuum to remove water. In some cases, it was necessary to use C$_7$H$_8$ as solvent and Dean-Stark setup to remove water. The $^{31}$P[¹H] NMR data for 4j are shown in Table 1. Reaction of 4j with excess elemental selenium in C$_7$H$_8$ gave the corresponding selenides as white solids in >80% isolated yields. The $^{31}$P[¹H] NMR spectra showed downfield singlets, flanked with $^{77}$Se satellites, with J$_{PSe}$ couplings around 700 Hz. Reaction with AlMe$_3$ resulted in loss of one of the –CH$_2$N(H)Ar arms.

Our group have previously shown that the –NH– group could be further modified to form unsymmetrical PCNCP ligands using a second equiv. of HOCH$_2$Pr$_2$ [76]. These
unsymmetrical ligands showed a range of coordination capabilities as a function of the more sterically encumbered R group. More recently, we have also shown the –NH– group could be deprotonated with base, and quenched with ClPPh2, to afford PCNP ligands (see Section 8).

6. PTA Chemistry

6.1. Synthesis of Selected Examples

PTA (1,3,5-triaza-7-phosphaadamantane, Figure 7) is a unique, air stable and water soluble trialkylphosphine that has been extensively studied [77] for its coordination capabilities [78–81], catalytic [77], and medicinal properties [82]. In 2015, an electron rich tricyclic analogue of PTA, namely CAP (1,4,7-triaza-9-phosphatricyclo[5.3.2.1]tridecane, was reported [77,83,84]. Both PTA and CAP could be prepared by Phospha-Mannich condensations of hexamethylenetetramine or 1,4,7-triazacyclononane and P(CH2OH)3 [77]. Typically, this procedure involved reaction of commercially available THPC and 1,4,7-triazacyclononane in water/NaOH to give CAP in 39% isolated yield as a white crystalline solid [84]. The 31P shows a singlet at 47.8 ppm in CDCl3 (Table 1).

Figure 7. Selected examples of PTA, CAP, and related compounds (A = anion).

Various “upper rim” functionalisations (5a, X = various enamines [85], phosphines [86], imidazolyl [87]) have been obtained, via a intermediate lithiated PTA species, thus enabling access to a greater pool of “PTA like” ligand systems. Frost and co-workers [85] showed that lithiated PTA intermediate with aromatic nitriles gave enamine modified ligands in 49–91% yields as white solids. The 31P NMR spectra show a typical single resonance around −87.0 ppm. All compounds were shown to slowly oxidise, in the solid state, but in solution this reactivity was more rapid (1 month in chlorinated solvents). Oxidation with H2O2 afforded the corresponding phosphine oxides. P,N-chelation could be demonstrated by coordination to a W(CO)4 fragment. Kwiatkowska and co-workers [88] recently reported the first examples of enantiomerically pure PTA ligands using a series of hydrolytic enzymes in a stereoselective acetylation performed under kinetic resolution conditions.

6.2. Importance of -N- Backbone Functionality in PTA and Related Compounds

Whilst various efforts have focused on “upper rim” modification of the carbon atom between P and N, the presence of N donor atoms has enabled alkylations of PTA to be performed using various benzylic halides and all showed good water solubility [89,90]. These alkylated PTA ligands 5b (A = Cl−, Br−, PF6−) could be used as Rh(I) catalyst precursors for the aqueous-biphasic hydroformylation of 1-octene [89] and as Au(I) complexes anticancer agents [90]. Other quaternisations have been reported and used to generate Ru complexes that showed cytotoxic activity towards cancer cell lines [82].

Both PTA and CAP display N-protonation characteristics that were be monitored by 31P[1H] NMR spectroscopy [77]. Our group found that cationic trialkylphosphines 5c are intramolecular H-bonded analogues of PTA and could function as effective ligands to Ru(II) and Rh(III) metal centres [91]. PTA was shown to undergo direct N-acetylation with benzoic anhydride affording 5d in 38% yield and was shown to be soluble in both water and other polar solvents [92].

