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Coordination Chemistry Reviews 249 (2005) 2056–2074
COORDINATION CHEMISTRY REVIEWS
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Review

The chemistry of phosphinoamides and related compounds

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Available online 22 April 2005

Contents

Abstract

This review commences with a survey of the general synthetic routes leading to aminophosphines containing the P—NH subgroup. Recent examples involving functionalised and chiral aminophosphines are included. The synthesis and structural properties of deprotonated aminophosphines, namely the phosphinoamides, are then described in detail. The reaction of phosphinoamides with main group elements/compounds and transition metal and lanthanide complexes, leading to the formation of inorganic chains, rings and phosphinoamido complexes is then discussed. The application of phosphinoamido complexes in olefin polymerisation catalysis is also covered.
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Keywords: Aminophosphines; Phosphinoamides; Diphosphinoamines; Iminodiphosphines; P—P coupling; Phosphinoamido complexes

1. Introduction

The chemistry of compounds containing phosphorus and nitrogen, with direct bonds between the two elements, has been known for many years, but continues to attract considerable attention, with applications in increasingly diverse

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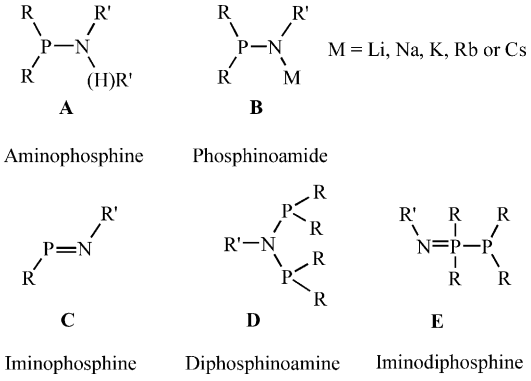
doi:10.1016/j.ccr.2005.03.014

fields [1,2]. Although traditional phosphorus chemistry is dominated by compounds containing P–C and P–O linkages (almost all naturally-occurring phosphorus compounds contain P–O bonds), P, N compounds now dominate in main group chemistry. Phosphorus, nitrogen compounds exhibit immense structural diversity and detailed structural information combined with theoretical rationalisation of their bonding, has helped to consolidate the field.

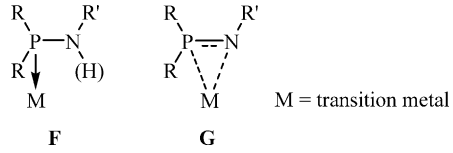
From a historical perspective, P, N chemistry concerning the P–N single bond is the oldest and is now well established. In contrast, the development of P, N chemistry involving P=N and P≡N bonds has been regarded as being somewhat 'exotic' [3,4]. The chemistry of P, N single and multiple bonds is now merging and expanding in a coherent fashion. Compounds containing P–N single bonds are called aminophosphines or phosphazanes, those with P=N double bonds are referred to as iminophosphines or phosphazenes and compounds with P≡N triple bond are called phosphazynes or phosphorus nitrides. The nomenclature used to describe some of their derivatives is somewhat more complicated and the lack of a generally accepted nomenclature for P, N systems makes the unambiguous designation of these compounds difficult, and has, on occasion, led to a confusion in the literature. In this review, we will use the name aminophosphine for type **A** compounds, deprotonated aminophosphines, type **B**, are referred to as aminophosphine anions or phosphinoamides (in this review we use the latter). Compounds containing P=N bonds, type **C**, are termed iminophosphines. Those with the P–N–P unit, type **D**, are termed diphosphinoamines and those of type **E**, with a N=P–P backbone are named iminodiphosphines.



The prototypical reaction used to prepare aminophosphines involves the reaction between an amine and a chlorophosphine with the elimination of HCl. The formation of P–N single bonds is usually facile, and as such, this method is well established and has been employed for many decades [5].

Among the aminophosphines of type **A**, those with P–NH are especially interesting as the acidic hydrogen is easily removed yielding phosphinoamides, type **B**, with a negative charge residing on P, N unit. The P–N bond in the anion is shorter than those observed in aminophosphines, but longer than in P=N-containing iminophosphines, type **C**, suggesting that the bond is intermediate between the two.

The traditional coordination chemistry related to neutral aminophosphines involves bonding via the phosphorus centre only, type **F** [6,7]. The partial double bond character of phosphinoamides enables η^2 coordination, forming complexes of type **G**. In addition, $R_2P–N(R')^-$ is *iso*-electronic with $R_2P–X^-$ (X = O, S and Se). The latter species have proven to be popular ligands, which often show extraordinary coordination behaviour, whereas the coordination chemistry of $R_2P–N(R')^-$ is still largely unexplored.



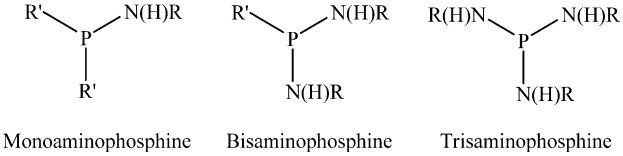
Although phosphinoamides have been known for many decades [8,9], in the past their chemistry has been explored (and interpreted) in the absence of detailed structural information. Since the 1990s [10] a large number of X-ray structures of phosphinoamides and their complexes have been reported, which has led to a renewed interest in the field.

In this review, as a foundation for the discussion, we commence by briefly describing the synthesis and characterisation of aminophosphines and their anions. Aminophosphines containing the basic structure $R_2P–N(H)R'$, mainly focussing on the most recent examples containing functionalised groups and chiral centres, will be described. The synthesis and characterization of their anions, with references mostly after 1992, where most of the anions have been investigated by single crystal X-ray analysis, will also be covered. The remainder of this review will focus on the use of phosphinoamides as ligands/nucleophiles, and the subsequent applications of phosphinoimido complexes in catalysis, notably olefin polymerisation.

2. Aminophosphines and their anions

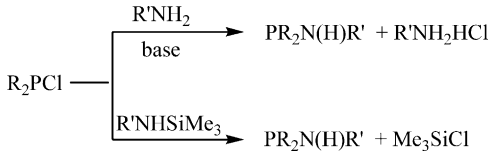
2.1. Aminophosphines

Aminophosphines can be classified according to the number of amine groups attached to the phosphorus centre. In general, as the numbers of the amine groups increases at the phosphorus centre, the stability of the aminophosphine decreases.



Monoaminophosphines, $R_2PN(H)R'$ (R, R′ = alkyl or aryl), tend to be stable and are generally easy to prepare. The aminolysis reaction, which involves reaction of an amine with a chlorophosphine, remains the most widely used method for their preparation [5]. The reaction is conducted in the presence of an organic base, typically triethylamine, to trap the

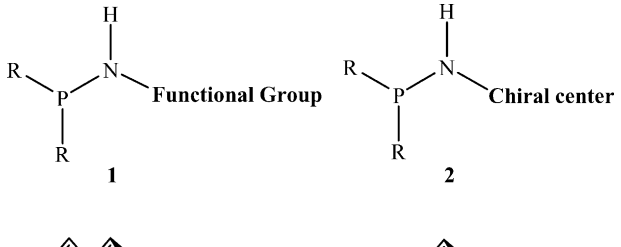
liberated HCl. An alternative reaction employs an aminosilane in place of an amine, which liberates trimethylchlorosilane, and has the advantage that it can easily be removed by distillation [11]. However, the method is limited by the comparatively low availability of aminosilane precursors.



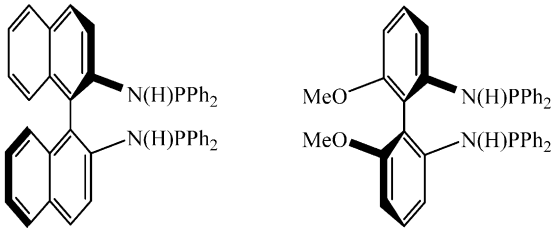
Other routes to $R_2PN(H)R'$ compounds have been reported, although yielding a more limited range of compounds. For example, there is a trend towards utilising organometallic bases in place of organic bases, which take place via metallated amide intermediates, M[RNH] (R = alkyl or aryl; M = Li, Na or K), and are important precursors in organic synthesis. Of the various metallated salts, lithiated amines are the most common, and many of their structures have been elucidated by single crystal X-ray diffraction [12,13]. However, since many lithiated species are unstable, even at low temperatures, they are often generated in situ prior to conversion to the desired product. The relatively strong basicity of such amides enables the rapid formation of P–N bonds. In particular, this methodology is especially useful for amines with bulky substituents where conventional organic bases like triethylamine are too slow to be synthetically useful.

$$R'NH_2 \xrightarrow{n\text{BuLi}} \text{Li[RNH]} \xrightarrow{R_2PCl} PR_2N(H)R'$$

Aminophosphines with one P–NH unit are the simplest to prepare and have been intensively investigated [14,15]. Due to their applications as ligands in coordination chemistry, many functionalised aminophosphines, e.g., with methoxyl, pyridyl and acetyl groups have been prepared [16], and aminophosphines with chiral centres have found applications in asymmetric catalysis [17,18]. In particular, the chiral aminophosphine BINOL-analogues **3** [19] and **4** [20], combined with various transition metals, exhibit excellent activity in asymmetric hydrogenation reactions.

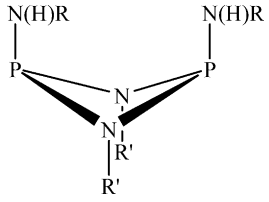


1 **2**



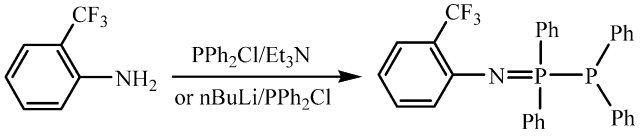
3 **4**

Ring systems tend to be more stable than open chain aminophosphines, a particular stable class are the cyclic species, type **5**. The stability of such ring systems has enabled the isolation of a series of complexes containing four-membered P, N rings. Such compounds have been studied for many years, with recent interests focussed on their reactivity towards main group elements [21].



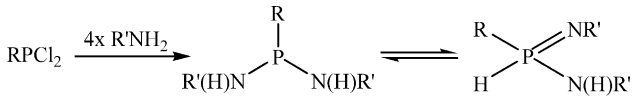
5

It is noteworthy that some aminophosphines with strong electron-withdrawing groups at the nitrogen centre are difficult to prepare using either the aminolysis method or via the amide. Neither the reaction of $C_6H_4(o\text{-}CF_3)NH_2$ with Ph_2PCl in dichloromethane in the presence of triethylamine, nor lithiation of $C_6H_4(o\text{-}CF_3)NH_2$ with *n*BuLi followed by addition of Ph_2PCl, affords the expected aminophosphine $PPh_2N(H)C_6H_4(o\text{-}CF_3)$. In both reactions, the only product observed is the iminodiphosphine $PPh_2{-}PPh_2{=}NC_6H_4(o\text{-}CF_3)$ **6** [22].



6

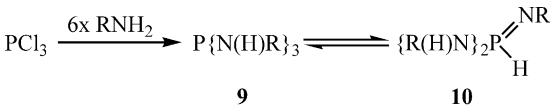
Diaminophosphines, $RP[N(H)R']_2$ (R, R′ = alkyl, aryl) **7** are generally less stable than monoaminophosphines, especially those with alkyl substituents, which can easily undergo condensation reactions to give N=P(IV)–N, type **8**, products. The two tautomers **7** and **8** co-exist in solution [23], although increasing the bulk of the substituents at the P- and N-centres can inhibit the process [5,24]. The position of the prototropic equilibrium **7** ↔ **8** depends on the solvent and the substituents at the phosphorus and nitrogen centres, which evidently influence the acidity of the NH and PH forms.



7 **8**

Diaminophosphines with aryl substituents are less prone to condensation reactions [25,26]. Their increased stability has been ascribed to the partial delocalisation of the electron lone pair at the phosphorus centre. An aryl substituent at the nitrogen also helps to distribute the electron density and reduce the nucleophilicity of the phosphorus towards the NH group.

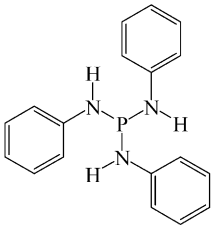
Trisaminophosphines $P\{N(H)R\}_3$ (R = alkyl or aryl) **9** have also been known for many years [27,28]. Over 100 years ago, Michaelis described an attempt to prepare tris(*n*-propylamino)phosphine, finally concluding that tris(alkylamino)phosphines were unstable [27]. The main problem is their tendency to undergo condensation. A recent report demonstrated that even using amines with very bulky substituents, condensation from $P\{N(H)R\}_3$ to $\{R(H)N\}_2PH{=}NR$ **10** cannot be prevented [29].



