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Review

N-phosphino carboxylic acid amides, lactams and ureas: Synthesis, properties and applications

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Dedicated to Prof. Masaaki Yoshifuji on the occasion of his 65th birthday, with my warmest congratulations and very best wishes.

Contents

Abbreviations: AMPP, aminophosphinephosphinite; COD, 1,5-cyclooctadiene; Cp, C_5H_5; Cp^*, C_5Me_5; Cpe, cyclopentyl; Cy, cyclohexyl; de, diastereomeric excess; ee, enantiomeric excess; LactaNOP, *N*-phosphino,*O*-phosphinito-(L)-lactic acid; LANOP, Hoffmann–La Roche term for lactaNOP; mandelNOP, *N*-phosphino,*O*-phosphinito-(*S*)-(+)-mandelic acid; NOP, phosphanylated at nitrogen and oxygen; oxo-proliNOP, *N*-phosphino,*O*-phosphinito-(*S*)-2-pyrrolidinone-5-carboxylic acid; oxo-proNOP, *N*-phosphino,*O*-phosphinito-(*S*)-5-(hydroxymethyl)-2-pyrrolidinone; pip, piperidine; ^{i}Pr, *iso*-propyl; proNOP, *N*-phosphino,*O*-phosphinito-(*S*)-5-(hydroxymethyl)-pyrrolidine; Py, pyridine; SHOP, Shell Higher Olefin Process; thf, tetrahydro furane; tht, tetrahydro thiophene; $C_1^1(4)$, chain, one hydrogen acceptor, one hydrogen donor, four atoms in the motif; $R_2^2(8)$, ring, two hydrogen acceptors, two hydrogen donors, eight atoms in the motif

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Abstract

The chemistry of a diverse range of compounds is reviewed that have the structural motif PNC=O(*S*) in common. The majority of compounds falls in the category of carboxylic acid phosphino amides, their cyclic representatives, the phosphino lactams, and phosphino ureas, the diamide of carbonic acid. Their chemistry is characterised by a rich and fascinating Main Group Chemistry as well as a plethora of diverse applications in catalysis, polymers, pharmacy, and the printing industry.

Keywords: Phosphino ureas; Phosphino lactams; Phosphino amides; Homogeneous catalysis; Phosphonylation; Asymmetric hydrogenation

1. Introduction

Ever since their advent as universal ligands for transition metals in homogenous catalysis the phosphanes have become a familiar sight, not only for the synthetic chemist [1–3]. They are usually thought of as containing P–C and P–O bonds; in the latter case they are known as phosphites. However, in recent years those compounds containing direct bonds between phosphorus and nitrogen atoms have made the transition from the backbenches to centre stage [4,5]. In the early days, they were frequently used as synthons for the synthesis of other phosphorus containing compounds due to the ease with which the amino group can be substituted, particularly under acidic conditions [6]. With the discovery of widespread applications in their own right [7,8], especially as ligands in homogenous catalysis [9–11], interest in them increased dramatically in recent years [12–16].

All phosphorus, nitrogen compounds containing a P–N single bond are known as phosphino amines and those that are anionic in nitrogen or have a metal atom bonded to the nitrogen centre are called phosphino amides. Coordination to transition metals usually occurs via the phosphorus end or as a M–N single bond in case of the phosphino amides [5]. Unfortunately, naming of phosphorus, nitrogen compounds is not consistent in the literature and thus the term phosphino amine is frequently used for compounds in which the phosphorus and the nitrogen atoms are separated by a carbon spacer unit such as $(CH_2)_x$ [17–20] or an aryl group [21–23]. Simple phosphino amines have recently been extensively reviewed [5,14,15], but with increasing importance of phosphino amines in a wide range of applications, various functional groups [24–26], stereocentres [27,28] or oxidation on phosphorus [29–31] were introduced to tune their properties to the intended application.

The present review will describe the chemistry of a class of phosphino amines that is best defined as *N*-phosphino carboxylic acid amides containing the structural motif O=CNP, a term that has its origin in organic chemistry. Unfortunately, it collides somewhat with the definition of a simple phosphino amide given above, but even that is consistent with the established nomenclature in Organic Chemistry. The scope of the review relies on a broad definition of carboxylic acid amides and thus includes phosphanylated representatives of linear carboxylic acid amides [32], lactams [12,13], ureas [33], biuret [34] and some nucleic acids [35]. The carbonyl group, directly bonded to the P–N entity at the nitrogen terminus, serves to render the phosphorus end somewhat electron deficient as seen by typical values for the Tolman Electronic Parameter, TEP [36,37] of around 2080 cm^{-1} for bisphosphino ureas [38,39], a value that is in the range for phosphites [36]. Thus, it should come as no surprise that applications of bisphosphino ureas include utilisation as ligands in catalysts for hydroformylation reactions [40]. It is equally unsurprising that the performance of catalysts based on phosphino lactams shall be significantly different from those systems where the lactam is reduced to an amine [12,13]. It is this influence of the carbonyl group that distinguishes the compounds described in the present review.

This review is structured by classes of compounds: carboxylic acid phosphinoamides, phosphino lactams and phosphino ureas as well as a section that includes all those compounds that do not fit very well into any of these three categories. Each chapter has four subdivisions: synthesis, properties/reactivity, transition metal complexes and applications. The sequence carboxylic acid amides, lactams, ureas was chosen for chemical reasons rather than the chronology of their phosphonylated derivatives. In this respect the phosphino ureas are entitled to claim precedence as does urea for the parent compounds. It should be mentioned that although a fair number of patents are mentioned, the present review does not claim full coverage of the patent literature. Indeed, no dedicated search of the patent literature was performed.

2. Carboxylic acid phosphinoamides

The first reports for this ligand class concerned synthesis in the coordination sphere of a transition metal [42]. Most often the reaction took place as nucleophilic attack of the nitrogen atom of a coordinated ligand on the carbonyl carbon atom bonded to the same metal. Planned synthesis of the free ligands occured much later [43] and was instigated by the expectation that these ligands would perform well in homogenous catalysis due to their similarities with P,O ligands used in the SHOP-process (Shell Higher Olefin Process) [44–46].

2.1. Synthesis of carboxylic acid phosphinoamides

Most general routes for the synthesis of these ligands make use of one of the three classic phosphanylation reactions exploiting the reactivity of the P–Cl bond. Firstly, $ClPR_2$ can be reacted with a primary or secondary carboxylic acid amide in the presence of an auxiliary base, typically triethyl amine. This reaction was employed by Woollins and coworkers [47] in the synthesis of diphenylphosphino benzoic acid amide using *p*-dimethylamino-pyridine to facilitate proton abstraction. Woollins and coworkers report only low yields in the synthesis of this compound (29%) and its pyridine analogue (32%)

using this route [48]. This seems to be in keeping with the accustomed low reactivity of carboxylic acid amides [49]. Secondly, reaction can proceed by a salt metathesis reaction with a lithiated carboxylic acid amide as reaction partner. Ando et al. [50] report moderate yields (40–56%) in the synthesis of *N*-methyl-*N*-(diphenylphosphino)acetamide after distillation. However, when Woollins et al. used this method in the synthesis of the bis-diphenylphosphino substituted *N*,*N*′-dibenzyl-1,3-isophthalamide they report a yield of 76% [51] without distillation. It should be mentioned that distillation, even without thermal decomposition of the product, reduces the yield as some of the product remains in the apparatus [49]. The low yield reported by Ando et al. could very well be for this reason and not for any sidereactions occuring in the formation. And thirdly, the proton of the carboxylic acid amide can be substituted by a $SiMe_3$-group in a first step and then reacted with the chlorophosphine [52–54]. In this reaction the low boiling chlorotrimethylsilane is liberated and can be distilled off in a continous way. The method was reported by Braunstein et al. [33] in the synthesis of diphenylphosphino acetamide with a yield of 84%. Although the latter method has the highest reported yield, it is also by far the most tedious and in reality a two step protocol since the silylated carboxylic acid amide has to be prepared first.

A rather special synthesis is that employed by Ando et al. [50] where a *N*-silylated phosphino amine was treated with acetic acid anhydride to yield the desired acetic acid phosphino amide and trimethylsilyl acetate in high yields of around 80%. The reaction proceeds with other carboxylic acid anhydrides, but seems to vary significantly in yield. For instance, propionic acid anhydride yields only 38% of the phosphino propionamide if treated with {methyl(trimethylsilyl)amino}di-*t*-butylphosphine, but 93% if treated with {methyl(trimethylsilyl)amino}diphenylphosphine.

Yoder and Miller reported the use of borane protected dimethylchlorophosphine and the appropriate lithium amide salts obtaining the respective carboxylic acid phosphino amides in 60–65% yield [52].

2.2. Properties of carboxylic acid phosphinoamides

Carboxylic acid phosphino amides are thermally stable, proton labile compounds that can easily be oxidised at the phosphorus atom. They prefer to coordinate to metals via the phosphorus terminus and can form chelate complexes using the carbonyl oxygen atom.

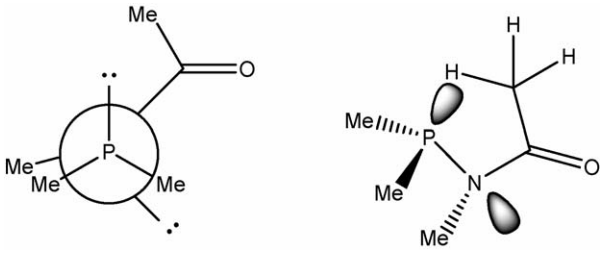


Fig. 1. Steric view of *N*-methyl-diphenylphosphino acetamide showing the relative positions of the substituents and the electron lone pairs on nitrogen and phosphorus.

The structures of these phosphino amides possess two very interesting features. From their NMR-spectra it is known that they can occupy two distinct conformations with respect to the relative positions of the phosphorus atom lone pair PALP and any C–H protons in β-position to it [50] as is the case in the acetamide series. The phenomenon is explained in terms of the dihedral angle between the PALP and the N–CH_3 bond. A large dihedral angle leads to a small J_{PH} or J_{PC} coupling constant and a small dihedral angle corresponds with a large coupling constant (see Fig. 1). The comparatively large $^4J_{PH}$ coupling constant (5 Hz) observed for the acetyl protons is attributed by the authors to an interaction between the PALP on phosphorus and the respective methyl protons [50]. A similarly large $^4J_{PH}$ coupling constant was observed by Hudson and Searle for NH proton of the urea derivatives $Ph_2PN(R)CONHR'$ [55,56].

The solid state structure is dominated by hydrogen bonding interactions between the carbonyl oxygen and the amide proton in those compounds that were derived from primary carboxylic acid amides. The two known examples $Ph_2P(S)NHC(O)Ph$ [47], a derivative of benzoic acid, and $Ph_2PNHC(O)Me$ [33], a drivative of acetamide, form one dimensional chains descripable as $C_1^1(4)$. The other possible structure in which two molecules form a dimer in the form of isolated rings, known as $R_2^2(8)$, has not been found yet (see Fig. 2).

This preference for hydrogen bond networks in the solid state comes as no surprise as carboxylic acid amides (including ureas) are noted for their extended and diverse multidimensional hydrogen bond networks [57–62]. In fact, they were used to develop the graph theory nomenclature used today to describe those complex structures [63–68].

The phosphorus terminus of these phosphino amides is easily oxidised by sulfur [47]. The oxidation was employed in a one-pot synthesis following phosphanylation of the benzoic acid amide used by just adding elemental sulfur at the end [47]

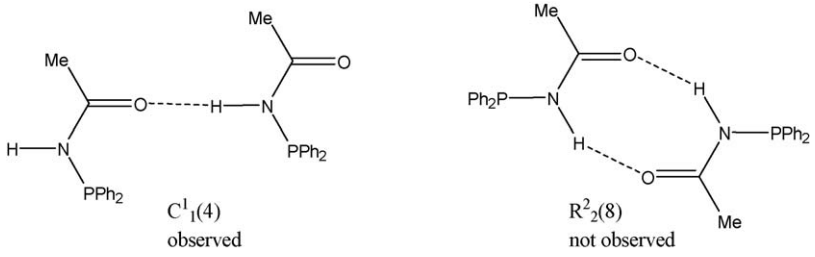
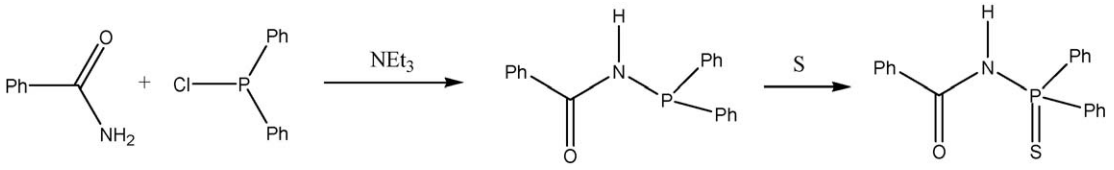
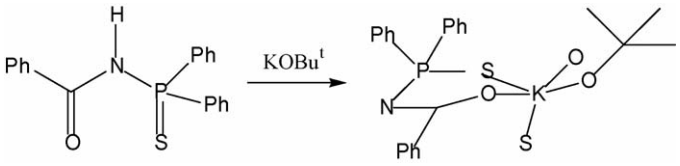


Fig. 2. Illustration of graph theory notation using diphenylphosphino acetamide as example.



Scheme 1. The auxiliary base method used in the synthesis of diphenylphosphino benzamide and its sulfurisation.



Scheme 2. Synthesis of the first six-membered "true heterocycle".

(see Scheme 1). The corresponding oxo-compounds are usually made as the orthophosphates by utilising the respective phosphorus(V) species [69,70].

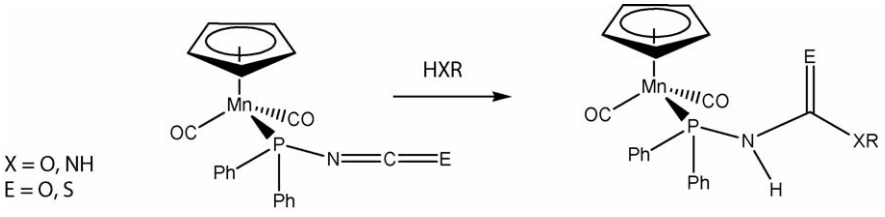
There has always been considerable speculation concerning the bond order of the P–N bond [71,72]. In the case of the carboxylic acid phosphino amides, the bond order can be assumed to be one in most cases judging from the reported bond lengths [33,47]. This is hardly surprising since the electron withdrawing nature of the acyl group would not allow for a considerable buildup of electronic density along the P–N bond vector. However, the anion displays a remarkable aptitude for electron delocalisation along the entire backbone as witnessed for the respective transition metal complexes. The compound $Ph_2P(S)NHC(O)Ph$ in its metallated form gave rise to the first six-membered "true" heterocycle [73] as the potassium salt [47] (see Scheme 2).

2.3. Transition metal complexes of carboxylic acid phosphinoamides

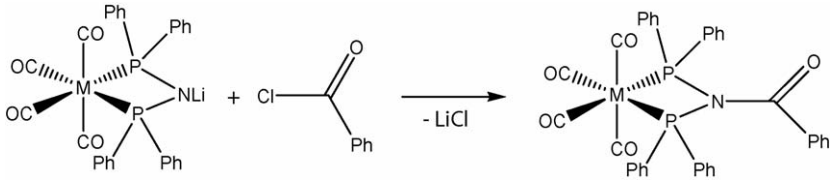
The earliest examples for carboxylic acid phosphino amides were synthesised in the ligand sphere of transition metals. As early as 1974 Höfler and Schnitzler reacted $[CpMn(CO)_2PPhCl_2]$ with pseudohalogens to effect complete substitution of chlorine by the respective pseudohalogen [42]. Of interest for us are the reactions with isocyanate and isothiocyanate. They lead to the isocyanato and isothiocyanato phosphino complexes which can be hydrolysed using an alcohol to give the respective phosphino carbamides or phosphino thiocarbamides or aminolysed to yield the respective phosphino ureas or phosphino thioureas coordinated to manganese (see Scheme 3). The reaction mechanism is assumed to be analogous to that of the well documented alcoholysis of isocyanates where a carbon atom takes the place of the phosphorus atom [74]. No attempt was made to release the free ligand.

Some 12 years later, Ellermann and Wend published a paper describing the reaction between the group 6 carbonyl complexes (M = Cr, Mo, W) of the well known chelate ligand $Ph_2PNHPPh_2$ and benzoic acid chloride in low (21%) to moderate (65%) yields (see Scheme 4) [75]. The lowest yield was reported for the molybdenum complex, a common trend in the group 6 triad. Attempts to synthesise the free ligand in the same way were not successful. Only 2 years later Ando et al. [50] report this route for their synthesis of phosphino acetamides. The answer could very well be that the second phosphino group on the same nitrogen atom changes the electronic situation and thus the reactivity sufficiently for some other reaction to occur instead. It might be worth mentioning that since then, it was observed that the negative charge on a phosphino amide can be located on phosphorus rather then on nitrogen with subsequent reactions on the phosphorus terminus (see Fig. 3) [16,19].

In the same year, Keim et al. [43,76] described the reaction of the phosphorus(V) ylide $RC(O)N{=}PPh_3$ with the Ni(0) species $[Ni(1,5\text{-}COD)_2]$ (1,5-COD = 1,5-cyclooctadiene) to



Scheme 3. Reaction of phosphino isocyanate and thioisocyanate with alcohols and amines in the ligand sphere of a manganese(I) complex.



Scheme 4. Acylation of a metal coordinated phosphinoamide.

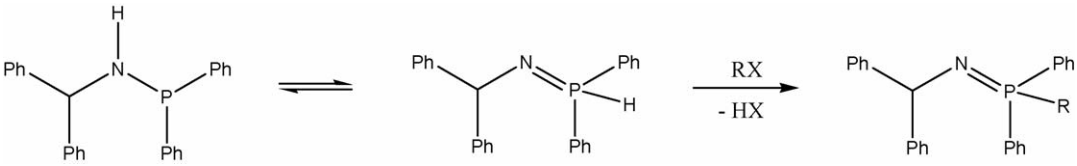
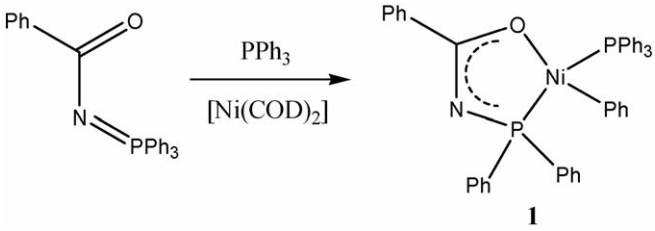


Fig. 3. Prototopic shift equilibrium leading to an imino phosphane.

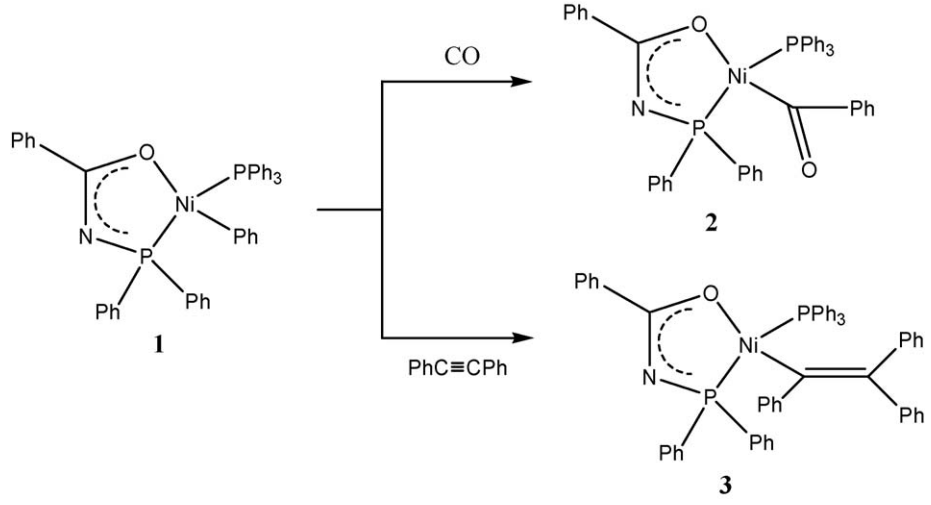


Scheme 5. Reaction of a phosphorus(V)ylide with $[Ni(COD)_2]$ to form a diphenylphosphino benzamide complex.

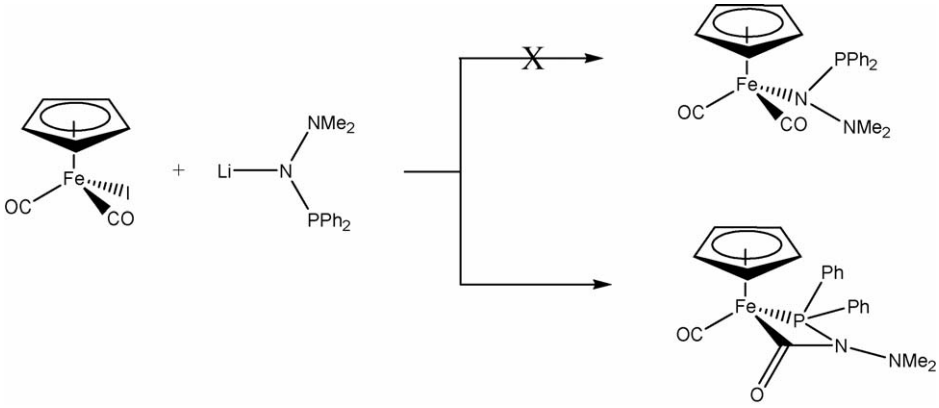
a P,O bonded Ni(II)-complex **1** (see Scheme 5). During the reaction a phenyl group is transferred from phosphorus to nickel in a formal reduction of phosphorus from +V to +III and oxidation of nickel from Ni(0) to Ni(II). The formerly neutral ligand becomes monoanionic in the process. Complex **1** was found to possess a reactive Ni–C bond of the phenyl group. This reactive centre could be exploited in reactions with hydrogen, carbon monoxide and tolane (see Scheme 6) whereby insertion into the Ni–C bond afforded the respective benzoyl-**2** and vinyl-complexes **3** in high yields. Both complexes could be reacted further to liberate the newly formed substituent. Treatment of compound **2** with methanol renders methyl benzoate and reaction with methyl iodide gave acetophenone. Similarily, the vinyl substituent of compound **3** could be liberated as triphenylethylene upon reaction with HCl.

Another synthesis in the same vein was reported by Wright and coworkers [77] with the reaction of the phosphino hydrazide $Li(Me_2NNPPh_2)$ and $[CpFe(CO)_2I]$ ($Cp = C_5H_5$). The intention was a simple salt metathesis reaction rendering a Fe–N single bond with the second amino group and the phosphino group pendant (see Scheme 7). Although this reaction might occur initially at low temperature, the product isolated after warmup is a compound whereby one of the terminal carbonyl groups is inserted into the Fe–N bond presumably through amide migration. Attempts to open the ring by addition of a more nucleophilic phosphine such as PMe_3 failed, but electrophilic attack on nitrogen with dry HCl affords ring opening as the N-protonated initial target molecule is formed (see Scheme 8). This ring opening reaction is fully reversible as addition of one equivalent of BuLi produces the metallacycle in quantitative yield.

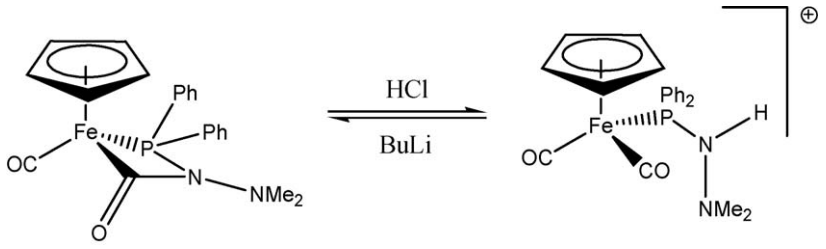
This amide migration reaction to form the carboxylic acid phosphino amide complex was also observed by Farrar and coworkers as part of a much wider rearrangement reaction involving a ruthenium carbonyl complex [78]. In a reaction sequence starting from triruthenium dodecacarbonyl, the mononuclear ruthenium carbonyl complex $[Ru(CO)_3(\kappa^2\text{-}PPh_2NMePPh_2)]$ **4** is formed first (see Scheme 9) in which the central ruthenium atom is electronically saturated, but coordinatively unsaturated. As a consequence rearrangement to a coordinatively saturated octahedral ruthenium complex takes place slowly in solution. The final product is a dinuclear complex where essentially only one of the two ruthenium atoms underwent rearrangement. In the process one of the P–N bonds in one of the two molecules breaks creating a phosphanide and a phosphino amide. The resulting intermediate then reacts with the second molecule of the starting material to form the final product. The breakage of the P–N bond results in a redox reaction as the starting compound **4** is a Ru(0) species and the product must be described as either a Ru(0)/Ru(II) or a Ru(I)/Ru(I) couple. Unfortunately, the authors did not elaborate.



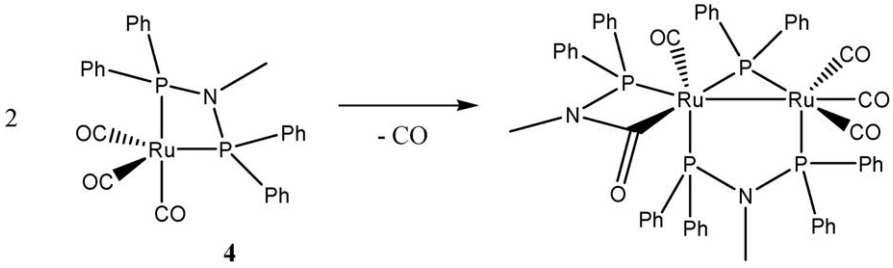
Scheme 6. Reaction of complex **1** with carbon monoxide and tolane.



Scheme 7. Acylation of diphenylphosphino hydrazide in the coordination sphere of $[CpFe(CO)_2I]$.



Scheme 8. Acylation and deacylation in the ligand sphere of Fe(II).



Scheme 9. Migratory acylation by decarbonylation in a ruthenium complex.

In more systematic studies, the research groups of Braunstein and Woollins explored the coordination chemistry of phosphino acetamides and phosphino benzamides, respectively. In the phosphino benzamide series, Woollins and coworkers reacted either the diphenylphosphino benzamide or the respective nicotinic acid derivative with Rh, Ru, Pt and Ni precursor complexes [79]. For $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ and $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}cymene)\}_2]$ cleavage of the dimer by the ligand takes place as expected. Similarly the two acetonitrile ligands are replaced by the phosphino amides when $[PtCl_2(MeCN)_2]$ is reacted with two equivalents of the phosphorus(III) compounds. In all cases the phosphino amides are monodentate coordinating through the phosphorus end (see Fig. 4). The authors attribute this to a general coordination behaviour of this and similar ligands such as $Ph_2PCH_2C(O)R$ [80–82] towards late transition metals. Since then examples refuting the claim became available for both lig-

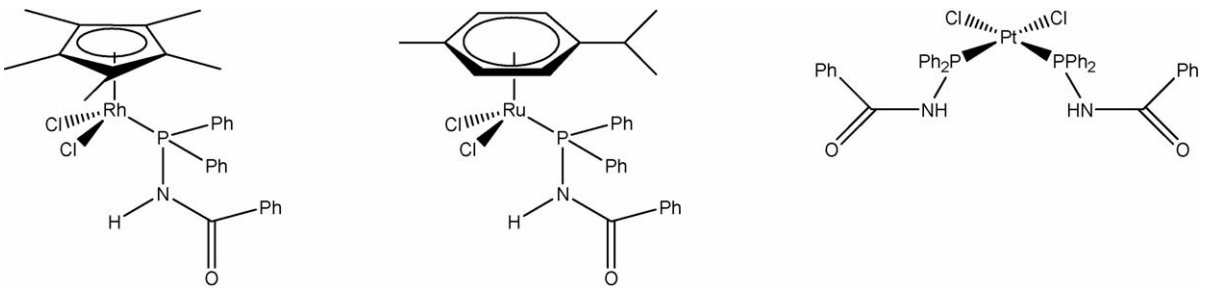
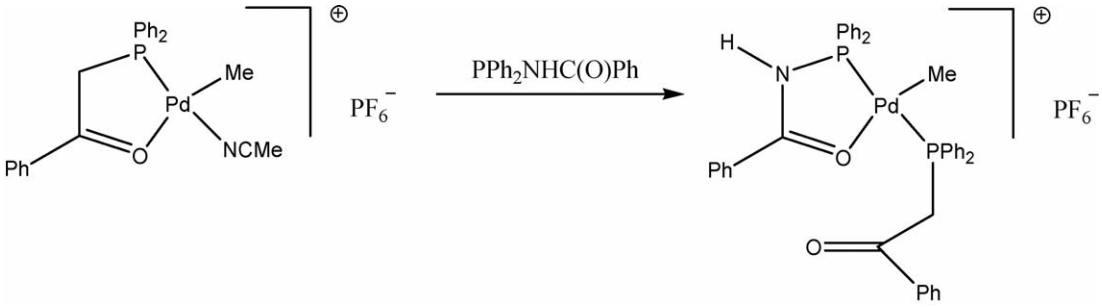


Fig. 4. Coordination Chemistry of diphenylphosphino benzamide.



Scheme 10. Ligating strength of diphenylphosphino benzamide as assessed by ligand displacement in a palladium complex.

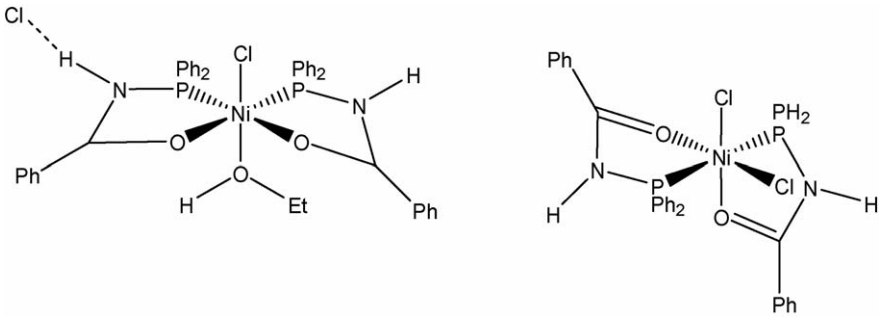
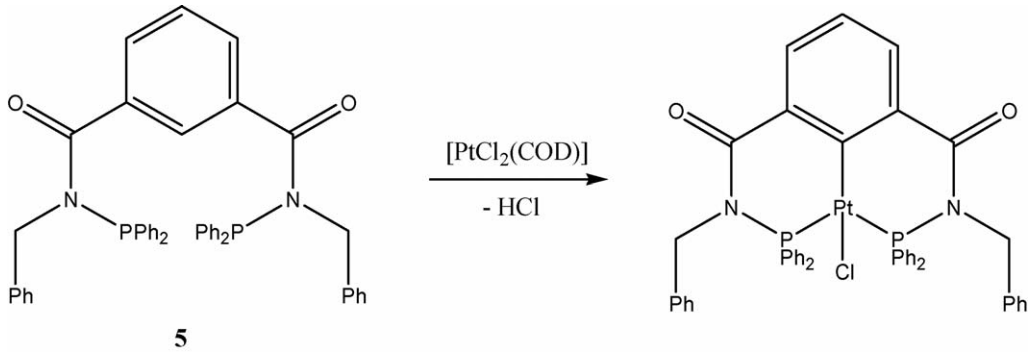


Fig. 5. The structure of a nickel double salt formed by diphenylphosphino benzamide.

and classes [33]. In fact, phosphino acetamide is a better chelate ligand then $Ph_2PCH_2C(O)Ph$ and replaces it in transition metal complexes (see Scheme 10) [33].