Whilst various examples of complexes of PTA are known, using exclusively the P-donor, it has also been possible to construct networks using both P/N donor atoms [93].
7. P–C–N–C–P Chemistry

7.1. Synthesis of Selected Examples

As analogues of dppp [bis(1,3-diphenylphosphino)propane], P–C–N–C–P ligands have received widespread appeal. In their excellent review, Balint and co-workers [94] highlighted various aspects of P–C–N–C–P (and P–C–N) ligands and the Reader is directed here for further insights. This type of synthesis methodology (Route B, Scheme 1) can be extended to various R/R' groups on both P and N donors and studied, for example in conjunction with Cr, for tri- and tetramerisation of ethylene [95]. In some cases, the ligands 6a (Figure 8) were found to be extremely air sensitive. Typical R groups on both P centres include Ph and Cy, whilst on N they include iPr, tBu, and Ph. The bisphosphine, 6b, could be prepared under similar conditions as an air stable colourless solid and showed a $^{31}$P signal at $-25.9$ ppm [96]. Ligand 6b was found to react with Au(I) and shown to act as a bridging or chelating diphosphine depending on stoichiometry. In all cases presented so far, the –PR$_2$ groups are identical. Our group reported the first examples of nonsymmetrical P–C–N–C–P ligands 6c using a two-step synthesis [76]. This was further corroborated by the presence of two $^{31}$P signals in the NMR spectrum consistent with inequivalent P nuclei.

We also observed these ligands could bind in various motifs (P-monodentate, PP-chelate, and PP-bridging two different metal centres). The differences in ligating behaviour could be attributed to the sterics of both R groups on the two P-centres. We have also reported the synthesis of a 2-alkenyl N-arene functionalised P–C–N–C–P ligand 6d [97]. N-pyridyl functionalised bis(phosphino)amines 6e and 6f (95% yield, $^{31}$P $-27.7$ ppm) could be synthesised from Ph$_2$PH, CH$_2$O and the appropriate pyridylamine [98–101]. Both 6e and 6f show diverse coordination chemistries with Group 11 metals. Bridging P–C–N (6g) [102], 2,2'-bipyridyl diphosphine (6h) [103] and the polyphosphine P–C–N–C–P (6i) [104,105] ligands have also been reported. Tetradeutate ligands 6i, based on a phenyl, naphthyl or biphenyl scaffold have been prepared and show (by single crystal XRD) weak C–H···π interactions upon complexation to Group 11 metal centres [105]. The air stable orange ferrocenyl bisphosphinoamine 6j could be prepared, in 87% yield, from double condensation of the ferrocenyl primary amine and Ph$_2$PCH$_2$OH and showed a $^{31}$P signal at $-23.5$ ppm [106]. The X-ray structure of this compound was also determined. Likewise the carborane functionalised phosphine 6k could be prepared from CH$_2$O, H$_2$NPh in DMF at 60 °C for 3 h and showed two singlets at 30.2 and 36.6 ppm (ratio 30:1 for racmeso) for the two diastereomers [107]. Our group recently described a novel diphosphane 6l, based on two five membered, bicyclic P$_2$C$_2$N, rings that could be prepared from [P(CH$_2$OH)$_4$]$^+$ and (4-Me$_2$N)C$_6$H$_4$NH$_2$ or (4-MeO)C$_6$H$_4$NH$_2$ [108,109]. Microwave assisted Kabachnik-Fields reaction of aminomethylphosphine oxides and (CH$_2$O)$_n$ and Ph$_2$P(O)H gave the corresponding (un)symmetrical phosphine oxides, such as 6m, in excellent (>90%) yield bearing a central –NH– or –NR– group [110].

Miller and co-workers [111–113] prepared tripodal phenyl and cyclopentyl phosphines, 6n, from Ph$_2$P(CH$_2$OH)$_2$ and NH$_3$. The latter in 59% yield and showed a $^{31}$P signal at $-18.4$ ppm. Tridentate ligands 6n can be prepared either from [Ph$_2$P(CH$_2$OH)$_2$]Cl or in situ, from P(C$_5$H$_9$)$_2$H/(CH$_2$O)$_n$ and NH$_3$. The $^{31}$P($^1$H) NMR spectrum showed a singlet at $-18.4$ ppm indicative of this substitution pattern. Both P$_3$- and P$_2$-coordination modes were observed at Ru metal centres. This is a common fragment that is present in a range of phosphine ligands that are finding excellent applications in catalysis and coordination chemistry. In 2011, Gade and co-workers reported the synthesis of tridentate 2,5-dimethyl- and 2,5-diphenylsubstituted phospholanes 6o using a similar synthetic methodology [114].
Whilst many studies have focused on the use of Ph2P(CH2OH)2, the more electron rich phos-
phines, with –CO2H and/or –OH functionalities in the N-arene backbone and have found positioning to be important in determining packing arrangements as seen for various Au(I), Pd(II), Pt(II), and Ru(II) metal centres studied [118–122]. The diphosphine forms an unusual hexameric structure in which the ligand acts as a P2O-tridentate ligand [121]. We have shown, by careful manipulation of the R group on the nitrogen atom, the ability to impact a range of packing motifs through H-bonding patterns at various late transition metal centres. In addition, the position of, for example, –CO2H groups could be shown related 1,2-substituted bis(phosphino)amines as a bridging ligand. In contrast, the groups of Yamashita [115] and Hill [116,117] have observed at Ru metal centres. This is a common fragment that is present in a range of complexes have been used for the catalytic hydrogenation of CO2 and found to be active with respect to formate formation.