9 **10**

R = *i*Pr, *t*Bu, Ph[Me(CH)]

The synthesis of trisaminophosphines with aryl substituents has been somewhat more successful. For example, the reaction of PCl_3 with aniline affords such a compound, although problems with reproducibility were encountered [30] the structure of tris(phenylamino)phosphine **11** was finally established beyond doubt [31]. In addition, the higher oligomers **12** and **13**, and polymers, from the same reaction of PCl_3 with aniline in various stoichiometries have been isolated [32]. Increase in the steric bulk of the substituent at the nitrogen of the primary amine facilitates the formation of tris(arylamino)phosphines [33], although often they are not stable and exist as mixtures with their corresponding tautomers.



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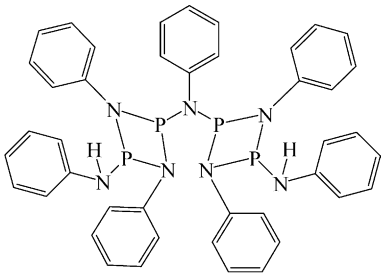

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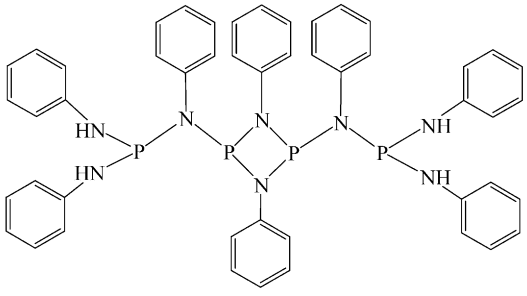
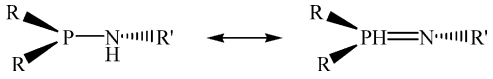
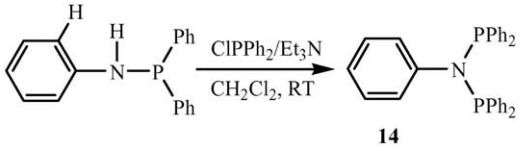


13

Schmidpeter and Rossknecht proposed that the reactivity of aminophosphines was dominated by the protoprotism of the N(H)P moiety, and subsequently, this proposition has proven extremely helpful in rationalising their reactivity [34]. Aminophosphine can exist, at least in principle, in two isomeric forms, $R_2P{-}N(H)R'$ and $R_2P(H){=}NR'$ [35]. The reaction of $R_2PN{-}(H)R'$ with chlorophosphines gives P–N–P products, whereas reaction of $R_2P(H){=}NR'$ affords N=P–P products [9c]. Similar phenomena were observed in the reactions of aminophosphines with metal complexes [36].



Factors that influence the equilibrium, $R_2P{-}N(H)R' \leftrightarrow R_2P(H){=}NR'$, include the nature of the substituents, the solvent and the temperature. The substituents are particularly important since they determine whether the aminophosphine reacts as $R_2P{-}N(H)R'$ or $R_2P(H){=}NR'$. For example, diphenylphosphinoaniline (Ph_2PNHPh) [37,38] is frequently used in coordination chemistry, whereas it is not used as a precursor to diphosphinoamines, e.g., bis(diphenylphosphino)aniline **14** [39]. As an illustrative example of the importance of the substituents on the outcome of the reaction, substitution of the proton in diphenylphosphinoaniline by a Ph_2P unit gave bis(diphenylphosphino)aniline **14** as the only product. In the same type of reaction, the nitrile-functionalised aminophosphine $Ph_2PN(H)C_6H_4$(*o*-CN) does not give the P–N–P product, instead the N=P–P containing compound **15** is formed. If the nitrile substituent is replaced by phenyl group, viz. $Ph_2PN(H)C_6H_4$(*o*-Ph), reaction with chlorodiphenylphosphine affords mainly the P–N–P product $(Ph_2P)_2NC_6H_4$(*o*-Ph) **16**; the N=P–P product $PPh_2{-}PPh_2{=}NC_6H_4$(*o*-Ph) **17** is obtained in only 2% yield [22,40].



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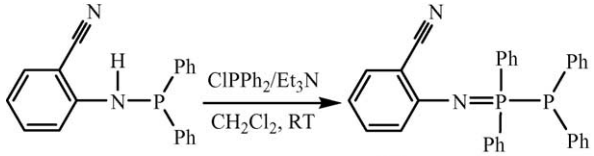

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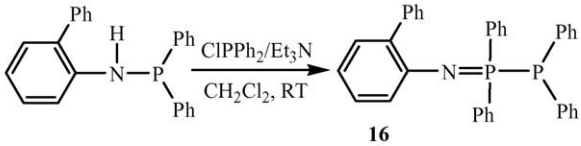

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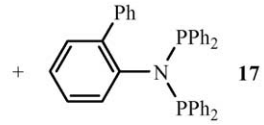
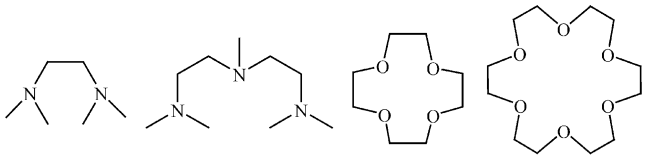


17

2.2. Phosphinoamides

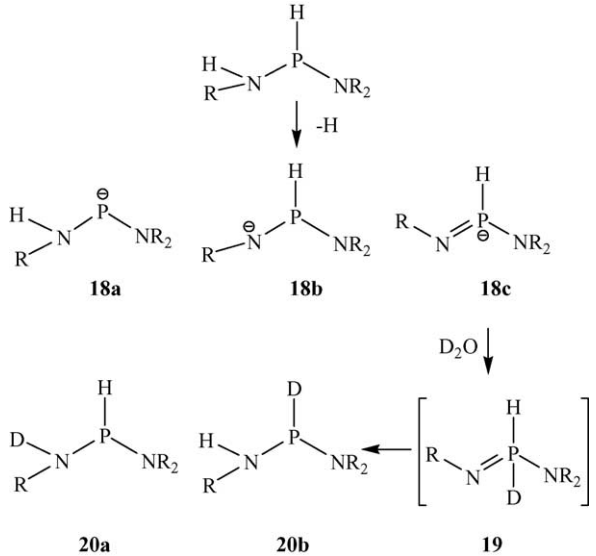
Group 1 metal salts of phosphinoamides are readily prepared by deprotonation using reagents such as *n*BuLi, MH (M = Na or K) or M(O*t*Bu) (M = K, Rb or Cs). The solid-state structures of these anions tend to contain diethyl ether or thf as supporting ligands, coordinated to the metal ion. In addition, other supporting ligands such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDTA), 12-crown-4 or 18-crown-6 are also employed as supporting ligands.



TMEDA PMDTA 12-Crown-4 18-Crown-6

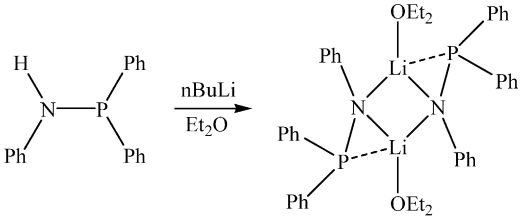
The preparation of such compounds tends to be straightforward, provided good stoichiometry of reactants is used, but the resulting products are air sensitive, and mounting crystalline products for X-ray analysis requires considerable skill. Prior to the structural analysis of such salts, phosphinoamides were used as precursors to iminobiphosphines [41] or transition metal complexes [42].

Efforts to determine the structure of phosphinoamides, especially with respect to locating the negative charge, have been made [43,44]. Deprotonation of $(SiMe_3)_2NP(H)–N(H)SiMe_3$, for example, could result in anions **18a**, **18b** or **18c**. Since these anions react with D_2O, possibly via intermediate **19**, to give a mixture of **20a** and **20b**, indicated by the presence of P–H and P–D bonds in the ^{31}P NMR spectrum, the structure of the anion was proposed to be like that of **18c**. Based on the structural information currently available it is not unreasonable to assume that the anion could have a more complicated structure.



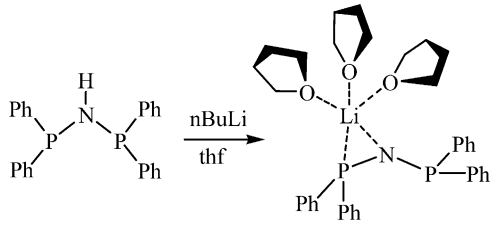
18a **18b** **18c** **20a** **20b** **19**

Ashby and Li published the structure of lithium diphenylphosphinoamide **21** [10], revealing a dimeric structure with the two N- and two Li-centres forming a four-membered ring. The P–N bond distance of 1.672 Å is intermediate between a P–N single bond and P=N double bond. The lone pair of electrons on the phosphorus is oriented toward the lithium ion that exhibits the shorter P–Li distance indicating the presence of P···Li interactions, despite this interaction not being observed in the solution.



21

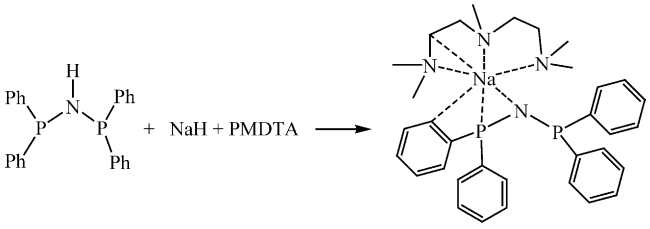
Subsequently, the structure of the lithium salt of **22** was reported, it is monomeric with the lithium cation interacting with both the P- and N-centres [45]. Compared to the neutral precursor, $(Ph_2P)_2NH$, the P–N distances are reduced from 1.692 to 1.658 Å and 1.686 Å, and the P–N–P angle increases from 118.9° in the neutral precursor to 124.7° in **22**. The ^{31}P NMR of **22** displays a singlet resonance at room temperature, which splits into two signals on cooling to −100 °C, suggesting that the P···Li interaction is maintained in solution, at least at low temperature. Interestingly, P···Li coupling could not be observed in solution by ^{31}P NMR spectroscopy, and it was not possible to observe the $^2J(PP)$ coupling although the two phosphorus centres are inequivalent in the solid state. For $Li[PPh_2]$, it has been suggested that, in thf, polymeric chain-like structures exist in solution [46]. However, in a recent paper, ^7Li pulsed-gradient spin-echo (PGSE) diffusion NMR spectroscopy was used to provide a clearer picture of the solution structure, which suggest that the structure is monomeric with the Li cation solvated as $[Li(thf)_4]^+$ [47].



22

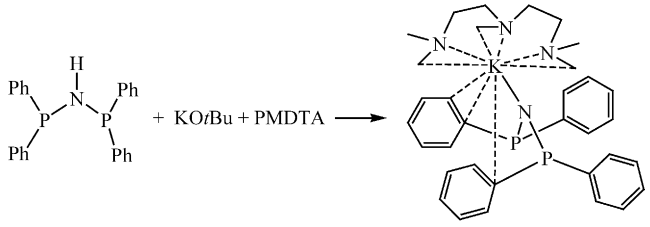
The P–N bond distances in **21** and **22** indicate some multiple-bond character is present, which explains why the both P- and N-centres can interact with metals, seldom the case for neutral aminophosphines. Anions derived from bis(diphenylphosphino)amine with other Group 1 cations have been prepared and their solid-state structures differ depending on the metal cation and the solvent.

Reaction of $(PPh_2)_2NH$ and NaH in the presence of PMDTA gives the sodium complex **23a** [48a]. Similar to the lithium salt **22**, the sodium ion in **23a** interacts with both the phosphorus and nitrogen centres in the solid state. In addition, weak interactions between the sodium ion and carbon atoms from a phenyl ring and an aliphatic carbon atom from the PMDTA ligand are also present.



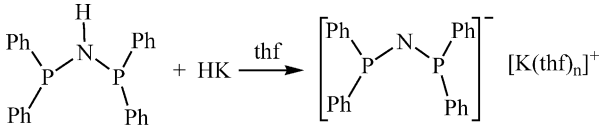
23a

In a similar manner, the reaction of $(PPh_2)_2NH$ and KO*t*Bu in the presence of PMDTA affords the potassium complex **23b**, which is structurally similar to **23a**, although in **23b**, there is no interaction between potassium cation and the phosphorus centres [48b]. The two P–N bond distances in **23a** are 1.664(2) and 1.667(2) Å, and in the potassium salt **23b** these values are essentially the same. In the lithium salt **22** they are 1.658(4) and 1.686(4) Å.

