FULL PAPER

Influence of the functional group on the synthesis of aminophosphines, diphosphinoamines and iminobiphosphines

Zhaofu Fei, Rosario Scopelliti and Paul J. Dyson*

Institut de Chimie Moléculaire et Biologique, Ecole Polytechnique Fédérale de Lausanne, EPFL-BCH, CH-1015 Lausanne, Switzerland. E-mail: paul.dyson@epfl.ch

Received 1st April 2003, Accepted 21st May 2003 First published as an Advance Article on the web 6th June 2003



The reaction of the anilines RNH_2 [$R = C_6H_4(o-CN)$, $C_6H_4(p-CN)$, $C_6H_4(m-CN)$, $C_6H_4(o-C_6H_5)$, C_6F_5 and C_6H_4 -(*o*-CF₃)] with Ph₂PCl and inorganic or organic bases in differing stoichiometry and in different solvents has been studied. The electronic properties and steric effects of the substituent groups, the base employed, the stoichiometry and the solvent all influence the outcome of the reaction and a series of aminophosphines, diphosphinoamines and iminobiphosphines have been isolated and characterised. The structures of three diphosphinoamines and three iminobiphosphines have been established using single-crystal X-ray diffraction.

Introduction

While phosphine ligands with exclusively P–C bonds are the most widely studied, aminophosphines, diphosphinoamines and iminobiphosphines (Chart 1) have also attracted increasing considerable attention. Interest in phosphines with P–N bonds arises from the different electronic properties transferred by the nitrogen centre to the phosphorus centre(s).^{1,2} A review describing the coordination chemistry of diphosphinoamines reveals a burgeoning and exciting field,³ and further possibilities are highlighted in a very recent review that describes diphosphines with inorganic backbones more generally.⁴ Although iminobiphosphines have also been known for many years,⁵ they have not been studied to the same extent as aminophosphines and diphosphinoamines, due to, at least in part, their relative instability compared to aminophosphines and diphosphinoamines.⁶



Among the routes used to prepare aminophosphines and diphosphinoamines, the most frequently used method involves aminolysis of a phosphine chloride.⁷ The reaction of phosphine chloride and the amine usually provides the target compound, RNHPR'₂ or RN(PR'₂)₂, in high yield. The HCl liberated from the reaction forms a salt with an organic base, for example triethylamine, which is insoluble in the reaction solvent, typically diethyl ether or thf, and therefore leads to facile separation and purification of the product. It is possible to replace the organic base with an inorganic base such as BuⁿLi, Na or K, which leads to deprotonation of the amine and formation of an amide anion. The anion can subsequently be converted into an aminophosphine⁸ or iminobiphosphine⁹ by reaction with a phosphine chloride. In contrast to the aminolysis method, this latter procedure using alkali bases has received little attention, presumably due to the sensitivity of the intermediate and the additional costs associated with such bases.

The solid-state structures of aminophosphines and diphosphinoamines have been extensively studied.¹⁰ In contrast, full structural characterisation of iminobiphosphine compounds is rare.¹¹ In addition, despite the availability of a wide range of functionalised amine and related phosphorus compounds,

functionalised aminophosphines are mostly limited to ether and pyridyl derivatives.¹ Since both steric and electronic effects exerted by a functional group on the amine play a significant role on the outcome of the reaction it is important to study their effect in more detail. Recently, we described how the lithiation of the functionalised amine C₆H₄(o-CN)NH₂ 1a, followed by addition of Ph₂PCl, afforded the aminophosphine C₆H₄-(o-CN)NHPPh, 2a in high yield.¹¹ During the course of our research, we found in the same reaction the iminobiphosphine C₆H₄(o-CN)N=PPh₂PPh₂ 4a is also formed and it was possible to isolate it. Compared to other anilines, the CN group exerts a determining effect on the reactivity of the aminophosphine, as evident from the reaction of the 2a with another equivalent of Ph₂PCl in the presence of triethylamine which gives the iminobiphosphine 4a in nearly quantitative yield, instead of the diphosphinoamine C₆H₄(o-CN)N(PPh)₂ 3a. The analogous reaction of Ph,PCl with PhNHPPh2 gave only the diphosphinoamine PhN(PPh₂)₂. In this paper we expand on our earlier studies by examining how both electronic and steric effects influence the formation of aminophosphines, diphosphinoamines and iminobiphosphines.

Results and discussion

In phosphorus chemistry, ³¹P NMR spectroscopy has been widely used to monitor reactions, which allows the rapid identification of products based on characteristic signals in the spectrum.¹² In general, arylaminodiphenylphosphines C₆H₄-(o-R)NHPPh₂ give rise to singlet resonances between 25 and 35 ppm [*cf.* 29.4 ppm in PhNH–PPh₂,¹³ 26.4 ppm in PyNH–PPh₂ (Py = 2-pyridyl),^{1a} 27.2 ppm in C₆H₄(o-OCH₃)NH–PPh₂,¹⁴ 29.6 ppm in C₆H₄(o-PPh₂)NH–PPh₂¹⁵]. Diphenylphosphinoamines also exhibit a singlet resonance, but at higher frequency, typically around 64–70 ppm [*cf.* 67.7 ppm in PhN(PPh₂)₂,¹⁶ 65.6 ppm in C₆H₄(o-OCH₃)N(PPh₂)₂¹⁷]. Iminobiphosphines display a distinctive AB system with a characteristic ¹J_{P-P} value of *ca.* 220–290 Hz.^{5,9} Using these data, it is possible to rapidly evaluate the products obtained from the reactions described herein.