7.2. Importance of –N(R)– Backbone Functionality in P–C–N–C–P Ligands

Previously, diphosphine 6g bearing two secondary amine groups, is capable of acting as a bridging ligand. In contrast, the groups of Yamashita [115] and Hill [116,117] have shown related 1,2-substituted bis(phosphino)amines 6p and 6q (Figure 9) are precursors to hydroborane and PCP pincer proligands. Hence, reaction of 1,2-phenylenedi-

amine with BH2 and CH2O gave 6p in 68% yield, with both –NH– groups available for further reaction, in this case with BH3,SM2 and Pr2NH to afford a hydroborane in this case. Whilst 6q was not isolated, it is clearly an intermediate which subsequently reacts with CH2O to form N,N'-bis(phosphinomethyl)-dihydroperimidines.

Our group have been interested, for a number of years, in highly decorated ditertiary phosphines with –CO2H and/or –OH functionalities in the N-arene backbone and have found positioning to be important in determining packing arrangements as seen for various
Au(I), Pd(II), Pt(II), and Ru(II) metal centres studied [118–122]. The diphosphine \(6r\) forms an unusual hexameric structure in which the ligand acts as a P\(_2\)O-tridentate ligand [121].

We have shown, by careful manipulation of the R group on the nitrogen atom, the ability to impact a range of packing motifs through H-bonding patterns at various late transition metal centres. In addition, the position of, for example, –CO\(_2\)H groups could also result in intramolecular protonation of one of the P–C bonds forming lactone functionalised P–C–N ligands at a coordinated metal centre [63]. A similar P–C bond cleavage has been observed in a piano-stool complex of \(4i\) (X = O) which, in the Ru(II) coordination sphere, shows a single secondary aminophosphine ligand and Cp/PPH\(_3\) ligands [123]. In \(6r\), where only a singly ortho hydroxy group is available, P\(_2\)O-tripodal coordination at Re(V) and Tc(V) oxo centres has very recently been observed [124].

One of the earliest demonstrations of the importance of the pendant amine is its susceptibility towards protonation, relevant to many catalytic processes involving hydrogen. For example, elegant work by Bullock and co-workers [125] has shown that the tricarbonyl iron complex Fe(CO)\(_3\) (8a) undergoes protonation, with [(Et\(_2\)O)\(_2\)H]\([\text{B}(\text{C}_6\text{F}_5)_4]\)\(^–\) at the Fe, whilst with HBF\(_4\).OEt\(_2\), protonation occurs at the iron and pendant N. Treatment with excess HOTf gives a dicationic complex where both the Fe and N centres are protonated. Protonation reactions have also been studied in disubstituted diiron systems as well [126]. In addition to the protonation capabilities at the pendant amine, the nitrogen can also participate in further bonding to a transition metal, acting as a facial P\(_2\)N-tridentate system as found in [Mo(Cp)(PNP-\(6s\))(CO)]\(^+\) [127].

Whilst many studies have focused on the use of Ph\(_2\)PCH\(_2\)OH, the more electron rich Et\(_2\)PCH\(_2\)OH has been used to access a range of amino acid ester ligands [128]. The Rh complexes have been used for the catalytic hydrogenation of CO\(_2\) and found to be active with respect to formate formation.

The ligand \(6u\) has been used to support a Ni(0) metal centre, and immobilised within a protein scaffold via in situ amide bond formation [129]. Finally, Li and co-workers have used a hybrid NHC-diphosphine \(6v\) as a facial coordinating ligand for the Ru-catalysed synthesis of N-substituted lactams by acceptorless dehydrogenative coupling of diols with primary amines [130].