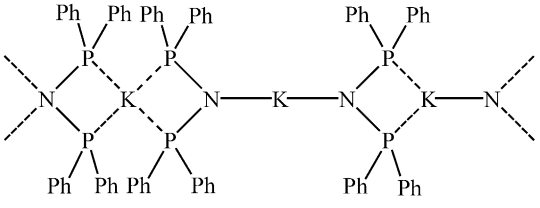


23b

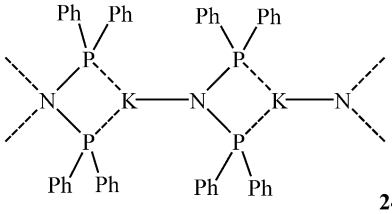
Treatment of $(PPh_2)_2NH$ with KH in thf under reflux affords **24** [49], the structure exists in two forms **24a** and **24b** crystallised as blocks and needles, respectively. Structures **24a** and **24b** consist of infinite chains that differ in their coordination environments.



24 n = 1.25 n = 1.5

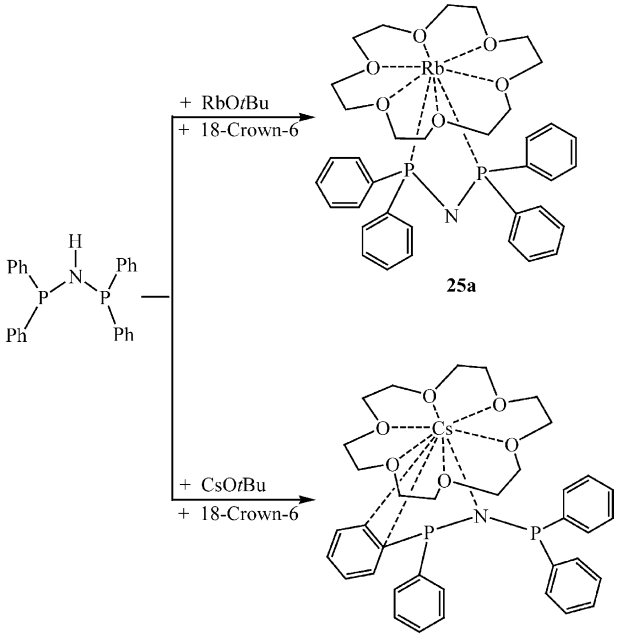


24a



24b

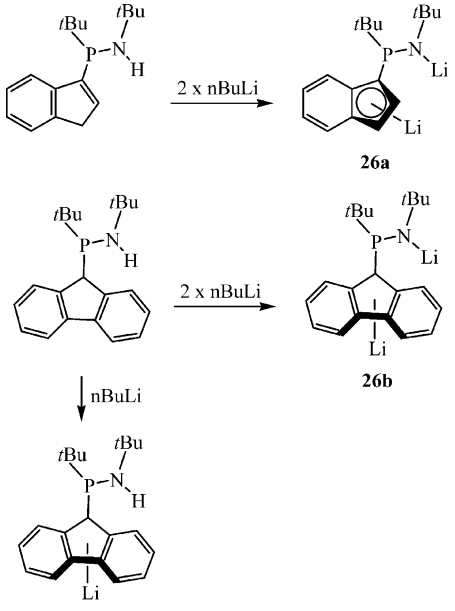
Interestingly, the reaction of $(PPh_2)_2NH$ and RbO*t*Bu followed by addition of PMDTA did not give a PMDTA complex, instead a compound of composition $Rb(NPPh_2)_2 \cdot 0.5thf$ was isolated [50]. However, if the reaction is conducted in the presence of 18-crown-6 then the crown complex **25a** is obtained, and surprisingly, there is no Rb–N bond. Replacing rubidium with caesium affords **25b**, which in contrast to **25a**, contains no Cs–P interaction. The two P–N bond distances are 1.658(3) and 1.656(3) Å in **25a** and 1.632(4) and 1.653(4) Å in **25b**.



25a

25b

An interesting class of phosphinoamide is represented by **26** and **27** [51]. Compounds **26a** and **26b** are prepared by treatment of the corresponding aminophosphines with two equivalents of *n*BuLi. Deprotonation can be controlled to afford **27** by adding one equivalent of *n*BuLi; deprotonation takes place at the cyclopentadiene ring rather than at the nitrogen. Both **26** and **27** can be transformed into the corresponding Me_3Si or Me_3Sn derivatives.

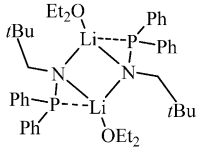


26a

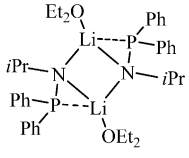
26b

27

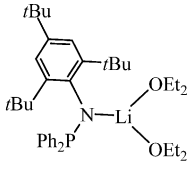
The lithium salts **28**–**32** are prepared by the same method, treatment of the corresponding aminophosphines with *n*BuLi in diethyl ether or thf [52]. Both **28** and **29** have dimeric structures in the solid state, being only marginally different from the anion **21**. The P–N bond lengths are 1.660(2) and 1.669(2) Å in **28** to 1.659(4) and 1.666(4) Å in **29**, and weak P···Li interactions are also observed in **28** (P···Li: 2.633(6) and 2.673(6) Å) and in **29** (P···Li: 2.693(7) and 2.913(7) Å). Compound **30** is monomeric with essentially no P···Li interactions in the solid state, presumably due to the steric bulk at the N-centre. Anion **31** has a dimeric structure, but the two lithium cations are inequivalent. Compound **32** represents the first example of a functionalised phosphinoamide. In the solid-state structure of **32** both lithium ions are equivalent and contribute towards the formation of a 12-membered ring [40]. In solution, the ^{31}P NMR spectra of all the lithium salts show a singlet at room temperature in thf, having chemical shifts at higher frequency than the neutral aminophosphines precursors.



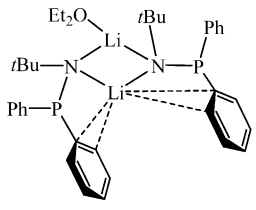
28



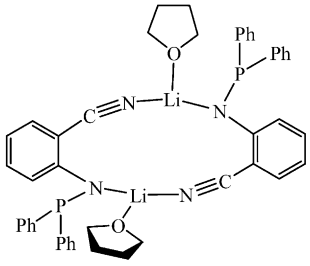
29



30

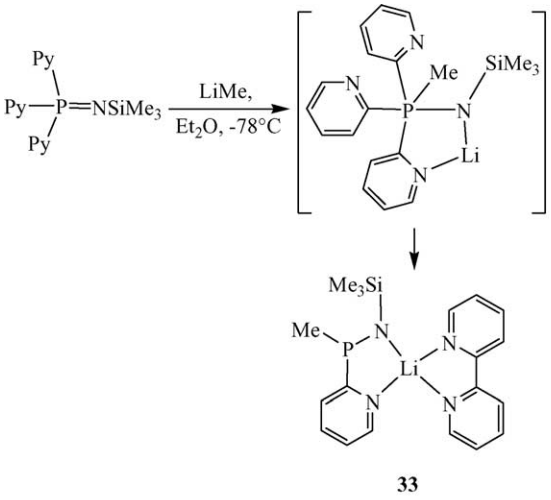


31

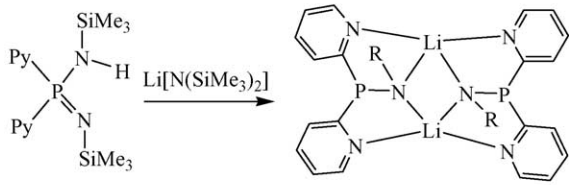


32

Cleavage of iminophosphoranes can also provide phosphinoamides. For example, reaction of the iminophosphorane $Py_3P{=}NSiMe_3$ (Py = 2-pyridyl) with LiMe affords **33** [53]. Formation of **33** was proposed to proceed via initial addition of LiMe to the P=N bond, in such a way that the methyl anion binds to the phosphorus centre, with the lithium ion trapped by the peripheral nitrogens. Rearrangement of the hypervalent species through substituent coupling to two pyridyl groups would lead to the formation of the 2,2′-bipyridyl adduct **33**. Similarly, reaction of $Py_2P(NHSiMe_3){=}NSiMe_3$ with $Li[N(SiMe_3)_2]$ in Et_2O gives **34** [54]. The electron-withdrawing effect of the 2-pyridyl group is believed to not only play a significant role in the cleavage of the P=N bond, but also in the stabilisation of the resulting lithium salt.

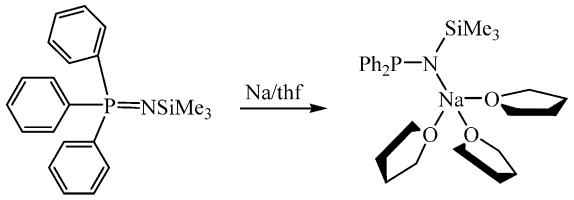


33



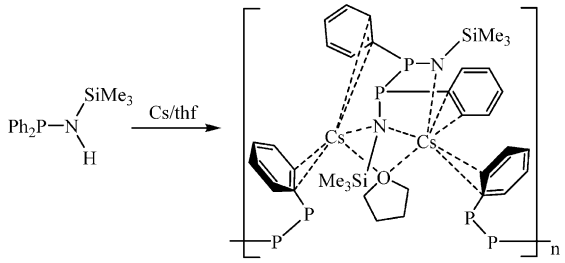
34 R = $SiMe_3$

The P–N distances in the lithium salts **33** and **34** are comparable with those observed in **28**–**32**, despite the differences in the peripheral ligands. Elemental sodium has also been shown to induce the cleavage of P=N bond in $Ph_3P{=}NSiMe_3$ to give phosphinoamides **35** [55]. The method has been successfully expanded into other systems with electron-withdrawing groups at P- and N-centres [56].



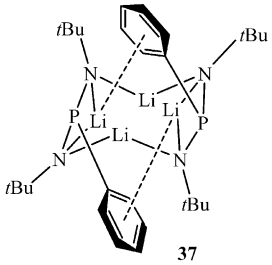
35

Deprotonation of aminophosphines using potassium, K–Na alloy [57] or metallic caesium [55] is also possible. However, deprotonation is sometimes accompanied by P–P formation. Reaction of $Ph_2PN(H)SiMe_3$ with elemental caesium results in the formation of a polymer, **36** [55]. Formation of the P–P bonds could be due to the high reactivity of elemental potassium and caesium, but other factors cannot be ruled out.

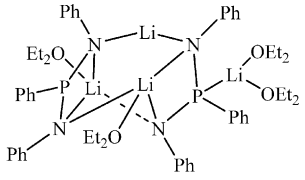


36

Deprotonation of diaminophosphines is also a facile reaction, but in general, the resulting structures are very complicated, presumably due to the greater probability of rotation around the P–N bonds. The solid-state structures of dianions also tend to vary significantly [58]. Lithiation of the diaminophosphine *t*BuP{N(H)*t*Bu}$_2$ using *n*BuLi affords the dimeric species **37**, in which each lithium ion is connected to two nitrogens. There are no solvent molecules present, which interact with the lithium centers, instead Li···π interactions with the phenyl rings are present. Lithiation of PhP{N(H)*t*Bu}$_2$ also affords a dimer, **38**, with three different lithium environments, having coordination numbers of two, three and four. Metallation of MeP{N(H)*i*Pr}$_2$ gives a tetramer **39**, whereas metallation of RP{N(H)*t*Bu}$_2$ (R = 2,4,6-tris(*tert*-butylphenyl)) with *n*BuLi yielded the *n*-butyl derivate **40**. Thus, reaction with *n*BuLi not only causes the deprotonation of the aminophosphine, but also induces an exchange of the phosphorus-bonded substituent.



37



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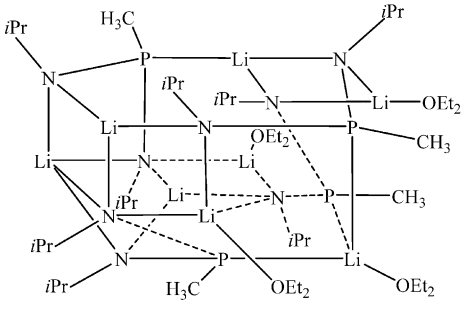
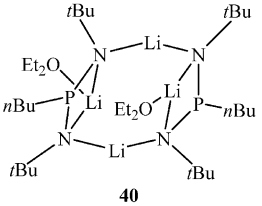


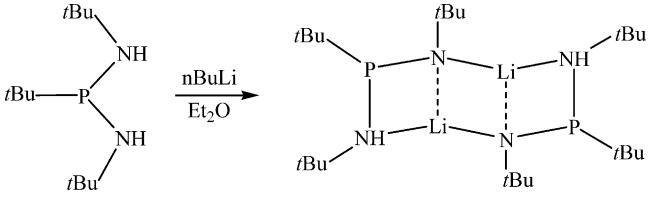
39



40

Unlike monophosphinoamides, which exhibit a singlet in their ^{31}P NMR spectra in thf, the dianions do not give sharp signals at room temperature. This feature could be interpreted as several different species being present in solution, but so far full characterisation in solution has not been achieved.