In the reaction of $Ph_2PNHC(O)Ph$ or $Ph_2PNHC(O)Py$ (Py = pyridine) with $NiCl_2{\cdot}6H_2O$ Woollins and coworkers report the formation of a nickel double salt in which the ligand is indeed bidentate throughout (see Fig. 5) [79] showing that it is capable of acting as a chelate ligand to the late transition metal nickel. The difference is most likely the ability of nickel to extend its coordination number to six in the present case whereas the central metal stays tetra-coordinated in the other complexes $[Cp^*RhCl_2L]$ ($Cp^* = C_5Me_5$), $[(\eta^6\text{-}p\text{-cymene})RuCl_2L]$ and *cis*-$[PtCl_2L_2]$, respectively. Reacting the platinum precursor complex with only one equivalent of the phosphino amide would most likely yield the respective P,O chelate complex *cis*-$[PtCl_2(P,O\text{-}\kappa^2\text{-}Ph_2PNHC(O)R)]$ (R = Ph, Py). The nickel double salt has the composition $[NiCl(EtOH)L_2]{\cdot}Cl{\cdot}[NiCl_2L_2]$ ($L = Ph_2PCH_2C(O)Ph$, $Ph_2PCH_2C(O)Py$) with the chloride anion hydrogen bonded to the OH group of the alcohol moiety.

Recently, the same group has reported on the *N*,*N*′-bisphosphino derivate of isophthaldiamide, a difunctional ligand [51]. The bisphosphino diamide **5** reacts with the platinum precursor $[PtCl_2(COD)]$ (COD = 1,5-cyclooctadiene) as a tridentate ligand coordinating through both phosphorus atoms and a carbon atom of the central phenyl ring after C–H activation and subsequent HCl elimination (see Scheme 11). C–H activation by platinum or palladium is frequent in related pincer ligands [83]. Reaction of **5** with a respective palladium precursor $[\{(C_3H_5)PdCl\}_2]$ did not result in C–H activation, but yielded the dinuclear complex $[\{(C_3H_5)PdCl\}_2$(**5**)] instead. The different outcome has probably its reason in the different stoichiometries rather then differences in reactivities. The phosphorus: metal ratio was two for platinum, but only one for palladium.



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Scheme 11. Pincer ligand behaviour of the bisphosphino diamide **5** and C–H activation by platinum.

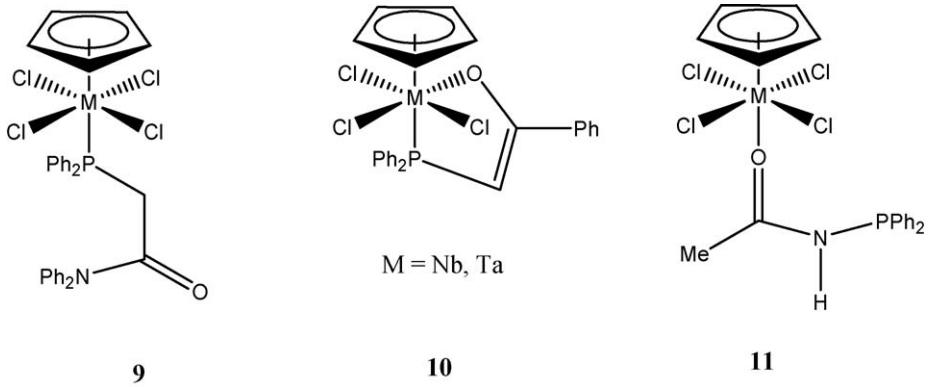
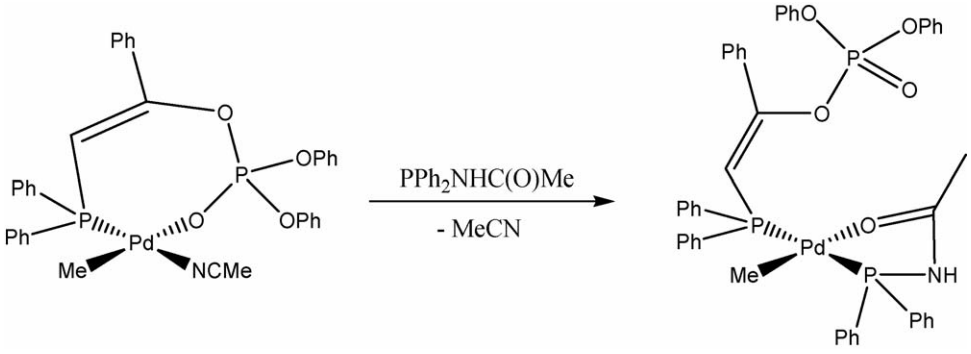


Fig. 6. The unique C═O─M bonding mode for diphenylphosphino acetamide.

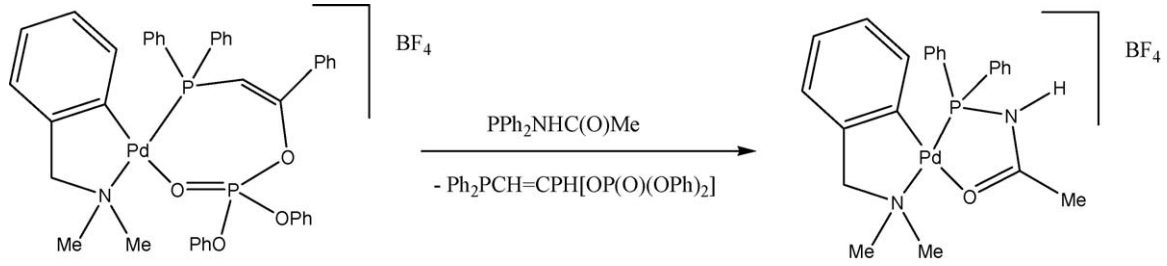
In the phosphino acetamide series Braunstein and coworkers investigated the coordination behaviour of $PPh_2NHC(O)Me$ **6** and the similar ligands $Ph_2PCH_2C(O)Ph$ **7** and $Ph_2PCH_2C(O)NPh_2$ **8** towards monocyclopentadienyl complexes of niobium, tantalum and tungsten $[Cp^LMCl_4]$ ($Cp^L = C_5H_5$, C_5Me_5 and M = Nb, Ta, Mo) **9–11** (see Fig. 6) [84]. Ligand **8** coordinates in the expected monodentate fashion through its phosphorus terminus whereas ligand **7** experiences C–H activation and subsequent P,O bidentate coordination after HCl elimination. The coordination mode of ligand **6** is exceptional in the behaviour of these three ligands and in that of **6** itself in as much as coordination is effected by the carbonyl oxygen. No explanation for this extraordinary coordination behaviour was given by the authors, but they pointed out that **6** is usually a better P,O chelate ligand than **7**. Only a very few examples are known where a functionalised phosphine coordinates monodentally through the alternative donor atom, nitrogen or oxygen instead of phosphorus [84,85].

The relative ability of the oxygen end for bonding to metal centres can be estimated by the reaction of ligand **6** with the palladium complexes $[PdMe(NCMe)\{P,O\text{-}\kappa^2\text{-}Ph_2PCH{=}CPh[OP(O)(OR)_2]\}]BF_4$ (R = Et, Ph) whereby ligand **6** replaces acetonitrile and forms a chelate ring with concurrent ring opening leaving the orthophosphate group pendant (see Scheme 12) [86]. Ligand **6** can even completely displace the P,O chelate ligand $Ph_2PCH{=}CPh[OP(O)(OR)_2]$ (R = Et, Ph) in a related complex (see Scheme 13) proving its considerable chelate strength.

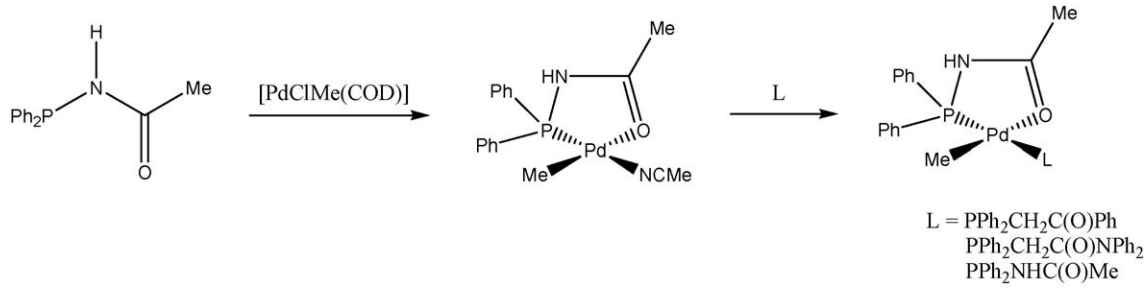
Chelate coordination of ligand **6** to late transition metals occurs readily. An example is the reaction of **6** with the palladium precursor [PdCl(Me)(COD)] (COD = 1,5-cyclooctadiene) [87]. After anion exchange with $AgBF_4$ the cationic chelate complex $[Pd(Me)(NCMe)(P,O\text{-}\kappa^2\text{-}\mathbf{6})]BF_4$ is formed readily (see



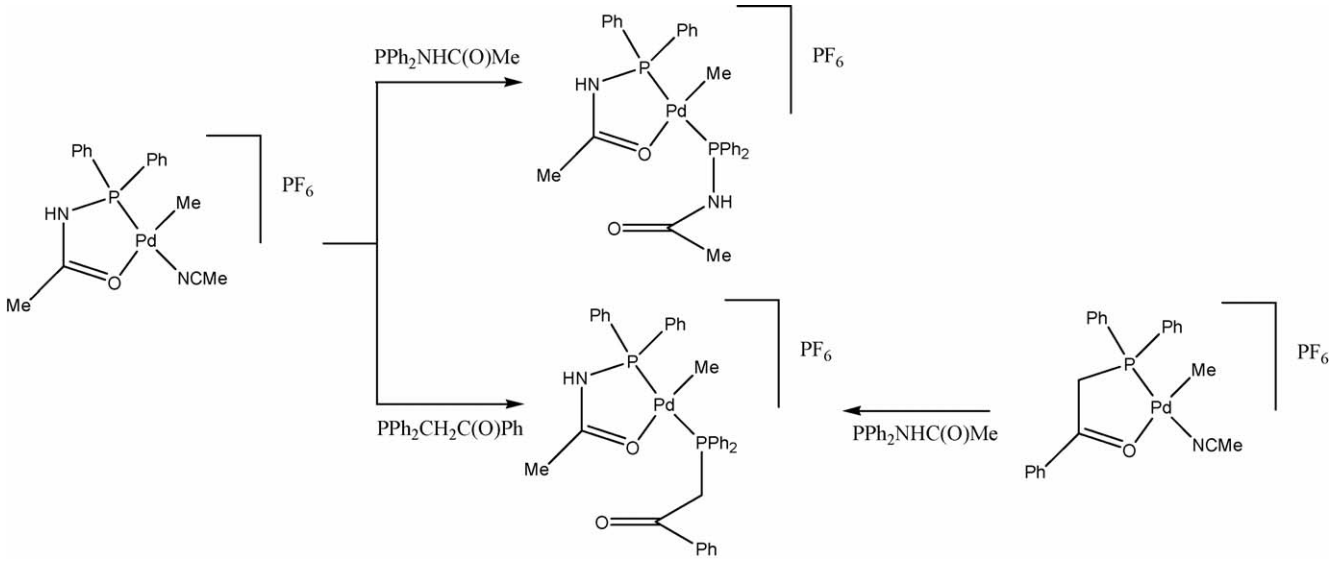
Scheme 12. Displacement of a phosphino phosphate by diphenylphosphino acetamide.



Scheme 13. Complete displacement of a phosphine by the C═O terminus of diphenylphosphino acetamide.



Scheme 14. Ligand strength assessment of diphenylphosphino acetamide.

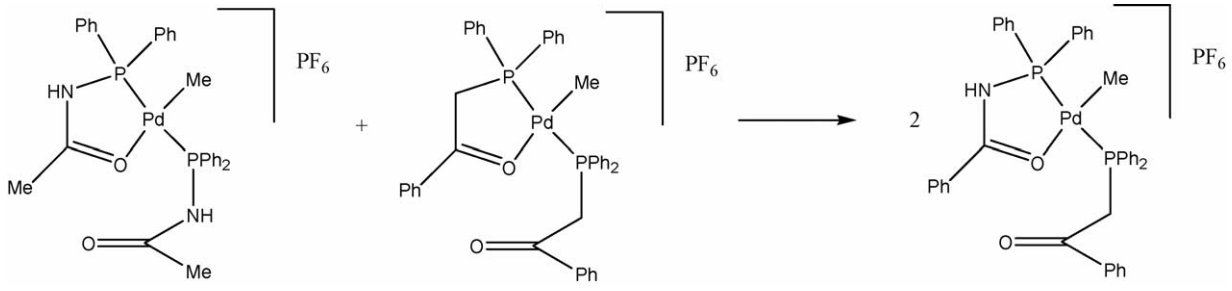


Scheme 15. The chelate strength of diphenylphosphino acetamide compared to a phosphino ketone.

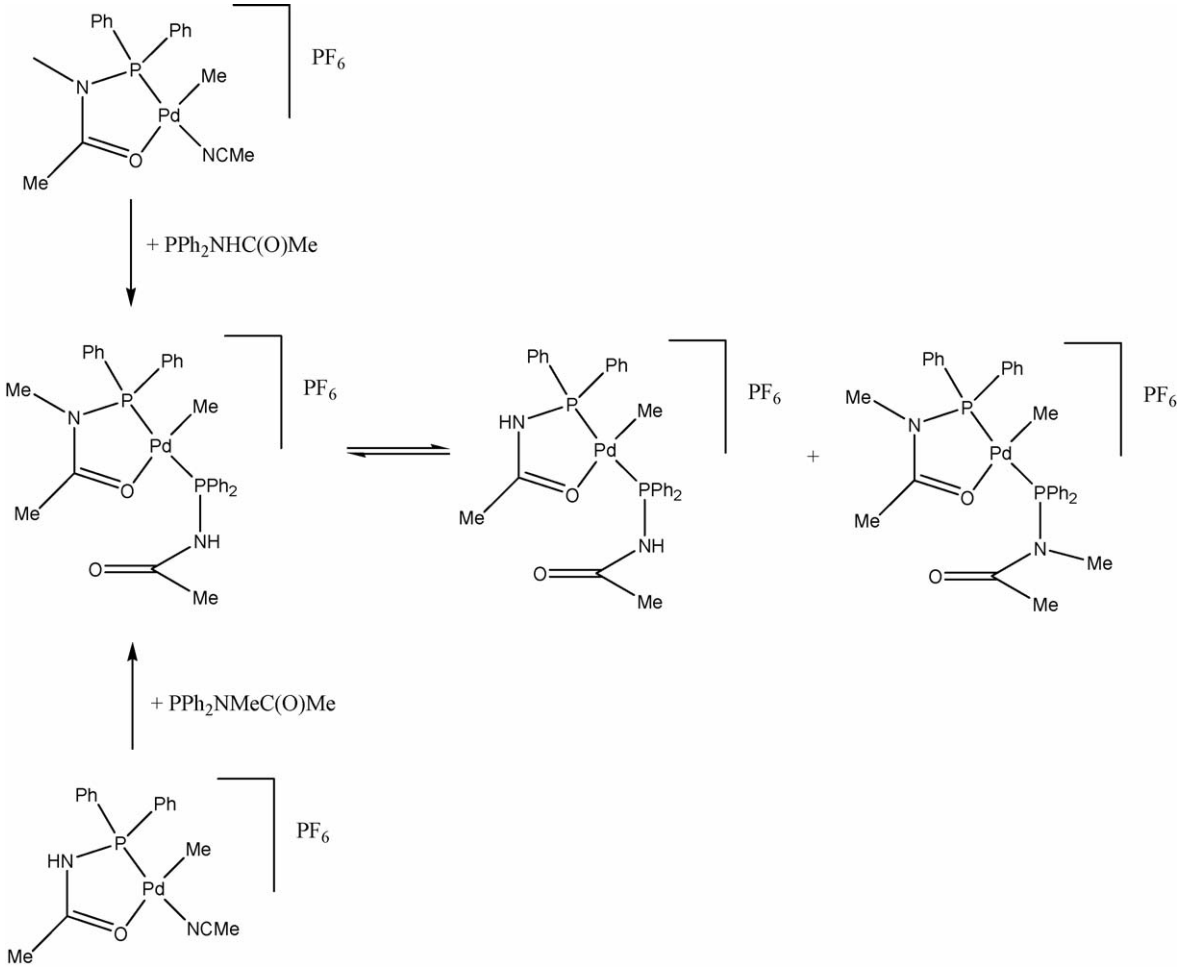
Scheme 14). Addition of a potentially bidentate ligand such as **7**, **8** or **6** leads to replacement of acetonitrile, but no ring opening of the coordinated ligand **6** is observed indicating that **6** is a better P,O chelate ligand than either **7** or **8**.

In a much broader study Braunstein et al. have investigated the chelate properties of ligand **6** using the complex [Pd(Me)(NCMe)(P,O-κ^2-**6**)]PF_6 [33]. Once formed, addition of either **6** or **7** as alternative ligand renders the complexes [Pd(Me)L(P,O-κ^2-**6**)]PF_6 (L = **6**, **7**) as acetonitrile is replaced (see Scheme 15). That **6** is a better chelate ligand than **7** is established by synthesising complex [Pd(Me)(**7**)(P,O-κ^2-**6**)]PF_6 from either side. Reacting [Pd(Me)(NCMe)(P,O-κ^2-**7**)]PF_6 with ligand **6** yields complex [Pd(Me)(**7**)(P,O-κ^2-**6**)]PF_6 as the oxygen end of ligand **6** replaces its counterpart from **7** in the chelate position. Compound [Pd(Me)(**7**)(P,O-κ^2-**6**)]PF_6 can also be formed by a ligand exchange reaction between [Pd(Me)(**6**)(P,O-κ^2-**6**)]PF_6 and [Pd(Me)(**7**)(P,O-κ^2-**7**)]PF_6 (see Scheme 16).

The methyl substituted ligand $PPh_2NMeC(O)Me$ **6**Me behaves in a similar way prompting the Braunstein group to investigate the relative chelate strengths of **6** and **6**Me [33]. The outcome of the experiment introducing the two ligands alternatively to the respective palladium complex [Pd(Me)(NCMe)(P,O-κ^2-L)]PF_6 (L = **6**, **6**Me) is as surprising as indecisive. Complex [Pd(Me)(**6**)(P,O-κ^2-**6**Me)]PF_6 undergoes an equilibrium ligand sym-proportionation reaction forming [Pd(Me)(**6**)(P,O-κ^2-**6**)]PF_6 and [Pd(Me)(**6**Me)(P,O-κ^2-**6**Me)]PF_6 (see Scheme 17).



Scheme 16. Ligand sym-proportionation.



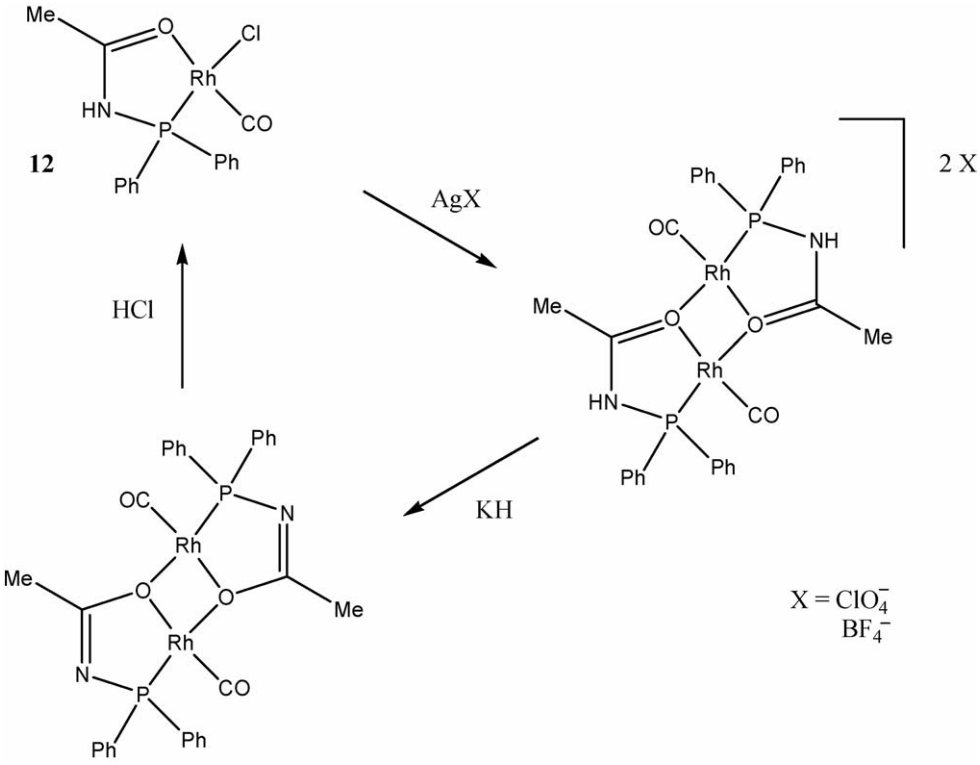
Scheme 17. Ligand sym-proportonation between diphenylphosphino acetamide and *N*-methyl-diphenylphosphino acetamide.

If **6** is reacted with the rhodium complex $[Rh(\mu\text{-}Cl)(CO)_2]_2$ the chelate complex $[RhCl(CO)(P,O\text{-}\kappa^2\text{-}\mathbf{6})]$ **12** is formed readily [88]. Salt metathesis yields the dimer $[Rh(CO)(P,O\text{-}\kappa^2\text{-}\mathbf{6})]_2\ X_2$ ($X = ClO_4^-$, BF_4^-) that is readily deprotonated to form the neutral dimeric complex. The monomer is readily reformed upon addition of dry HCl (see Scheme 18). A similar dimer can be formed following chloride abstraction with AgX ($X = ClO_4^-$ BF_4^-), but retaining two positive charges. Complex **12** was reacted with several alternative ligands to determine the relative ligand strength of **6**. The chelate ring is opened up upon addition of isonitriles while **6** can be completely displaced by triphenyl phosphine. Displacement of **6** can also be afforded by addition of 2-phosphinomethyl-pyridine.

The same reaction pattern as with the dimeric rhodium precursor complexes can be observed with the Mo(II) complexes $[\{(\eta^6\text{-}C_6H_5R)Mo(C_3H_5)(\mu\text{-}Cl)\}_2]$ (R = H, Ph) easily accessible from $[(\eta^6\text{-}C_6H_5R)_2Mo]$ and allyl chloride [89]. Reaction of the molybdenum dimer with ligand **6** in toluene renders the monodentate, phosphorus coordinated complex $[(\eta^6\text{-}C_6H_5R)Mo(C_3H_5)Cl(\mathbf{6})]$ whereas the same reaction carried out with sodium methanolate in methanol yields the chelate complex $[(\eta^6\text{-}C_6H_5R)Mo(C_3H_5)(P,O\text{-}\kappa^2\text{-}PPh_2N{=}C(O)Me)]$ after deprotonation of the coordinated ligand **6** (see Scheme 19). Without addition of a base to afford proton abstraction or when ligand **6**Me is used instead of ligand **6**, the reaction produces the salt complex $[(\eta^6\text{-}C_6H_5R)Mo(C_3H_5)(P,O\text{-}\kappa^2\text{-}PPh_2NRC(O)Me)]PF_6$ (R = H, Me) after anion exchange with NH_4PF_6.

The molybdenum chelate complexes adopt a three legged piano stool structure with an essentially tetrahedral geometry around the metal centre. As all four substituents are different, the metal is asymmetric and the complex chiral at molybdenum. All the complexes crystallise in the racemic form (see Scheme 20). The metallacycle is planar as are the respective metallacycles for all the known P,O chelate complexes of this ligand class.

Pregosin and coworkers [90] reacted the commercially available amidophosphine-phosphinite chelate ligand (*S*)-Ph-*t*-LANOP with the rhodium precursor $[RhCl(COD)]_2$ obtaining two dinuclear complexes (see Scheme 21). In the major product one of the (*S*)-Ph-*t*-LANOP ligands replaces the COD on one of the rhodium centres and the other (*S*)-Ph-*t*-LANOP ligand replaces one of the two bridging chlorines. In the minor product both COD ligands are replaced leaving the central $[Rh_2Cl_2]$ ring fragment intact. In each case (*S*)-Ph-*t*-LANOP acts as a chelate ligand, but in the major product it also serves as a bridge between the two metal centres. The LANOP ligands are synthesised from oxo-prolinol (see Scheme 22) [91] using an asymmetric hydrogenation reaction as the first step.



Scheme 18. Dimerisation and monomerisation of a rhodium(I) diphenylphosphino acetamide complex.

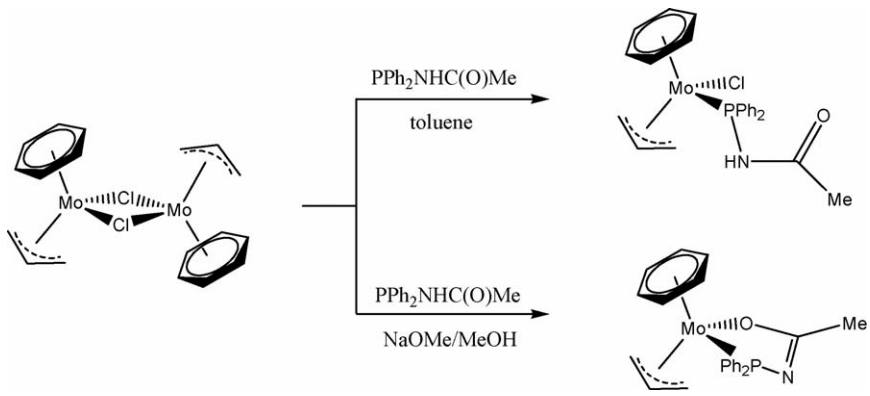
The major product rearranges slowly, over several weeks, in methylene chloride to form the minor product. The minor product exists in the *syn–trans* and in the *syn–cis* form, respectively (see Fig. 7). The COD ligand in the major product can be replaced to give the respective triligand complex, if another (*S*)Ph-*t*-LANOP moiety is added to it. Mononuclear rhodium (I) complexes are accessible by removing the chloride *in situ* using a silver salt. The resulting cationic complex has both a COD and a (*S*)-Ph-*t*-LANOP chelate ligand. The COD ligand can subsequently be replaced by other donor ligands such as phosphines. Other approaches to mononuclear complexes include the reaction of $[RhCl(PPh_3)_3]$ with (*S*)-Ph-*t*-LANOP or the minor product with isonitriles.

Interestingly enough, the same reaction carried out with $[M(COD)_2]BF_4$ (M = Rh, Ir) as the metal precursor complex renders the mononuclear complexes as sole products (see Scheme 23) [91]. Similarly, the palladium complex **13** gives only the expected ligand substitution product **14** (see Scheme 24).

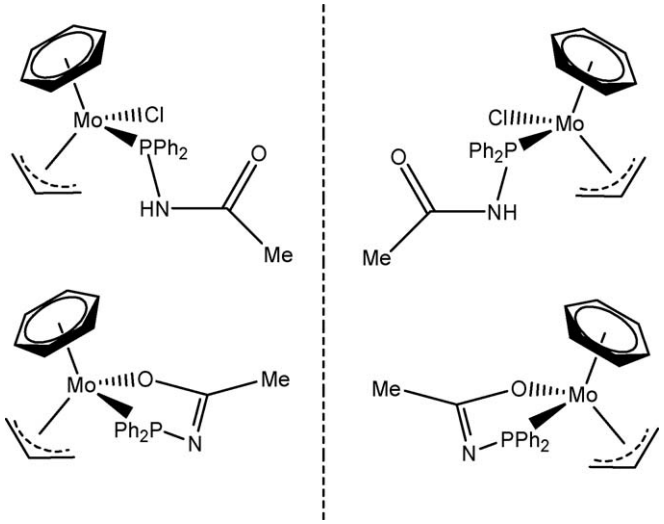
2.4. Applications of carboxylic acid phosphinoamides

Few applications for these ligand systems have been reported in the literature so far [43,91,92], but some investigations leading to possible applications in the field of homogenous catalysis have already been carried out [33,88,93]. In particular, the behaviour of some rhodium and palladium complexes towards CO was investigated. CO is one of the feedstock monomers in hydroformylation and CO/olefin copolymerisation reactions [94–96].

It was found, that CO readily displaces the oxygen terminus from the metal if the phosphino amide acts as a chelate ligand [88]. The reaction is usually reversible, but in some cases carbon monoxide is powerful enough to replace the phosphino amide



Scheme 19. Reaction between diphenylphosphino acetamide and $[(\eta^6\text{-}C_6H_6)Mo(C_3H_3)Cl]_2$.

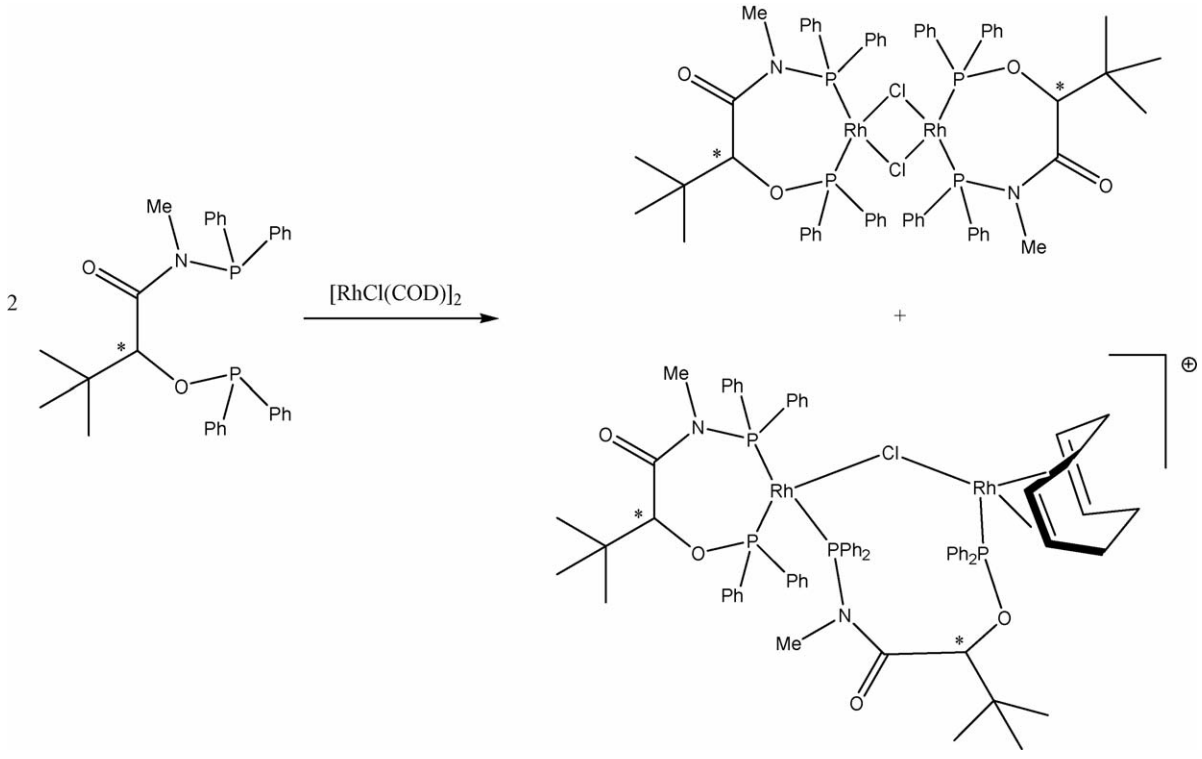


Scheme 20. The stereochemistry of the products from Scheme 19.