8. P–C–N–P and P–N–N–P Ligands

Synthesis of Selected Examples

Recent work by our group has shown that rare examples of P–C–N–P ligands \(7a\) (Figure 10), with an N-backbone group, could be synthesised by reaction of the singly substituted naphthyl P–C–N precursors, with CIPPh\(_2\) in the presence of LDA [131]. These ligands coordinate to Cr(0) centres generating the corresponding octahedral tetracarbonyl complexes. Furthermore, these ligands were also shown to be effective, in the presence of Cr(acac)\(_3\) and MMAO-3A, for ethylene tri-/tetramerisations. Conversely, starting from \(^1\)Bu\(_2\)PNC\(_3\)H\(_3\)N and deprotonation with \(^9\)BuLi at \(-78\) °C then quenching with \(^8\)Bu\(_2\)PCl at low temperature then warming to r.t. gave \(7b\) in 71% isolated yield [132]. Two doublets in the \(^{31}\)P NMR support the non-symmetric structure. Only 5% P–N hydrolysis took place in CDCl\(_3\) indicating \(7b\) has good solution stability under these conditions. The same approach could be used to access a series of diphosphinoindole ligands \(7c\) [133]. Reaction of the P(III) intermediate with \(^9\)BuLi, in Et\(_2\)O, at \(-78\) °C and reaction with CIPPh\(_2\) gave the chelating ligands \(7e\) in 35–73% isolated yields. The NMR spectra showed one doublet around 39 ppm for the phosphinoamine and a further second doublet around \(-25\) ppm. In relation to PNP and PCNCP ligands this is a hitherto new class of ligand that has received only limited attention so far.
The THF and could be isolated as a viscous oil showing a $8a$

In this context, the central N atom can be viewed as either neutral palindromic or anionic palindromic ligands depending on the charge at nitrogen. Usually the central –NR– group is either a secondary amine, tertiary amine or 2,6-pyridyl group for example. In this case, the role of the central N atom can be more influential on the reactivity of the complex, via electron effects and the variation of the trans influence. Some illustrative examples of ligands of this type are shown in Figure 11 and a brief discussion of the synthesis and reactivity are described here. It is important that these pincer ligands can import good stability and hence often chosen for this property.

We use some recent elegant examples, from the literature, to highlight these classes of diphosphines. As will also be mentioned, these ligands can display noninnocent behaviour and can expand the application of such complexes in transition metal chemistry. This will involve formation of a C=N double bond as will be illustrated and how this can be used to impart further reactivity, either in catalysis and/or through bond activation. Note also, the pincer arrangement also allows outer sphere effects, like what previously seen for the PCNCP ligands with regard to protonation.

The first type of R$_2$P–N–N–PAr$_2$ pincer ligands to consider (Figure 11) are those with a central –N(H)– group where R = Ph (8a) [136,137], Cy (8b) [138], tBu (8c) [139]. The Ph derivative 8a was synthesised from Ph$_2$PH, tBuOK and (ClCH$_2$CH$_2$)$_2$NH$_2$·Cl$^-$ in THF and could be isolated as a viscous oil showing a $^{31}$P shift at −20.6 ppm (C$_6$D$_6$) [136]. The tBu analogue 8c was prepared from tBu$_2$PLi and Me$_2$SiN(CH$_2$CH$_2$Cl)$_2$ at −60 °C in THF and isolated as a viscous light yellow liquid in 76% yield showing a $^{31}$P signal at 22.3 ppm (in C$_6$D$_6$). Tertiary alkylamine diphosphinoamine ligands 8d [140] and the phenyl-substituted 8e [141,142] are also known and could easily be obtained, in 44% yield, from reaction of the lithium salt and the bis(chloroethyl)amine HCl salt.

PNP pincer ligands with a pyridyl N atom are also known, both with –CH$_2$PR$_2$ groups and with –CM$_2$PR$_2$ (8f) [143,144] or –CH(CH$_2$(2-C$_5$H$_4$N))PR$_2$ (8g) [145] substituents. Furthermore, the spacer can also be a –N(H)– group, as opposed to a –CH$_2$– group, as is the case for 8h [146] and prepared by the P–N coupling of ClP(C$_6$H$_4$CO$_2$Bu)$_2$ with 2,6-diaminopyridine in the presence of NEt$_3$ and showed a $^{31}$P signal at 25.4 ppm (in CDCl$_3$). Unsymmetrical PNP-pincer ligands such as 8i is an excellent ligand, in conjunction with metals such as Mn [147–150] or Ru [151] for various catalytic transformations.