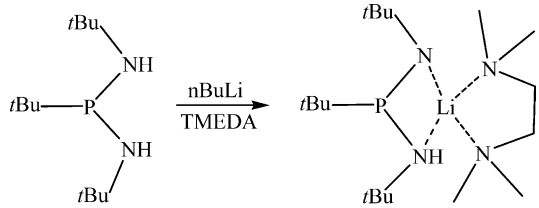
Diaminophosphines can also be selectively deprotonated. The reaction of *t*BuP{N(H)*t*Bu}$_2$ with equimolar amounts of *n*BuLi in Et$_2$O at −78 °C affords the monolithiated compound **41** in almost quantitative yield [59].



41

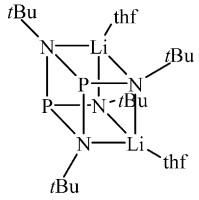
The ^{31}P NMR spectrum of **41** in non-coordinating solvents such as hexane and C$_6$D$_6$ only show one singlet at ca. 104 ppm. In contrast, the ^{31}P NMR spectra of both isolated and in situ prepared **41** in Et$_2$O show an additional signal of ca. 10% relative intensity at 108 ppm indicating that **41** is solvated, with both forms being equilibrium. The structure of **41** in the solid state comprises a non-planar eight membered P$_2$N$_4$Li$_2$ heterocycle formed from two (anionic) di(amino)phosphine moieties and two Li cations.

Reaction of **41** with TMEDA, or alternatively deprotonation of *t*BuP{N(H)*t*Bu}$_2$ with *n*BuLi in the presence of TMEDA, yields **42** in high yield. In solutions containing TMEDA **41**, converts to **42**, which points to the formation of an equilibrium between TMEDA-coordinated **42** and unsolvated **41** in non-coordinating solvents. The equilibrium is temperature dependent, at −60 °C **42** dominates, but at higher temperature the unsolvated species **41** is the main species present. The P–N bond distances in **42** also differ by almost 0.13 Å [1.784(2) Å and 1.654(2) Å].

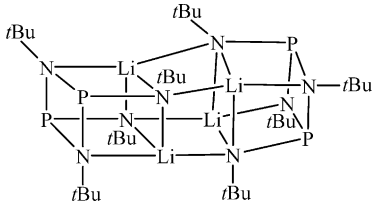


42

Cyclic aminophosphines derived from type **5** compounds can form polycyclic cages in the solid state like **43**, or larger structures such as **44** [60]. This class of phosphinoamides can form a number of complexes with Group 13 elements such as boron [61], aluminium [62], gallium [63], indium and thallium [64] and they were recently reviewed [21].

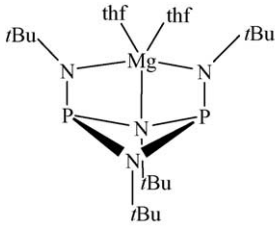


43

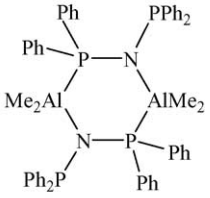


44

Metallation of aminophosphines with Grignard reagents, $AlMe_3$ or $ZnMe_2$ affords **45** [21], **46** [65] and **47** [55], respectively.



45



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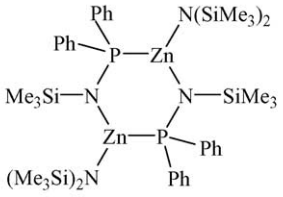
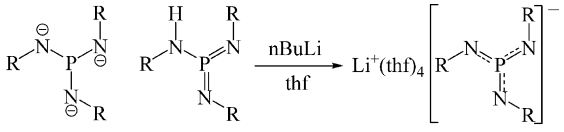


47

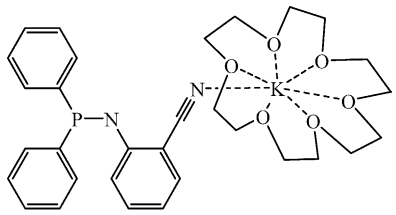
Trianions of type **48** are rare since the strong electron donation from the nitrogen anions to the phosphorus centre increases the nucleophilicity at the phosphorus centre and consequently they are unstable. However, monomeric tri(imino)metaphosphates have been isolated. Reaction of the di(imino)aminophosphine with *n*BuLi affords **49** [66]. The P–N bond in **49** is very short [1.565(2) Å] suggesting almost pure double bond character.



48

49 R = 2,4,6-tris(*tert*-butylphenyl)

Phosphinoamides where neither the N- nor P-centres interact with a cation were predicted to be different from the conventional metallated adducts. Addition of a crown ether to trap the metal ion during the synthesis of phosphinoamides was not sufficient to prevent interaction between the P and the N centres and the cation [50]. However, using this strategy in combination with a nitrile functional group on the aminophosphine, successfully led to a structure with an isolated phosphinoamide [67]. The reaction of $Ph_2PN(H)C_6H_4$(*o*-CN) with elemental potassium in the presence of 18-crown-6 gave the free anion **50** in high yield, which displays a sharp singlet at room temperature in the ^{31}P NMR spectrum. The solid-state structure of **50** reveals a P–N bond length of 1.675(5) Å, which is slightly shorter than that in the lithium analogue **32**, confirming a theoretical study that predicted a shortening of the bond [68]. The bond lengths associated with the P, N unit and the aromatic ring and the nitrile substituent show delocalization of the negative charge along the ring and, to some extent, towards the P-centre.

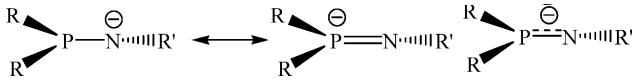


50

The isolated anionic P, N unit is more reactive than anions that interact with the counter cation. For example, reaction of **50** with H_2O does not lead to the reformation of the aminophosphine precursor, instead, cleavage of the P–N bond takes place, leading to formation of $K[Ph_2PO]$ and C_6H_4(*o*-CN)NH_2.

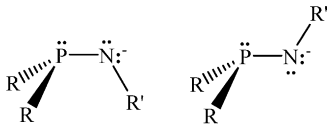
Theoretical studies on phosphinoamides have been used to probe the location of the negative charge, the character of the P–N bond, the nature of P···Li interactions and the configuration around the P–N bond [52,68]. In all the lithium salts analysed by single crystal X-ray diffraction, N···Li interactions are always present indicating that the charge is nitrogen centred. The other noteworthy feature is the change of the P–N bond length. In most cases, the P–N bond distance is shorter in the lithium salts than in the neutral aminophosphine; although in dianions and cyclic anions the P–N bond can elongate (in cyclic structures) as well as decrease in length. A comparison of the structural parameters of aminophosphines with their lithiated derivatives is difficult since only a few pairs are available. In all cases, the P–N bond length decreases after deprotonation, although to varying extents. The greatest decrease in P–N bond length is observed in monoaminophosphines while in diaminophosphines the decrease in bond length is small. Although P···Li interactions are often present in the solid state the reasons for such variations remain unclear.

It has been suggested that the anion $R_2P–N–R'$ could formally be described as a resonance hybrid with the corresponding iminophosphides, $R_2P^-=NR'$ [10,52,68].



Form $R_2P–N–R'$ is expected to predominate if the greater electronegativity of the nitrogen atom is the dominate factor; however, form $R_2P^-=NR'$, in which phosphorus has expanded its octet, results in additional stabilization due to resonance delocalization of the charge and P–N multiple bonding. Ab initio calculations indicate that hyperconjugation is not sufficient to describe most phosphinoamide derivatives as iminophosphides,

$R_2P^-{=}NR'$, although electron-withdrawing substituents at the phosphorus strengthen the P–N bond. While most simple alkyl- and aryl-substituted derivatives are best described as phosphinoamides, $R_2P{-}N^-R'$, with the negative charge located mainly on nitrogen, calculations suggest that there is sufficient hyperconjugative bonding to enforce two ground-state conformations, *cis* and *trans*.



cis *trans*

The majority of structurally characterised monophosphinoamides exhibit *cis*-geometries, although *trans* structures have been observed in **30**, **32** and **35**. Compounds **30** and **35** have bulky substituents that probably give rise to the *trans*-configuration, which also probably explains why they are monomers. In the case of **32**, the additional functional group is the likely factor, which accounts for the *trans* configuration.

3. Reactions of phosphinoamides with main group elements and compounds

The reactivity of phosphinoamides has been intensively investigated, and they are generally regarded as good nucleophiles. They react with most of the representative main group elements, i.e., P_4, S, Se and I_2, and compounds of Groups 13–16, such as $AlCl_3$, AsI_3, SbI_3 and $BiBr_3$. Phosphinoamides have also been used as starting material for synthesis of P–P and P–M (M = As, Sb or Si) compounds which exhibit chain and ring structures.

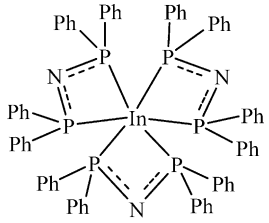
3.1. (Re)protonation reaction

It has been demonstrated that aminophosphines can be regenerated from phosphinoamides by protonation with water or methanol. These re-protonation reactions helped to establish the nature of such anions prior to their characterisation by X-ray diffraction methods, although the reaction provides little information about the actual structure of the anion [43]. For example, the lithium ion in $Li[(Ph_2P)_2N]$ **22**, interacts with both the P- and N-centres, but reacts with MeOD to give the aminophosphine $(Ph_2P)_2ND$ as the only product [69]. The disparity between the structural data and reactivity of the anion can be rationalised using hard–soft acid base theory, since the nitrogen is a hard base, it reacts preferentially with H^+.

Re-protonation of phosphinoamide **32** also affords the aminophosphine precursor; but re-protonation of the free anion **50** does not give the original aminophosphine, instead P–N cleavage takes place [67]. The addition of water to a thf solution of the potassium-18-crown-6 salt of **50** gives initially $K[Ph_2PO]$, not the expected aminophosphine, even at low temperature (−20 °C). The $K[Ph_2PO]$ was then further oxidized to $K[Ph_2P(:O)O]$, which crystallises together with the amine giving a host–guest complex connected by an N–H···O hydrogen bond.

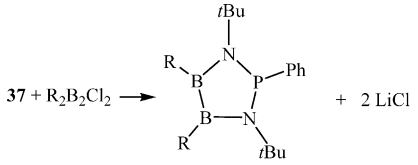
3.2. Reactions with Group 13 chlorides

Among the numerous reports on reactivity studies of phosphinoamides, there is little coverage on reactions of open-chain phosphinoamides with Group 13 elements and compounds. Compound **22** reacts with $InCl_3$ in a 3:1 molar ratio in thf at room temperature to give the neutral compound **51** [70]. The four-membered P–N–P–In chelate rings in the solid-state structure of **51** are oriented in a propeller-like conformation.



51

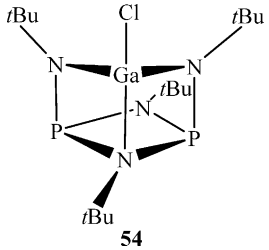
The reaction of **37** with $R_2B_2Cl_2$ (R = 2,4,6-tris(*tert*-butylphenyl)) affords the ring compound **52** [58]. The ring in **52** is almost planar and the B–N bond lengths [1.428(7) and 1.436(7) Å] are characteristic of unsaturated bonds, whereas the B–B bond distance of 1.710 Å is typical of a single bond.



52: R = 2,4,6-tris(*tert*-butylphenyl)

The reaction of **41** with one equivalent of $GaCl_3$ in Et_2O results in the formation of *t*BuP{N(H)*t*Bu)N(*t*Bu)}$GaCl_2$ **53**, which was characterised by spectroscopy [59].

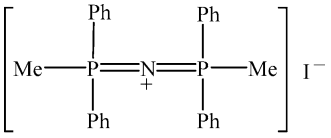
In contrast to open-chain phosphinoamides, bridged anions such as **43** can react with Group 13 chlorides like $GaCl_3$ to give cage-like complexes such as **54**. This area has been recently reviewed [21], although some further examples have since been published [71].



54

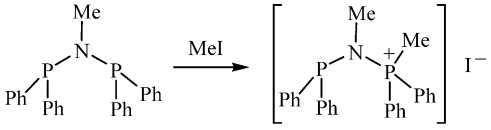
3.3. Reactions with Group 14 halides

Compound **22** reacts with MeI to give bis(diphenylmethylphosphino)iminium iodide $[(Ph_2MeP)_2N]I$ **55** in which two P–C bonds have formed (instead of the expected formation of C–N bonds) [72].