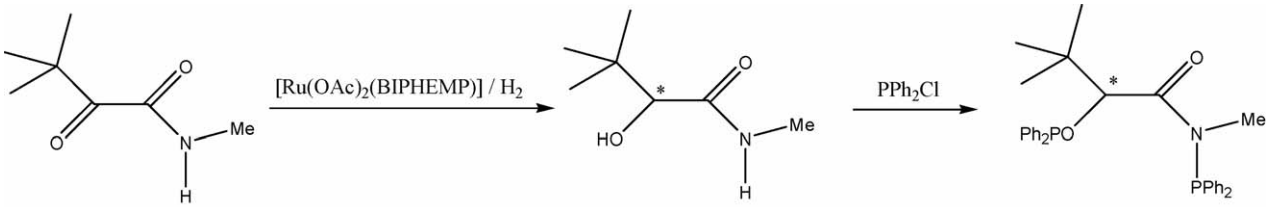
completely. In one reported case the resulting complex *trans*-$[Rh(CO)_2(PPh_3)_2]ClO_4$ takes up a third CO to form the trigonal bipyramidal complex *trans*-$[Rh(CO)_3(PPh_3)_2]ClO_4$ [88]. In palladium complexes insertion of CO into the Pd-alkyl bond was observed [97], a necessary requirement for chain propagation in CO/olefin copolymerisation [98–102] as well as the hydroformylation of olefins [94–96]. Braunstein et al. investigated the early chain propagation steps of the copolymerisation between CO and ethylene on the phosphinoacetamide/palladium system shown in Scheme 25 in a rare study not involving strained alkenes [97].

Keim et al. [43] remarked upon the suitability of phosphino amino ylides to replace the phosphino ketones as ligands in the nickel(0) catalysed olefin oligomerisation reaction known as the SHOP process (Shell Higher Olefin Process) [44–46]. No definitive examples were reported, but some studies concerning the insertion of CO and tolane into the Ni–C bond were carried out.

Hoffmann–La Roche have patented a process for the asymmetric hydrogenation of 4-oxoisophorone enol acetate to (*S*)-



Scheme 21. Formation of a rhodium(I) *t*-LANOP complex.



BIPHEMP = (6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)

Scheme 22. Asymmetric hydrogenation in the synthesis of *t*-LANOP.

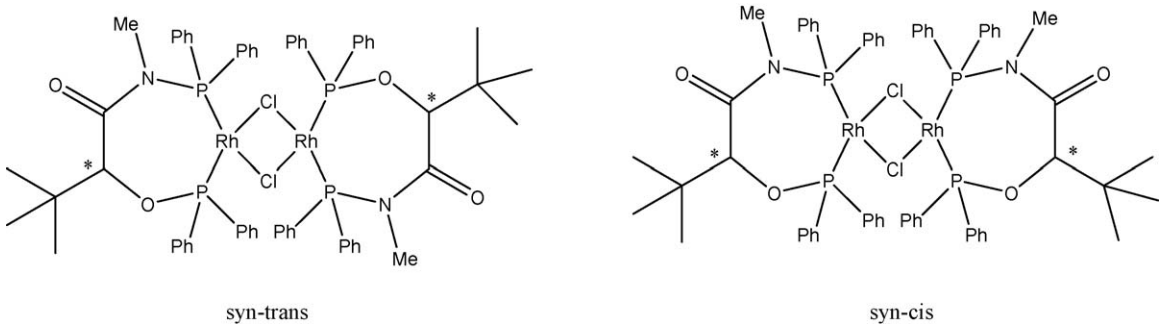
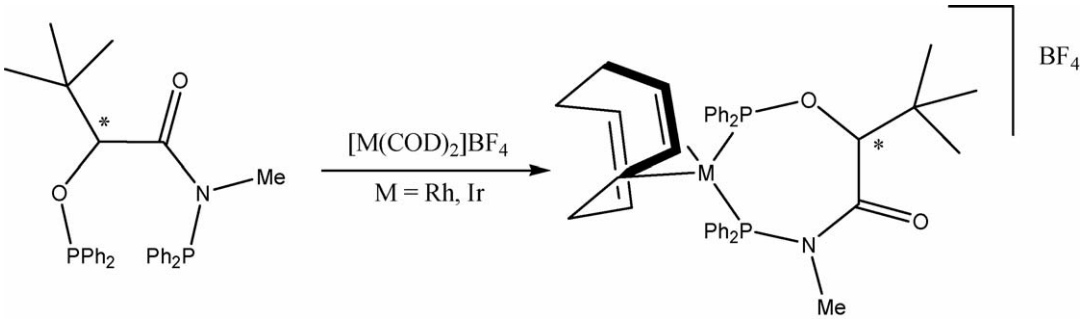
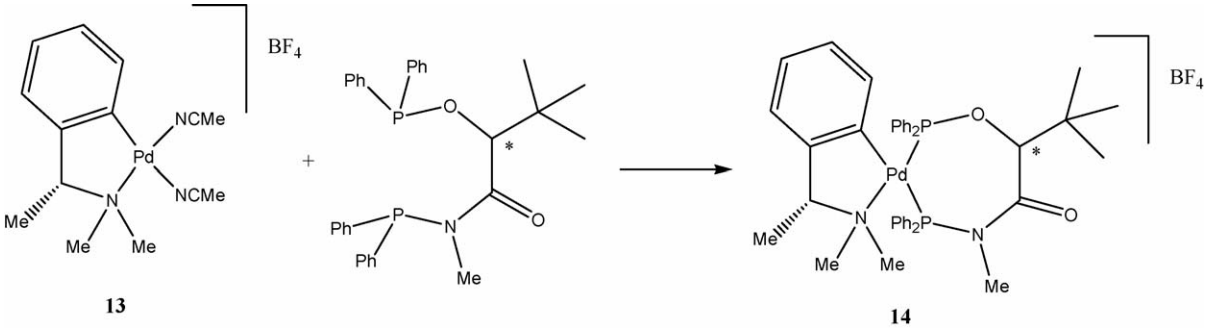


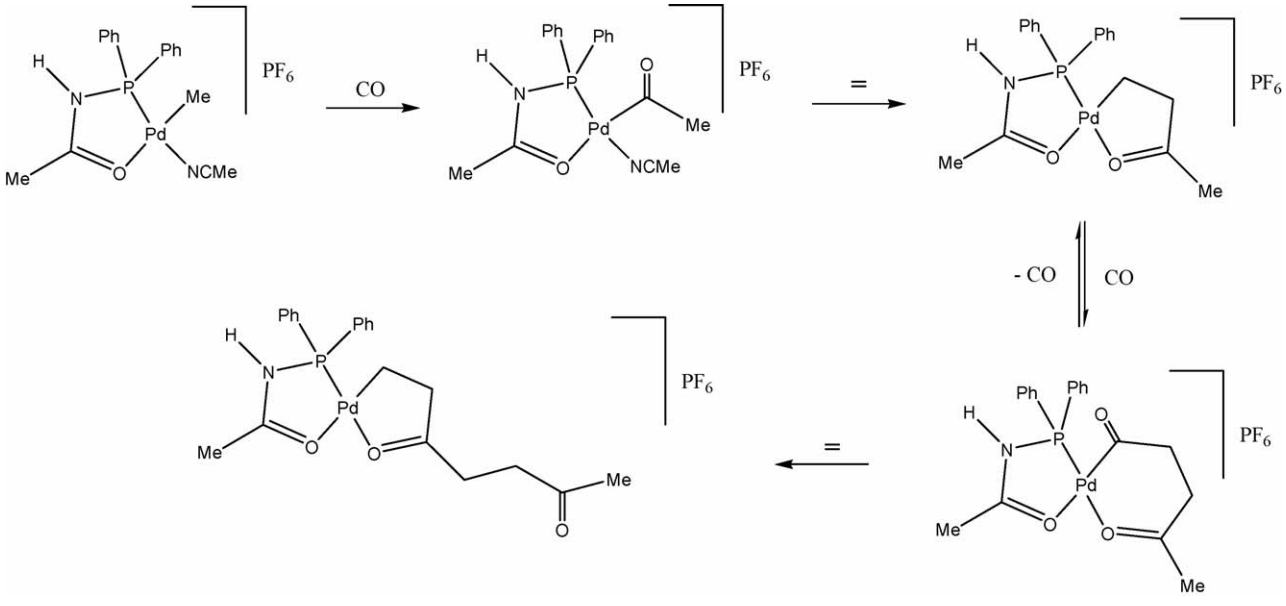
Fig. 7. The stereochemistry of the rhodium(I) *t*-LANOP dimers.



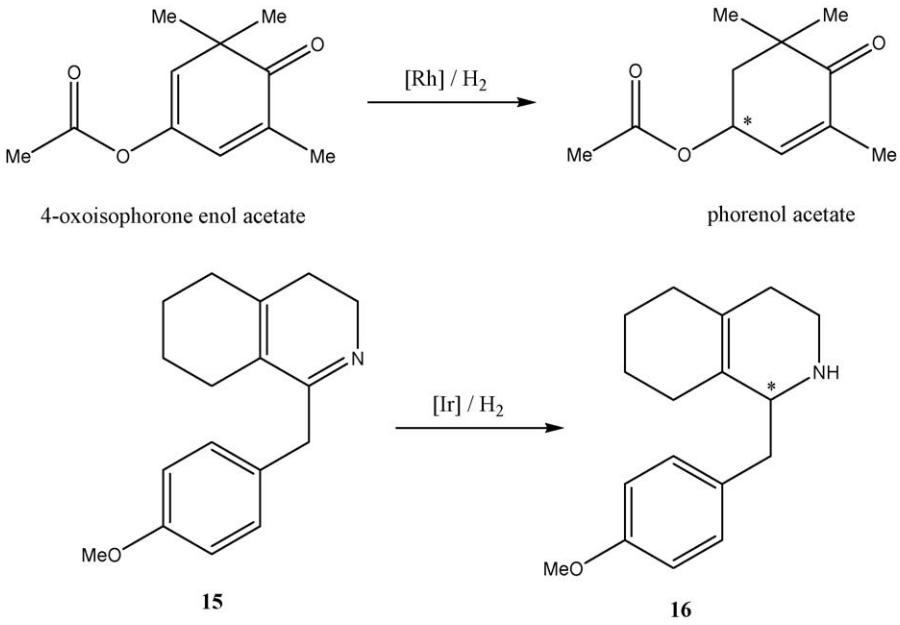
Scheme 23. Formation of monomeric rhodium(I)/*t*-LANOP cmplexes.



Scheme 24. Reaction of a palladium(II) complex with *t*-LANOP.



Scheme 25. The early stages of ethylene/CO copolymerisation as seen with a Pd(II)/diphenylphosphino acetamide system.



Scheme 26. The asymmetric hydrogenation of 4-oxoisophorone enol acetate and **15**.

phorenol acetate using a rhodium catalyst in 71% ee and of cyclic iminium salts like **15** to the corresponding cyclic secondary amines like (*S*)-**16** using iridium catalysts in 86% ee (see Scheme 26) [91,103]. (*S*)-phorenol acetate is a valuable intermediate in the synthesis of retinoides used for therapy and prophylaxis of dermatological deceases [104] and (*S*)-**16** is a valuable intermediate for pharmaceutical products like Dextromethorphan and Levorphanol.

Mortreux and coworkers reported the use of the mandelNOP family (see Fig. 8), an earlier representative of the same class of ligands termed *t*-LANOP by Scalone et al., for the asymmetric hydrogenation of activated ketones using rhodium catalysts [92]. In the asymmetric hydrogenation of Dihydro-4,4-dimethyl-2,3-furandione and *N*-Benzylbenzoylformamide to the optically active α-hydroxy compounds (see Scheme 27), both identically P- and differently P-substituted ligands were

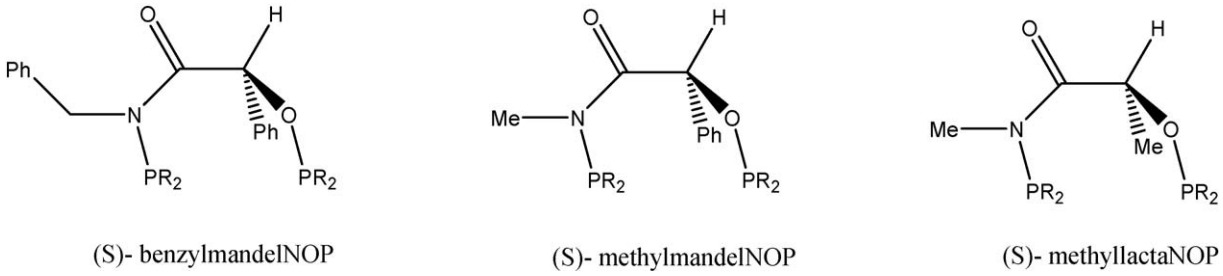
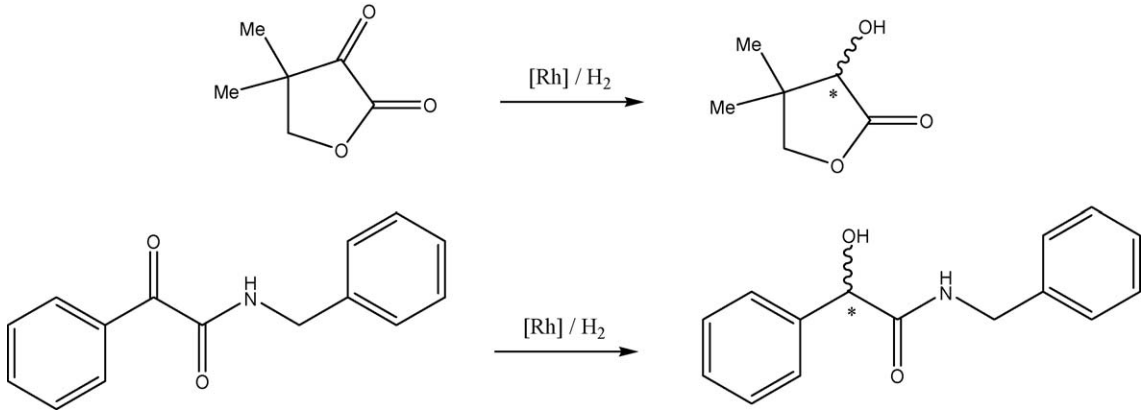


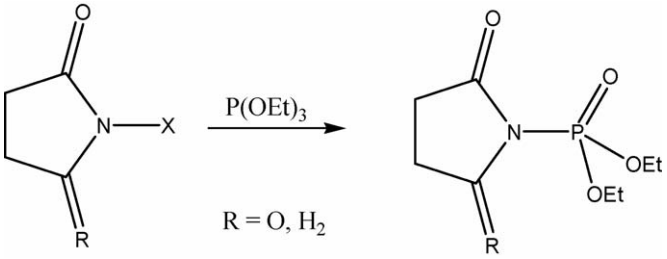
Fig. 8. The mandelNOP family of ligands.



Scheme 27. The asymmetric hydrogenation of dihydro-4,4-dimethyl-2,3-furandione and *N*-benzylbenzoylformamide to the optically active α-hydroxy compounds.

used giving dramatically different reported ees in the final product.

Whereas the identically P-substituted ligands (*S*)-Ph,Ph-benzylmandelNOP, (*S*)-Ph,Ph-methylmandelNOP and (*S*)-Ph,Ph-methyllactaNOP gave poor to mediocre reported ees in the 13–55% range, the differently P-substituted analogues (*S*)-Ph,Cpe-benzylmandelNOP, (*S*)-Ph,Cpe-methylmandelNOP and (*S*)-Ph,Cpe-methyllactaNOP rendered the products in mediocre to good ees of 51–90%. The catalyst is the dinuclear species discussed in the next chapter.



Scheme 29. Arbuzov reaction leading to a lactam phosphate.

3. Phosphino lactams

Interest in phosphino lactams emerged in a very diverse selection of research areas, but was almost always fueled by application driven expectations. Although the main focus has been asymmetric hydrogenation [105], another centre of research activities evolved around use as a reactive coupling agent for block copolymers [106], while still others were simply interested in P,O chelate coordination leading to five membered metallacycles [107]. Reflecting the different intended purposes, phosphino lactams rapidly evolved from the parent compounds **17** to functionalised phosphino lactams carrying different phosphino groups with diverse electronic and steric properties as well as asymmetric centres in the carbon backbone **18** (see Fig. 9).

Whereas most phosphino lactams are derived from the series of monocarboxylic acids, there are quite a few examples of lactams whose parent compounds possess two carboxylic acid functions such as phthalic acid imide **19** [108].

3.1. Synthesis

Synthesis of the phosphino lactams is almost always accomplished by reacting the respective lactam with a suitable P–Cl compound. To my best knowledge, no case has ever been reported whereby the P–N bond was formed first to create the linear carboxylic acid phosphino amide followed by ring closure to the phosphino lactam. This is probably due to the reported instability of the P–N bond [6].

The amidophosphine-phosphinite compounds **18** known as oxo-proNOP ligands and developed by Mortreux et al. from the commercially available (*S*)-5-(hydroxymethyl)-2-pyrrolidinone pose a very interesting challenge. They display two reactive centres in their precursor compounds, namely an N–H and an O–H bond featuring different reactivities towards chlorophosphines or chloro-phosphites. Careful exploitation of these different reactivities leads to the introduction of different phosphino groups on the N- and O-termini of the ligand. Successive reaction with two different P–Cl compounds usually leads to substitution on oxygen first and nitrogen later [105,109] (see Scheme 28).

An interesting alternative to the general route is the reaction between *N*-halogeno-succinimide (halogen = Cl, Br) or *N*-2-bromo-2-pyrrolidinone and triethylphosphite to the respective Arbuzov products (see Scheme 29) employed by Desmarchelier and Fukuto [108]. The reaction cannot be extended to related compounds. For instance, *N*-chloro-*N*-alkylamides render imidoyl chlorides and trialkyl phosphates [110] whereas reactions

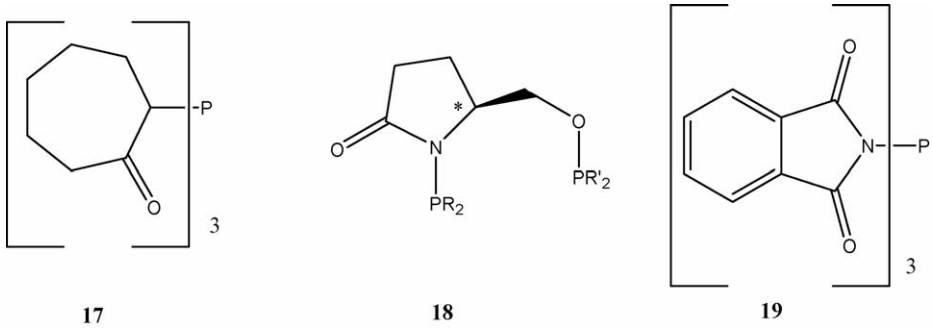
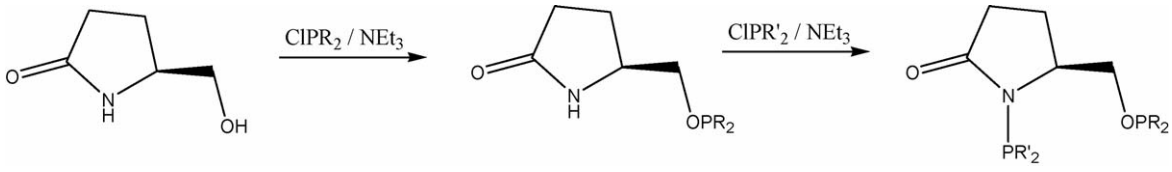
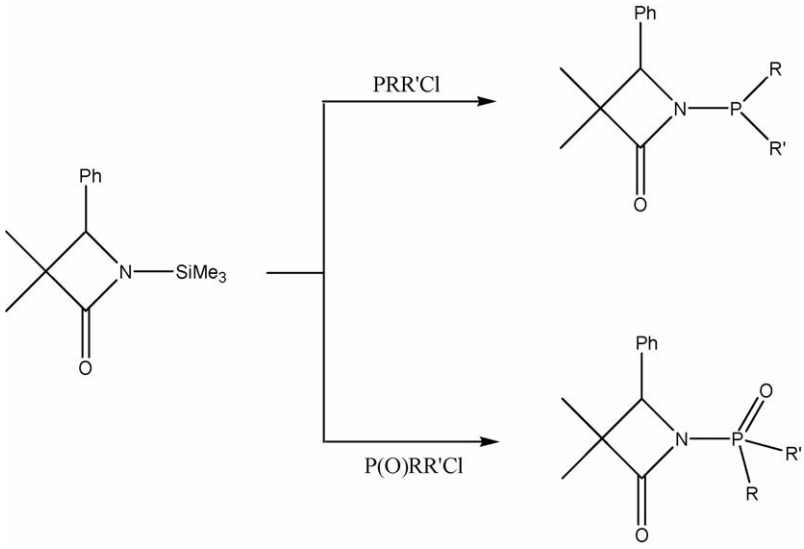


Fig. 9. Phosphino lactam ligands.



Scheme 28. Stepwise phosphanylation in the synthesis of oxo-proNOP ligands.



Scheme 30. Phosphanylation of four membered lactams.

with phosphines result in the formation of phosphine oxides without formation of a P–N bond [111,112].

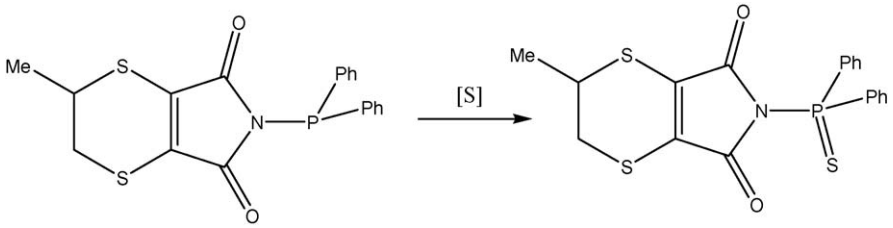
It is equally possible to use silylated lactams in the reaction with PCl_3, thus avoiding the use of an auxiliary base to trap the hydrochloric acid formed [54,113,114]. Particularly interesting is the synthesis of phosphino lactams where the lactam has a short ring size (see Scheme 30) [113]. Only the P=O products were isolated as the λ^3-phosphines were too moisture sensitive [113].

3.2. Properties of phosphino lactams

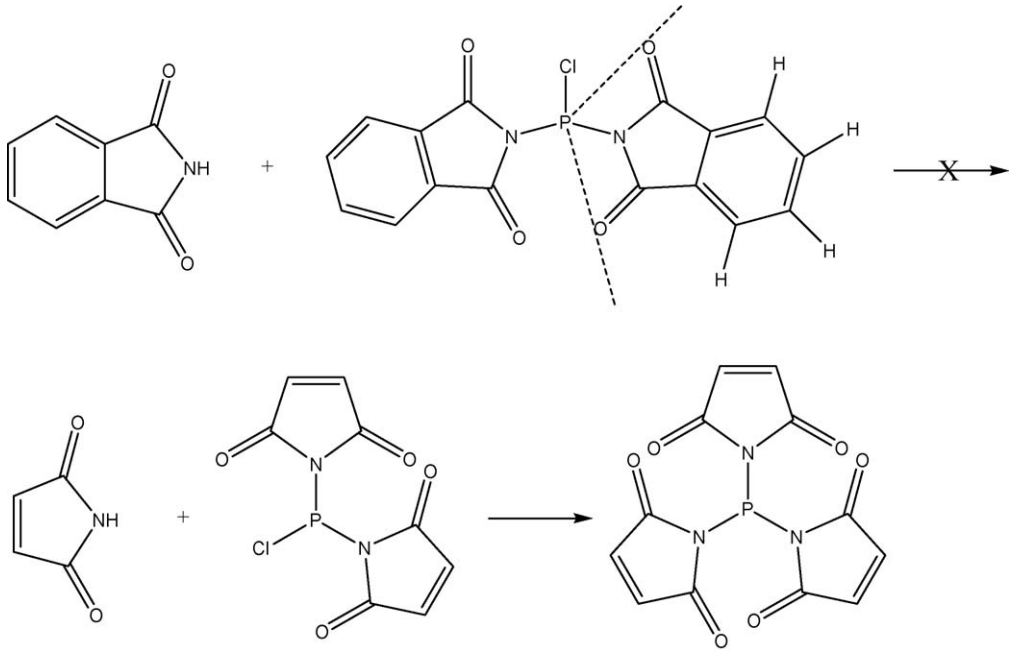
Like the linear carboxylic acid phosphino amides phosphino lactams are electron deficient compared to their phosphino amide counterparts not carrying an oxo-group on the amino carbon atom. The electron withdrawing effect is transmitted to the phosphino group making the phosphino lactam essentially an electron deficient ligand.

The phosphorus terminus of a phosphino lactam is susceptible to oxidation. Prolonged exposure to air will oxidise the phosphino lactam to the respective phosphorus(V) oxo-compound [114,115] whereas the analogous sulfurisation can be accomplished by reacting the phosphino lactam with elemental sulfur [116] (see Scheme 31). A more convenient way to obtain the P=O product is oxidisation with NO [114]. Phosphino lactams are easily hydrolised [113].

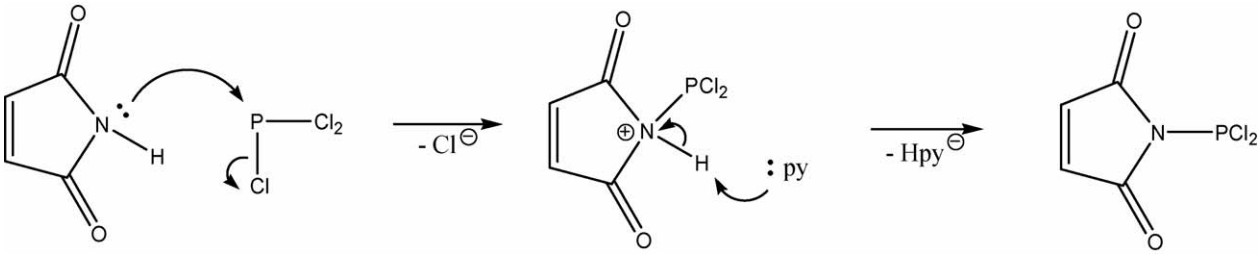
The electronic properties of phosphino lactams are probably best illustrated in the attempts to synthesise a series of phosphorus trilactams starting from PCl_3 and phthalimide, succinimide and maleimide as the lactam component [117]. All reactions were carried out in stoichiometric ratios in acetone with pyridine added as the auxilary base. All reactions yielded the expected product except when trisubstitution on phosphorus was intended. The third substitution using phthalimide failed even with prolonged heating to reflux whereas the same reaction using succinimide or maleimide rendered the expected triimide (see Scheme 32). The authors claimed steric factors for this behaviour, but on closer inspection it becomes apparent that the annelated phenyl ring in phthalimide has no steric influence at nitrogen since the phenyl ring is completely in the shadow of the two CO groups. However there is a significant annelation effect present that results in removal of electron density from the nitrogen centre [118–120]. The reaction mechanism proposed by the authors [117] cites nucleophilic attack of the nitrogen atom on the phosphorus centre as the first step (see Scheme 33). That is inconsistent with the electronic properties of the imides employed. However, if the first step in the third substitution reaction is assumed to be nucleophilic attack of the phosphorus on the NH proton, the nucleophilicity mirrors the reactivity (see Scheme 34). In this context it should be noted that the phosphorus centre becomes significantly more nucleophilic as chlorides are replaced by the lactam substituents.



Scheme 31. Sulfurisation of phosphino lactams.

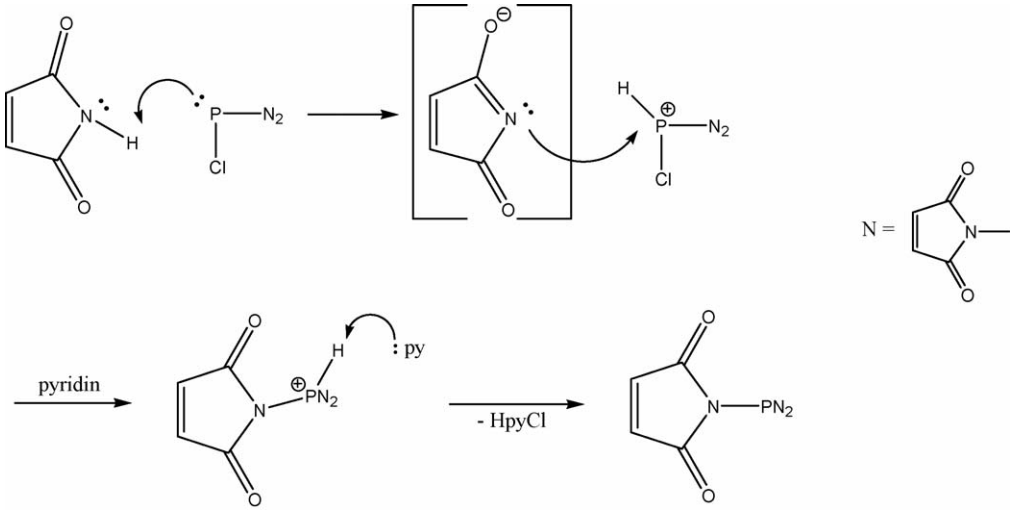


Scheme 32. Differences in the reactivities of succineimide and phthalimide towards $ClP(lactam)_2$.



Scheme 33. Proposed reaction mechanism in the phosphanylation of lactam.

Another interesting approach to arrive at trilactam phosphines was realised by Lorenz et al. [121] in their $PCl_n(Naphtholactam)_{n-3}$ ($n = 1$–3) series of ligands. The base used to deprotonate the naphtolactam was $Na\{N(SiMe_3)_2\}$ and the resulting naphtholactam phosphines displayed different isomers. The isomers differ in the relative position of the lactam oxo-group relative to the phosphorus atom; they can either be above or below the plane defined by the three nitrogen atoms (see Fig. 10).



Scheme 34. Probable mechanism in the phosphanylation of lactams.

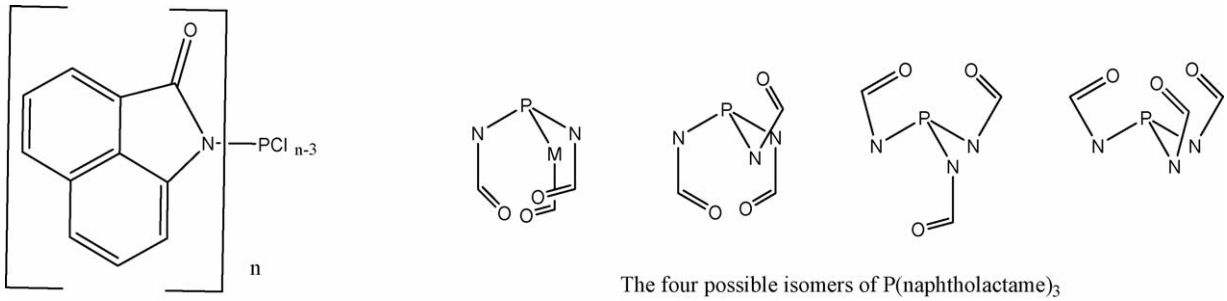
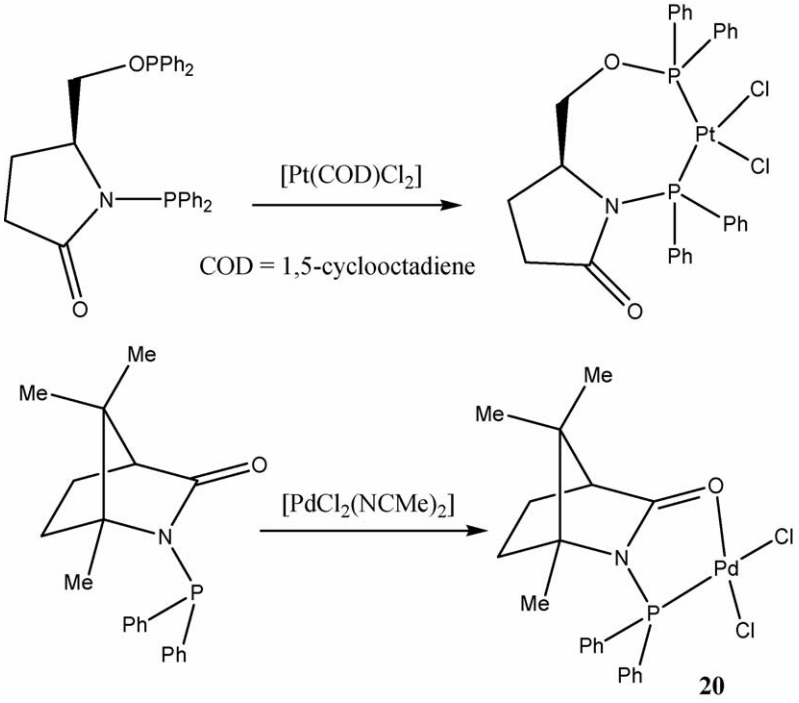


Fig. 10. The possible isomers of $P(Nl)_3$.