Pyridal appended (8j) [152], tetradentate P–C–N–C–C–P (8k) [152] and watersoluble derivatives (8l) [153] have also been prepared, the latter via the diprimary phosphine intermediate (H$_2$PCH$_2$CH$_2$)$_2$N(CH$_2$CH$_2$OMe).

Figure 10. Selected examples of P–C–N–P diphosphines.

Simple Ar$_2$P–N–N–PAr$_2$ ligands, 7d, can be accessed through the direct reaction of the appropriate hydrazine and ClPR$_2$ (Ar = 2-MeC$_6$H$_4$, 2MeOC$_6$H$_4$) [48].

9. P–C–N–C–C–P Ligands

9.1. Synthesis of Selected Examples

The basic backbone here represents an important ligand class of terdentate ligand, or “pincer” ligands [134,135] given they can occupy three coordination sites at a metal site.
9.2. Importance of –N(R)– Backbone Functionality in P–C–C–N–C–C–P Ligands

In a recent study in 2022 [154], the synthesis of a large family of N-amide functionalised PNP ligands 8m, including water-soluble variants [155], has been reported using an acyl chloride, NH₂(CH₂CH₂PPh₂)₂+Cl⁻ and NEt₃ in CH₂Cl₂. The ³¹P{¹H} NMR spectra show typically two singlets around −20 ppm, due to restricted amide bond rotation.

Deprotonation of the secondary amine can result in a facial PNP coordination in which there is an amido group. This can be appreciated in several examples (8n, 8o) of compounds shown in Figure 12 [156,157]. Dearomatisation is also important as a function of deprotonation and extensive studies have been undertaken in this field [135].

![Figure 11. Selected examples of P–C–C–N–C–C–P diphosphines and related analogues.](image)

![Figure 12. Selected examples of P–C–C–N–C–C–P diphosphines.](image)

10. Small/Medium Ring Based Cyclic Ligands

10.1. Synthesis of Selected Examples

The Mannich condensation reaction can be used to form chiral seven membered macrocycles [158]. As is normal for this synthesis protocol, reaction of the bis(phosphine) with (CH₂O)₃ at around 100 °C led to rac/meso hydroxymethyl functionalised diphosphine which, upon treatment with chiral amines, gave 1-aza-3,6-diphosphacycloheptanes 9a as air-stable crystalline solids (Figure 13). The X-ray structure revealed short P…P distances (3.120 and 3.118 Å) in comparison to known rac isomers. Condensations with amines such as aniline, p-toluidine and 5 aminoisophthalic acid and benzylamine were undertaken. Two ⁳¹P peaks at −25 and −27 ppm for the amines and −33.5 and −31.8 for benzylamine were observed (Table 1). The reaction of Ph(H)P(CH₂)₃P(H)Ph with CH₂O, afforded the corresponding hydroxymethyl diphosphine, then reaction with ¹PentNH₂, in DMF, gave a mixture of products as verified by ³¹P NMR [159]. Isolation of the macrocycle was possible in 21% yield and confirmed by X-ray crystallography. Helm and co-workers [160] expanded this seven-membered ring ligand family to other 4-C₆H₄X analogues (X= OMe, H, Me, Br, Cl, CF₃) and a subsequent series of Ni-based electrocatalysts for hydrogen generation.
Various eight membered cyclo-P$_2$N$_2$ macrocycles have received attention and been described. For example, cyclic diphosphines P$^R_2$N$^R'$_2 (R = Ph, tBu; R' = Ph, Bn, 9b) have been used to prepare diiron [161] and ruthenium [162] complexes. A water-soluble variant of 9b, bearing –CO$_2$H groups, has also been reported by Hey-Hawkins and co-workers [163]. The 1,5-diaza-3,7-diphosphacyclooctane 9c could be conveniently prepared from (2-C$_5$H$_4$N)P(CH$_2$OH)$_2$ and condensation with primary amines leading to a range of air-stable crystalline products. Only one signal was observed in the $^{31}$P$^{[1]}$H NMR spectra in the region −33 to −63 ppm [164]. Other modifications of the pyridyl cyclic diphosphines [165–167] could also be achieved, following similar procedures to that employed for 9c, and suitably disposed for various coordination studies to be undertaken.

A synthetic strategy based on dynamic covalent chemistry of macrocyclic aminomethylphosphines has been developed for various 14- [168], 16- [169], 18- [170] and 20-membered P$_4$N$_2$ macrocycles. These reactions start with bis(phosphino)alkanes, formaldehyde and primary amines resulting in multiple products. The amine in question is again also important and influences the outcome of the condensation reaction. Again, the lability of the P–CH$_2$–N fragment is important for these dynamic systems.