55

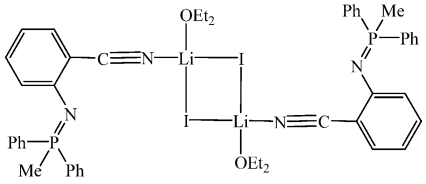
The isomer of **55**, viz. **56**, with the charge formally residing on the phosphorus, is not observed. However, such a compound can be prepared from the reaction of bis(diphenylphosphino)methylamine with MeI.



56

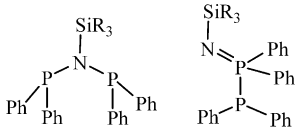
Interestingly, the reaction of **22** with CH_2Cl_2 or $CHCl_3$ also gives **55** [73]. It is thought that CH_2Cl_2 and $CHCl_3$ are reduced to CH_3Cl, which is the active alkylating agent. In the reaction mixture, traces of $CHCl_3$ and $ClCH_2CH_2Cl$ were detected.

Similarly, the reaction of **32** with MeI gave a P–C coupling product, viz. **57**, although there is no P–Li interaction in the solid-state structure of **32** [40].



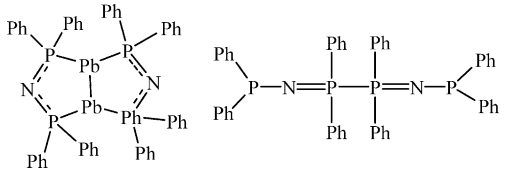
57

Compound **22** reacts with chlorosilanes $ClSiR_3$ to give diphosphinoamines $(Ph_2P)_2NSiR_3$ **58** and $Ph_2P–PPh_2=NSiR_3$ **59**; the ratio of products depends on the nature of the SiR_3 groups and the reaction conditions, although the two isomers exist in equilibrium [74].



58 **59**

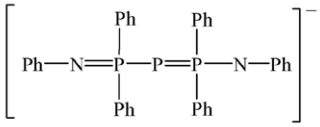
The reaction of **22** with $PbCl_2$ affords the binuclear lead complex **60** together with the free ligand **61** [75]. The Pb–Pb distance in **60** is 3.041(1) Å, considerably shorter than the interatomic Pb···Pb distance [3.49 Å] in elemental lead [76], indicating the presence of a covalent Pb^{1+}–Pb^{1+} bond. Conformation of this hypothesis is provided by ^{207}Pb NMR spectroscopy of the ^{207}Pb-labelled compound, which shows a large ^{207}Pb, ^{207}Pb-coupling constant of 7708 Hz. The formation of the by-product, **61**, is frequently observed in the reactions of **22** and is isolated either as the free ligand or in a coordinated form. For example, treatment of **22** with FeF_3 or CuF_2 in thf affords **61** [77].



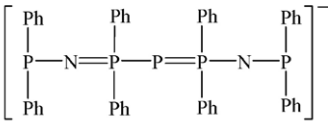
60 **61**

3.4. Reactions with Group 15 elements and halides

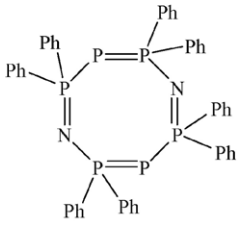
Reaction of **21** with elemental phosphorus in thf under reflux gives anion **62** [41b]. The reaction can be accelerated by addition of tetramethylethylenediamine, possibly because it sequesters the lithium from **21** thereby increasing the nucleophility of the anion. Similarly, reaction of **22** with elemental phosphorus gave anion **63**, which reacts with further elemental phosphorus to give the eight-membered ring system **64** [41b].



62

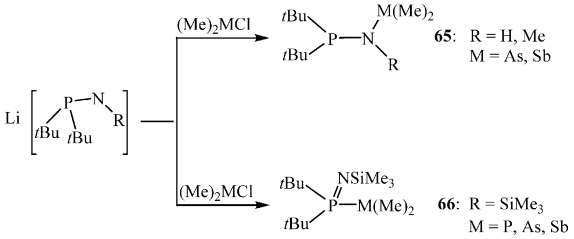


63

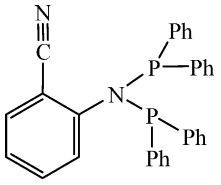


64

The reaction of lithium salts of formula $Li[tBu_2PNR]$ with Group 15 chlorides affords P–N–M compounds, **65**, when R is H or Me and N=P–M products, **66**, if the substituent on the anion is large, viz. $R = SiMe_3$ [9c]. These observations are in keeping with the reactions of **22** with chlorosilanes [74]. Here, the substituents on $[tBu_2PNR]^-$ anions determine the outcome of the reaction, with the more bulky substituent at the nitrogen favouring the formation of an N=M double bond, while the less bulky substituents favour the formation of an N–M single bond.

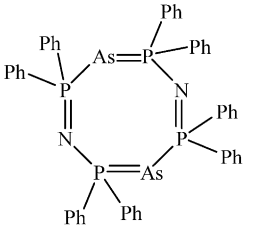


The formation of N=P–M products provides further evidence that the substituents play a determining role in the reactivity of phosphinoamides. In this context, it is interesting to compare the reactions of the lithium salts of **21** and **32** with Ph_2PCl [40]. In the solid state, the Li ion in **21** interacts with both P- and N-centres, although the reaction gives exclusively the P–N–P product, $(PPh_2)_2NPh$ **14**. In contrast, in the solid state of **32**, there is no P–Li interaction, but the reaction of **32** with Ph_2PCl affords the N=P–P product, **15**, only. Formation of the diphosphinoamine **67** is not observed.

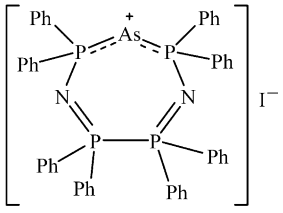


67

Reaction of **22** with PCl_3 affords a mixture of **61** and **64** [78]. Isolation of **64** from this reaction is interesting, since it can be regarded as P–P coupling direct from the anion **22**. Similarly, reaction of **22** and $BiBr_3$, SbI_3 and AsI_3 in a 3:1 ratio gives the free ligand **61** [79], and in the reaction with AsI_3 the eight-membered ring compound **68** is also isolated. Reaction of **22** with AsI_3 in a 2:1 ratio affords the cationic seven-membered ring **69**.



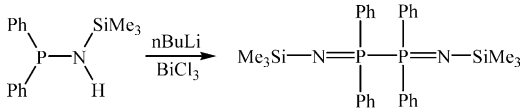
68



69

The solid-state structure of **69** indicates that the P–As bonds [2.253(2) and 2.260(2) Å] have partially double bond character.

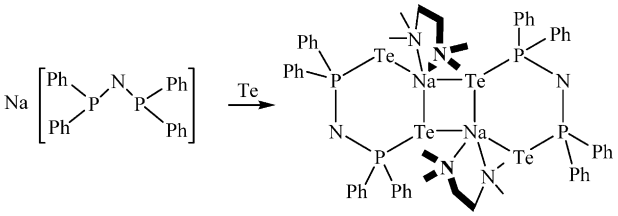
Reaction of $Ph_2PN(H)SiMe_3$ with *n*BuLi followed by addition of $BiCl_3$ gives **70** and elemental bismuth [55]. The oxidative P–P coupling is important since the compound **70** cannot be prepared from $Ph_2P–PPh_2$ with Me_3SiN_3 using the Staudinger reaction.



70

3.5. Reactions with tellurium and I_2

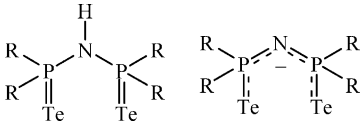
The reaction of $Na[Ph_2PNPPh_2]$ with tellurium powder in toluene under reflux in the presence of TMEDA affords **71** [80].



71

The ^{31}P and ^{125}Te NMR spectra of **71** in thf at 235 K reveal single environments for both the phosphorus and tellurium nuclei. This observation may be attributed to a fast exchange process involving a monomer in which the sodium ions are solvated by thf. In the solid-state structure, the central Na_2Te_2 ring is almost planar. The P–Te bond lengths of 2.383(1) and 2.403(1) Å are slightly longer than the values of ca. 2.37 Å determined for *t*BuP = Te [81] and not too different from amino-substituent tellurophosphorane [82].

This method, starting from the anion, represents a new approach to metallated imino and amido tellurophsphoranes, which is advantageous since the tellurophosphinic amine precursors $[P(Te)R_2]_2NH$ are difficult to prepare. Oxidation of bisphosphinoamine with tellurium usually gives the mono-oxidized product, so that anionic tellurophosphide $[P(Te)R_2]_2N^-$ were previously unknown.



Oxidative P–P coupling of **22** also takes place in the reaction with iodine affording **61** in near quantitative yield [78]. This reaction is similar to those reported by Schmidpeter and Burget using P_4 as a P–P coupling agent [41b].

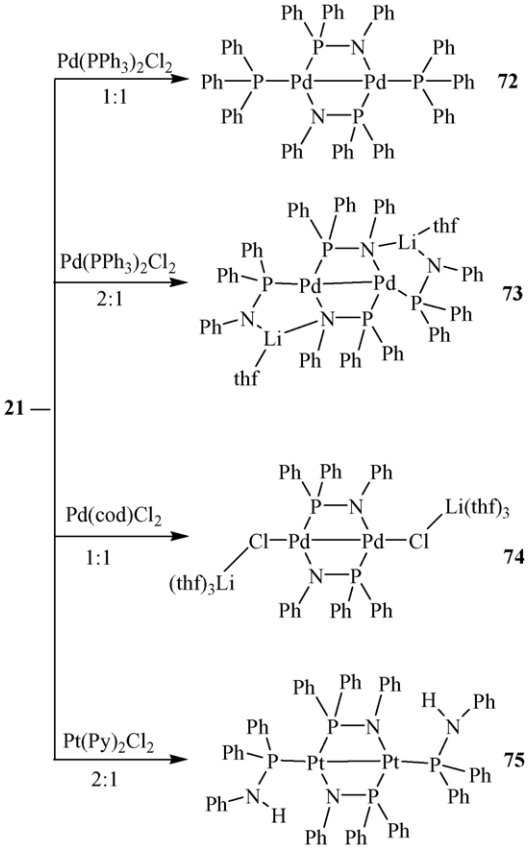
4. Reactions of phosphinoamides with transition metal complexes

Phosphinoamides possess both hard (N^-) and soft (P) donor centres, and accordingly can coordinate to main group, transition, lanthanide and actinide metals. Despite extensive studies involving main group compounds, transition metal complexes have been prepared with relative few salts, notably **21**, **22**, **24** and **43**. Some aspects of the coordination chemistry of phosphinoamides have been reviewed previously [21,83]. Only the synthesis and characterisation of transition metal complexes using the phosphinoamides **21** and **22** and **24** published after 1992 will be described here.

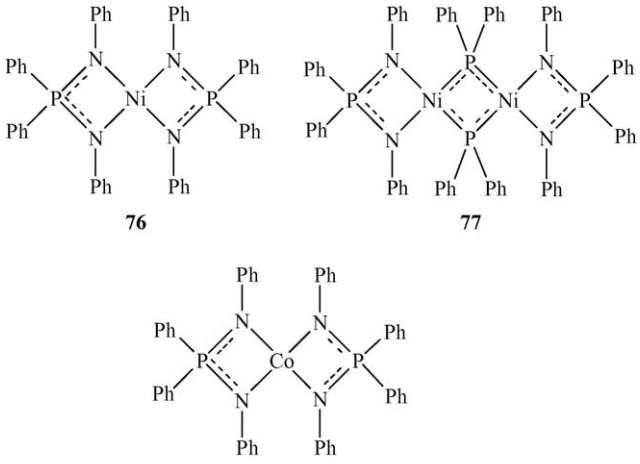
4.1. Reactions of $Li[Ph_2PNPh]$

In the reactions of **21** with transition metal complexes the $[Ph_2PNPh]^-$ group can act as both a bridging and terminal ligand; in some cases P–N bond cleavage is also observed [84]. The reaction of **21** with $Pd(PPh_3)_2Cl_2$ in a 1:1 and

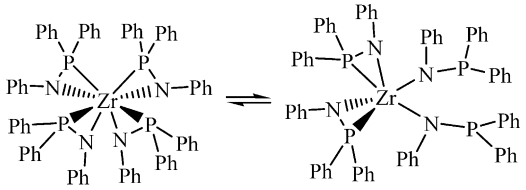
2:1 molar ratio affords **72** and **73**, respectively. In a similar reaction of **21** with $Pd(cod)Cl_2$ (cod = cyclooctadiene) in 1:1 ratio **74** is isolated. Complexes **72**, **73** and **74** are dimeric and contain a Pd–Pd bond, with the distances ranging from 2.515(2) Å in **72** to 2.587(2) Å in **74**. The P–N distances in **72** and **74** are shorter than those observed in the precursor [84]. Reaction of **21** with $Pt(Py)_2Cl_2$ (Py = 2-pyridyl) in a 2:1 molar ratio in thf affords **75**; it is interesting to note that this complex contains a neutral aminophosphine ligand, and it is not clear if the H atom is derived from the solvent, or from hydrolysis of phosphinoamide [84].