Scheme 35. Metal coordination modes for phosphino lactams.

The ligand properties deteriorate as more naphtholactam moieties are added to the phosphorus centre and the naphtholactam substituent withdraws eletron density from the phosphorus centre making it less nucleophilic. Likewise, the naphtholactam substituent is considerably bulkier than the standard phenyl group creating significant steric hindrance at the coordinating atom.

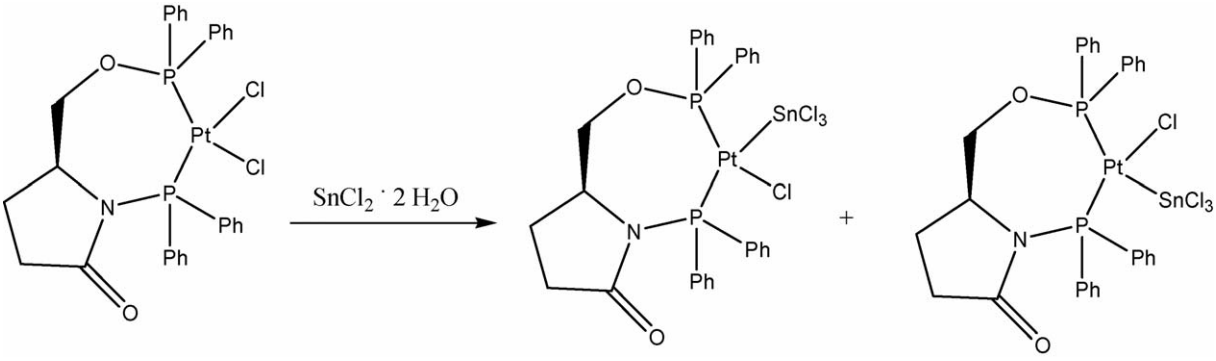
3.3. Transition metal complexes

Phosphino lactams coordinate readily to transition metal complexes through phosphorus [12,13] and in other cases their carbonyl oxygen to form chelate complexes [107] whenever possible (see Scheme 35).

Mortreux et al. reacted the AMPP[1] ligands (*S*)-1-(di-R-phosphino)-2-(((di-R′-phosphino)oxy)methyl)-pyrrolidinone (R, R′ = phenyl ph, cyclohexyl cy, cyclopentyl cpe) with [Pt(COD)Cl_2] (COD = 1,5-cyclooctadiene) to form the respective P, P chelate complexes after COD substitution (see Scheme 35 for an example) [122]. These seven membered metallacycles are described as rigid due to fusion with the proline cycle [123–127] with four (P, Pt, P, O) of their seven atoms in a common plane. The complexes are off-white solids that can be handled and stored in air for prolonged periods of time. They are also stable towards moisture. Thus, when the platinum-AMPP complexes are reacted with undried tin(II) chloride, the tin(II) chloride readily inserts into one of the two Pt–Cl bonds (see Scheme 36).

The distribution of the two possible isomers, with the trichlorostannyl-group *trans* to either the P(*N*) or the P(*O*) phosphorus, is largely dependent upon the substituents on phosphorus and the proline ring, but completely indifferent to solvent effects [128]. Only the *trans*-P(*N*) complex is observed when both phosphorus atoms bear the same substituents (Ph,Ph; Cy,Cy; Cpe,Cpe) and the proline ring misses the oxo-group, i.e. the pyrrolidine rather than the pyrrolidinone derivatives are used.

[1] AMPP is a collective term used for proNOP (derived from pyrrolidine) and oxo-proNOP (derived from pyrrolidinone) ligands.



Scheme 36. Reaction of [Pt(oxo-proNOP)Cl_2] with $SnCl_2$.

The ratio changes to as much as 80/20 for the pyrrolidinone derivatives with identical substitution on phosphorus and to 55/45 for the most different combination (Ph, ^{i}Pr) in the pyrrolidine series. This effect is explained by the authors with the relative electron densities on the two phosphorus atoms and the resulting differences in the *trans* effects for the incoming $SnCl_2$ group issuing from them. The P(*N*) phosphorus is identified as the intrinsically more electron rich site compared to P(*O*), but that is said to be mitigated by the oxo-group in the pyrrolidinone series resulting in a smaller ratio of up to 80/20 instead of 100/0 for the identically substituted derivatives in the pyrrolidinone series.

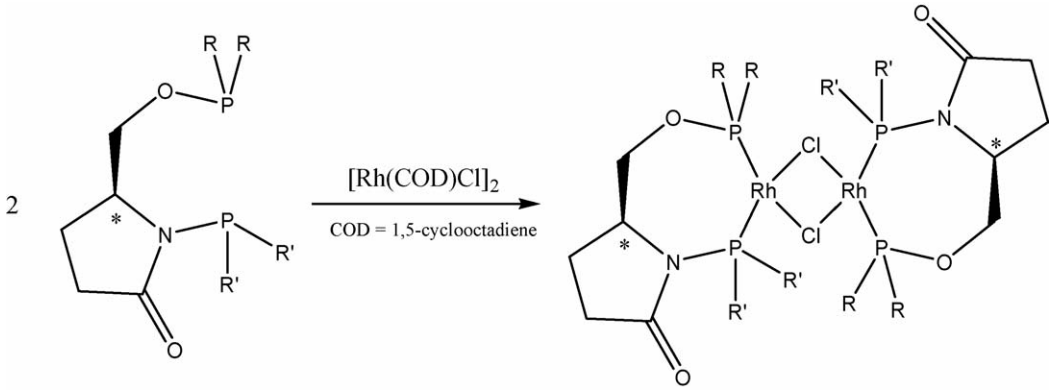
Jacobson in his effort to test a series of phosphino amide ligands for their performance in homogenously catalysed hydroformylation reactions reacted *in situ* 1-diphenylphosphino-pyrrolidinone with the rhodium(I) precursor complexes $[Rh(CO)_2Cl]_2$, $[Rh(C_8H_{14})_2Cl]_2$, $[Rh(C_2H_4)_2Cl]_2$ and [Rh(CO)$(PPh_3)_2$Cl], respectively [129]. Although the complexes were not isolated and no ^{31}P NMR spectra of the respective solutions recorded, the author assumed that five membered P,O chelate complexes were formed. The assumption could have been easily verified by the characteristic downfield shift experienced for five membered chelate rings in their ^{31}P NMR spectra [130].

However, the assignment, speculative as it may be on Jacobson's part, was supported by Mortreux and coworkers some 9 years later when they published their findings on the reaction of some AMPP ligands with the rhodium(I) precursor complex [Rh(COD)Cl]$_2$ [92]. It should be noted, however, that AMPP ligands form P,P chelate complexes and not P,O chelates as claimed by Jocobson whose ligand lacks a second phosphorus centre. In the reaction featuring the AMPP ligands, the products are dimeric μ-chloro bridged rhodium complexes where the AMPP ligand acts as a P,P-chelate (see Scheme 37). No information regarding the ratio between the two possible isomers (*syn–cis* and *syn–trans*) for the relative positions of the P(*O*) and P(*N*) phosphorus atoms was given.

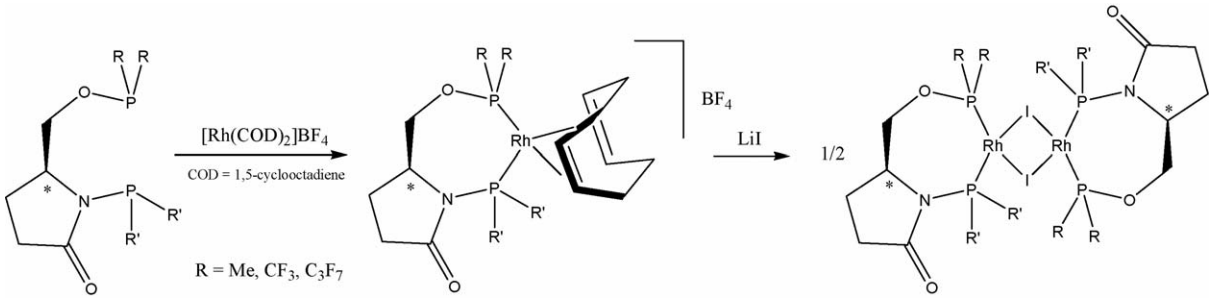
Other rhodium(I) precursors included $[Rh(COD)_2]BF_4$ and $[Rh(COD)(OCOR)]_2$ (R = Me, CF_3, C_3F_7) resulting in a monomeric complex (see Scheme 38) and the μ-acetato bridged dimers (see Scheme 39).

In a related reaction Mortreux and coworkers reacted the ligands Ph,Ph-oxo-proNOP and Cy,Cy-oxo-proNOP with $[Ni(COD)_2]$ to obtain the respective nickel(0) complexes (see Scheme 40) *in situ* [131]. Here no isomers (*syn–cis, syn–trans*) are expected due to the tetrahedral coordination around the nickel centre.

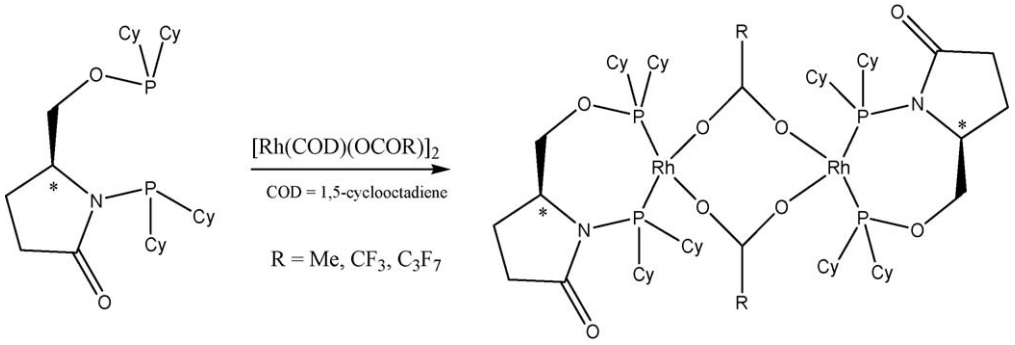
Other transition metal complexes of oxo-proNOP ligands include those derived from the ruthenium(II) precursor [Ru(COD)(methylallyl)$_2$] (COD = 1,5-cyclooctadiene) [132–134]. When [Ru(COD)(methylallyl)$_2$] is reacted with (*S*)-1-(diphenylphosphino)-2-((((di-phenylphosphino)oxy)methyl)-pyrrolidinone the monomeric bis-methylallyl complex is obtained which can be further reacted with carboxylic acids to render the respective dicarboxylates (see Scheme 41). The alternative procedure, i.e. reaction of [Ru(COD)$(O_2CR)_2$] with (*S*)-1-



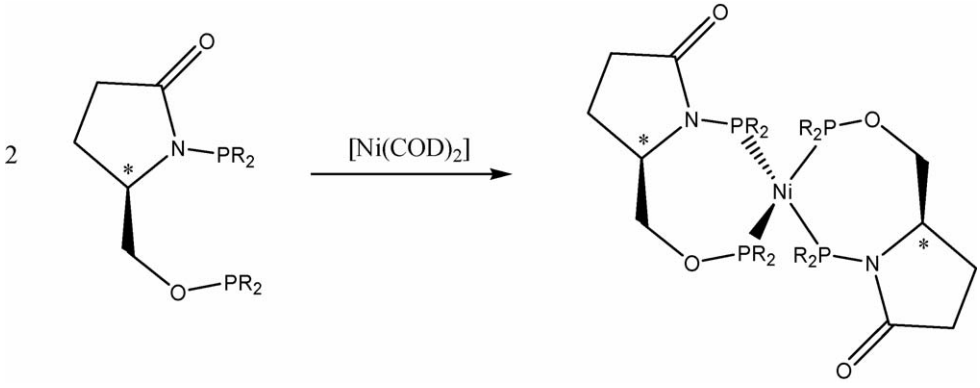
Scheme 37. Formation of dimeric rhodium(I)/oxo-proNOP complexes.



Scheme 38. Dimerisation of a monomeric rhodium(I)/oxo-proNOP complex.



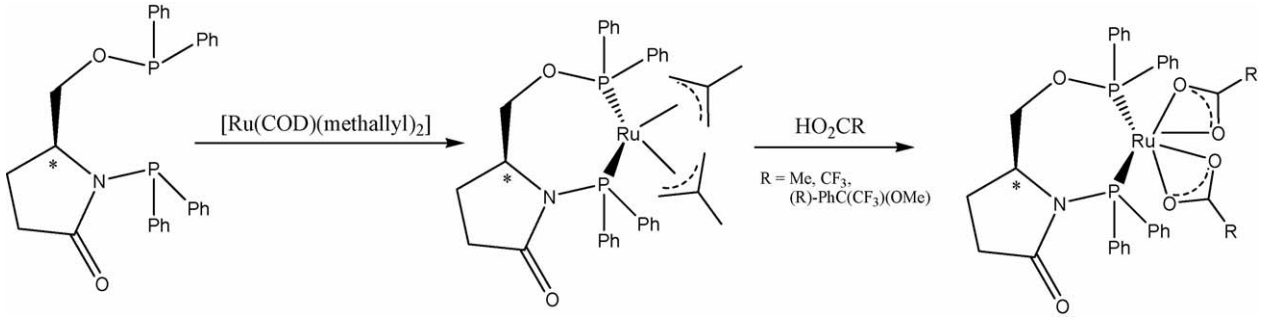
Scheme 39. Carboxylato bridged dimeric rhodium(I)/oxo-proNOP complexes.



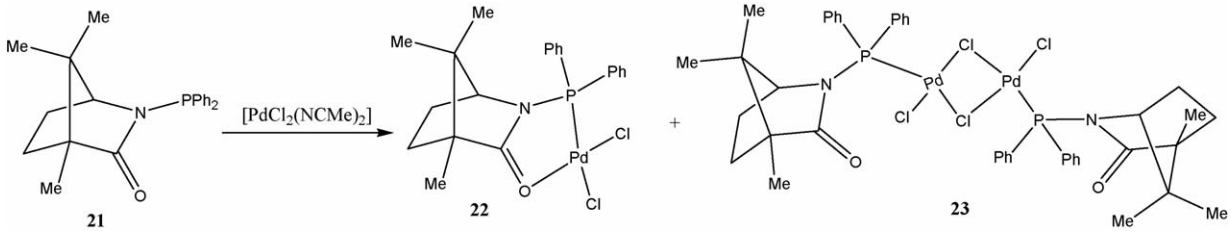
Scheme 40. Isomer free, tetrahedrally coordinated Ni(0) complexes of oxo-proNOP.

(di-phenylphosphino)-2-(((di-phenylphosphino)oxy)methyl)-pyrrolidinone was not attempted by the authors after the analogous reaction with the respective pyrrolidine ligands failed to produce a pure product [132].

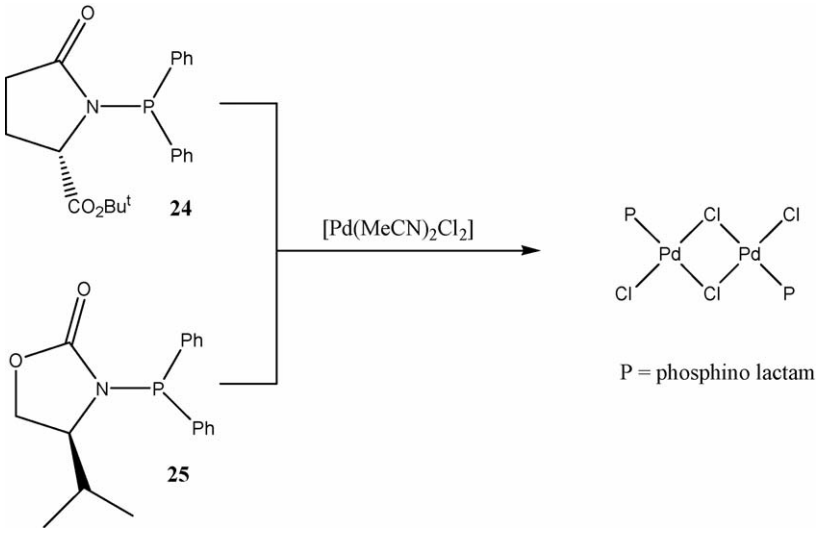
In fact, the ruthenium complexes are usually isolated as diastereomeric mixtures. These diastereoisomers result from enantiomeric configurations of the methylallyl or carboxylato ligands, respectively [133]. An observation that was also made



Scheme 41. Formation of and ligand exchange on ruthenium(II)/oxo-proNOP complexes.



Scheme 42. Palladium coordination on camphor phosphino lactams.

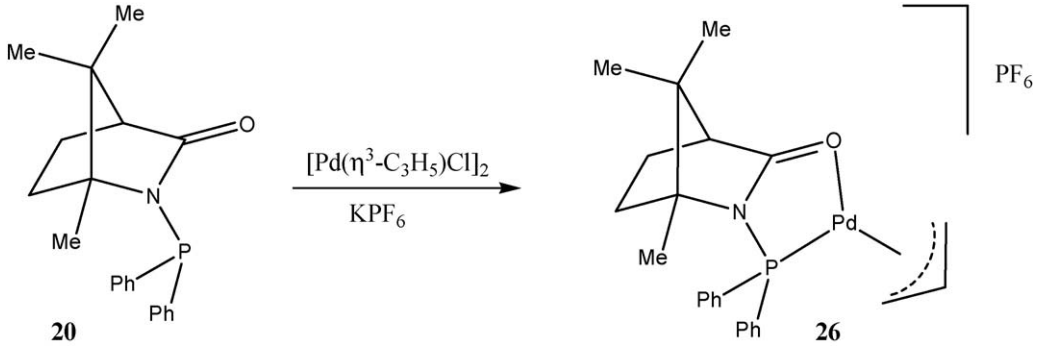


Scheme 43. Monodentate coordination mode of oxo-proNOP.

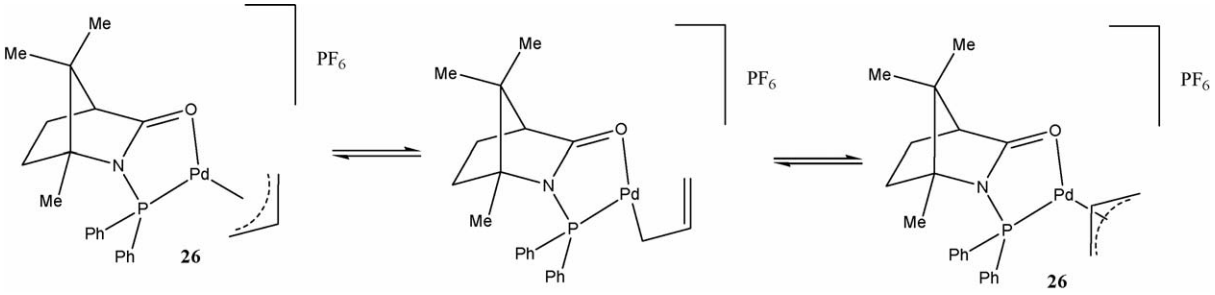
for $[P_2Ru((acac)_2]$ complexes [135]. Interestingly, there the ratio of the diastereoisomers in the final product is normally more favourable, if the route in Scheme 41 is followed. The Ru-oxo-proNOP complexes are air sensitive, a marked contrast to their platinum counterparts.

A phosphino lactam **20** derived from D-camphoric acid [107,136] was reacted with $[Pd(MeCN)_2Cl_2]$ to yield the P,O chelate complex in 93% yield (see Scheme 36). The isomeric phosphino lactam **21** prepared from D-camphor [136] produced two palladium complexes, a mononuclear monodentate **22** one in 77% and a dinuclear **22** one in 11% yield, under otherwise identical conditions (see Scheme 42).

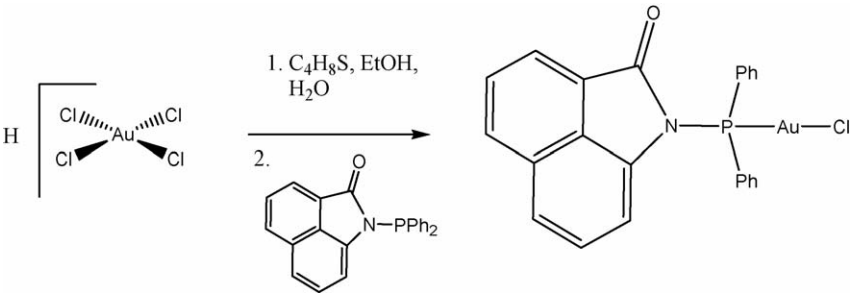
As Hosokawa et al. have pointed out, phosphino lactams do not necessarily bind in a bidentate fashion to palladium [107]. Instead, the phosphino lactam **24** and the phosphino oxazolidinone **25** form the dimeric palladium dichloride complexes with η^1-P ligands (see Scheme 43). Whether η^1- or η^2-coordination is preferred seems to depend on the electron density at phosphorus, the η^1-ligands bearing an electron withdrawing group in close proximity to the phosphorus atom. When $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ is reacted with the phosphino lactam **20**, the mononuclear complex $[Pd(P,O\text{-}\mathbf{20})(\eta^3\text{-}C_3H_5)]PF_6$ is formed in 75% yield after anion exchange using KPF_6 (see Scheme 44). In $[Pd(P,O\text{-}\mathbf{20})(\eta^3\text{-}C_3H_5)]PF_6$ **26** the chiral phosphino lactam ligand is responsible for the formation of diastereoisomers depending on the relative orientation of the allyl-ligand in relation to the stereocentre of the camphor backbone (see Scheme 45). The equilibrium is observable by ^{1}H NMR. A similar mechanism is operating with



Scheme 44. Synthesis of a camphor phosphino lactam palladium allyl complex.



Scheme 45. Isomerisation mechanism of the allyl substituent in the campher phosphino lactam palladium allyl complex.

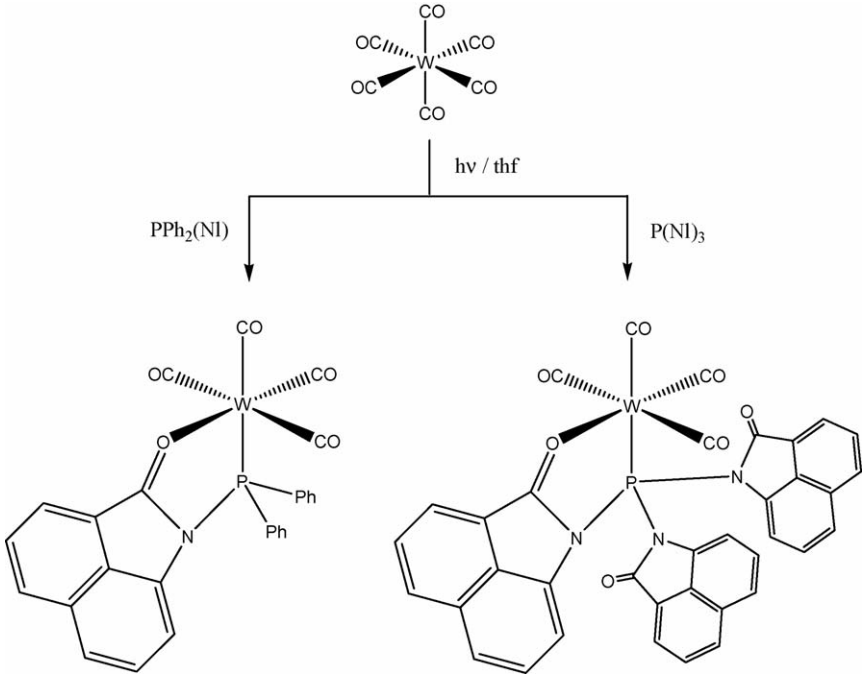


Scheme 46. Synthesis of [Au(PPh$_2$Nl)Cl].

the preceeding ruthenium methyallyl and ruthenium carboxylate complexes, respectively.

Lorenz et al. reacted their phosphino naphtholactams with gold and tungsten complexes to determine their ligand behaviour experimentally [121]. In the reaction between P(Nl)Ph$_2$ (Nl = naphtholactame) and [HAuCl$_4$]$^-$ the presumably linear [ClAuP(Nl)Ph$_2$] complex was obtained (see Scheme 46). The complex is very unstable and decomposes appreciably at elevated temperatures (temperature reported by authors: 60 °C). The product could not be isolated as a pure compound and was detected only as a mixture with unreacted starting material. The ligand P(Nl)$_3$ did not react with [Au(tht)Cl] (tht = tetrahydrothiophene).

Reaction with [W(CO)$_6$] proved to be more successful (see Scheme 47). When [W(CO)$_6$] was irradiated with light at −20 °C, treated with either P(Nl)Ph$_2$ or P(Nl)$_3$ and slowly warmed to ambient temperature, the respective coordination products were obtained. The resulting products were charac-



Scheme 47. Synthesis of *cis*-[W(PPh$_2$Nl)(CO)$_4$] and *cis*-[W(PNl$_3$)(CO)$_4$].

terised as *cis*-[W(CO)$_4${κ^2-P,O-P(Nl)Ph$_2$}] and *cis*-[W(CO)$_4$ {κ^2-P,O-P(Nl)$_3$}], respectively. Coordination of the lactam oxygen on the tungsten atom is weak in *cis*-[W(CO)$_4${κ^2-P,O-P(Nl)$_3$}]. The ligand becomes easily monodentate, if the complex is exposed to donating solvents, even as weakly donating as acetone.

3.4. Applications

Applications for the use of phosphino lactams cover a surprisingly diverse range starting at asymmetric hydrogenation of olefins [105,137] and carbonyl compounds [138,139] over fungicides [117] to cooling agents [140] and compatibility agents for block copolymers [106,141–145]. The reported applications are summarised in the four subheadings: hydrogenation, hydroformylation, compatibilisation agents for block copolymers and other applications to give the reader a better overview.

3.4.1. Hydrogenation

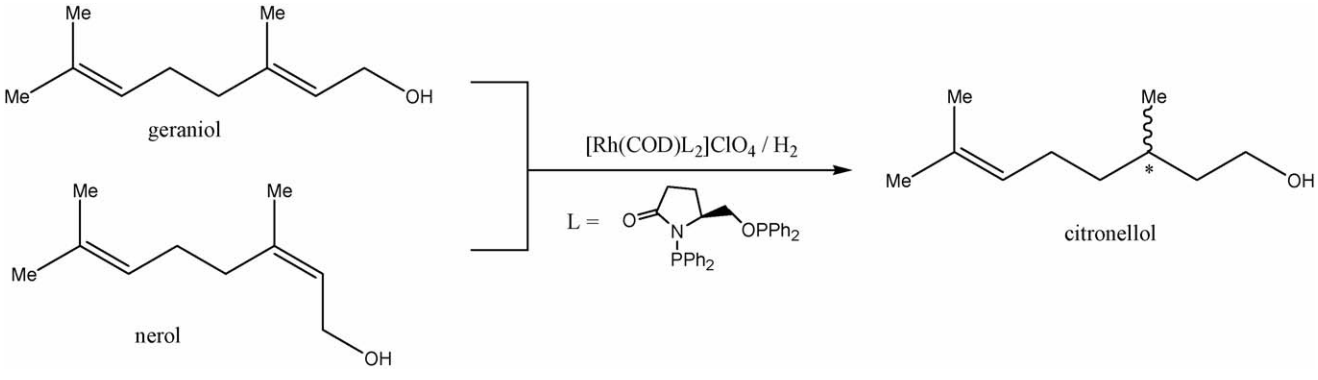
Most hydrogenations performed with phosphino lactams involve functional olefins or carbonyl groups with many carbonyl substrates carrying other functional groups. The intended product was almost always chiral. The notable exception to the rule was reported by Chevallier et al. in their study to hydrogenate styrene [137] The only phosphino lactam ligand used in this study was diphenylphosphino valerolactam with [Rh(C$_2$H$_4$)Cl]$_2$ as catalyst precursor and no reaction was observed.

A quarter of a century later Karim and coworkers reported the synthesis of citronellol by the rhodium catalysed asymmetric hydrogenation of the *cis*/*trans* isomers nerol and geraniol, two allyl alcohols (see Scheme 48) [105]. The observed ee of the product depends largely on the solvent (thf, ethanol, benzene) used with thf having only 26–30% ee, but ethanol (77–81% ee) and benzene (80.5–84.5% ee) giving much better results. Interestingly, the chirality of the product depended both on the solvent and on the starting material with geraniol giving (R)-citronellol and nerol rendering the (*S*)-enantiomer. However, in thf as solvent, the chirality was reversed. Changing the ligand from oxo-proNOP to proNOP that is to a species without the 5-oxo group has the same effect, but with lower ees compared to the ligands used.

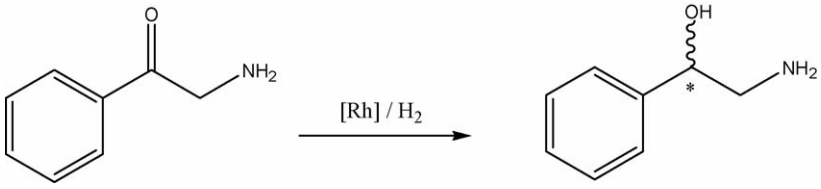
When the carbonyl compounds dihydro-4,4-dimethyl-2,3-furandione (ketopantolactone), *N*-benzylbenzoylformamide (*N*-benzylphenylglyoxamide) (see Scheme 26) or 2-aminoacetophenone (see Scheme 49) are used as substrates, the solvent was invariably toluene [146–148], a choice based on the experience made in the synthesis of citronellol. Reported ees were high except for *N*-benzylphenylglyoxamide where the reported ee dropped to 61–67% and independent of the anionic ligand on rhodium (Cl, CF_3CO_2). The reported enantiomers were (R)-hydroxypantolactone and (*S*) for the two nitrogen containing compounds. Using the proNOP instead of the oxo-proNOP ligand again resulted in a marked drop in the reported ees [147]. A very recent study on the solvent dependency for these three substrates again confirmed the order reported earlier [146]. Reported ees drop sharply in the order toluene > methanol.

In related studies [92,149,150], oxo-proNOP ligands were used in the rhodium catalysed asymmetric hydrogenation of various amines and amides (see Fig. 11). Reported ees for all substrates were generally in the mid to high 90s (%) with only the ketoamide reported to be much lower at room temperature (47–87%) [92], but 92% at 80 °C [149].

A study on the asymmetric hydrogenation of trifluoromethyl ketones using rhodium/oxo-proNOP catalysts reported excellent ees for alkyl and benzyl substituents (97%) that



Scheme 48. Synthesis of citronellol by asymmetric hydrogenation of geraniol and nerol.



Scheme 49. Asymmetric hydrogenation of 2-aminoacetophenone.