### 10.2. Importance of –N(R)– Backbone Functionality in Cyclic Diphosphines

As seen in previous sections within this review, the interaction of the pendant amine in complexes of cyclic diphosphines of 9c (and related analogues) has previously been studied towards protonation reactions [171], heterolytic splitting of H$_2$ [172], electrocatalytic alcohol oxidation [173], and hydroalkoxylation [174].

Immobilation of ligands of the type 9c have been undertaken in which a suitable para substituted group on the N arene groups has been introduced enabling anchoring to a metal oxide surface (via phosphonic acid groups) [175], glassy carbon electrodes (via a Cu$^2+$ catalysed alkyne-azole cycloaddition) [176], or a carbon electrode (via amide bond formation) [177]. Recently, Kubiak and co-workers [178] prepared a partially substituted derivative through a multistep approach. The penultimate step, involved lithiation of a bromo intermediate and reaction with CIP(O)(OEt)$_2$ in THF at −108 °C. The phosphonate P$_2$N$_2$ ligand was isolated in 76% yield. A $^{31}$P spectrum showed a singlet at −49.4 ppm (in CDCl$_3$). Here, the group achieved immobilisation via modification of the arene on the P donors (as opposed instead to the N donors as described previously).

### 11. P–C–P–C–N–C–P–C–P and P–C$_2$–N–C$_2$–N–C$_2$–P Ligands

#### 11.1. Synthesis of Selected Examples

In this penultimate section, some examples bearing one (or two) amine groups in a diphosphine backbone (Figure 14) are highlighted. Ligand 10a could be prepared from Ph$_2$PCH$_2$P(Ph)CH$_2$OH and BnNH$_2$ as a mixture of meso-/rac- diastereomers [179]. Disso-

olution in CH$_3$CN enabled precipitation of the meso isomer in 25% yield. The $^{31}$P$^{[1]}$H NMR showed two doublets at −41.7 and −22.3 ppm for the meso form. 1,8-naphthyridine ligands 10b (R = 'Pr, tBu) [180,181] and 1,10-phenanthroline ligands 10c (R = Cy, Ph) [182,183] and 10d [184] are all examples of PNNP-tetratendate ligands. Finally, 10e could be prepared, as the potassium salt, via reaction of KPPh$_2$ with N,N'-bis(2-fluorophenyl)-formamidine in CH$_2$Cl$_2$ in excellent yield and showed a $^{31}$P signal at −14.3 ppm (d$^8$-THF) [185–187]. The

![Figure 13. Selected examples of ring structures incorporating P–C–N backbones.](image-url)
3,3′-azo-benzene phosphine 10f (31P = 4.9 ppm, CDCl3) was prepared in 66% yield from HPPh2, meta-diiodo-azobenzene and Pd(PPh3)4/NEt3 in C7H8 at 100 °C [188].

**Figure 14.** Selected examples of P–C–P–C–N–C–P, P–Cm–N–Cn–N–Cm–P and P–C3–N–C3–P–P ligands (m = 2, 5; n = 1, 2).

### 11.2. Importance of –N(R)– Backbone Functionality

A bisamido, dianionic ligand could be accessed through the neutral parent proligand bisamine 10g (Figure 15) and deprotonation achieved through reaction with Mg(18Bu)2/C7H8 [189] or reaction with a dimesityliron(II) dimer in THF [190]. Lee and Thomas [191] recently found a nickel templated replacement approach of Ph substituents on P could be achieved leading to different –PR2 substitutions [with Me, tPr or –(CH2)3− groups]. Deprotonation of ligands 10h [192] and 10i [193] gave β-diketiminate ligands whose structural flexibility can be realised through complexation to various metal centres.

**Figure 15.** Selected proligands to anionic P–C2–N–C2–P and P–C2–N–C3–N–C2–P ligands.

**Table 1.** 31P{[1H]} NMR data for selected ligands discussed in this review.

| Ligand | S(P)/ppm | NMR Solvent | Reference |
|--------|----------|-------------|-----------|
| 1a     | 25.9     | CDCl3       | [25]      |
| 1b     | 26.4     | CDCl3       | [11]      |
| 1c     | 38.5     | CDCl3       | [12]      |
| 1d     | 42.2     | CDCl3       | [13]      |
| 1e     | 42.1     | CDCl3       | [13]      |
| 1f     | 26.1     | CDCl3       | [13]      |
| 1g     | 71.3     | CDCl3       | [14]      |
| 1j     | 32.6 (and 12.6) | C6D6 | [17] |
| 1k     | 63.9     | C6D6        | [18]      |
| 1l     | 106.4    | CDCl3       | [19]      |
| 1m     | 77.9     | C6D6        | [20]      |
| 1n     | 126      | CD3CN       | [23]      |
| dppa   | 43.1     | CDCl3       | [31]      |
| 2a     | 50.1     | CDCl3       | [32]      |
| 2b     | 62.1     | CDCl3       | [35]      |
Table 1. Cont.