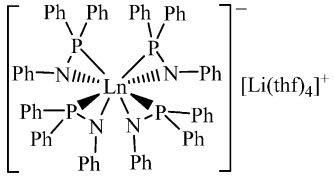
The reaction of **21** with $Ni(PPh_3)_2Cl_2$ in a 2:1 molar ratio gives **76** in thf and **77** in DME. The reaction of **21** with $Co(PPh_3)_2Cl_2$ in 2:1 molar ratio gives compound **78** [84]. In all these compounds, cleavage of the P–N bond has taken place, but the mechanism is not clear [84]. The P–N bond lengths in **76**–**78** are shorter than in the anion **21**, falling in the range 1.605(3)–1.618(8) Å, which is very close in value to a formal P=N double bond.



Compound **21** reacts with $ZrCl_4$ in a 4:1 molar ratio to give the homoleptic phosphinoamide complex **79** [85]. In the solid-state structure of **79** four $PhNPPh_2$ ligands coordinate to the metal centre in a η^2 fashion. In solution, **79** undergo a dynamic process, apparently existing in equilibrium with **80**, in which two of the ligands are η^1 coordinated via the nitrogen.



Compound **21** also react with lanthanides affording η^2 bonded moieties like those observed in the zirconium systems. However, in contrast to the reaction with $ZrCl_4$, reaction with $LnCl_3$ (Ln = Y, Yb or Lu) gives a salt, **81**, composed of a $[Li(thf)_4]^+$ cation and a $[Ln(Ph_2PNPh)_4]^-$ anion. Even with an excess of $LnCl_3$ complex **81** is the only product that can be isolated [86].

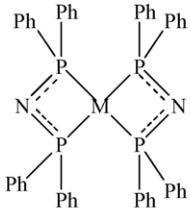


81

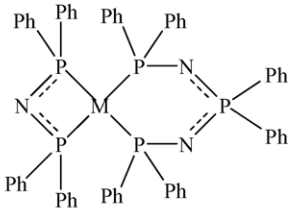
Despite the presence of the strained three-membered rings, the P–N distances in all the lanthanide complexes do not differ significantly from that observed in the anion, all being in the range 1.672(8)–1.696(3) Å.

4.2. Reactions of $M[(Ph_2P)_2N]$ (M = Li or K)

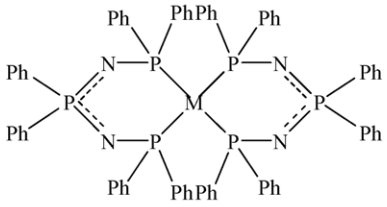
The reaction of **22** with MCl_2 (M = Ni or Pd), in a 2:1 ratio affords complexes with the general structure of **81** [87,88]. The reaction is sensitive to many factors and the actual product(s) depend on the type of metal chloride employed and the molar ratio of the starting materials, leading to complexes **82** and **83**, in which P–N bond scission and formation of new P–N bonds has taken place [77].



81

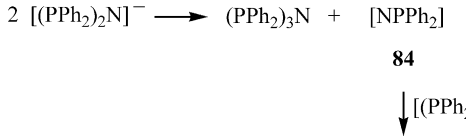


82

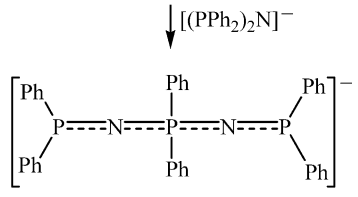


83

During the formation of complexes **82** and **83**, it is assumed that **22** is oxidized to give $(PPh_2)_3N$ and $[NPPh_2]$ **84**, whereas the metal halide is reduced. The intermediate, **84**, may be trapped by addition of a further equivalent of **22** with the formation of **85**, which then reacts with transition metal to form **82** or **83** depending on the conditions.

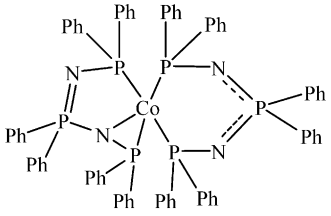


84



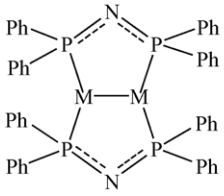
85

The reaction of **22** with $CoCl_2$ affords **86**, which comprises three different (three, five and six) rings [88]. The P–N–P unit from the parent anion acts as a bidentate ligand and as a tridentate ligand. In addition to **86**, tris(diphenylphosphino)amine, cobalt metal and LiCl are isolated.

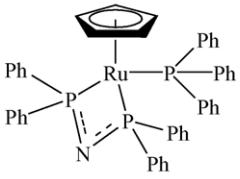


86

A number of transition metal complexes based on silver and gold **87** [89,90], and ruthenium **88** [91] have been prepared from **22**. The reactions appear to follow a similar route and while structures of the complexes vary, the coordination mode of the ligands is essentially the same, i.e., chelation via the phosphorus centres.



87a: M = Ag
87b: M = Au



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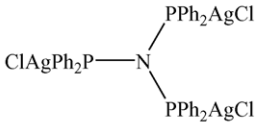
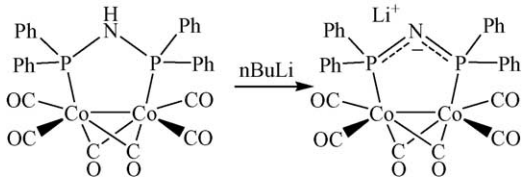
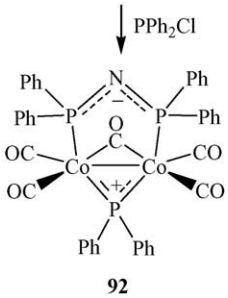


89

The dimeric silver compound **87a** reacts with Ph_2PCl affording the monomeric compound **89**. Lithiation of the aminophosphine complex **90**, prepared from the reaction of diphosphinoamine and cobalt carbonyls, affords **91**, which reacts with PPh_2Cl to give the PPh_2 bridging complex **92** [92].

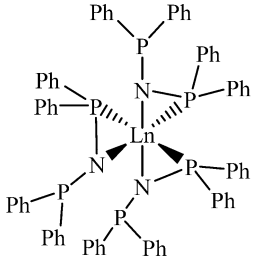


90 **91**



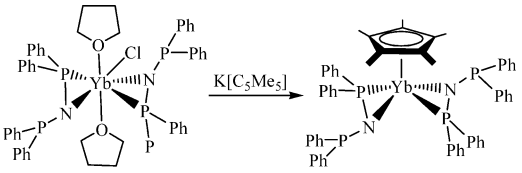
92

The reaction of **24** with anhydrous yttrium or lanthanide trichlorides in a 3:1 molar ratio affords the bis(phosphanyl)amide complexes $[Ln\{N(PPh_2)_2\}_3]$ **93** in good yield [93]. The solid-state structures of **93a** and **93b** show two inequivalent P-centres. In solution, however, complex **93a** shows one sharp signal in the room temperature ^{31}P NMR spectrum. Only at low temperature (173 K) are two different phosphorus environments observed.



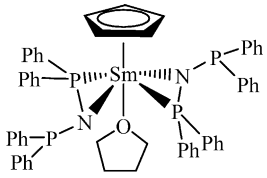
93a: Ln = Y
93b: Ln = Er

Reaction of **24** with anhydrous ytterbium trichloride in thf in a 2:1 molar ratio affords a mixture containing $[Yb\{(Ph_2P)_2N\}_2Cl(thf)_2]$ **94** and $[Yb\{(Ph_2P)_2N\}Cl_2(thf)_3]$ [94]. If the reaction is carried out with a slight excess of **24** only **94** and $[Yb\{N(PPh_2)_2\}_3]$ are formed.



94 **95**

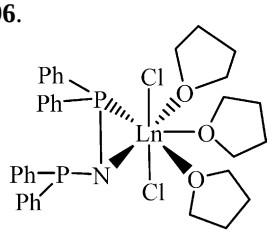
The solid-state structure of **94** reveals that the metal centre adopts a distorted pentagonal bipyramidal arrangement in which thf molecules are located in the axial positions. Similar to **93**, the diphosphanylamide ligand is η^2 coordinated via the nitrogen and one of the phosphorus centres. Treatment of **94** with an excess of $K[C_5Me_5]$ in thf, affords the pentamethylcyclopentadienyl complex **95**. The lengths of the coordinated P–N bonds in **95** are shorter [1.664(2) and 1.671(2) Å] than the free P–N bond [1.722(2) and 1.724(2) Å]. A closely related organometallic compound to **95**, viz. **96**, may be prepared in a single step from the reaction of **24** and $[Sm(C_5H_5)Cl_2(thf)_3]$ in a 2:1 molar ratio [94].



96

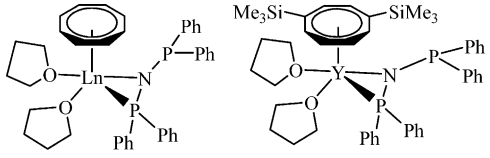
The ^{31}P NMR spectrum of **96** at room temperature contains a broad signal at 58.0 ppm indicating that the phosphorus centres are equivalent in solution. Similar dynamic behaviour is observed for the other related lanthanide compounds.

The reaction of **24** with $LnCl_3$ (Ln = Y, Sm, Er or Yb) in a 1:1 molar ratio affords complexes of type **97** [95]. The diphosphanylamide ligand in these complexes coordinates in η^2 mode through the nitrogen and one of the phosphorus centres and the P–N bond lengths are comparable with those observed in **93**–**96**.



97a: Ln = Y
97b: Ln = Sm
97c: Ln = Er
97d: Ln = Yb

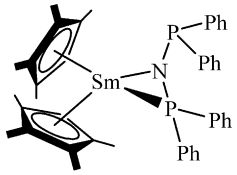
Reaction of $Ln(\eta^8\text{-}C_8H_8)(thf)_3I$ (Ln = La or Sm) with **24** in equimolar quantities in thf at room temperature affords the corresponding diphosphanylamide complexes of type **98**. Compound **98b** has also been obtained from the reaction of $K_2[C_8H_8]$ with **97b** [95]. Transmetallation of dilithium 1,4-bis(trimethylsilyl)cyclooctatetraene, $Li_2[1,4\text{-}(Me_3Si)_2\text{-}C_8H_6]$, with anhydrous yttrium chloride in a 1:1 molar ratio in thf at room temperature followed by the addition of one equivalent of **24** affords **99**, which is closely related to **98** [95]. The ^{89}Y NMR spectrum of **99** contains a triplet resonance resulting from coupling with the two phosphorus centres, indicating that the phosphorus centres are equivalent in solution. Accordingly, the ^{31}P NMR spectrum of **99** contains a doublet at 38.1 ppm, which is comparable to those signals found for related compounds.



98a: Ln = La
98b: Ln = Sm

99

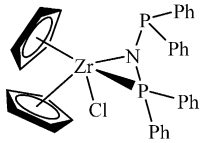
Reaction of **24** with $K[Sm(C_5Me_5)Cl_2]$ in a 1:1 molar ratio in thf, gives the expected metallocene complex **100**, albeit in low yield [96]. Compound **100** can also be obtained in a one-pot reaction commencing with $SmCl_3$ and **24** followed by addition of $K[C_5Me_5]$.



100

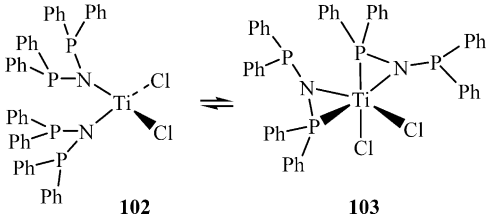
The ^1H NMR spectrum of **100** exhibits a sharp singlet for the methyl group protons of the C_5Me_5 unit. The two phosphorus centres are equivalent in the ^{31}P NMR spectrum displaying a signal at 56.6 ppm, which is close in value to that of **24**, viz. 58.6 ppm.

Reaction of **24** with zirconocene dichloride in a 2:1 molar ratio in thf, does not yield the expected bis(diphosphinoamido) complex, instead the monoamido complex **101** is obtained [97]. In solution, no dynamic process is observed for the η^2 diphosphanylamide ligand which contrasts with related complexes (see above). The ^{31}P NMR spectrum of **101** at room temperature shows two broad signals at −3.8 and 62.2 ppm, but the $^2J_{P-P}$ coupling constant could not be resolved. The solid-state structure of **101** is very similar to complex **100**. In **100,** the two P–N distances are 1.660(3) and 1.692(4) Å, and in **101** they are 1.642(5) and 1.708(5) Å.