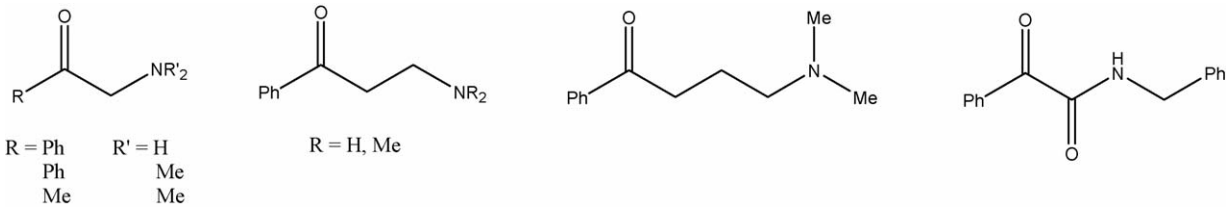
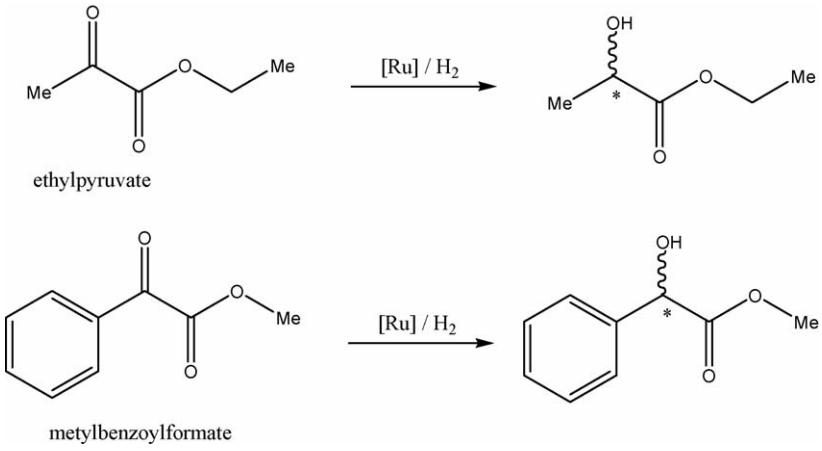


Fig. 11. Some amines and amides used in oxo-proNOP catalysed asymmetric hydrogenation reactions.

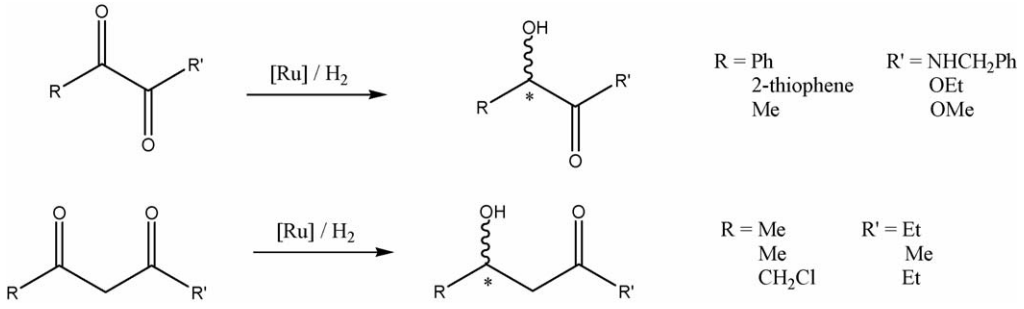


Scheme 50. Asymmetric hydrogenation of ethylpyruvate and methylbenzoylformate.

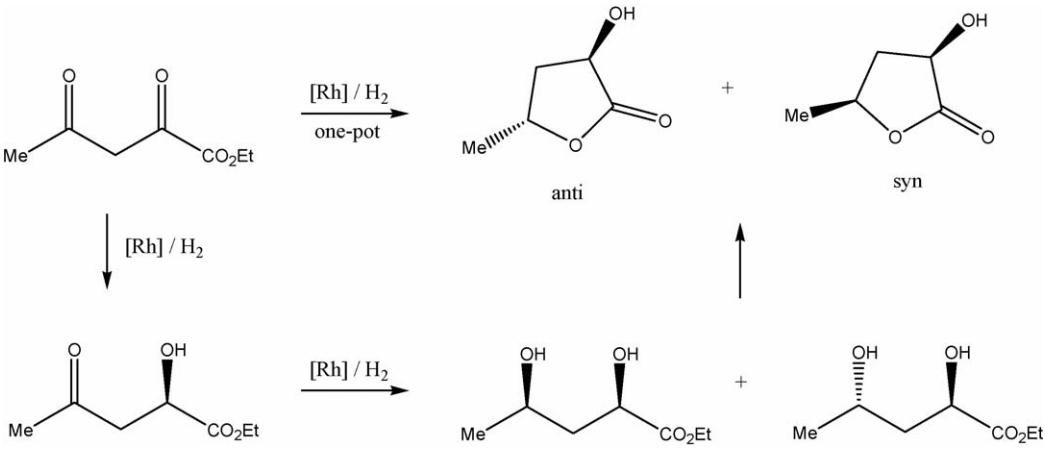
dropped markedly when phenyl (73% ee), anisolyl (83% ee), $PhCH_2OCH_2$ (86% ee) or *p*-chlorphenyl (38% ee) was the substituent [150]. Apparently, electron withdrawing substituents are detrimental to the chiral resolution. Interestingly, changing the degree of fluorination on the methyl group had a similarly bad influence on the enantiomeric excess and the yield. The CH_3 substituted starting material yields less than 2% with an ee of about 8.

In a theoretical study using molecular mechanics and extended Hückel calculations, Mortreux and coworkers established that the enantioselectivity in the asymmetric hydrogenation of ketopantolactone using chiral rhodium/oxo-proNOP catalysts is likely due to thermodynamic rather than kinetic control in the addition of molecular hydrogen onto the chiral ketopantolactone–chlororhodium complexes bearing the phosphino lactam ligand [151].

Other prochiral functionalised ketones used in asymmetric hydrogenations with chiral phosphino lactams include ethylpyruvate and methylbenzoylformate (see Scheme 50) [132,133] and related α- and β-keto carboxylic acid derivatives like esters and amides (see Scheme 51) [152,153]. Conversion rates and reported ees were generally low for ethylpyruvate and methylbenzoylformiate using [Ru(COD)(2-methylallyl)$_2$] as the precatalyst. That the low conversion rates and ees are indeed a property of the ruthenium catalyst and not of the substrate was established in the asymmetric hydrogenation of ketopantolactone. The ees for rhodium catalysts [109] were significantly higher than for the ruthenium ones [132,133]. Similar observations were made with the α-keto carboxylic acid derivates shown in Scheme 51. The amide shows the highest ee followed by the thienyl ketoester and the methyl ketoester brings up the rear [152]. The β-ketoesters show significantly higher reported ees in the range of 50–85% ee with the best results obtained by the ruthenium methylallyl precursors at low temperature. Raising the temperature markedly decreases the obtained ees, from 85% at 20 °C to 47% at 95 °C.



Scheme 51. Asymmetric hydrogenation of α- and β-carboxylates.

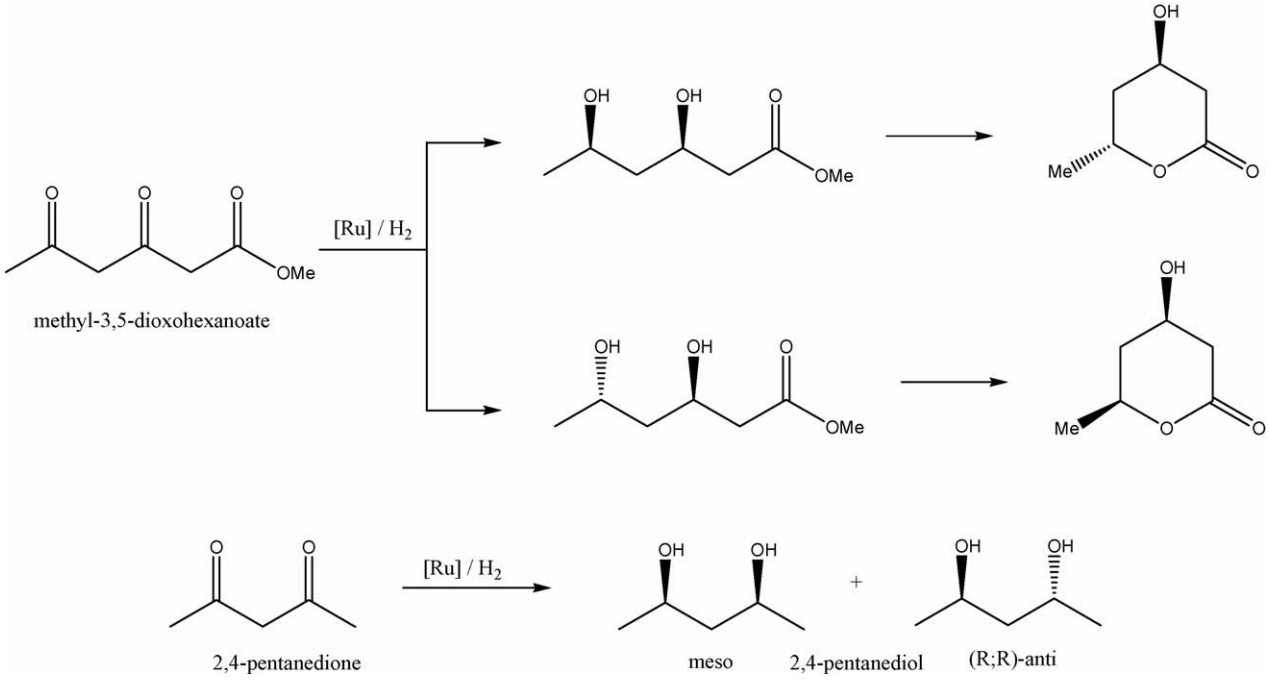


Scheme 52. *Anti*- and *syn*-α-hydroxy-γ-butyrolactone from the asymmetric hydrogenation of 2,4-dioxovalerate.

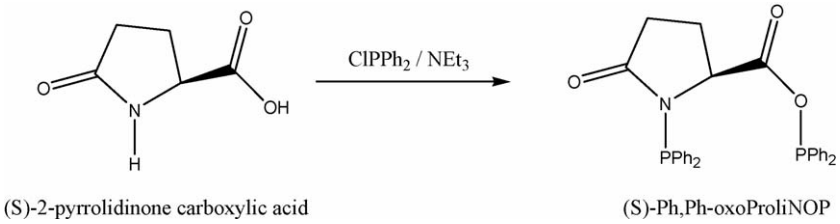
An interesting one-pot synthesis of α-hydroxy-γ-butyrolactone by sequential asymmetric hydrogenation of 2,4-dioxovalerate using chiral rhodium catalysts was reported by Carpentier and coworkers (see Scheme 52) [153]. Reported ees are rather good (72–80% for *syn* and 86–87% for *anti*, respectively), but in the same study ruthenium-BINAP catalysts were reported to be better.

In a related study, Hosokawa et al. showed the solvent dependency in the asymmetric hydrogenation of methyl-3,5-dioxohexanoate and 2,4-pentanedione using phosphino lactam–ruthenium catalysts and a ruthenium-(*S*)-BINAP catalyst for comparison (see Scheme 53) [107]. Again, the Ru-BINAP catalyst showed much higher ees, but the syn/anti ratio could be tuned using the appropriate anion/solvent combination with the phosphino lactam ruthenium catalysts. For instance, with $CF_3CO_2^-$ as the anion in the asymmetric hydrogenation of methyl-3,5-dioxohexanoate a 68:32 *syn*/*anti* ratio was obtained in methylene chloride while an equal mixture between methylene chloride and methanol resulted in a *syn*/*anti* ratio of 14:86. (R)-MTPA {(R)-α-methoxy-α(trifluoromethyl)phenylacetate} as anion showed an even greater effect with a 96:4 *syn*/*anti* ratio in methylene chloride and 8:92 when methanol was added as above. 2,4-Pentanedione produced almost identical results, except that now good ees (86–93%) were reported for reaction in pure methylene chloride.

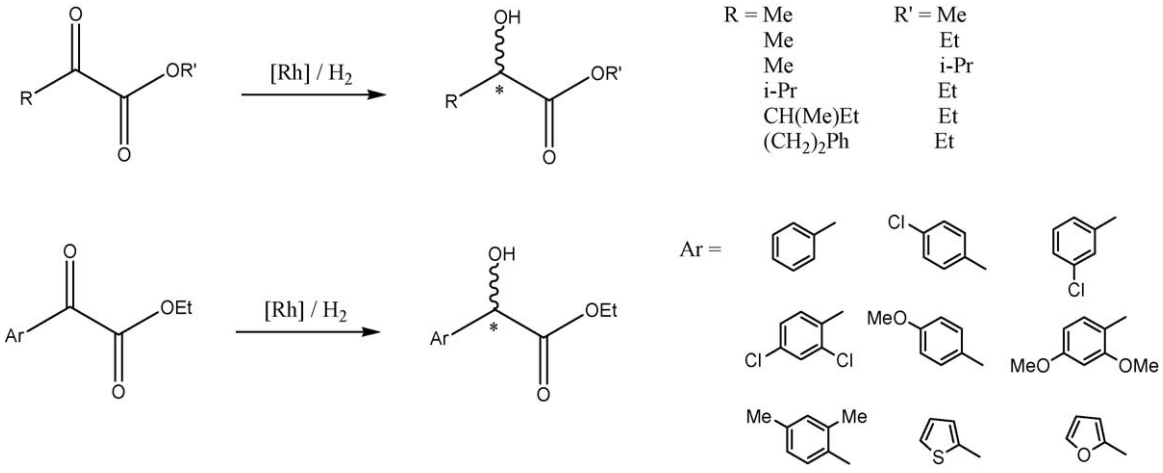
In a comparative study involving the use of phosphino lactam ligands of the oxo-proNOP family in asymmetric hydrogenation and in hydroformylation reactions, Agbossou and coworkers introduced a new ligand named oxoProliNOP (see Scheme 54) [154]. The new ligand showed no improvement over existing ligands in the asymmetric hydrogenation of ketopantolactone using ruthenium precursors.



Scheme 53. Asymmetric hydrogenation of methyl-3,5-dioxohexanoate and 2,4-pentanedione.



Scheme 54. Synthesis of oxo-proliNOP from 2-pyrrolidinone carboxylic acid.



Scheme 55. Asymmetric hydrogenation of α-ketoesters.

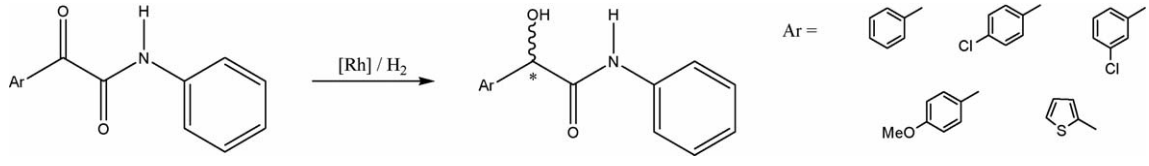
An interesting investigation of the reasons for chiral resolution in the asymmetric hydrogenation of α-ketoesters using rhodium-phosphino lactam catalysts was published by Carpentier and Mortreux [155]. They investigated a series of aliphatic and aromatic α-ketoesters (see Scheme 55) as well as some aryl-α-keto carboxylic acid benzylamides (see Scheme 56). They concluded that stereochemical discrimination is achieved by steric rather than electronic means. The argument runs as follows: the bigger the substituent at the alkoxycarbonyl moiety (R′ in Scheme 55) and the smaller the α-substituent at C=O (R in Scheme 56) the higher the ee. Observations on the other substrates were similar.

An interesting exception to the rather small substrates usually employed in these asymmetric hydrogenation reactions is the stereoselective hydrogenation of folic acid on immobilised chiral rhodium–diphosphane catalysts reported by Brunner et al. (see Scheme 57) [156]. Using oxo-proNOP as ligand results in a low reported de (de = diastereomeric excess) of only some 30% while DIOP, BINAP and others yielded a reported de of around 50%.

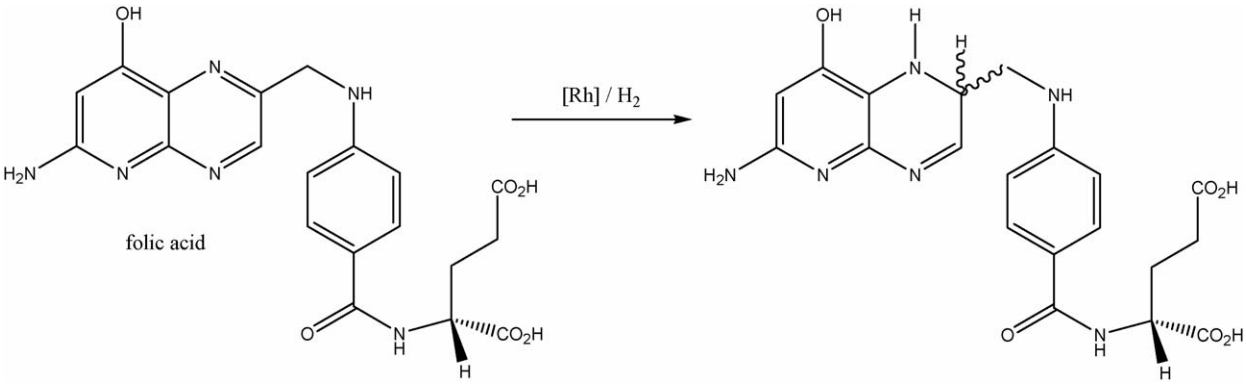
Using $(CO)_3$Cr-benza anellated proNOP ligands for asymmetric hydrogenation reactions did not improve the performance compared to the oxo-proNOP catalysts [157].

3.4.2. Hydroformylation

Relatively few reports concerning the use of phosphino lactams in catalytic hydroformylation reactions are found in the literature [122,129,154]. Jacobson reported that paraformaldehyde can be hydroformylated to glycol aldehyde using phosphinoalkylidene lactams and rhodium(I) precursors, mainly $[Rh(CO)_2Cl]_2$ [129]. Best results were obtained using six membered chelate rings like the one formed by *N*,*N*-dimethyl-3-(diphenylphosphino)propionamide. In sharp contrast to this ligand, the *N*-(diphenylphosphino)-2-pyrrolidinone forming a five membered chelate ring yielded no glycol aldehyde at all.



Scheme 56. Asymmetric hydrogenation of α-keto carboxylic acid amides.



Scheme 57. Asymmetric hydrogenation of folic acid.

Mortreux and coworkers tested their oxo-proNOP ligands (closely related to Jacobson's pyrrolidinone derivative, but chiral) in the asymmetric hydroformylation of styrene (see Scheme 58) [122,154]. Styrene is noted for its tendency to form branched products in hydroformylation reactions [158,159], which are chiral.

The role of an optically active catalyst therefore is to discriminate in favour of either enantiomer while maintaining the preference for branched products. Both, regioselectivity and stereoselectivity were poor with reported ees in the range of 40–56% and linear to branched ratios well above 1.0. Comparison of the oxo-proNOP to the proNOP ligand family led the authors to conclude that "the catalytic activity of the [catalysts] is mainly controlled by the aminophosphine moiety of the ligand and suggests that the reaction rate increases with the reduction of the electron density on the P(*N*) atom" [154].

3.4.3. Compatibilisation agents for block copolymers

In polymer chemistry polymers are frequently "mixed" to form a new material combining the favourable properties of the constituting parts. A particularly easy method of "mixing" is a process known as melt blending whereby the individual polymers are melted together, processed and cooled. A serious problem arises when the polymers are immiscible in the melt or crystallise separately upon cooling. Akkapeddi et al. encountered such a challenge when they attempted the melt blending of PPE (poly{2,6-dimethyl-1,4-phenylene ether}) and PET (polyethylene terephthalate) [106,141]. They solved their problem by finding a suitable reactive coupling agent that would assist in the reaction between the two end groups of the constituting polymers. In the present case the reaction would be between an aryl carboxylic acid and a phenol to form the respective ester. As both end groups are not reactive enough, Akkapeddi and Chung [142] and Glans and Akkapeddi [144] added phosphorus trilactams to the melt as coupling agents (see Scheme 59).

Other applications as reactive coupling agent for block-copolymers include polyphenyleneoxides/polyesters [145], polyester/amine functionalised elastomers [143] and as an ester-interchange inhibitor for polyalkylene terephthalate/polyarylate polymer compositions [142].

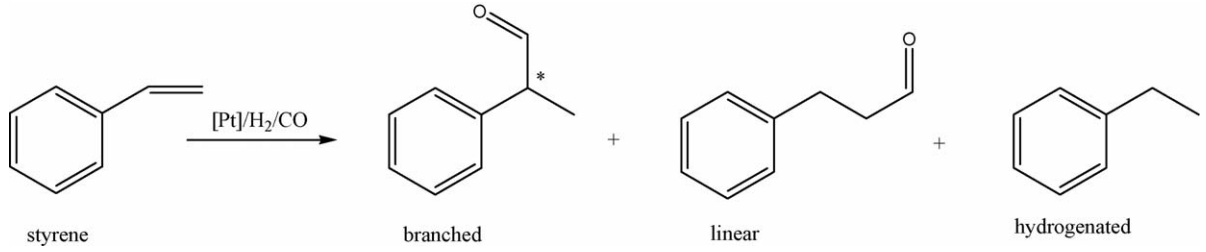
Another application for P(caprolactam)$_3$ was reported by Khitzin et al. [160] as anti-ageing agent for the synthetic rubber elastomer SKI-3.

3.4.4. Other applications for phosphino lactams

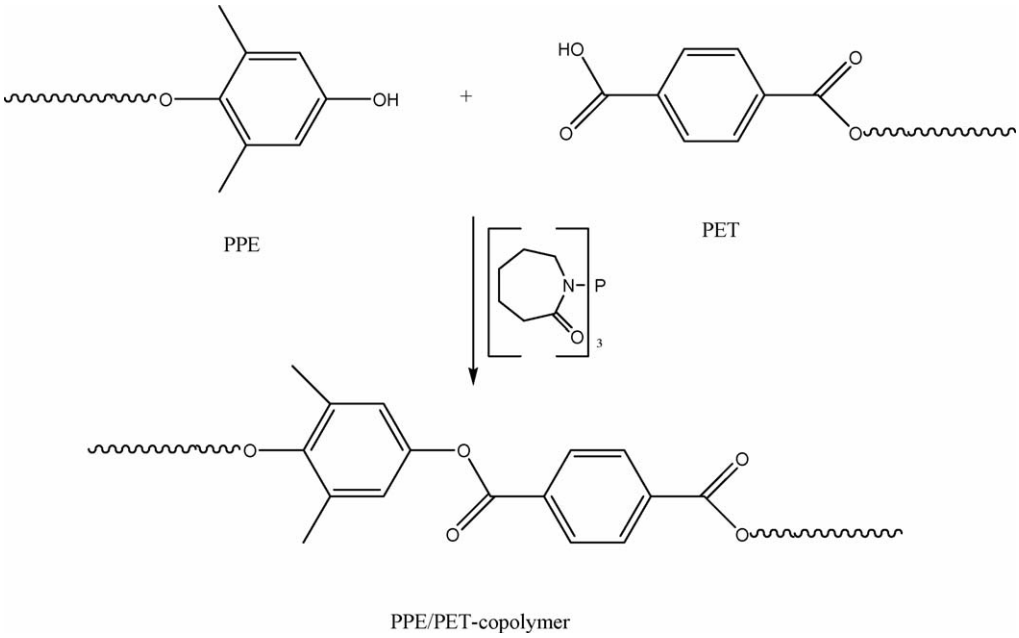
In other applications for phosphino lactams, Narrain and Kumar investigated the utility of this compound class for fungitoxicity (see Scheme 32) [117]. The compounds were found to be active against *H. oryzae* and *A. flavus* with the phosphino lactams derived from succinimide and maleimide being only moderately fungitoxic, but the phthalimide derivative showed very high fungitoxicity. The chlorophosphino lactams were even more powerful due to the P–Cl bond, a finding that was expected, but has no practical significance as P–Cl compounds are not suitable for commercial applications for obvious reasons.

Izeki et al. have patented the use of oxo-proNOP ligands for use in the manufacture of fluorinated refrigerating agents derived from the asymmetric hydrogenation of fluorinated carbonyl compounds (see page 32) [140].

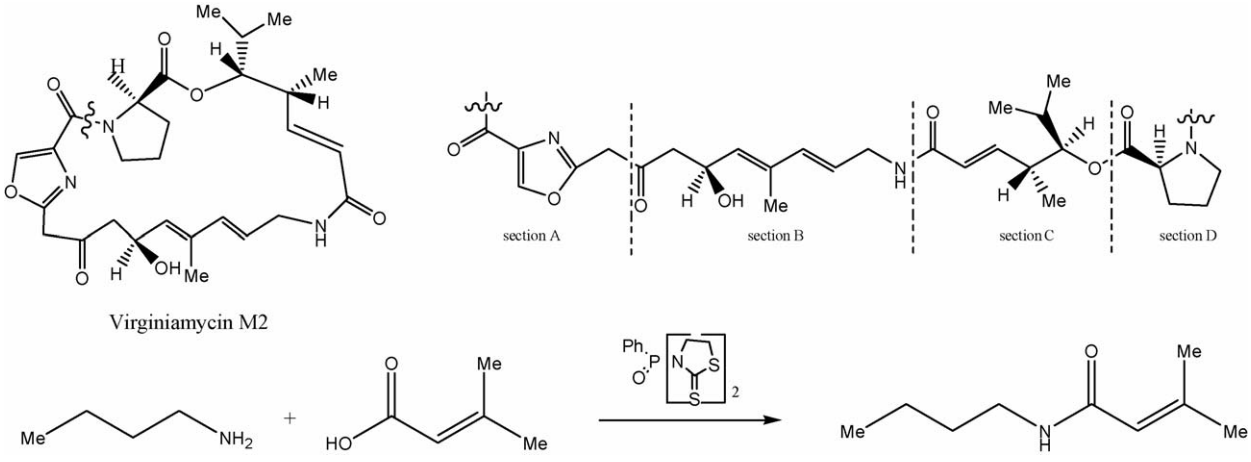
Nagao et al. used a phosphino thiocarbamate in the total synthesis of the antibiotic *Virginamycin M2* (see Scheme 60) particularly in the step linking segment B and C [161].



Scheme 58. Hydroformylation of styrene with a chiral catalyst.



Scheme 59. Phosphino lactams as coupling agents for PPE/PET block copolymers.



Scheme 60. Utilisation of a phosphino thiocarbamate in the total synthesis of *Virginiamycin M2*.

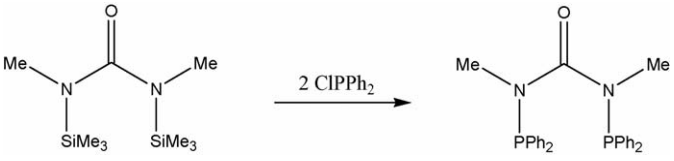
4. Phosphinoureas and thioureas

Studies with phosphino ureas date back into the 1960s [162] with interest originating from the chemistry of the P–N bond. Development of the field remained to be the domain of Main Group chemists with interest in cyclic compounds containing a P–P bridge [163–167], the synthesis of cyclic phosphino ureas and their reactivity towards small molecules [168–170]. Coordination Chemistry and the usefulness of phosphino ureas as ligands for transition metals [40] as well as applications in catalysis [41] have only emerged quite recently.

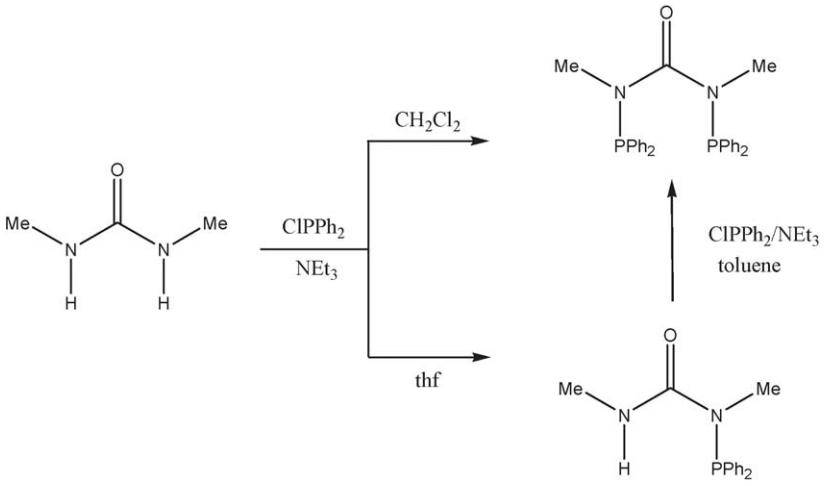
4.1. Synthesis

Phosphino ureas can be prepared in numerous ways, but two general procedures seem to have evolved in the last half century or so. The first employs silylated urea and a chlorophosphine (see Scheme 61). The two substances are heated without solvent and special care needs to be taken as to the reaction conditions and stoichiometries as otherwise follow-on reactions will lower the yield considerably [171]. The second comprises reacting the respective urea derivative with a chlorophosphine in the presence of an auxiliary base (see Scheme 62) [172–174].

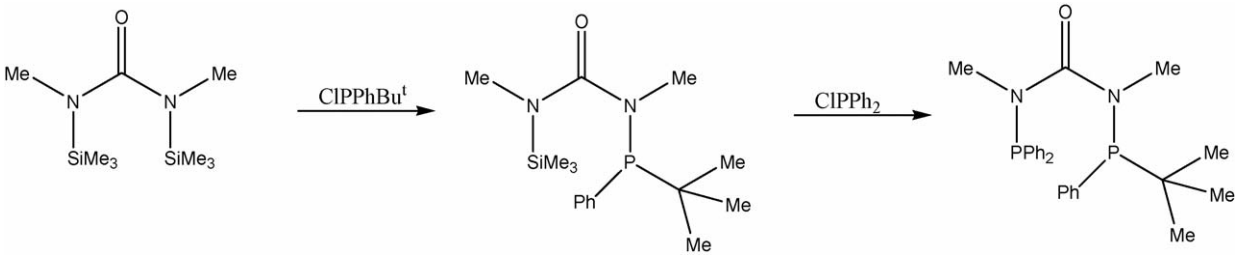
The silyl urea method developed by Schmutzler and coworkers has opened a rich and interesting chemistry of which the phosphino ureas are only the entrance gate. The initially formed



Scheme 61. Phosphanylation of bis-silylureas.



Scheme 62. Solvent dependent synthesis of mono or bisphosphino ureas.



Scheme 63. Rare synthesis of an unsymmetric bisphosphino urea using the silylurea method.

phosphino ureas react further under the conditions employed and give rise to a multitude of condensation and rearrangement products (see Section 4.2). Monophosphino ureas are seldom obtained as the isolated product as they usually react further to the bisphosphino ureas [170,175]. The notable exception is $ClPPhBu^t$, a chlorophosphine whose substituents are bulky enough to prevent the second substitution under controlled conditions [175]. Instead, the monophosphino urea can be reacted in the same way with $ClPPh_2$ to form the respective unsymmetrical bisphosphino urea (see Scheme 63) [171,176].

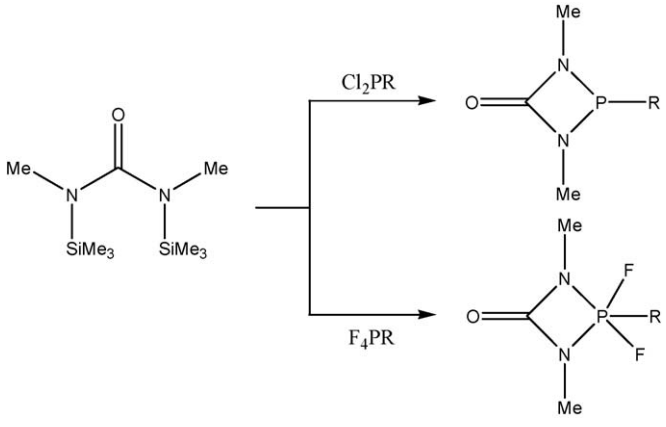
An interesting approach to cyclic products is the reaction of silylated ureas with dichlorophosphines [163,165,170] and related species carrying at least two halogen atoms on phosphorus [169] (see Scheme 64).

Reaction of silyl urea with a chlorinated bisphosphine produces the expected cyclic bisphosphino urea (see Scheme 65) [177].