Reaction of the anilines 1(a-f) with Bu^nLi and Ph_2PCl in diethyl ether

Alkali-metalated amide anions of type RNHM (R = alkyl, aryl, M = Li, Na, K) are important precursors in organic synthesis. Lithiated amines are the most common and many structures have been elucidated by X-ray crystallography.^{18–20} However, since many lithiated species are not very stable, even at low temperature, the amide anions are often generated *in situ* and

Table 1 Relative ratio of the products from the reaction of the anilines 1(a-f) with BuⁿLi and Ph₂PCl in 1 : 1 : 1 ratio in diethyl ether based on ³¹P NMR spectroscopy

1	: RNH ₂	2: RNHPPh ₂ (%)	3: RN(PPh ₂) ₂ (%)	4: RN=P(PPh ₂)-PPh ₂ (%)
1	a: C ₆ H ₄ (o-CN)NH ₂	2a : 85	3a : < 1	4a : 15
1	b : $C_6H_4(p-CN)NH_2$	2b : 45	3b : ~5	4b : 50
1	$c: C_6H_4(m-CN)NH_2$	2c : 30	3c : ~ 5	4c : 65
1	d: $C_6H_4(o-Ph)NH_2$	2d: 95	3d : 0	4d : ~5
1	e: C ₆ F ₅ NH ₂	2e : 0	3e : 0	4e : 100
1	f : $C_6H_4(o-CF_3)NH_2$	2f : 65	3f : 0	4f : 35

converted into the desired product. Lithiation of the functionalised aniline C₆H₄(o-CN)NH₂ 1a using BuⁿLi in diethyl ether resulted in the precipitation of a solid, which was then reacted with Ph₂PCl. When no further reaction takes place, as evidenced by ³¹P NMR spectroscopy, the solvent and volatile components were removed under vacuum. The resulting solid was dissolved in thf and analysed by ³¹P NMR spectroscopy which showed the presence of three compounds. A signal at 29.0 ppm with a relative intensity of ca. 85% can be assigned to the aminophosphine C₆H₄(o-CN)NHPPh₂ 2a. About 15% of the iminobiphosphine C₆H₄(o-CN)N=PPh₂-PPh₂ 4a is present; it gives rise to two sets of doublets at 7.5 ppm and -15.5 ppm with a ${}^{1}J_{P-P}$ value of 262 Hz. There are also traces of the diphosphinoamine C₆H₄(o-CN)N(PPh₂)₂ 3a, tentatively characterised on the basis of a singlet at 67.0 ppm, with a very low relative intensity (less than 1%).

In an analogous reaction using the *para*-isomer C_6H_4 -(*p*-CN)NH₂ **1b**, which exhibits a very similar electron withdrawing effect, but is clearly of less steric hindrance than the *ortho*-isomer **1a**, the formation of the aminophosphine C_6H_4 -(*p*-CN)NHPPh₂ **2b** is lower (*ca.* 45%), and the formation of the iminobiphosphine $C_6H_4(p$ -CN)N=PPh₂-PPh₂ **4b** and diphosphinoamine $C_6H_4(p$ -CN)N(PPh₂)_2 **3b** is significantly higher (*ca.* 50 and 5%, respectively). Using the *meta*-isomer C_6H_4 -(*m*-CN)NH₂ **1c** as the starting material the amount of the aminophosphine $C_6H_4(m$ -CN)NHPPh₂ **2c** decreased further to about 30% and the quantity of the iminobiphosphine C_6H_4 -(*m*-CN)N=PPh₂-PPh₂ **4c** increased to *ca.* 65% compared to the other isomers. Diphosphinoamine $C_6H_4(p$ -CN)N(PPh₂)_2 **3c** is formed in low yield. These reactions are summarised in Scheme 1 and the relative amounts of each product are listed in Table 1.

	i. 1 x nBuLi ii. 1 x Ph. PC1				
RNH_2	$\frac{\text{II. I X I II_2I CI}}{\text{Et}_2\text{O}}$	RNHPPh ₂ +	$RN(PPh_2)_2 +$	RN=P(Ph ₂)-PPh ₂ +	free amine
1	-	2	3	4	

Scheme 1 Reactions of the anilines 1 with Bu^nLi and $Ph_2PCl(1:1:1)$ in diethyl ether.