101

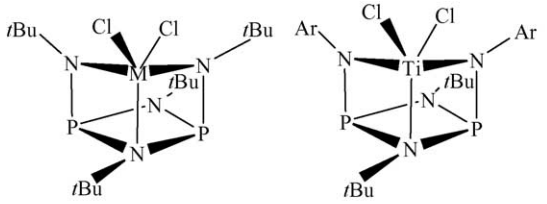
Compound **22** reacts with $TiCl_4$ in a 2:1 molar ratio to give **102**, which is in equilibrium with **103**. At room temperature, the dominant species is **102**, but at low temperature the relative amount of compound of **103** increases [85].



102 **103**

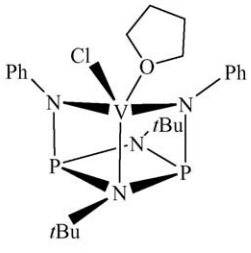
4.3. Reactions of cyclic phosphinoamides

The reaction of MCl_4 (M = Zr and Hf) in a 1:1 ratio with **43** generated in situ affords complexes of type **104** [98,99]. Similarly, reaction of **43** with titanium and vanadium complexes $TiCl_4$ and VCl_3 affords complexes **105** and **106**, respectively [99].



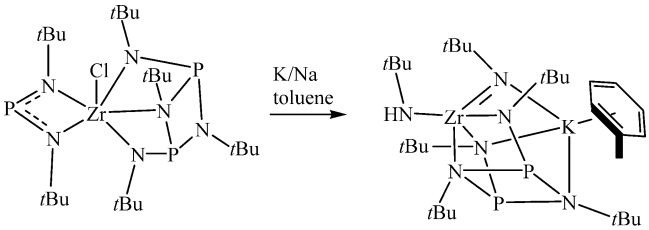
104a: M = Zr
104b: M = Hf

105a: Ar = Ph
105b: Ar = *m*-tol
105c: Ar = *p*-tol



106

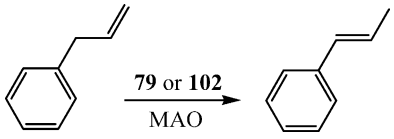
Reaction of **104** with a further equivalent of **43** affords compounds composed of more cyclic anions, for example, reaction of **43** with the zirconium complex **104a** in a 1:2 ratio in toluene at 80 °C leads to the formation of **107** in moderate yield [100]. Subsequent reaction of **107** with two equivalents of K–Na alloy in toluene yields the amido, imido zirconium complex **108**. In this reaction the cleavage of the two P–N bonds results in the formation of a compound containing a Zr=N double bond. Presumably, the bulky ligands on zirconium are essential for stabilising the imido zirconium monomer **108**. The Zr–N_{imido} distance is 1.893(9) Å, typical of Zr=N double bond [101].



107 **108**

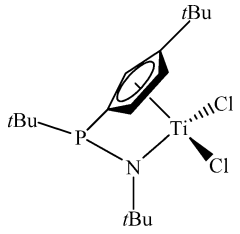
4.4. Application of phosphinoamido complexes in catalysis

Phosphinoamido complexes of the early transition metals are electronically unsaturated and tend to be effective polymerisation catalysts, although they can also catalyse other reactions [102,103]. For example, in the presence of methylalumoxane (MAO) the zirconium and titanium complexes **79** and **102** catalyse the formation of high molecular weight elastomeric polypropylene, a consequence of an epimerisation mechanism in which the growing polymer does not detach from the metal centre during the polymerisation [85]. In order to support such a mechanism the same catalysts were shown to promote the isomerisation of alkenes. Selective conversion of allybenzene to *trans*-methylstyrene can be achieved, complex **79** being more effective than **102**. Isomerisation of 1-octene to *trans*-2-octene can also be promoted with these catalysts, but several other minor products are also formed with the **102**/MAO system.



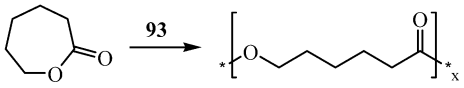
Compound **105a** also catalyses the polymerisation of ethylene in the presence of MAO [activity 2.0×10^3 g PE (mol catalyst)$^{-1}$ h^{-1} bar^{-1}] [99]. Related compounds **104a** and **104b**, with bulky substituents were also screened, but were found to be inactive. The titanium compound **109** is only a moderately active catalyst for the polymerisation of ethylene in the presence of MAO [activity 1.0×10^3 g PE (mol catalyst)$^{-1}$ h^{-1} bar^{-1}] [51]. However, the discovery of new non-metallocene olefin polymerisation catalysts is now

progressing at a considerable rate [104] and it is likely that many other phosphinoamido complexes will be evaluated over the next few years.



109

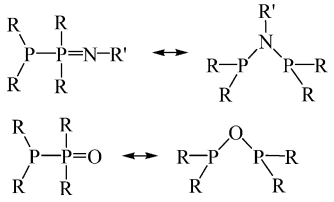
The lanthanide complexes **93a** and **93b** shows high activity in the poylmerisation of caprolactone [93]. Molar monomer/catalyst ratios of 150:1 afforded the corresponding polycaprolactone in excellent yield (95–99%) within 1 min. It was suggested that the initial step of the polymerisation involves the coordination of the carbonyl group to the metal centre, forming a sevenfold coordination sphere around the central atom.



5. Summary and outlook

This review shows that essentially every aminophosphine containing the P–NH unit can be deprotonated by bases such as *n*BuLi, NaH and KH, etc. Although the number of isolated phosphinoamides is relatively small compared to the parent aminophosphines, the number of well-characterised compounds continues to expand. The large number of functionalised aminophosphines prepared in recent years should enable a rich chemistry of functionalised phosphinoamides, although this area remains largely unexplored, and phosphinoamides with chiral centres are unknown.

It has been shown that phosphinoamides can react with chlorophosphines to give diphosphinoamines or iminodiphosphines. While the coordination chemistry of diphosphinoamines has been explored in detail and reviewed previously, the related coordination chemistry of iminodiphosphines is largely unexplored [105,106]. In addition, transformations involving diphosphinoamines or iminodiphosphines are in their infancy [107], although it is comparable with the Arbuzov reaction.



The reduction of phosphinoamides represents a useful route to P–P coupled compounds; however, the mechanism of the reduction, especially the initial cleavage of the P–N bond, is poorly understood.

Phosphinoamides can coordinate to virtually all metals of the periodic table, using either N or P as monodentate ligand, or using the P–N unit in η^2 modes. It is too early to say whether phosphinoamides are superior ligands to neutral aminophosphines, since the coordination chemistry of the former have been investigated to a lesser extent. However, in many cases, phosphinoamides are much stronger donors than the neutral aminophosphine. Despite this, a number of recent studies have shown that phosphinoamide complexes are promising olefin polymerisation catalysts, providing an alternative to the metallocenes.

Acknowledgements

We thank the Swiss National Science Foundation and the EPFL for the financial support.

References

[1] F.R. Hartley, The Chemistry of Organophosphorus Compounds, vol. 1, Wiley, Manchester, 1990.
[2] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1984, p. 619.
[3] E. Niecke, M. Nieger, F. Reichert, Angew. Chem. Int. Ed. 24 (1988) 1715.
[4] O.J. Scherer, Multiple Bonds and Low Coordination in Phosphorus Chemistry, Georg Thieme Verlag, Stuttgart, 1990.
[5] G. Ewart, A.P. Lane, J. McKechnie, D.S. Payne, J. Chem. Soc. Sect. A (1964) 1543.
[6] M.S. Balakrishna, V. Sreenivasa Reddy, S.S. Krishnamurthy, J.F. Nixon, J.C.T.R. Burckett, St. Laurent, Coord. Chem. Rev. 129 (1994) 1.
[7] T. Appleby, J.D. Woollins, Coord. Chem. Rev. 235 (2002) 121.
[8] J. Singh, A.B. Burg, J. Am. Chem. Soc. 88 (1966) 718.
[9] (a) H. Nöth, L. Meinel, Z. Anorg. Allg. Chem. 349 (1967) 225; (b) O.J. Scherer, G. Schieder, Chem. Ber. 101 (1968) 4184; (c) O.J. Scherer, W.M. Janssen, J. Organomet. Chem. 20 (1969) 111.
[10] M.T. Ashby, Z. Li, Inorg. Chem. 31 (1992) 1321.
[11] (a) Z. Fei, Y. Lu, M. Freytag, P.G. Jones, R. Schmutzler, Z. Anorg. Allg. Chem. 626 (2000) 969; (b) Z. Fei, H. Thonnessen, P.G. Jones, L. Crowe, R.K. Harris, R. Schmutzler, Z. Anorg. Allg. Chem. 626 (2000) 1763; (c) Z. Fei, A.M.Z. Slawin, J.D. Woollins, Polyhedron 20 (2001) 3355.
[12] (a) P.P. Power, Acc. Chem. Res. 21 (1988) 147; (b) F.T. Edelmann, F. Pauer, M. Wedler, D. Stalke, Inorg. Chem. 31 (1992) 4143.
[13] (a) D.R. Armstrong, A. Carstairs, K.W. Henderson, Organometallics 18 (1999) 3589; (b) K.W. Henderson, P.G. Williard, Organometallics 18 (1999) 5620.
[14] A.H. Cowley, M.J.S. Dewar, W.R. Jackson Jr., W.B. Jennings, J. Am. Chem. Soc. 92 (1970) 5206.
[15] I.G. Csizmadia, A.H. Cowley, M.W. Taylor, L.M. Tel, S. Wolfe, Chem. Commun. (1972) 1147.
[16] (a) A.D. Burrows, M.F. Mahon, M.T. Palmer, J. Chem. Soc. Dalton Trans. (2000) 1669;

(b) S.M. Aucott, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc. Dalton Trans. (2000) 2559;
(c) S.M. Aucott, M.L. Clarke, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc. Dalton Trans. (2001) 972;
(d) M.L. Clarke, A.M.Z. Slawin, M.V. Wheatley, J.D. Woollins, J. Chem. Soc. Dalton Trans. (2001) 3421;
(e) N. Biricik, Z. Fei, R. Scopelliti, P.J. Dyson, Helv. Chem. Acta 86 (2003) 3281;
(f) N. Biricik, Z. Fei, R. Scopelliti, P.J. Dyson, Eur. J. Inorg. Chem. (2004) 4232.

[17] (a) J.-M. Camus, J. Andrieu, R. Poli, P. Richard, C. Baldoli, S. Maiorana, Inorg. Chem. 42 (2003) 2384;
(b) C. Blanc, F. Agbossou-Niedercorn, Tetrahedron: Asymmetry 15 (2004) 757;
(c) G.-P. Calabrò, D. Drommi, G. Bruno, F. Faraone, J. Chem. Soc. Dalton Trans. (2004) 81.

[18] (a) O.I. Kolodiazhnyi, E.V. Gryshkun, N.V. Andrushko, M. Freytag, P.G. Jones, R. Schmutzler, Tetrahedron: Asymmetry 14 (2003) 181;
(b) E.V. Gryshkun, N.V. Andrushko, O.I. Kolodiazhnyi, Phosphorus Sulfur Silicon Relat. Elem. 179 (2004) 1027.

[19] M. Rodriguez, I. Zubiri, H.L. Milton, D.J. Cole-Hamilton, A.M.Z. Slawin, J.D. Woollins, Polyhedron 23 (2004) 693.

[20] Y.-X. Chen, Y.-M. Li, K.-H. Lam, A.S.-C. Chan, Chin. J. Chem. 21 (2003) 66.

[21] L. Stahl, Coord. Chem. Rev. 210 (2000) 203.

[22] Z. Fei, R. Scopelliti, P.J. Dyson, J. Chem. Soc. Dalton Trans. (2003) 2772.

[23] O.I. Kolodyazhnyi, N. Prynada, Tetrahedron Lett. 41 (2000) 7997.

[24] M.G. Barlow, R.N. Haszeldine, H.G. Higson, J. Chem. Soc. C (1966) 1592.

[25] Y.G. Trishin, V.N. Chistokletov, Zh. Obsh. Khim. 49 (1979) 39–44.

[26] M.G. Lappert, M.J. Hade, A. Singh, J.L. Atwood, R.D. Rogus, R. Shakir, J. Am. Chem. Soc. 105 (1983) 302.

[27] G. Michaelis, Liebigs Ann. Chem. 326 (1903) 129.

[28] H. Binder, R. Fischer, Chem. Ber. 107 (1974) 205.

[29] O.I. Kolodyazhnyi, N. Prinada, Russ. J. General Chem. 71 (2001) 646.

[30] (a) H.J. Vetter, H. Nöth, Chem. Ber. 96 (1963) 1308;
(b) Y.G. Trishin, V.N. Christokletov, A.A. Petrov, V.V. Kosovtsev, Zh. Org. Khim. 11 (1975) 1749.