| Ligand | δ(P)/ppm | NMR Solvent | Reference |
|--------|----------|-------------|-----------|
| 2f     | −6.4     | CD$_2$Cl$_2$ | [39]      |
| 2g     | 69.0     | CDCl$_3$    | [41]      |
| 2h$^a$ | 137.9/135.3 | C$_2$D$_8$  | [42]      |
| 2i     | 69.3     | CDCl$_3$    | [44]      |
| 2m     | 59.5     | CDCl$_3$    | [52]      |
| 2n     | 17.2 and −20.0 (J$_{PP}$ 277 Hz) | CD$_2$Cl$_2$ | [52]      |
| 3a     | 159.8    | CDCl$_3$    | [55]      |
| 3c     | −77.0    | CDCl$_3$    | [56]      |
| 4a     | −16.7    | C$_6$D$_6$  | [57]      |
| 4b     | −19.4    | C$_6$D$_6$  | [57]      |
| 4c     | −17.1    | CDCl$_3$    | [58]      |
| 4d     | −18.6    | CDCl$_3$    | [59]      |
| 4f     | −26.3    | C$_6$D$_6$  | [62]      |
| 4h     | −19.6    | C$_6$D$_6$  | [64]      |
| 4i     | ca. −61.0 | CD$_2$COCD$_3$ | [67] |
| 4j     | −29.6 to −33.6 | C$_6$D$_6$ | [68,69] |
| 4k     | ca. −42.0 | CD$_2$SOCD$_3$ | [74] |
| PTA    | −98.3    | D$_2$O      | [77]      |
| CAP    | 46.7     | D$_2$O      | [77]      |
| 5a     | ca. −87.0 | CDCl$_3$   | [85]      |
| 5c     | ca. −55.0 | CD$_2$SOCD$_3$ | [91] |
| 5d     | −77.9    | CDCl$_3$    | [92]      |
| 6a$^b$ | −26.5    | C$_6$D$_6$  | [95]      |
| 6b     | −25.9    | CDCl$_3$    | [96]      |
| 6c     | −27.4 and −41.5 (J$_{PP}$ 4 Hz) | CDCl$_3$ | [76] |
| 6d     | −27.3    | CDCl$_3$    | [97]      |
| 6e     | −28.0    | CD$_2$SOCD$_3$ | [98] |
| 6f     | −27.7    | CDCl$_3$    | [101]     |
| 6h     | −19.7    | CDCl$_3$    | [103]     |
| 6j     | −25.3    | CDCl$_3$    | [106]     |
| 6k     | 30.2 and 36.7 | -  | [107] |
| 6l     | ca. −34.5 | CDCl$_3$ | [108,109] |
| 6n$^c$ | −28.0    | CDCl$_3$    | [112]     |
| 6p     | 29.5     | C$_6$D$_6$  | [115]     |
| 6q$^c$ | −26.0    | C$_6$D$_6$  | [116]     |
| 6r     | −22.1 to −28.1 | CDCl$_3$ | [120] |
| 7a$^d$ | 67.0 and −21.7 | CDCl$_3$ | [131] |
| 7b     | 79.6 and 7.0 (J$_{PP}$ ~101 Hz) | CDCl$_3$ | [132] |
| 7d$^e$ | 47.3     | CDCl$_3$    | [48]      |
| 8c     | 22.3     | C$_6$D$_6$  | [139]     |
| 8d     | ca. −19.0 | CDCl$_3$   | [140]     |
| 8e     | −0.4     | C$_6$D$_6$  | [141]     |
| 8f$^f$ | 25.4     | CDCl$_3$    | [146]     |
| 8g$^g$ | −7.0 and −19.6 | CDCl$_3$ | [152] |
| 8h$^e$ | −52.8    | CDCl$_3$    | [153]     |
| 8m     | −20.7 and −21.5 | CDCl$_3$ | [154] |
### Table 1. Cont.