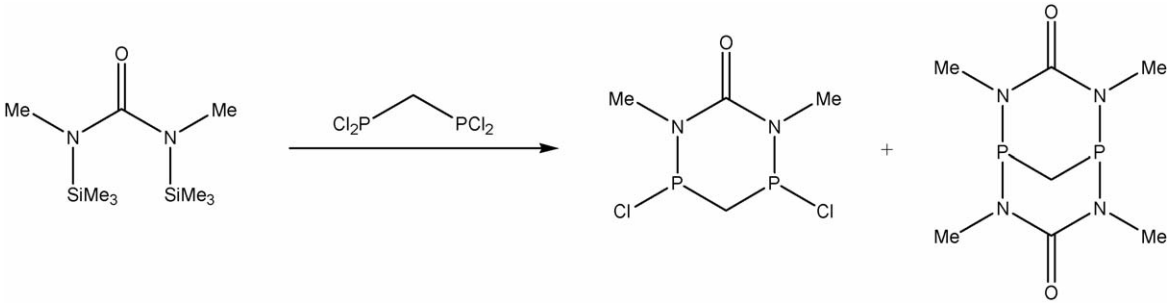
The auxiliary base method developed originally by Schmutzler and coworkers [172,178,179] and later refined by Woollins and coworkers [173,180] is more predictable in its outcome, but did not give rise to the same wealth of unexpected and beautiful chemistry as the silyl urea method did.

A fascinating reaction in this context is that between $(Me_3SiNH)_2CO$ and $ClPPh_2$ giving the system the choice between elimination of $SiMe_3Cl$ and HCl, respectively. As it turns out, the isolated product is $(Ph_2PNH)_2CO$ whereby the chlorophosphine has reacted with the silyl moiety [173].

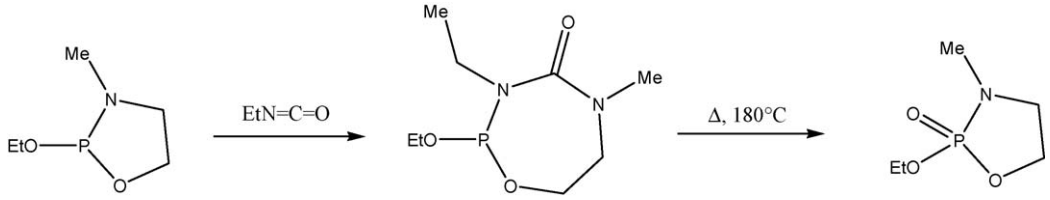
Schmutzler et al. developed the auxiliary base method for thiourea derivatives as silylated thiourea did not give satisfactory results in the silyl method. In the auxiliary base method thioureas again react differently from the urea analogues. Thioureas react with chlorophosphines in ethereal solvents first to the mono [179] and then to the bisphosphino [181] derivatives in marked contrast to the respective ureas which can be held at the monophosphino stage only in thf [182]. In three publications, Gruber and Schmutzler describe the synthesis of monophosphino thioureas [179], symmetrical bisphosphino thioureas [178] and unsymmetrical bisphosphino



Scheme 64. Synthesis of cyclic phosphino ureas using dichlorophosphines.



Scheme 65. Synthesis of cyclic phosphino ureas using "bidentate" bis-chlorophosphines.



Scheme 66. Isocyantae insertion into a cyclic phosphinamidinate.

thioureas [181]. All compounds were synthesised using the auxiliary base method. It should be mentioned here, even though it falls under the heading of reactivity of phosphino thioureas, that symmetrical bisphosphino thioureas can be obtained upon leaving a solution of monophosphino thiourea standing for 2 days [181]. The isolated products of the reaction were the original thiourea derivative carrying a hydrogen atom on each nitrogen and the respective symmetrical bisphosphino thiourea.

The reactivity of urea derivatives is markedly different. Woollins et al. obtained only symmetrical bisphosphino ureas upon reacting the appropriate urea with chlorophosphines in the presence of triethyl amine as auxiliary base and dichloromethane as solvent, even at equimolar amounts [173,180]. Kühl [174] and Kühl and Lönnecke [182] then showed that the monophosphino ureas can be easily obtained, if thf were used as solvent. Thus, reacting *N*,*N*′-dimethyl urea with an excess (up to 2.2 equivalents) of chlorodiphenylphosphine in thf produces only the monophosphino derivative [182]. Similarly, the monophosphino urea **27** is the only product, if $ClP(OC_6H_3Bu^t_2\text{-}2,4)_2$ is used. Reaction of $PPh_2NMeC(O)NMeH$ with $ClP(OC_6H_3Bu^t_2\text{-}2,4)_2$ yields the respective unsymmetrical bisphosphino urea **28** [174].

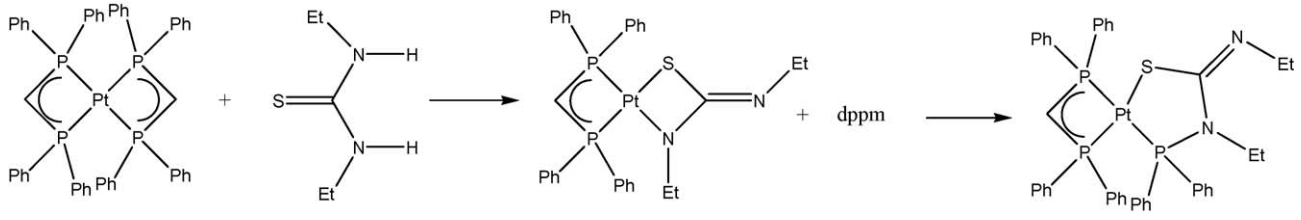
Other routes to phosphino ureas or thioureas are much less common, but have the potential for a general route. For instance, if $Ph_2P(S)N{=}C{=}S$ is reacted with a secondary amine, the monophosphorylated thiourea derivative $Ph_2P(S)NHC(S)NR_2$ is formed [183]. Another method utilises the more classical approach to ureas by reacting an aminophosphine with isocyanate [34,55]. Hudson and Searle inserted ethylisocyanate into a cyclic phosphinoamidate obtaining the respective cyclic phosphino ureate (see Scheme 66) [56].

A patent filed by Hoechst describes the synthesis of $Cl_2P(O)NHC(O)NHR_2$ by the reaction of $Cl_2P(O)N{=}C{=}O$ with a primary amine at low temperature (−25 to −30 °C) [162].

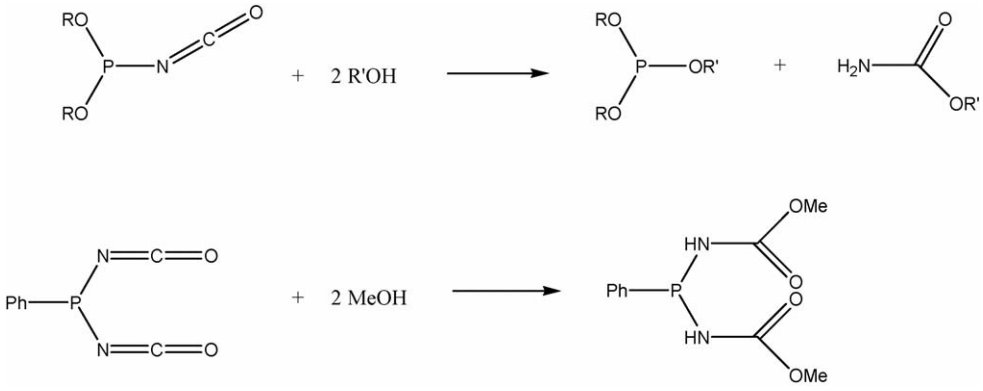
In a complicated metal mediated reaction *N*,*N*′-diethyl thiourea forms a monophosphino thiourea derivative apparently using the dppm (bis-diphenylphosphino methane) monoanion as the phosphorus source (see Scheme 67) [184].

The reactivity of the phosphorus moiety prompted researchers to devise methods of synthesising phosphino ureas from phosphino isocyanates in the coordination sphere of transition metals, particularly rhodium [185,186]. Usually, phosphino isocyanates react with alcohols at the more reactive phosphorus atom rather than the unsaturated isocyanate system (see Scheme 68) [187,188] leading to a complex mixture. By coordinating the phosphino isocyanate to a transition metal like rhodium, the phosphorus centre is protected from attack by the nucleophile and the reaction proceeds smoothly at the isoyanate end (see Scheme 69).

The reaction of phosphino isocyanates with alcohols or amines is easily monitored using IR spectroscopy. During the course of the reaction, the band for the isocyanate moiety at



Scheme 67. Phosphonylation of thiourea in the ligand sphere of platinum(II).



Scheme 68. Alcoholysis of phosphino isocyanates.

2230–2250 cm^{-1} disappears and a new carbonyl band around 1730 cm^{-1} appears [185]. Sterically demanding compounds like (−) menthol were reported not to react [185].

4.2. Properties

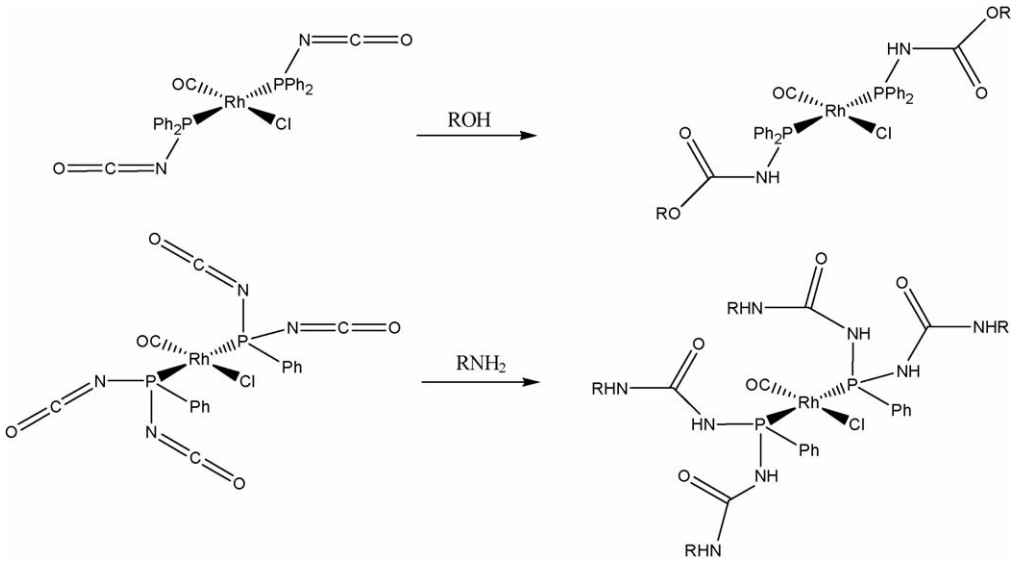
Phosphino ureas are rather reactive compounds that have a pronounced tendency towards rearrangement reactions. They are readily oxidised with oxygen, sulfur and selenium [173] at the phosphorus end and add to unsaturated compounds like isocyanates [169]. Like their parent compounds [57–62], phosphino ureas and thioureas form hydrogen bond networks with their remaining NH groups. For examples see Fig. 12 [173].

When Hudson [55] and Hudson and Searle [56] synthesised phosphino ureas by reacting phosphino amines with isocyanates, they noticed the occurence of two products distinguished by different carbon substituents on the respective nitrogen atoms. The existence of the two phosphino ureas could only be explained by a rearrangement reaction (see Scheme 70) [56]. By a similar rearrangement, the phosphino group can insert into the C=O bond (see Scheme 71) [55].

It should be mentioned that the reaction between Ph_2PNHPh and *n*-propyl isocyanate yields the same product, $Ph_2PNPhC(O)NHPr$, as the reaction between Ph_2PNHPr and phenyl isocyanate [56]. The NH proton showed an unusually high J_{PH} coupling constant of 16 Hz similar to that observed by Ando et al. for $Me_2PNMeC(O)Me$ ([50], chapter 2). Quite interestingly, Hudson et al. reported a cyclic conformation for $Ph_2PNEtC(O)NHPh$ with intramolecular hydrogen bonding to the phosphorus atom based on spectroscopic data. The structure was confirmed by X-ray analysis on the related compound $Ph_2PNEtC(O)NHPh$ by Kühl and Lönnecke 30 years later [182] with an additional intermolecular hydrogen bond to the adjacent C=O in the solid state.

A similar rearrangement was also encountered by Schmutzler et al. for the four membered ring system **29** (see Scheme 72). The rearrangement proceeds with catalytic amounts of isocyanate. Alternatively, a mechanism requiring only two molecules of **29** without isocyanate as mediator was postulated.

The four membered ring system can be oxidised by *o*-chloranil rendering five coordinated phosphorus [168,189]. It was suggested by Schmutzler and coworkers that *bis*-



Scheme 69. Alcoholysis and aminolysis of rhodium coordinated phosphino isocyanates.

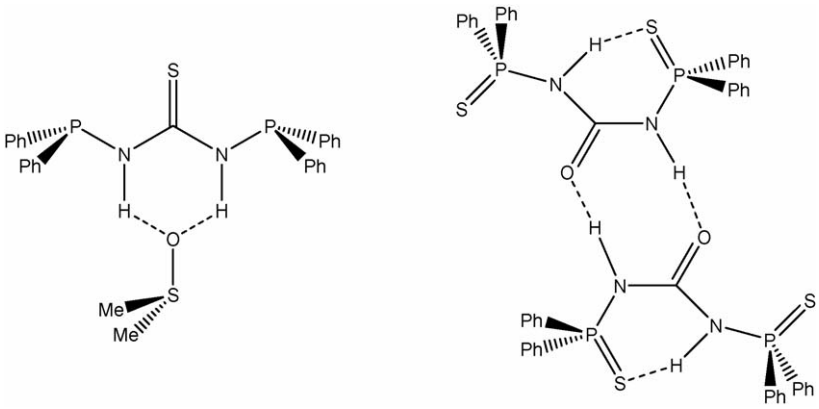
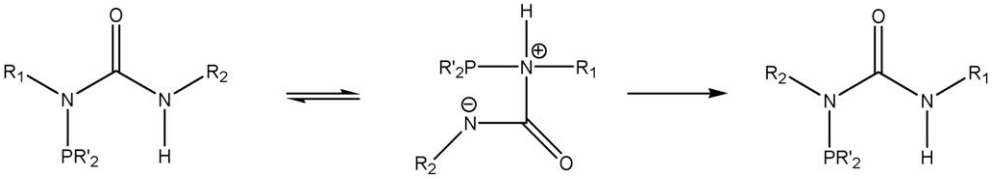
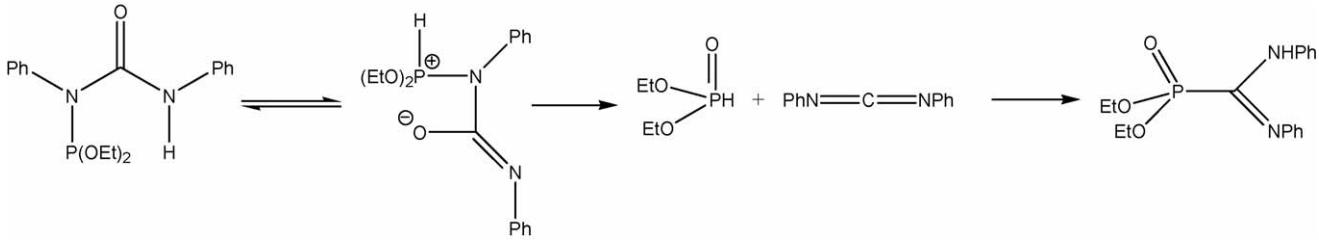


Fig. 12. Hydrogen bonding in phosphino urea and thiourea ligands.



Scheme 70. *N*,*N*′-substituent exchange in phosphino ureas.



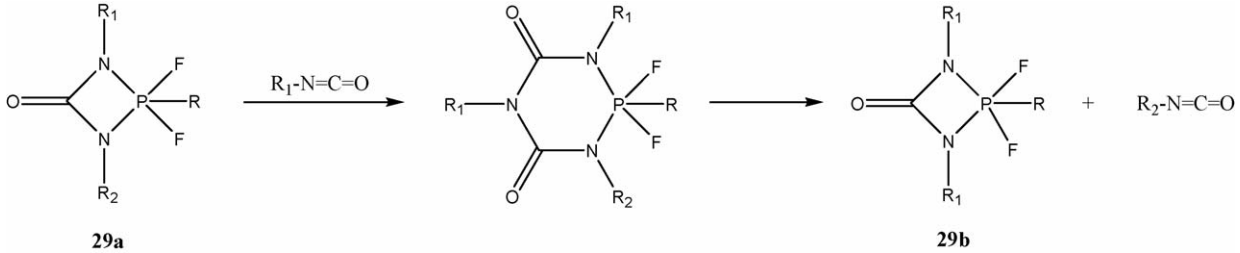
Scheme 71. Rearrangement pathway for diethylphosphite substituted *N*,*N*′-diphenylurea.

silyl dimethyl urea reacts with two equivalents of dichlorophenylphosphine via the four membered ring to a five membered ring system in an insertion reaction [163]. Later the reaction was found to produce the respective bisphosphino urea first and formation of the cyclic compound in a second step (see Scheme 73) [190].

The compound can exist in three different structures distinguished by bonding of chlorine to phosphorus (see Scheme 74) [190]. If the chlorine atom bonds to both phosphorus atoms, a PPCl three membered ring is formed. Upon breakage of the bond to the pentavalent phosphorus a zwitterionic structure emerges that turns into a phosphonium salt structure if the remaining P–Cl bond is cleaved. Which of the three possible structures is realised depends largely on the steric bulk and the electronic properties of the substituent R. Reaction with $NaBPh_4$ introduces the non-bonding anion BPh_4^- and results in the formation of the respective phosphonium salt.

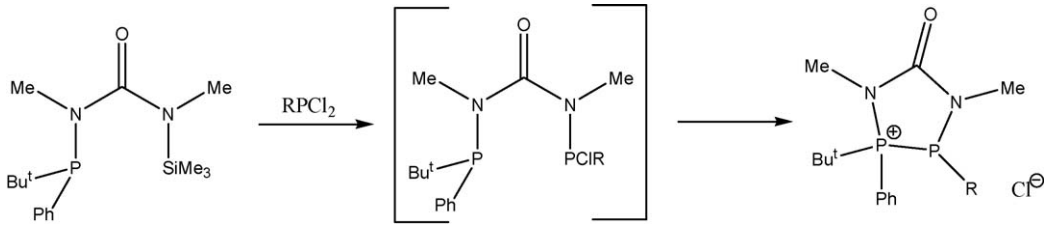
The homologues are obtained if Cl_2ER (E = As, Sb) is used instead of the dichlorophosphine. Reaction with Me_2SnCl_2 leads to the compound $[P\text{-}Sn]_2[Me_2SnCl_4]$ where PR is replaced by $SnMe_2$ in the cation.

A similar structure, but without a direct P–P bond is formed if bis-silylurea is reacted with the cyclic perchloro diphosphane $[ClPCCl_2]_2$ [191]. Here, two CCl_2 moieties bridge the P–P vec-

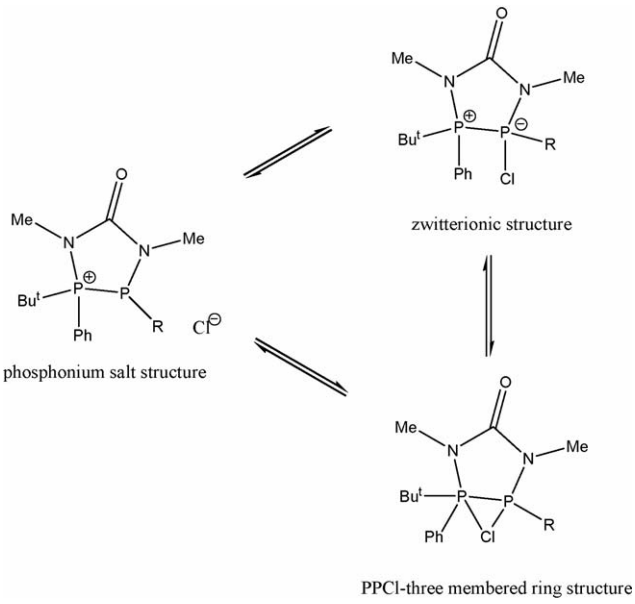


29a **29b**

Scheme 72. Proposed substituent exchange mechanism on cyclic phosphino ureas via isocyanate insertion-elimination.



Scheme 73. Ring closure reaction in P-chloro bisphosphino ureas by P—P bond formation.



Scheme 74. Structural isomers of cyclic P(PhBu^t)N(Me)C(*O*)N(Me)P(R)Cl.

tor. Reaction of bis-silylurea with $Cl_2PCCl_2PCl_2$ results in the formation of the expected six membered ring and the respective bicyclic system if two equivalents of bis-silylurea are used.

Another product from the reaction between bis-silylurea and dichlorophosphine is a P-spiro compound shown in Scheme 75 [166,170]. It decomposes by elimination of the NCN unit of the four membered ring leaving the five membered ring in its P-oxidised form intact [164]. Another reaction, affecting the five membered ring, is shown in Scheme 76 [165]. A PPh moiety is effectively eliminated by oxidation with either Cl_2 or PCl_5.

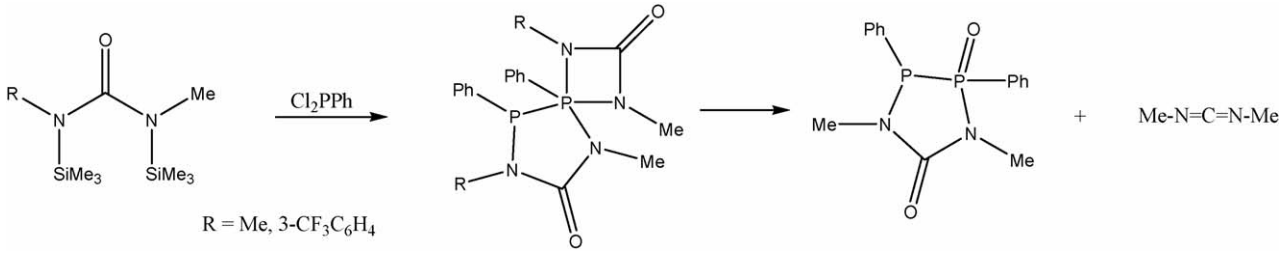
Schmutzler and coworkers have studied the chemistry of phosphino thiourea in a series of publications [172,178,179,181] and found it quite different from that of the urea analogues. In an attempt to synthesise diphenylphosphino thiourea from thiourea and chlorodiphenyl phosphine using the auxiliary base method, they isolated $Ph_2PP(S)Ph_2$ instead of the intended product [172]. For *N*,*N*′-dimethyl thiourea the same group reports a tautomeric equilibrium between the NH group and the sulfur atom resulting in partial phosphonylation at the sulfur terminus [179]. This finding is supported by their observations leading to the formation of $Ph_2PP(S)Ph_2$. The sulfur phosphonylated compound reverts back to the nitrogen phosphonylated one (see Scheme 77).

The monophosphino thioureas can be reacted with chlorophosphines $ClPR_2$ to the symmetrical [178] and unsymmetrical [181] bisphosphino thiourea. There seem to be no limitations as to the substituents R that can be employed.

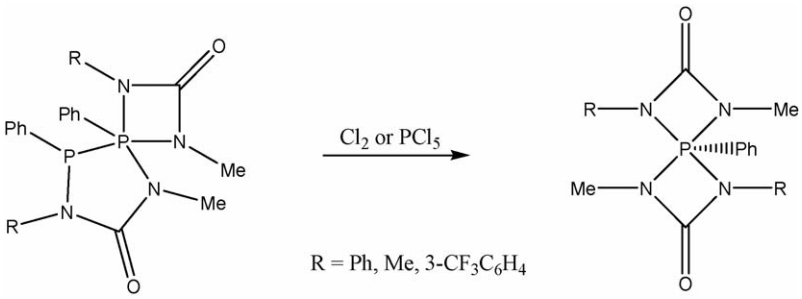
4.3. Transition metal complexes

As already mentioned in the introduction to this chapter, interest in the coordination chemistry of phosphino ureas developed very slowly. It took some three decades after the first report of phosphino ureas for the Schmutzler group to publish the first report on the X-ray structure of $(PhBu^tPNMe)_2CO$ **30** coordinated to a $[M(CO)_4]$ moiety (M = Cr, Mo) [175]. In the same publication Schmutzler et al. described the reaction of **30** with $[Fe_2(CO)_9]$ and $[Pt(COD)Cl_2]$ (COD = 1,5-cyclooctadiene). In the reaction between $(PhBu^tPNMe)_2CO$ and *cis*-[M(norbornadiene)$(CO)_4$] (M = Cr, Mo, W) the expected product is *cis*-$[M\{P,P\text{-}\kappa^2\text{-}(PhBu^tPNMe)_2CO\}(CO)_4]$, the P,P-chelate complex. However, not entirely unexpected, the actual product proved to be the P,O-chelate *cis*-$[M\{P,O\text{-}\kappa^2\text{-}(PhBu^tPNMe)_2CO\}(CO)_4]$ featuring a MPNCO five membered ring and "true heterocycle" (see Scheme 78), incidentally the same "true heterocycle" [73] as for the transition metal complexes of the carboxylic acid phosphinoamides discussed earlier.

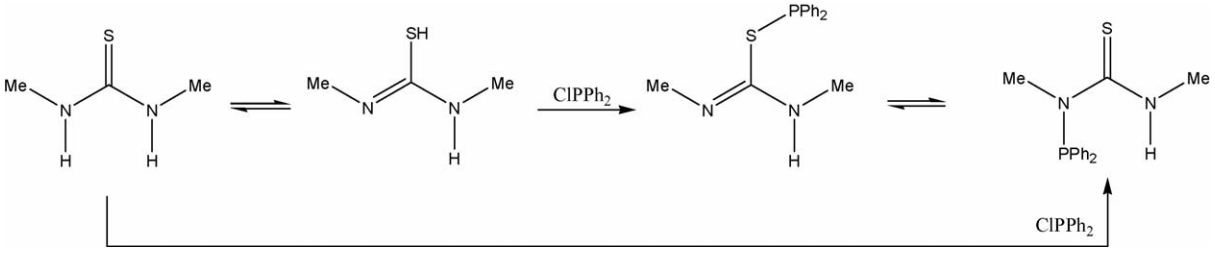
Reaction of $(PhBu^tPNMe)_2CO$ with $[Pt(COD)Cl_2]$ results in the displacement of COD by the bisphosphino urea ligand and the synthesis of $[Pt\{PhBu^tPNMe)_2CO\}Cl_2]$ (see Scheme 79).



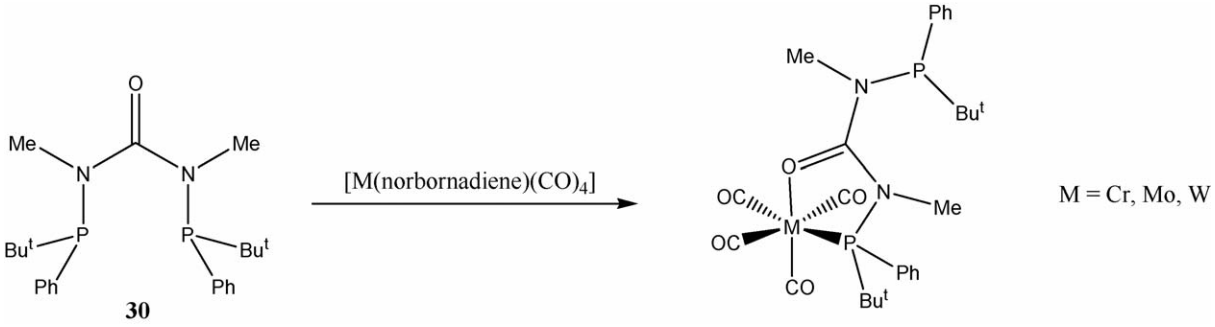
Scheme 75. Formation of spiro-phosphines from bis-silylureas.



Scheme 76. Ring contraction in spiro-phosphino ureas.

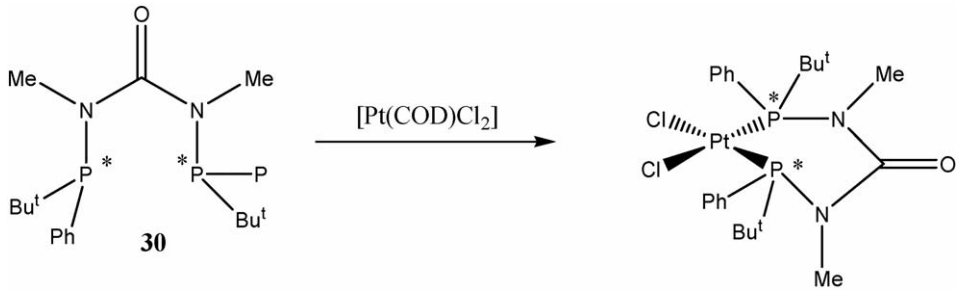


Scheme 77. Proposed mechanism in the phosphanylation of thiourea using the auxiliary base method.

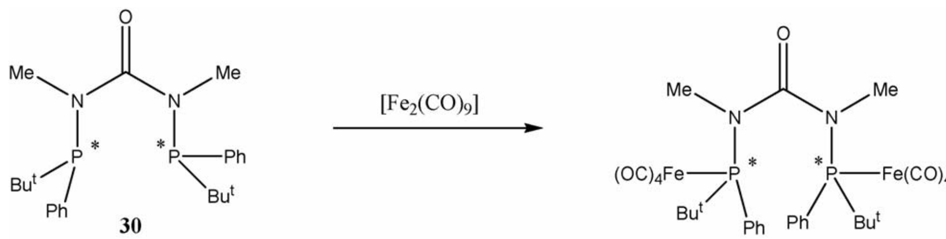


Scheme 78. Formation of P,O-chelate complexes using the sterically crowded bisphosphino urea (PhBu^{t}PNMe)$_2$CO.

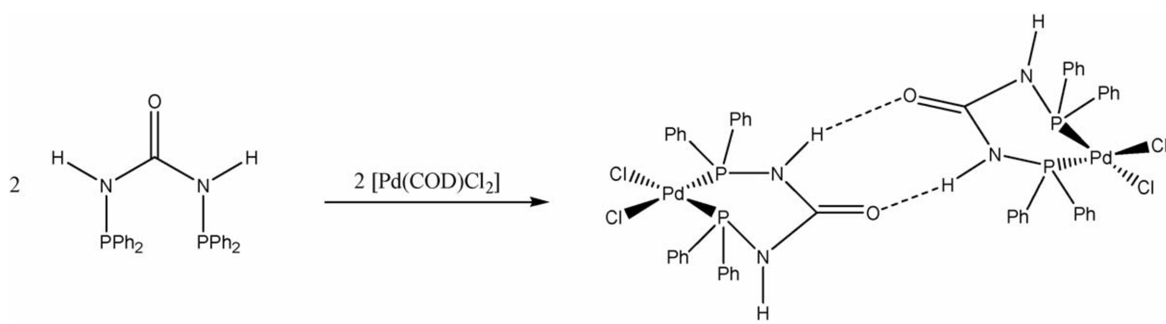
The structure of the complex was published some 11 years after the report of the synthesis, almost as an afterthought [176]. Nonetheless, the structure is typical for many bisphosphino urea transition metal complexes and worth discussing in some detail. As expected, platinum is coordinated by two chlorine and two phosphorus atoms in a square planar fashion. The MPNCNP six membered ring is not planar, but folded along the P–N vector. This renders the two phosphorus atoms non-equivalent as one lies on the fold vector and the other does not. It should be mentioned that [Pt{PhBu^{t}PNMe)$_2$CO}Cl$_2$] is chiral in both phosphorus centres creating two diastereomers. In theory that should be reflected by two phosphorus signals in the ^{31}P NMR spectrum. In practice, only one signal at $\delta = 76.0$ ppm was detected and no comment made by the authors as to the chirality of the complex. It is conceivable that steric reasons and the high temperatures employed in the synthesis of the ligands favour the *meso*-form as the thermodynamically preferred diastereoisomer.



Scheme 79. Formation of a P,P-chelate complex using the sterically crowded bisphosphino urea ligand (PhBu^{t}PNMe)$_2$CO.



Scheme 80. Formation of a bis-monodentate dinuclear complex using the sterically crowded bisphosphino urea ligand $(PhBu^tPNMe)_2CO$.