[31] A. Tarassoli, R.C. Haltiwanger, A.D. Norman, Inorg. Nucl. Chem. Lett. 16 (1980) 27.

[32] M.L. Thompson, A. Tarassoli, R.C. Haltiwanger, A.D. Norman, Inorg. Chem. 26 (1987) 684.

[33] N. Burford, T.S. Cameron, K.D. Conroy, B. Ellis, C.L.B. Macdonald, R. Ovans, A.D. Phillips, P.J. Ragogna, D. Walsh, Can. J. Chem. 80 (2002) 1404.

[34] A. Schmidpeter, H. Rossknecht, Angew. Chem. Int. Ed. 8 (1969) 614.

[35] N. Burford, J.A.C. Clyburne, S. Mason, J.F. Richardson, Inorg. Chem. 32 (1993) 4988.

[36] (a) G. Schick, M. Raab, D. Gudat, M. Nieger, E. Niecke, Angew. Chem. Int. Ed. 37 (1998) 2390;
(b) S. Schulz, M. Raab, M. Nieger, E. Niecke, Organometallics 19 (2000) 2616.

[37] R.F. Hudson, R.J.G. Searle, F.H. Devitt, J. Chem. Soc. C (1966) 1001.

[38] W. Wiegräbe, H. Boch, Chem. Ber. 101 (1968) 1414.

[39] W. Seidel, M. Alexiev, Z. Anorg. Allg. Chem. 438 (1978) 68.

[40] Z. Fei, R. Scopelliti, P.J. Dyson, Inorg. Chem. 42 (2003) 2125.

[41] (a) A. Schmidpeter, G. Burget, Z. Naturforsch. 40b (1985) 1306;
(b) A. Schmidpeter, G. Burget, Angew. Chem. Int. Ed. 97 (1985) 580.

[42] (a) M.G. Newton, R.B. King, M. Chang, J. Gimeno, J. Am. Chem. Soc. 100 (1978) 1632;
(b) N. Dufour, J.-P. Majoral, A.-M. Caminade, R. Choukroun, Y. Dromzee, Organometallics 10 (1991) 45;
(c) J.T. Mague, Z. Lin, Organometallics 11 (1992) 4139.

[43] (a) A.H. Cowley, R.A. Kemp, Chem. Commun. (1982) 319;
(b) A.H. Cowley, R.A. Kemp, Inorg. Chem. 22 (1983) 547.

[44] (a) E. Niecke, W. Flick, Angew. Chem. Int. Ed. 12 (1973) 585;
(b) E. Niecke, G. Ringel, Angew. Chem. Int. Ed. 16 (1977) 486;
(c) E. Niecke, A. Nickloweit-Lüke, R. Rüger, Angew. Chem. Int. Ed. 20 (1981) 385.

[45] T. Kremer, F. Hampel, F.A. Knoch, W. Bauer, A. Schmidt, P. Gabold, M. Schütz, J. Ellermann, P.V.R. Schleyer, Organometallics 15 (1996) 4776.

[46] (a) A. Zschunke, H. Bauer, H. Schimdt, K. Issleib, Z. Anorg. Allg. Chem. 495 (1982) 115;
(b) Y. Yokoyama, K. Takahashi, Bull. Chem. Soc. Jpn. 60 (1987) 3485.

[47] I. Fernandez, E. Martinez-Viviente, P.S. Pregosin, Inorg. Chem. 43 (2004) 4555.

[48] (a) J. Ellermann, M. Schütz, F.W. Heinemann, M. Moll, Z. Anorg. Allg. Chem. 624 (1998) 257;
(b) J. Ellermann, M. Schütz, F.W. Heinemann, M. Moll, W. Bauer, Chem. Ber. 130 (1997) 141.

[49] P.W. Roesky, M.T. Gamer, M. Puchner, A. Greiner, Chem. Eur. J. (2002) 5265.

[50] J. Ellermann, W. Bauer, M. Schütz, F.W. Heinemann, M. Moll, Monatshefte für Chemie 129 (1998) 547.

[51] V.V. Kotov, E.V. Avtomonov, J. Sundermeyer, K. Harms, D.A. Lemenovskii, Eur. J. Inorg. Chem. (2002) 678.

[52] N. Poetschke, M. Nieger, M.A. Khan, E. Niecke, M.T. Ashby, Inorg. Chem. 36 (1997) 4087.

[53] A. Steiner, D. Stalke, Angew. Chem. Int. Ed. Engl. 34 (1995) 1752.

[54] F. Baier, Z. Fei, H. Gornitzka, A. Murso, S. Neufeld, M. Pfeiffer, I. Rüdenauer, A. Steiner, T. Stey, D. Stalke, J. Organomet. Chem. 661 (2002) 111.

[55] S. Wingerter, M. Pfeiffer, F. Baier, T. Stey, D. Stalke, Z. Anorg. Allg. Chem. 626 (2000) 1121.

[56] (a) N. Kocher, D. Leusser, A. Murso, D. Stalke, Chem. Eur. J. (2004) 3622;
(b) A. Murso, D. Stalke, Z. Anorg. Allg. Chem. 630 (2004) 1025.

[57] G. Bai, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, J. Chem. Soc. Dalton Trans. (2002) 2437.

[58] B. Eichhorn, H. Nöth, T. Seifert, Eur. J. Inorg. Chem. 12 (1999) 2355.

[59] T. Bauer, S. Schulz, M. Nieger, W. Kessler, Organometallics 22 (2003) 3134.

[60] (a) I. Schranz, L. Stahl, R.J. Staples, Inorg. Chem. 37 (1998) 1493;
(b) J.K. Brask, T. Chivers, M.L. Kahn, M. Parez, Inorg. Chem. 38 (1999) 290.

[61] G. Linti, H. Nöth, E. Schneider, W. Storch, Chem. Ber. 126 (1993) 619.

[62] N. Burford, D.J. LeBlanc, Inorg. Chem. 38 (1999) 2248.

[63] I. Schranz, D.F. Moser, L. Stahl, R.J. Staples, Inorg. Chem. 38 (1999) 5814.

[64] (a) L. Grocholl, I. Schranz, L. Stahl, R.J. Staples, Inorg. Chem. 37 (1998) 2496;
(b) M. Veith, F. Goffing, S. Becker, V. Huch, J. Organomet. Chem. 406 (1991) 105.

[65] P. Braunstein, R. Hasselbring, D. Stalke, New J. Chem. 20 (1996) 337.

[66] E. Niecke, M. Frost, M. Nieger, V. von der Goenna, A. Ruban, W.W. Schoeller, Angew. Chem. Int. Ed. 33 (1994) 2111.

[67] Z. Fei, R. Scopelliti, P.J. Dyson, Eur. J. Inorg. Chem. (2003) 3527.

[68] G. Tringuier, M.T. Ashby, Inorg. Chem. 33 (1994) 1306.

[69] J. Ellermann, M. Lietz, Z. Naturforsch. 35b (1980) 64.

[70] A. Winkler, W. Bauer, F.W. Heinemann, V. Gracia-Montalvo, M. Moll, J. Ellermann, Eur. J. Inorg. Chem. (1998) 437.

[71] G.R. Lief, I. Schranz, L. Stahl, Phosphorus Sulfur Silicon Relat. Elem. 179 (2004) 813.
[72] J. Ellermann, M. Lietz, K. Geibel, Z. Anorg. Allg. Chem. 492 (1982) 122–134.
[73] A. Winkler, F.W. Heinemann, M. Moll, J. Ellermann, Inorg. Chim. Acta 284 (1999) 288.
[74] H. Schmidbaur, S. Lauteschlaeger, F.H. Koehler, J. Organomet. Chem. 271 (1984) 173.
[75] A. Winkler, W. Bauer, F.W. Heinemann, V. Garcia-Montalvo, M. Moll, J. Ellermann, Eur. J. Inorg. Chem. (1998) 437.
[76] A.F. Wells, Structural Inorganic Chemistry, fifth ed., Clarendon Press, Oxford, 1984, p. 1279.
[77] J. Ellermann, P. Gabold, F.A. Knoch, M. Moll, A. Schmidt, M. Schütz, Z. Naturforsch. 51b (1996) 201.
[78] P. Braunstein, R. Hasselbring, A. Tiripicchio, F. Ugozzoli, Chem. Commun. (1995) 37.
[79] M. Dotzler, A. Schmid, J. Ellermann, F.A. Knoch, M. Moll, W. Baur, Polyhedron 15 (1996) 4425.
[80] G.G. Briand, T. Chivers, M. Parvez, Angew. Chem. Int. Ed. 41 (2002) 3468.
[81] N. Kuhn, H. Schumann, G. Wolmershäuser, Z. Naturforsch. 42b (1987) 674.
[82] S. Pohl, Z. Naturforsch. 34b (1979) 256.
[83] (a) M. Witt, H.W. Roesky, Chem. Rev. 94 (1994) 1163;
(b) P.W. Roesky, Heteroat. Chem. 13 (2002) 514.
[84] D. Fenske, B. Maczek, K. Maczek, Z. Anorg. Allg. Chem. 623 (1997) 1113.
[85] O. Kühl, T. Koch, F.B. Somoza, P.C. Junk, E. Hey-Hawkins, M.S. Eisen, J. Organomet. Chem. 604 (2000) 116.
[86] T.G. Wetzel, S. Dehnen, P.W. Roesky, Angew. Chem. Int. Ed. 38 (1999) 1086.
[87] J. Ellermann, J. Sutter, C. Schelle, F.A. Knoch, M. Moll, Z. Anorg. Allg. Chem. 619 (1993) 2006.
[88] J. Ellermann, J. Sutter, F.A. Knoch, M. Moll, Angew. Chem. Int. Ed. 32 (1993) 700.
[89] J. Ellermann, J. Utz, F.A. Knoch, M. Moll, Z. Anorg. Allg. Chem. 622 (1996) 1871.
[90] J. Ellermann, W. Wend, Z. Anorg. Allg. Chem. 543 (1986) 169.
[91] J. Ellermann, C. Schelle, F.A. Knoch, M. Moll, D. Pohl, Monatshefte für Chemie 127 (1996) 783.
[92] D. Pohl, J. Ellermann, F.A. Knoch, M. Moll, W. Baur, J. Organomet. Chem. 481 (1994) 259.
[93] P.W. Roesky, M.T. Gamer, M. Puchner, A. Greiner, Chem. Eur. J. (2002) 5265.
[94] M.T. Gamer, P.W. Roesky, Inorg. Chem. 43 (2004) 4903.
[95] P.W. Roesky, M. Gamer, N. Marinos, Chem. Eur. J. 10 (2004) 3537.
[96] M.T. Gamer, G. Canseco-Melchor, P.W. Roesky, Z. Anorg. Allg. Chem. 629 (2003) 2113.
[97] M.T. Gamer, M. Rastätter, P.W. Roesky, Z. Anorg. Allg. Chem. 628 (2002) 2269.
[98] G. Bai, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, Organometallics 20 (2001) 2962.
[99] D.F. Moser, L. Grocholl, L. Stahl, R.J. Staples, J. Chem. Soc. Dalton Trans. (2003) 1402.
[100] G. Bai, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Organometallics 21 (2002) 2789.
[101] (a) M.D. Fryzuk, J.B. Love, S.J. Rettig, Organometallics 17 (1998) 846;
(b) J.L. Thorman, I.A. Guzei, V.G. Young Jr., L.K. Woo, Inorg. Chem. 38 (1999) 3814.
[102] (a) P.J. Walsh, F.J. Hollander, R.G. Bergmann, J. Am. Chem. Soc. 110 (1988) 8729;
(b) C.C. Cummins, S.M. Baxter, P.T. Wolczanski, J. Am. Chem. Soc. 110 (1988) 8731.
[103] (a) D.W. Stephan, Angew. Chem. Int. Ed. Engl. 39 (2002) 315;
(b) F.T. Edelmann, D.M.M. Freckmann, H. Schumann, Chem. Rev. 102 (2002) 1851.
[104] V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283.
[105] Z. Fei, R. Scopelliti, P.J. Dyson, Eur. J. Inorg. Chem. (2004) 530.
[106] (a) N. Burford, T.S. Cameron, K.D. Conroy, B. Ellis, M. Lumsden, C.L.B. Macdonald, R. McDonald, A.D. Phillips, P.J. Ragogna, R.W. Schurko, D. Walsh, R.E. Wasylishen, J. Am. Chem. Soc. 124 (2002) 14012;
(b) N. Burford, P.J. Ragogna, J. Chem. Soc, Dalton Trans. (2002) 4307.
[107] Z. Fei, N. Biricik, D. Zhao, R. Scopelliti, P.J. Dyson, Inorg. Chem. 43 (2004) 2228.