| Ligand | δ(P)/ppm | NMR Solvent | Reference |
|--------|----------|-------------|-----------|
| 9a<sup>c</sup> | −25.8 and −26.6 | C<sub>6</sub>D<sub>6</sub> | [158] |
| 9c<sup>i</sup> | −33.5 | CDCl<sub>3</sub> | [164] |
| 10a | −22.3 and (J<sub>PP</sub> 121 Hz) | CDCl<sub>3</sub> | [177] |
| 10b | 11.8 | C<sub>6</sub>D<sub>6</sub> | [178] |
| 10e | −14.3 | d<sup>8</sup>-THF | [186] |
| 10f | −4.9 | CDCl<sub>3</sub> | [188] |
| 10h | −14.5 | CDCl<sub>3</sub> | [192] |

<sup>a</sup> R = Ph, R’ = Me;<sup>b</sup> R = Ph, R’ = iPr;<sup>c</sup> R = Ph;<sup>d</sup> X = H, Y = CH;<sup>e</sup> Ar = 2-MeC<sub>6</sub>H<sub>4</sub>;<sup>f</sup> Ar = 4-CO<sub>2</sub>Me<sub>2</sub>BuC<sub>6</sub>H<sub>4</sub>;<sup>g</sup> R = Cy;<sup>h</sup> R = Me;<sup>i</sup> R = 2-C<sub>5</sub>H<sub>4</sub>N.

#### 12. Catalysis

There has been considerable interest in the development and application of monodentate, bidentate, and polydentate phosphorus containing ligands of various metal complexes as catalysts for wide ranging transformations of academic and industrial relevance. This is also true for phosphine ligands encompassing one (or more) nitrogen donor sites in their ligand backbone structure. The manganese(I) complex MnBr(CO)₃(P,N-1b) was shown to act as a pre-catalyst for the alkylation of amines via reductive amination of aldehydes using molecular H<sub>2</sub> as reductant [194]. The ruthenium(I) pincer complex RuH(Cl)CO(PN<sub>2</sub>-1i) has been shown to hydrogenate catalytically challenging arenols to their corresponding tetrahydronaphthols or cyclohexanols [16,195]. Significant advances have been achieved with chromium catalysts of PNP ligands, for example 2a, for selective ethylene tri-/tetramerizations [32–34]. Furthermore recent examples of note include incorporation of an N-trityl group into the PNP backbone [196], the introduction of bulky -SiR<sub>3</sub> groups thereby avoiding use of methylaluminoxane [197], and the preparation of new unsymmetrical PNP ligands from Ph₂PNH(cyclopentyl) [198]. The isopropyl PNP bis(phosphinoamine) ligand 2a has also been successfully applied to the gold catalysed alkylation of aryl boronic acids [199], manganese catalysed dehydroisilylation and hydroisilylation of alkenes [200], and the 2,6-(Ph<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)PNP ligand 2f (and its C<sub>6</sub>H<sub>5</sub> analogue) were effective in the Buchwald-Hartwig coupling of various sterically hindered substrates [201].

The ready tuneability of PNP bis(phosphinoamine) ligands can be elegantly illustrated by the preparation of PNPO monoxides which can act as P,O-chelating ligands to Pd(II) and Ni(II) to afford catalysts for the copolymerization of ethylene with carbon monoxide [202,203]. Nickel(II) catalysts with cyclic diphosphine ligands incorporating pendant amines have been extensively studied as electrocatalysts for both the oxidation and production of H<sub>2</sub> [204]. Richeson and co-workers [205] have shown that Ni(II) complexes with the PNP pincer ligands 2,6-[Ph₂PNR]₂(NC<sub>5</sub>H<sub>3</sub>) (R = H, Me) can electrocatalytically generate hydrogen from H<sub>2</sub>O/MeCN solutions. Mononuclear iridium(I) complexes of bulky PNNP tetridentate ligands have been shown to be efficient photocatalysts for CO₂ reduction [206].

#### 13. Conclusions

It is without doubt that phosphorus ligands are an important class of compound widely appreciated by the coordination chemistry community. Whilst considerable focus has long been on all carbon backbone P-ligands, there is a considerable growing interest in the incorporation of one (or more) nitrogen atoms. The importance of this class can be released through the facile syntheses of such ligands and the tuneability, in terms of additional reactivities, that can be imparted through the central nitrogen centre. These types of ligands will continue to play a pivotal role in future avenues of phosphorus and transition metal chemistry.
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