Scheme 81. Hydrogen bonding in bisphosphino urea complexes.

Reaction of $(PhBu^tPNMe)_2CO$ with $[Fe_2(CO)_9]$ results in a dinuclear complex whereby the ligand bridges two $[Fe(CO)_4]$ moieties in a bis-*monohapto* fashion (see Scheme 80). Again, the asymmetric phosphorus atoms should give rise to two signals in the ^{31}P NMR spectrum, but unfortuately they do not. The bis-*monohapto* coordination of bisphosphino ureas is not unique, but was also encountered in gold(I) complexes [40].

A few years later Woollins et al. reacted $(Ph_2PNH)_2CO$ with $[Pd(COD)Cl_2]$ (COD = 1,5-cyclooctadiene) and obtained an X-ray crystal structure of $[Pd\{P,P\text{-}\kappa^2\text{-}(Ph_2PNH)_2CO\}Cl_2]$ describing the PdPNCNP-ring as being in a pseudo-boat conformation [173]. Interestingly, $[Pd\{P,P\text{-}\kappa^2\text{-}(Ph_2PNH)_2CO\}Cl_2]$ forms hydrogen bonded dimers of the $R_2^2(8)$ type via the H and O atoms of the urea moiety (see Scheme 81).

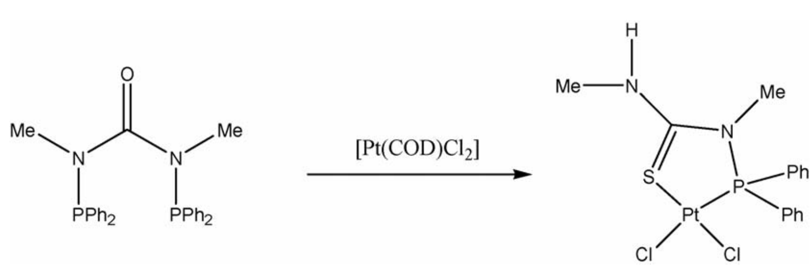
Similar complexes are obtained, if $(Ph_2PNH)_2CO$ is reacted with [Pd(COD)MeCl] or $[Pd(COD)Me_2]$, although no crystal structures were published [173].

The reaction of bisphosphino ureas and thioureas with the precious metal compounds $[M(COD)Cl_2]$ (M = Pd, Pt) continued to yield interesting results. When Woollins et al. reacted $(Ph_2PNR)_2CE$ (R = Me, Et; E = O, S) with $[M(COD)Cl_2]$ (M = Pd, Pt), the bisphosphino ureas rendered the expected simple coordination complexes $[M((Ph_2PNR)_2CO)Cl_2]$ (M = Pd, Pt; R = Me, Et), but the bisphosphino thiourea ligands underwent a P–N bond cleavage reaction and coordinated as P,S-chelates, very much like the carboxylic acid phosphinoamides (see Scheme 82).

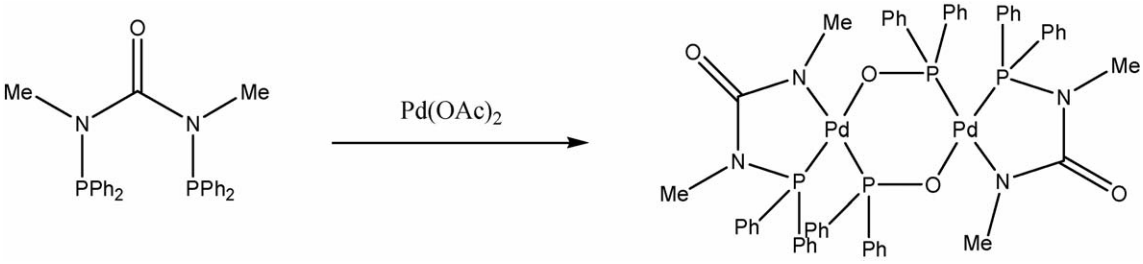
Although bisphosphino ureas seem to be less prone to P–N bond cleavage reactions than their thiourea counterparts, P–N bond cleavage does occur when $Pd(OAc)_2$ (OAc = acetate) is used as the palladium source (see Scheme 83) [180]. Concomitantly, the cleaved PPh_2 moiety is oxidised and incorporated as a P–O bridging ligand to form the central $Pd_2P_2O_2$ six membered ring of the ensuing dinuclear complex. The two flanking PdPNCN rings are planar and the central PdPOPdPO six membered ring adopts a cyclohexane chair type geometry giving the whole molecule two-fold symmetry.

The bisphosphino thiourea ligand $(Ph_2PNH)_2CS$ is sufficiently reactive to undergo P–N bond cleavage when reacted with nickel(II)chloride hexahydrate in methanol (see Scheme 84) [192]. As could be expected, the "spiro" nickel complex $[Ni(PPh_2NHC(NH_2)S)_2]Cl_2$ displays an intermolecular hydrogen bond network between the NH protons and the chloride anions.

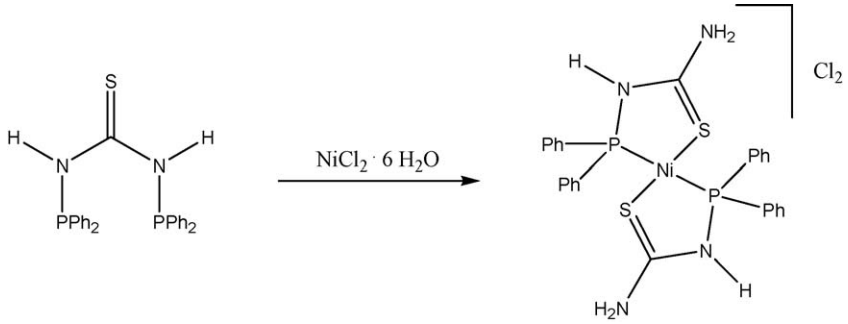
The choice of solvent is noteworthy as usually methylene chloride is used. However, nickel(II)chloride is soluble in



Scheme 82. P—N bond cleavage mediated by platinum.



Scheme 83. P—N bond cleavage mediated by palladium.



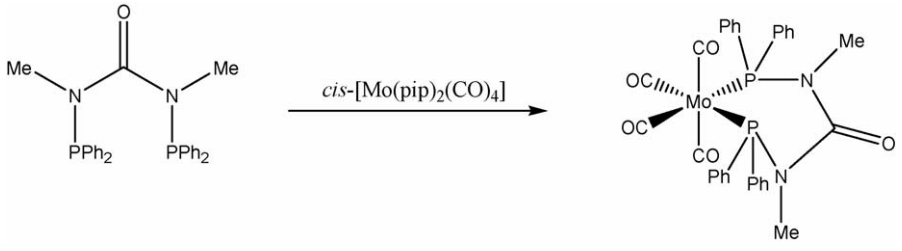
Scheme 84. P—N bond cleavage mediated by nickel.

methanol, but not in methylene chloride explaining the choice of the experimentators. Care was taken to establish that both $(Ph_2PNH)_2CS$ and the product $[Ni(PPh_2NHC(NH_2)S)_2]Cl_2$ are stable in methanol under the cited conditions and the authors conclude that coordination to the metal caused P–N bond cleavage.

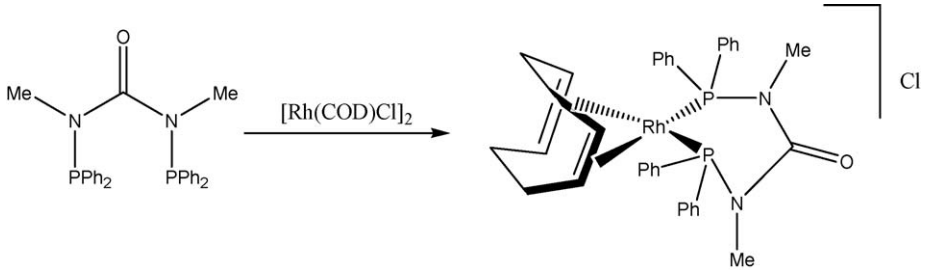
Following these preliminary reports, Woollins and coworkers published a comprehensive research paper detailing their work on the coordination chemistry of bisphosphino urea and thiourea compounds [40]. Apart from giving an overview of the previously published platinum and palladium complexes [180,192] it adds some gold(I), rhodium(I) and molybdenum(0) complexes to the general picture.

The molybdenum complex *cis*-$[Mo\{P,P\text{-}\kappa^2\text{-}(Ph_2PNMe)_2CO\}(CO)_4]$ is the product of the reaction between $(Ph_2PNMe)_2CO$ and *cis*-$[Mo(pip)_2(CO)_4]$ (pip = piperidine). Whereas the same reaction using the more bulky ligand $(PhBu^tPNMe)_2CO$ resulted in the P,O-chelate complex, this time coordination is effected via both phosphorus ends (see Scheme 85).

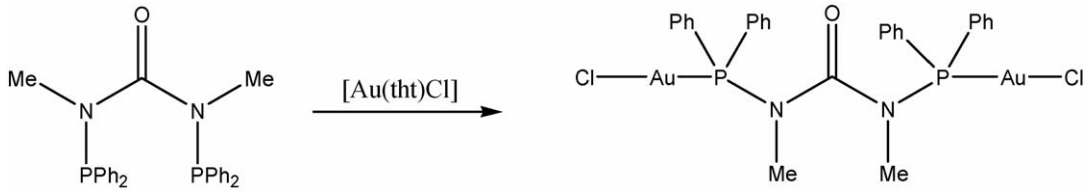
The same reaction carried out with $[Rh(COD)Cl]_2$ results in the replacement of the chloride rather than the olefinic ligand as could have been expected (see Scheme 86). Otherwise, the structure is very much like that of the isoelectronic palladium and platinum complexes discussed earlier. It



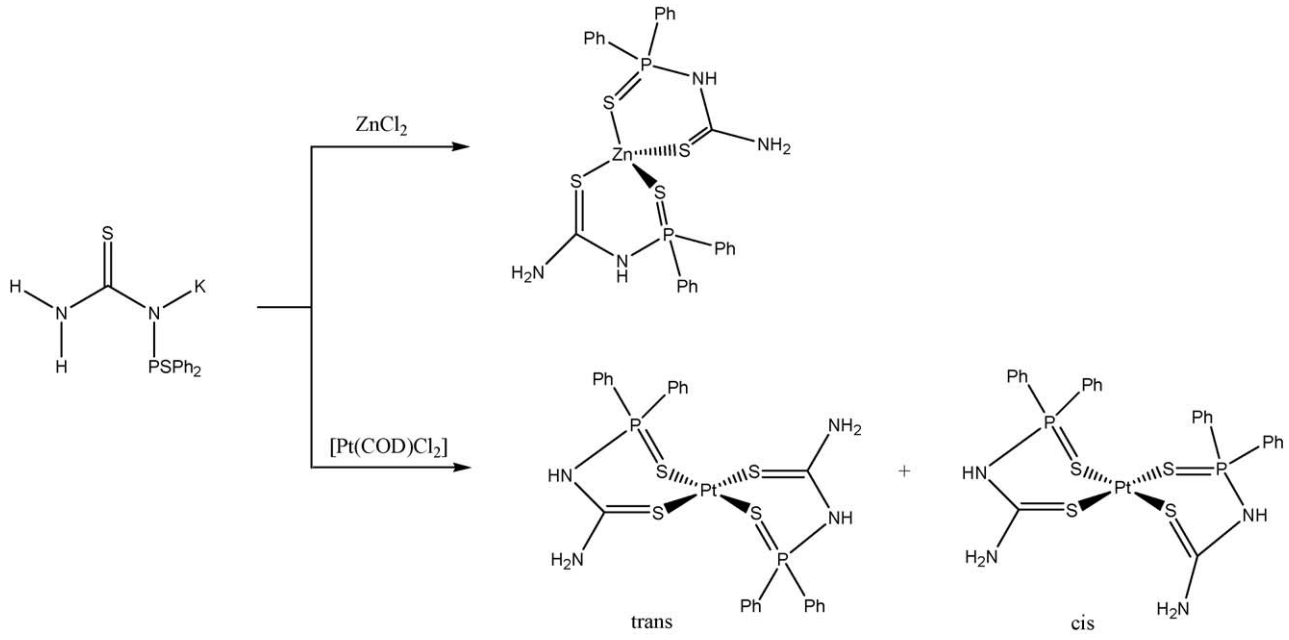
Scheme 85. Synthesis of a folded P,P-chelate molybdenum complex of $(Ph_2PNMe)_2CO$.



Scheme 86. Synthesis of a folded P,P-chelate rhodium complex of $(Ph_2PNMe)_2CO$.



Scheme 87. Synthesis of a dinuclear $(Ph_2PNMe)_2CO$ bridged gold complex.



Scheme 88. Formation of zinc and platinum complexes of $H_2NC(S)NHP(S)Ph_2$.

should be mentioned however that the rhodium complex is cationic.

The reaction of $(Ph_2PNMe)_2CO$ with [Au(tht)Cl] (tht = tetrahydrothiophene) produces the expected dinuclear complex whereby the bisphosphino urea ligand bridges the two gold atoms in a bis-*monohapto* fashion due to the inability of gold(I) to form chelates (see Scheme 87). This inability has its reason in the incompatibility of the metal preferred bite angle of 180° for gold(I) with the preferred bite angle of the ligand that is likely to be below 100° judging from its metal complexes. The structure of $[\{Ph_2P(AuCl)NMe\}_2CO]$ was confirmed by an X-ray crystal structure determination revealing that the two substituents on nitrogen resume positions that place the bulky substituents at maximum distance to each other. In particular, the phosphorus atoms move from an "endocyclic" position in the free ligands to "exocyclic" positions in $[\{Ph_2P(AuCl)NMe\}_2CO]$. This structure was postulated some 10 years earlier by Schmutzler et al. for the complex $[(PhBu^tP\{Fe(CO)_4\}NMe)_2CO]$ [175].

Woollins et al. were not only interested in the coordination chemistry of bisphosphino urea and thiourea compounds, but also oxidised the phosphorus termini of these compounds using oxygen and sulfur and proceeded to coordinate the ligands via the chalcogenides to transition metals [183]. An interesting example is the $H_2NC(S)NHP(S)Ph_2$ that after deprotonation on the phosphino nitrogen coordinates to zinc and platinum. The zinc complex being tetrahedral at metal renders only one isomer whereas platinum(II) being square planar yields a *cis*- and a *trans*-isomer, respectively (see Scheme 88).

Ojima et al. [193,194] proposed a structure for the nickel(II) complex of the P-sulfurised phosphino thiourea complex $[Ni\{Ph_2PNC(S)NHMe\}_2]$ whose structure was later confirmed by Iwamoto et al. using X-ray structure analysis (see Fig. 13) [195]. The NiSPNCS rings are essentially planar.

It was said earlier that the preferred bite angle for gold(I) of 180° is incompatible with the natural bite angle for the bisphosphino ureas based on the existing structural parameters of their complexes. That of course is not a valid method

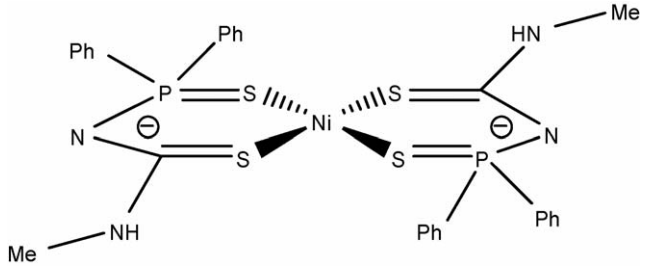
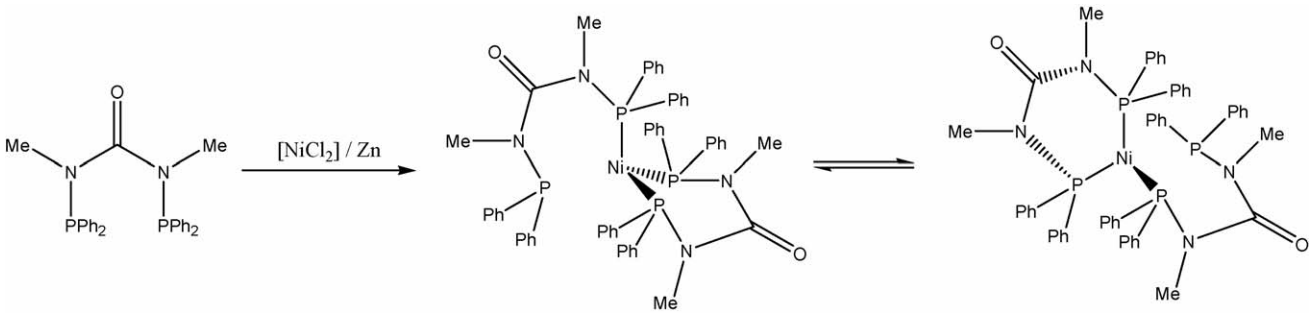


Fig. 13. Structure of the P-sulfurised phosphino thiourea complex $[Ni\{Ph_2PNC(S)NHMe\}_2]$.

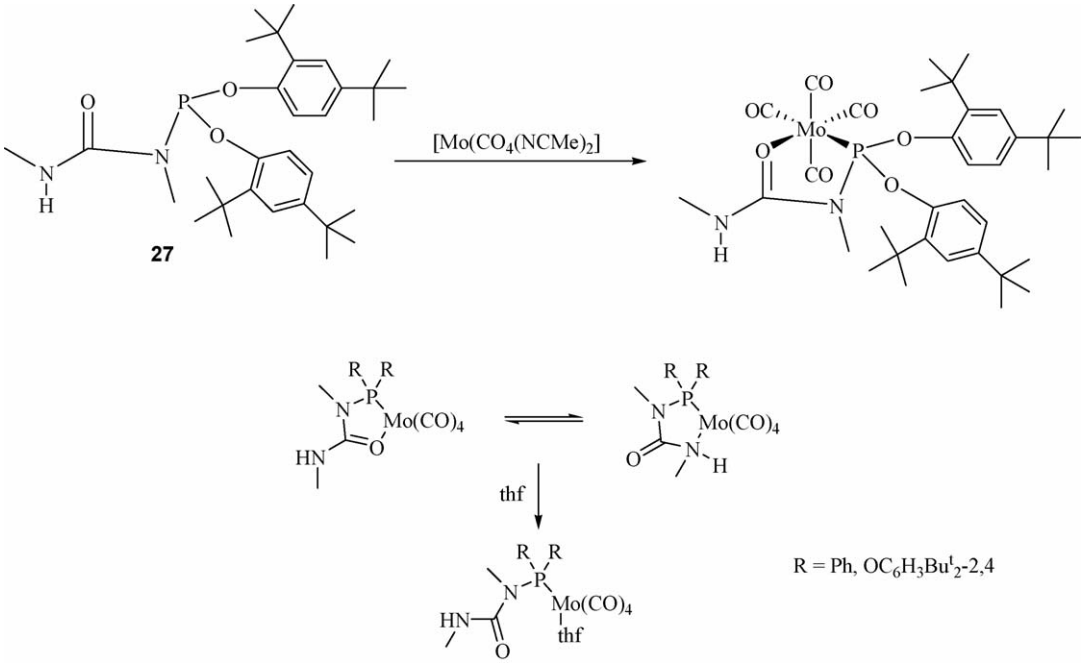


Scheme 89. Synthesis and proposed structure of [Ni((Ph$_2$PNMe)$_2$CO)$_2$] in solution.

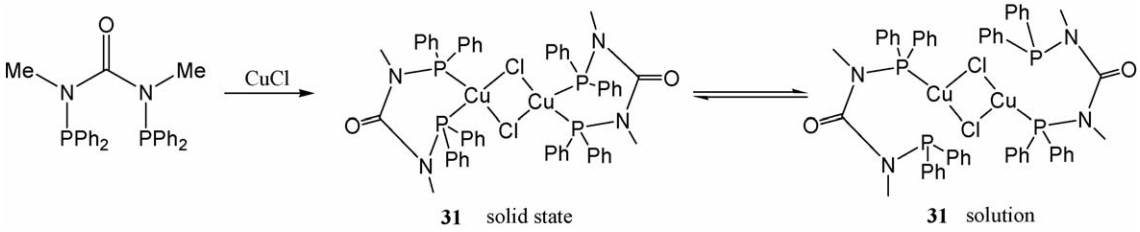
for the determination of ligand preferred bite angles as preference by ligand would suggest that their is no metal influence. That is not the case in a real metal–ligand complex. For that reason a "dummy metal" is used in molecular modelling calculations of natural bite angles as ligand preferred bite angles are named in the literature [196,197]. When Kühl and Langel determined the natural bite angle of (Ph$_2$PNMe)$_2$CO [198], X-ray crystal structures of bisphosphino urea metal complexes were limited to those examples were the metal features a preferred bite angle of 90° as in Pd(II), Pt(II), Ni(II), Rh(I), Cr(0) and Mo(0) with the exception of the previously described Au(I) complex.

Kühl et al. reacted (Ph$_2$PNMe)$_2$CO with nickel(II)chloride hexahydrate and an excess of zinc as reducing agent [198,199] to afford [Ni((Ph$_2$PNMe)$_2$CO)$_2$] in virtually quantitative yield. No crystals suitable for an X-ray crystal structure determination could be obtained. The yellow complex showed dynamic behaviour in the ^{31}P NMR spectrum indicative of alternative ring opening of either of the two NiPNCNP six membered rings (see Scheme 89). The authors gave incompatibility of the ligand preferred bite angle (95°–104°) with the metal preferred bite angle (109.5°) as the likely cause of this dynamic behaviour. Apparently Ni(0) tolerates only one chelate ring with an acute angle.

The only other phosphino urea ligands for which dynamic behaviour was reported are the two monophosphino ureas R$_2$PNMeC(*O*)NHMe (R = Ph, OC$_6$H$_3$Bu$^t_2$-2, 4 **28**). They form complexes with *cis*-[Mo(CNMe)$_2$(CO)$_4$] acting as chelate ligands with coordination via the phosphorus and either the oxygen or nitrogen terminus (see Scheme 90) [174]. The monophosphino urea acts as a hemilabile ligand [97], the phosphorus side binds firmly to the molybdenum atom, but coordination by either the oxygen or nitrogen moiety is weak allowing the ligand to switch between the two. This behaviour can be ascertained by comparing the IR spectra in the solid state (KBr) with that in solution (CH_2Cl_2) for the complex *cis*-[Mo{Ph$_2$PNMeC(*O*)NHMe}(CO)$_4$] [182]. Whereas in the solid state only one NH band at 3422 cm^{-1} and one for the ligand C=O



Scheme 90. Synthesis of *cis*-[Mo{R$_2$PNMeC(*O*)NHMe}(CO)$_4$] (R = Ph, OC$_6$H$_3$Bu$^t_2$-2, 4) and hemilabile behaviour of the coordinated monophosphino urea ligand in solution.



Scheme 91. Synthesis and structure of $[Cu\{(Ph_2PNMe)_2CO\}Cl]_2$ in the solid state and in solution.

group at 1605 cm^{-1} can be observed, the solution spectrum displays a second band for each group (3473 cm^{-1} and 1678 cm^{-1}, respectively).

Another d^{10}-metal isoelectronic to Ni(0) is copper(I) which is also characterised by a rich phosphine chemistry [200]. However, since copper(I) is a cation by necessity and nickel(0) is not, the resulting coordination complexes are not isostructural. Whereas nickel(0) binds two bisphosphino urea ligands, the copper(I) precursor CuCl binds only one such ligand preferring to form a $[Cu_2Cl_2]$ core structure instead (see Scheme 91) [201]. Like nickel(0) copper(I) displays a tetrahedral coordination sphere and is faced with the necessity to accommodate two acute angles in the two chelate rings it forms: the $[Cu_2Cl_2]$ core and the CuPNCNP ring with the bisphosphino ligand. Because of the Cu_2Cl_2 core, the copper(I) complex **31** is dinuclear and features two bisphosphino urea moieties.

In the solid state $[Cu\{(Ph_2PNMe)_2CO\}Cl]_2$ forms 1D chains using π–π interactions of the phenyl rings of the phosphino groups. The same general principle, but weaker π–π interactions are used to extend that initial 1D chain into a 2D network (see Fig. 14).

A very interesting feature of $[Cu\{(Ph_2PNMe)_2CO\}Cl]_2$ is the chirality of its CuPNCNP rings caused by the P–N fold vector. This chirality was first evidenced from the ^{31}P NMR spectra of *cis*-[Mo(**28**)$(CO)_4$] [174] **32** and fully desribed using the palladium complex [Pd(**28**)Cl_2] **33** (see Scheme 92) [202]. Folding of the six membered ring MPNCNP along the P–N vector creates two non-equivalent positions for the phosphorus atoms. The ligand $PPh_2NMeC(O)NMeP(OC_6H_3Bu^t_2\text{-}2,4)_2$ possesses two different phosphino groups. Thus the ^{31}P NMR spectrum of the metal complex shows two sets of doublets. In the case of the molybdenum complex, the ^{31}P NMR spectrum shows two sets of doublets for each expected signal in a ratio of 85:15. The authors explained this by showing that the metallacycle can fold along either of two possible P–N vectors leaving the respective phosphino groups in different geometrical environments. In the absence of a sufficiently accurate crystal structure, the authors had to leave the full description of the chirality of these complexes to the palladium compound **33**.

The chirality is more complex than expected since the fold vector creates two planes (PMPN and PNCN) and an axis (itself) each of which is an element of chirality. The three elements of chirality are not independent of each other and the complexes can be described using either one of them (see Figs. 15 and 16).

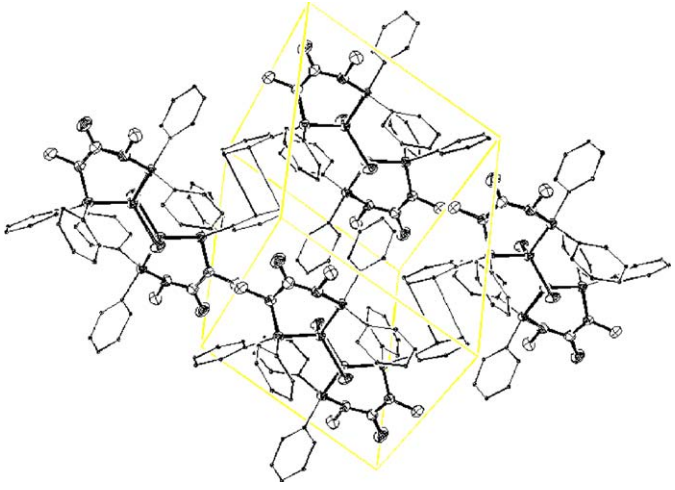


Fig. 14. Unit cell of **31** (*meso*-form) showing the π–π stacking interaction between the phenyl rings (long bonds). The weak π–π stacking interaction is located in the centre of the unit cell.

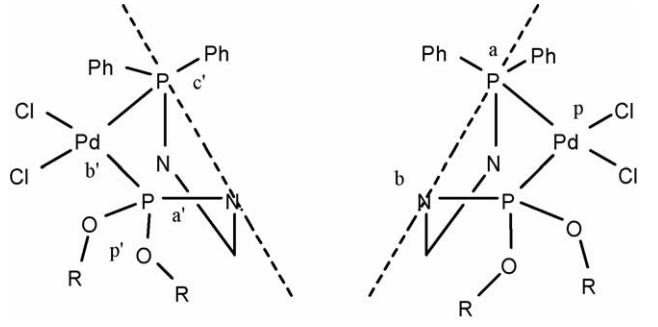


Fig. 15. The chirality of the metal complexes (shown for **33**) as described by the chiral planes.

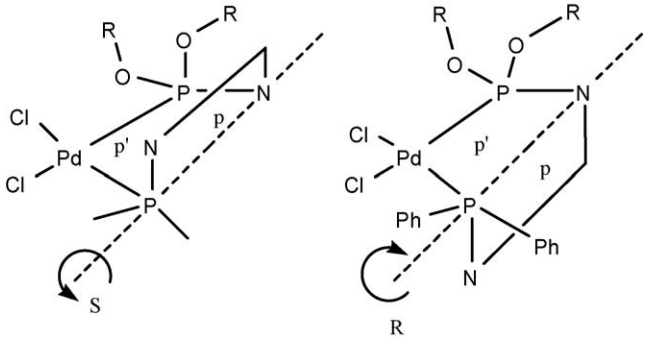
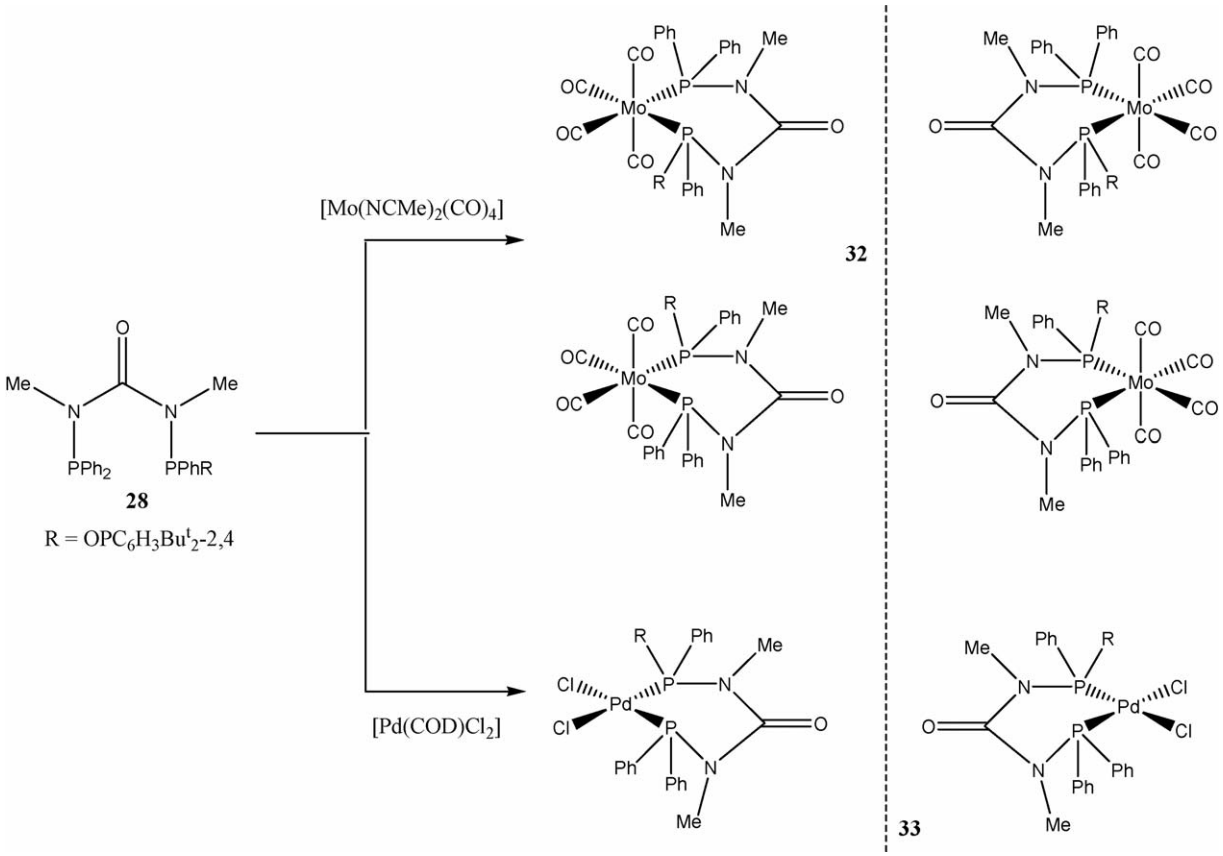


Fig. 16. The chirality of the metal complexes (shown for **33**) as described by A2 (dotted line).



Scheme 92. The observed enantiomers in the complexes **32** and **33**.

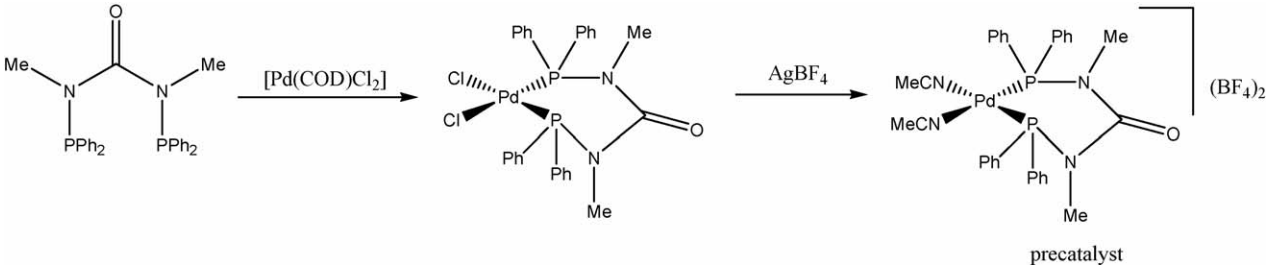
Thus, one bisphosphino urea ligand creates one independent element of chirality and gives rise to two enantiomers.

Not all possible diastereomers could be observed for all complexes. For example, whereas the ^{31}P NMR spectrum of the molybdenum complex **32** shows the presence of both diastereomers, only one diastereomer of the palladium complex **33** could be observed in either solution or the crystal state. Similarly the copper complex **31** realises only the *meso*-form in the crystal structure and suffers ring opening and thus racemisation in solution. For the earlier transition metal complexes with mostly symmetrical bisphosphino urea ligands, chirality was not even mentioned by the authors even though they are chiral. Presumably, the lack of a second set of signals in their respective phosphorus NMR spectra kept their chirality hidden.

4.4. Applications

Phosphino ureas have not enjoyed as much attention in applications as the phosphino lactams have, but their potential is shown by the diversity of uses. Iretskii et al. used rhodium(I) complexes of phosphino ureas (see Scheme 69) in the hydrosilylation of phenylacetylene, heptene-1, acetophenone and ethanol [185,186]. The rhodium(I) phosphino urea complexes show high activity whereas the parent rhodium(I) phosphino isocyanates show very low activity.

In more commercial applications Dossett and Stewart showed the usefulness of $(Ph_2PNMe)_2CO$ as a ligand in the nickel catalysed hydroformylation of α-olefins [41]. The catalyst is present as a dication, rather unusual for hydroformylation reactions (see Scheme 93).



Scheme 93. Formation of the catalyst precursor in the palladium/bisphosphino urea catalysed hydroformylation of α-olefins.

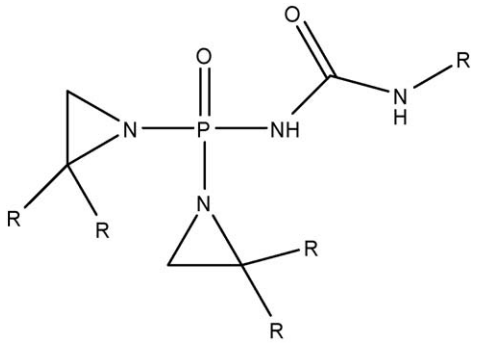


Fig. 17. *N*-(dialkyleneimido-phosphanyl)-ureas for use as cross linking agents.

The Hoechst AG was granted a patent to use *N*-(dialkyleneimido-phosphanyl)-ureas (see Fig. 17) as cross linking agents in a process for fixing pigments on fibrous materials and foils [162]. The urea compounds were used to improve the shelf life of printing dyes and to reduce the hazards posed by these dyes to those that are working with them.

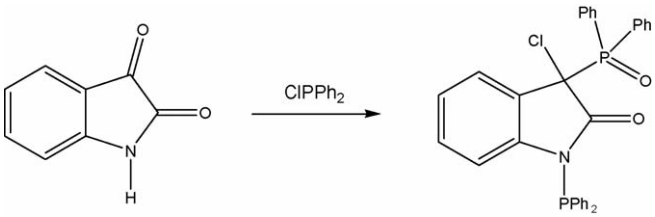
Sisler and Smith used phosphino ureas in the preparation of aminophosphonium halides useful as fuel additives [203]. They prepared the monophosphino urea by reacting urea first with elemental sodium and then with $ClPPh_2$.

5. Other compounds displaying the PNC=O structural motif

Some of the compounds discussed in this section might look strangely familiar and so they should. Quite often they can be seen as derivatives of compounds discussed in chapter 2–4, but with alterations sufficient to place them outside the categories of *N*-phosphanylated carboxilic acid amides, lactams or ureas. The interested reader might even successfully argue the case of a specific example.

The most obvious of these is probably the reaction between chlorodiphenylphosphine and an α-ketolactam reported by Razumov et al. in 1977 (see Scheme 94) [204]. It is not entirely clear whether the chlorophosphine attacks first the N–H bond or the α-carbonyl group. However, from other reports concerning HNC=O compounds possessing functional groups in close proximity to the NH moiety it seems likely that the amide reacts first [35,36,205,206].

Another functional HNC=O compound is biuret, a molecule that can be imagined as being derived from the condensation reaction of two urea molecules under elimination of ammonia.

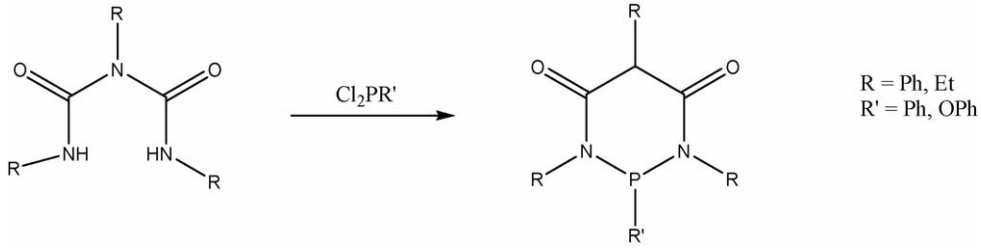


Scheme 94. Phosphanylation of an α-ketolactam.

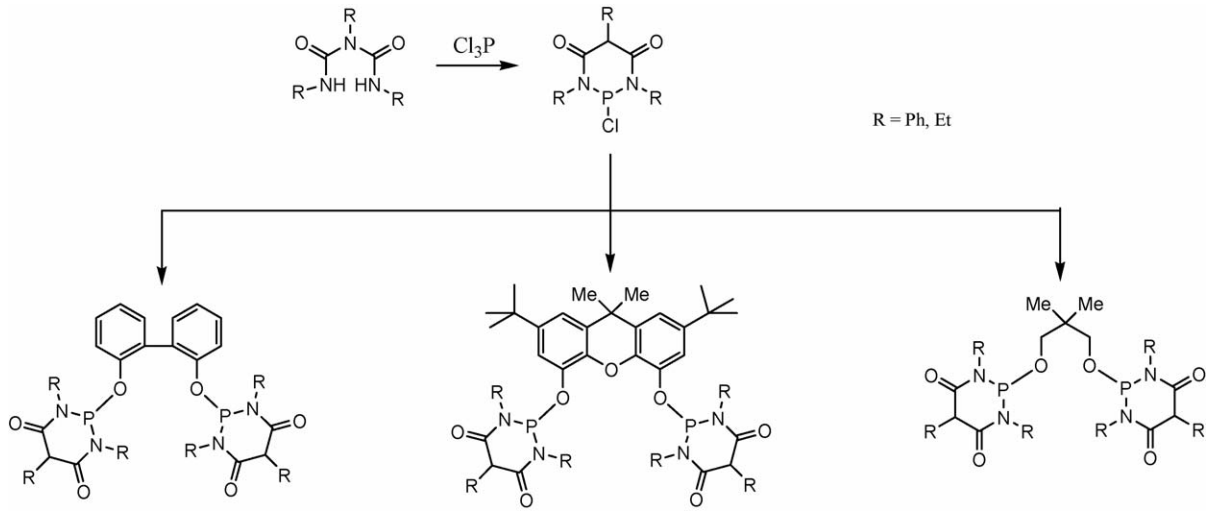
Thus, *N*,*N*′,*N*″-trisubstituted biuret is predisposed to form a six membered ring system if reacted with a dichlorophosphine (see Scheme 95) [35,206] and maintains a synthetically useful P–Cl group if reacted with PCl_3 (see Scheme 96). Van Leeuwen et al. used this system to design new mono- and bidentate phosphinoamide and phosphinoamidinate ligands for rhodium catalysed hydroformylation reactions. The νCO values in the IR spectra of their rhodium carbonyl complexes can be converted into TEP values of 2074–2079 cm^{-1} [39] placing them into the phosphite range [37].

The ligands were tested in hydroformylation reactions using *trans*-[Rh(CO)L_2Cl] as the precatalyst and 1-octene as substrate. The monodentate ligands form very active catalysts, but with a disadvantageous linear to branched ratio of the products. The product ratio for the chelate ligands was improved and the activity was only slightly lower [35]. The monodentate ligands were also tested in the intramolecular hydroformylation of allyldiphenylphosphine resulting in the usual three products, branched and linear aldehyde and the alkane from hydrogenation, but all still bonded to rhodium with their terminal carbon atoms (see Scheme 97) [206].

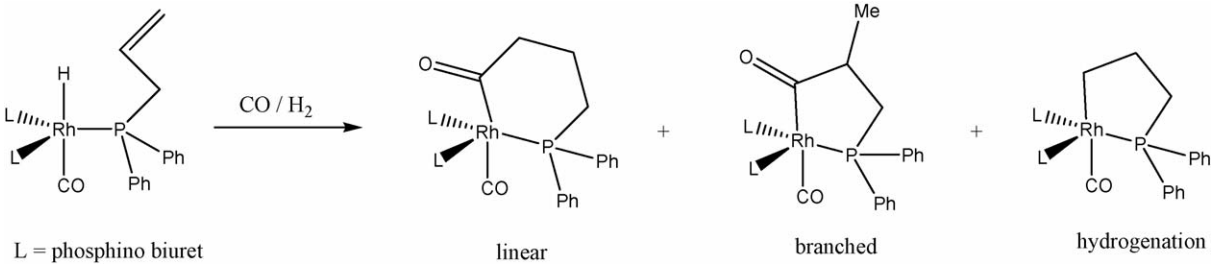
Another interesting system was introduced by Ellermann and Demuth, when they reacted 5-bromo uracile with chlorodiphenylphosphine [36]. Reaction occurs in two steps, first at N1 and then at N3 (see Scheme 98). Activation of the bromine can be effected in a very complicated reaction involving rearrangement, elimination and hydrolysis and resulting in the loss of a phosphino group. The structure of 5-diphenylphosphino uracile was confirmed by an X-ray crystal structure determination [207]. This complex reaction prompted the question whether the 5-phosphino uracile species is not more easily obtained from a reaction between 5-bromo uracile and sodium diphenylphosphide according to Hewertson and Demuth [205] and Hewertson and Watson [208]. The attempt failed. Instead 17% of 5-bromo-1-diphenylphosphino uracile was obtained instead of 82% using the earlier method.



Scheme 95. Phosphanylation of biuret.



Scheme 96. Formation of chelate ligands useful in catalytic hydroformylations using chlorophosphino biuret.



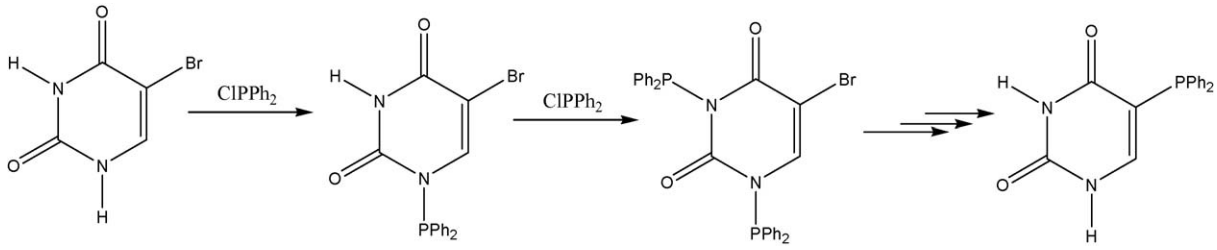
Scheme 97. Intramolecular hydroformylation of an allyldiphenylphosphine.

The coordination chemistry of 5-diphenylphosphino uracile was investigated using pentacarbonyl complexes of the group 6 metals chromium, molybdenum and tungsten [209]. The resulting carbonyl complexes were obtained as light sensitive crystals, but no crystal structure was reported. However, full spectroscopic characterisation was performed and a solid state structure proposed based on that evidence (see Fig. 18). As complexes containing the nitrosylcobalt(I) dicarbonyl moiety are usually more stable against light [210], the respective cobalt(I) complex of 5-diphenylphosphino uracile was prepared and a X-ray crystal structure obtained (see Scheme 99) [211].

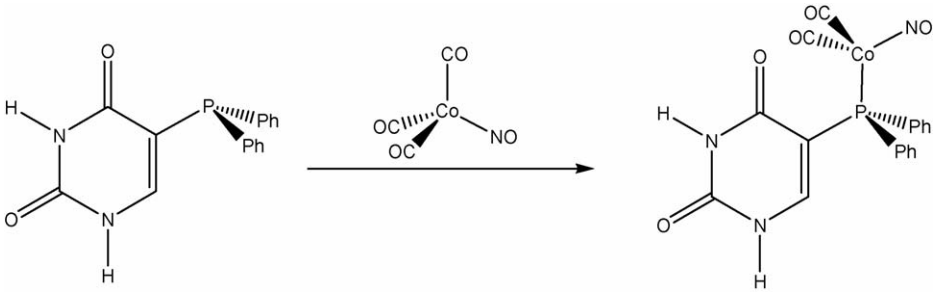
Some 10 years later, Ellermann et al. returned to the system when they investigated the phosphonylated 5-fluoro uracile [212]. The phosphanylation of the N1 and N3 protons is essentially the same as in the 5-bromo uracile system. However, an interesting tautomeric equilibrium was observed for the bisphosphino compound (see Scheme 100). In the tautomeric equilibrium the phoshino substituents are shifted from N1 and N3 to the oxygen atoms bonded to C2 and C4. Hydrolysis of the bisphosphino compounds affords the two monophosphino compounds and Ph_2PPOPh_2 in analogy to the respective 5-bromo compound.

Other examples of derivates from "natural products" include a theoretical study of N2 substituted saccharins at the HF (RHF/6-31G) level reported by Naumov et al. [213] in an approach to investigate the effect of *N*-substitution on this artificial sweetener. The study is concerned with the effect on the structural parameters of the saccharine backbone by the substituent on N2 (see Scheme 101). However, no value for the calculated P–N bond was given.

In a wider study of the reactions of (silylamino)phoaphines with organic halides Morton and Neilson give an example for



Scheme 98. Stepwise phosphanylation of 5-bromo uracile.



Scheme 99. Synthesis of $[CoNO(CO)_2L]$ (L = 5-diphenylphosphino uracile).

the reaction of a silylamino phosphine with methyl chloroformate (see Scheme 102) [214]. The product is the respective *N*-methoxycarbonyl-substituted dimethylphosphino amide, the carbonic acid analogon to the carboxylic acid phosphino amides discussed in chapter 2.

Molecules carrying a P–H, As–H or Sb–H functional group can be added to the N=N double bond of suitable azo compounds like dialkyl azodicarboxylates [215,216]. If the azo compound carries a C=O group on nitrogen the product might well be the PNC=O structural motif that forms the basis of the present review (see Scheme 103). The reactivity of the phosphorus containing species drops in the expected order $HPR_2 > HP(O)R_2 \sim HP(S)R_2 > HP(O)(OR)R \sim HP(O)(OR)_2$. The arsanes are very sensitive to hydrolysis and oxidation whereas the respective stibanes are extremely air, moisture, light and temperature sensitive. They cannot be stored for more than a couple of days even at −17 °C and exclusion of air, moisture and light.

As the work published by Linke and Brandt was written in German, an article describing very similar results by an Australian research group appeared in a British journal some 14 years later without citing the earlier articles [217]. However, the results presented by Jenkins et al. contain the crystal structures that were not provided by the Linke group.

The hydrogen atom in the phosphines can be substituted by the isolobal iron(II) fragment $[Cp^*Fe(CO)_2]$ ($Cp^* = C_5Me_5$) [218]. The transition metal involvement opens up new reaction pathways of which only the one leading to the PNC=O compound after CH activation on one of the Cp^*-methyl groups is of interest for us (see Scheme 104).

If one of the NMe_2 moieties in the starting material is substituted by phenyl, the Cp^* ring converts into the respective

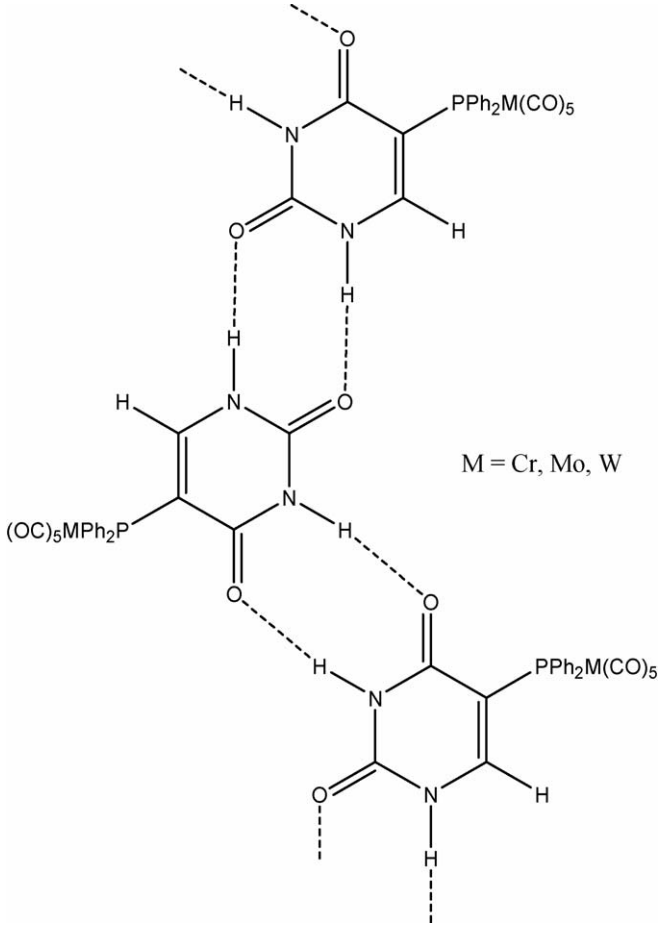
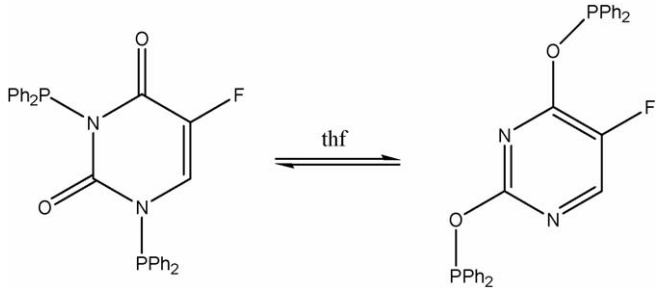
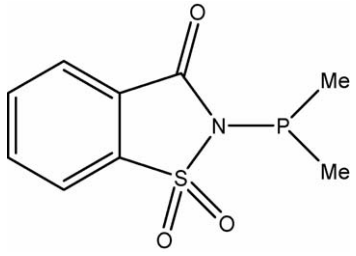


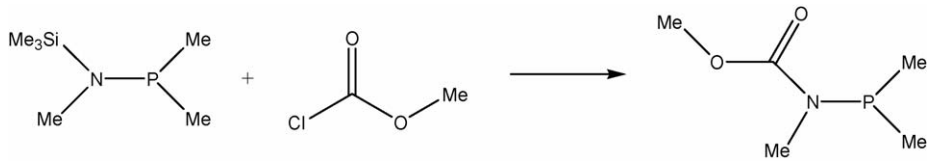
Fig. 18. Proposed hydrogen bond network in transition metal complexes of 5-diphenylphosphino uracile.



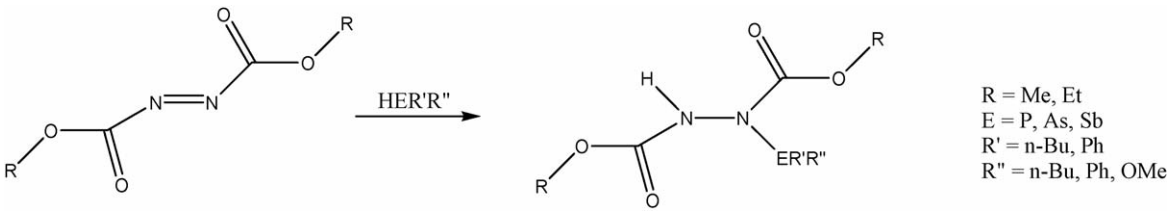
Scheme 100. Tautomeric equilibrium of 1,3-bis-diphenylphosphino-5-fluoro uracile in thf solution.



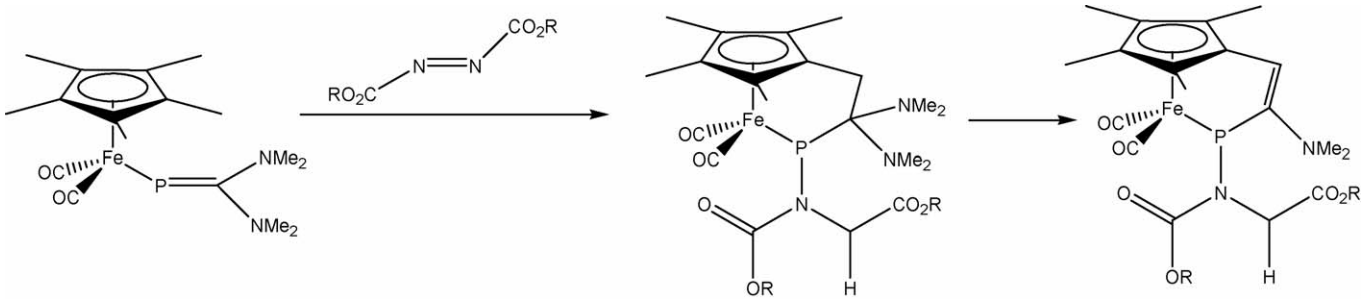
Scheme 101. *N*-Dimethylphosphino saccharin.



Scheme 102. Reaction of a silylamino phosphine with methyl chloroformate.



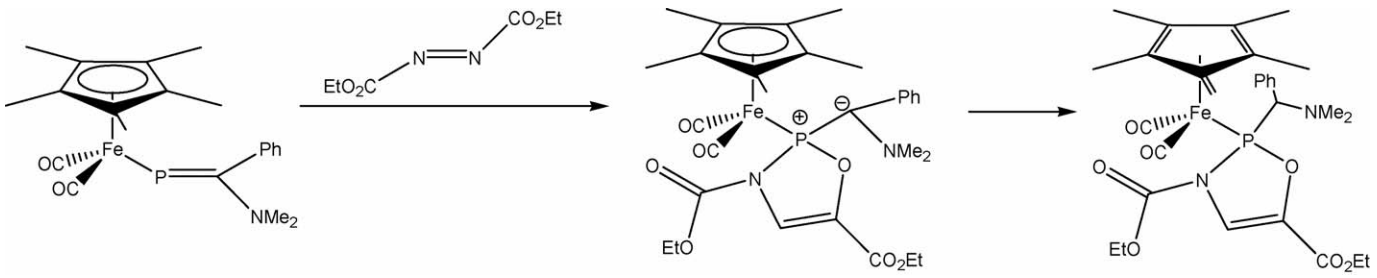
Scheme 103. Addition of phosphines, arsanes and stibanes across the N=N double bond of dialkyl diazocarboxylates.



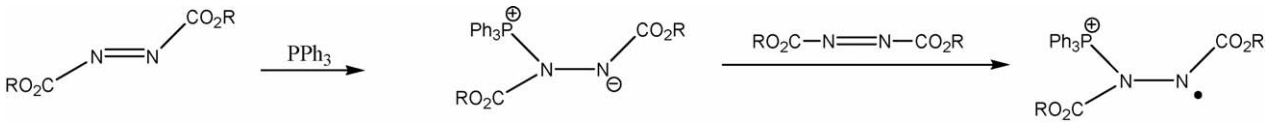
Scheme 104. Reaction of an iron phosphide with dialkyl diazocarboxylate.

fulvalene without ring closure with the carbon atom on phosphorus (see Scheme 105) [219]. Instead, ring closure occurs at phosphorus by activation of the C=O oxygen of the ester function.

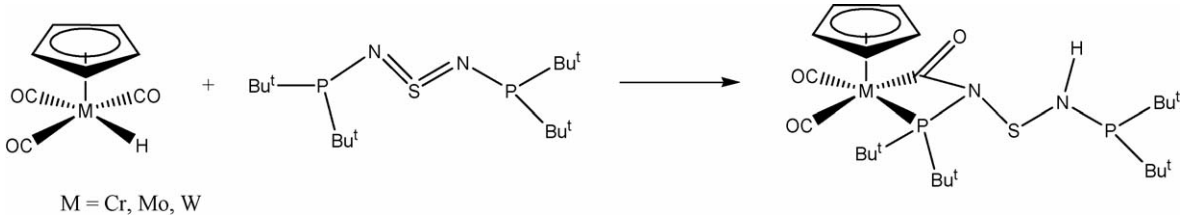
The rekindled interest in the reaction between dialkyl azodicarboxylates and phosphines stems from the Mitsunobu reaction whereby a carboxylic acid and a nucleophile is reacted with the aid of a dialkyl azodicarboxylate and triphenyl phosphine [220]. The study is not so much concerned with the synthesis of the Mitsunobu product RCO_2Nu, but with the mechanism of attack of the phosphine on the dialkyl azodicarboxylate that starts the Mitsunobu reaction. The initial product is a zwitterion, a phosphobetaine (see Scheme 106) which is a PNC=O species. This species can be oxidised by a second molecule of the dialkyl



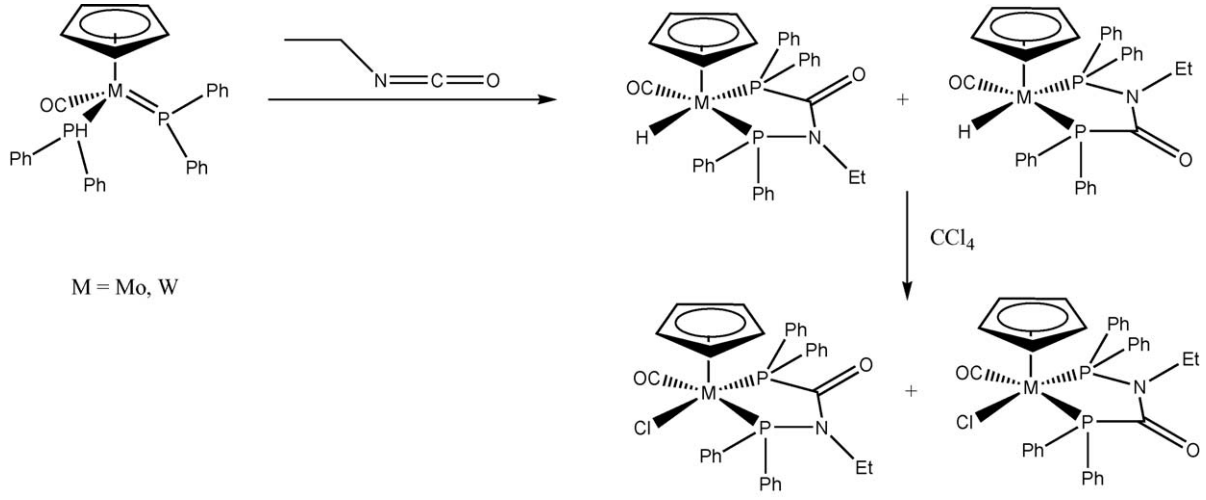
Scheme 105. Changing the reactivity of the iron phosphide.



Scheme 106. Attack of triphenylphosphine on dialkyl diazocarboxylate.



Scheme 107. Reacting a sulfurdiimide with a transition metal hydrido species.



Scheme 108. The reaction of an isocyanate with a transition metal phosphide.

azodicarboxylate to form a persistent radical, if no species with an acidic proton is present.

A similar reaction to that reported by Linke et al. was investigated by Heberhold et al. in the reaction between $H[CpM(CO)_3]$ ($Cp = C_5H_5$, M = Cr, Mo, W) and bis-(di-*tert*-butyl-E)sulfurdiimide (E = P, As) [221]. The reaction proceeds with formation of a N–C bond between the diimide and a metal carbonyl group (see Scheme 107). The proposed structure is one of three possible structures and was determined by spectroscopic means.

A transition metal carbonyl species carrying a phosphinidene and a secondary phosphine as ligands was reacted with an isocyanate by Malisch and Pfister [222]. As we remember from chapter 4, the reaction of phosphinoamines with isocyanates leads to phosphino ureas and in analogy to the dialkyl azodicarboxylates, a phosphine might react with an isocyanate to form a carboxylic acid phosphinoamide. However, the second phosphino group participates in the reaction and the observed product is a P,P-chelate complex of $PPh_2C(O)NEtPPh_2$ (see Scheme 108). $PPh_2C(O)NEtPPh_2$ can best be described as a *N*-phosphino, *N*′-phospha urea derivative, the second PPh_2-group taking the place of a nitrogen moiety in the urea parent compound.

The isocyanate adds to the two phosphorus substituents in two different orientations, leading to products where the hydride is either *cis* or *trans* to the P(*N*)-phosphorus. The respective ratios for the molybdenum and tungsten complexes are 5:2 and 2:1 in favour of the *cis*-P(*N*) compound, respectively. Scheme 108 shows only the diastereomers, the respective enantiomers can be obtained by the usual symmetry operation (the interested reader might want to exchange the CO and H(Cl) ligands to arrive at the mirror image). It should be mentioned that the hydrido complex reacts with carbon tetrachloride to form the respective chloro-complex.

6. Summary and outlook

This review has shown that the structural motif PNC=O(*S*) is found in a diverse range of compounds, but mainly focussed on carboxylic acid phosphinoamides, phosphino lactams, and phosphino ureas, gives rise to a rich chemistry not restricted to phosphorus, but reaching out into Coordination Chemistry, Organometallic Chemistry, catalysis, Polymer Science, Pharmacy, and Medicinal Chemistry to name a few. Although the Main Group Chemistry of the phosphino ureas is reasonably well explored, it is still far from being known. Other compounds like the phosphino lactams and the carboxylic acid phosphinoamides themselves have only been explored using a very limited number of representatives in an equally limited number of reactions. However, from the results available, an interesting and rewarding chemistry can be envisaged.

Their electronic properties are similar to those of phosphites and like them can be easily functionalised. Functinalisation and introduction of chirality, both in the backbone and at phosphorus, can be achieved in more ways and tapping more sources than it is possible in the synthesis of phosphites. The consti-

tuting parts of carboxylic acid phosphino amides include both amines and carboxylic acids. These are prominent, numerous, and inexpensive members of the chiral pool and an equally rich source of "naturally functionalised" molecules whose potential in the synthesis of PNC=O containing molecules still waits to be exploited.

A small number of chiral phosphino lactams, carboxylic acid phosphino amides, and phosphino ureas have been synthesised and tested, mainly in the hydrogenation of prochiral ketones useful as intermediates in the synthesis of pharmaceuticals. An equally interesting, but largely unexplored, application of chirality are the planar and axially chiral transition metal complexes of bisphosphino ureas. Their chirality is neither present in the metal fragment nor in the phosphino urea ligand, but is a consequence of the coordination process. The field of chiral ligands and complexes containing the PNC=O group as a whole lies largely bare waiting to be discovered.

Whether the chemistry of the PNC=O compounds can rival the chemistry of phosphites, the widely used and immensely better studies phosphorus ligand class with similar electronic properties is impossible to tell. For such a verdict more data needs to be accumulated for the PNC=O compounds. However, the existing range of applications given the comparatively small number of publications gives a clear indication that the potential exists and indeed exists not only in those fields where exploration has already begun.

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