Replacing the *ortho*-nitrile substituent by a phenyl group in the starting material, *viz*. $C_6H_4(o-C_6H_5)NH_2$ **1d**, results in the formation of almost exclusively the aminophosphine C_6H_4 - $(o-C_6H_5)NHPPh_2$ **2d**, only about 5% of $C_6H_4(o-C_6H_5)N=PPh_2$ -PPh₂ **4d** is found and the formation of the diphosphinoamine $C_6H_4(o-C_6H_5)N(PPh_2)_2$ **3d** is not observed. Starting from the aniline **1e** $C_6F_5N=PPh_2-PPh_2$ 4e was detected as the single phosphorus-containing product, the aminophosphine $C_6F_5NHPPh_2$ 2e and the diphosphinoamine $C_6F_5N(PPh_2)_2$ 3e were not formed. Using the aniline $C_6H_4(o-CF_3)NH_2$ 1f the result is similar as from the reaction from 1a, a high yield of the aminophosphine $C_6H_4(o-CF_3)$ -NHPPh₂ 2f was found, whereas $C_6H_4(o-CF_3)N=PPh_2-PPh_2$ 4f was formed in relatively low yield and the formation of $C_6H_4(o-CF_3)N(PPh_2)_2$ 3f was not observed.

The diphosphinoamines 3 and iminobiphosphines 4 are presumably derived from aminophosphine anions (2X in Scheme 2), generated by deprotonation of the newly formed aminophosphine with the lithiated amine RNHLi. In the solution, 2X can undergo a metatropism reaction into 2Y. There is a precedent for this type of reaction and such intermediates have been proposed previously.^{10b,21,22} It is not unreasonable to assume that reaction of the 2X-type anion with Ph2PCl will give the P-N-P product, whereas reaction of the 2Y-type anion with Ph₂PCl will give the N=P-P product. Based on this hypothesis the ratio of 2X and 2Y is clearly dependent on the substituent, with electron withdrawing groups at the ortho-position stabilising the 2Y-type anion, thereby increasing ratio of the N=P-P product, for example, C₆F₅NH₂ affords exclusively the iminobiphosphines product. It is also possible that the solubility of the lithiated anilines contribute to the outcome of the reactions. Addition of BuⁿLi to the anilines 1a, 1b, 1c, 1d and 1f in diethyl ether gives a suspension. The lithaited anilines are clearly poorly soluble in diethyl ether. Only in the case of 1e a clear solution is formed, which gives the highest yield of the N=P-P product 4e. A comparison of the reaction of 1a, 1b and 1c indicates that steric influences also play a role. Steric hindrance of the CN group at the ortho-position prevents further deprotonation of the formed aminophosphine 2a; so that 2a is the main product. A similar result is found for 1f. In the case of 1d, the yield of N=P-P product is very low, maybe the electron withdrawing effect is not appreciable and the steric hindrance of the more bulky phenyl group is much higher than the smaller CN group, so that the phenyl group prevents the deprotonation at the nitrogen. In the case of 1e, there is no steric hinderance and the electron withdrawing effect of the C₆F₅ group plays a dominant role, so that only N=P-P formation was observed.

In all cases, iminobiphosphines 4(a-f) could be isolated in pure form with low-to-moderate yield, due to differences in solubility of the other compounds. After removal of the solvent from the reaction mixture, the solid residue is copiously washed with diethyl ether removing both the aminophosphine, diphosphinoamine and any unreacted amine. The remaining solid contains the iminobiphosphine 4(a-f) and LiCl, the latter of which





Table 2 Relative ratio of the products from the reaction of the anilines 1(a-f) with Ph₂PCl and Et₃N in 1 : 1 : 1 ratio in dichloromethane based on ³¹P NMR spectroscopy

1 : RNH ₂	2 : RNHPPh ₂ (%)	3: RN(PPh ₂) ₂ (%)	4: RN=PPh ₂ -PPh ₂ (%)	
$\begin{array}{c} \textbf{1a: } C_6H_4(o\text{-}CN)NH_2\\ \textbf{1b: } C_6H_4(p\text{-}CN)NH_2\\ \textbf{1c: } C_6H_4(m\text{-}CN)NH_2\\ \textbf{1c: } C_6H_4(o\text{-}N)NH_2\\ \textbf{1d: } C_6H_4(o\text{-}Ph)NH_2\\ \textbf{1e: } C_6F_5NH_2\\ \textbf{1f: } C_6H_4(o\text{-}CF_3)NH_2\\ \end{array}$	2a : ~5 2b : 65 2e : 90 2d : 100 2e : 0 2f : 0	3a : 10 3b : 35 3c : 10 3d : 0 3e : 25 3f : 0	4a : 85 4b : 0 4c : 0 4d : 0 4e : 75 4f : 100	

could be isolated with CH₂Cl₂, affording a highly pure product. Among the iminobiphosphines **4(a–f)**, only **4e** is highly soluble in diethyl ether, and separation from the free amine is possible by recrystallisation at low temperature with **4e** crystallising first from the solution. Only the aminophosphine products **2a** and **2d** could be isolated in high yield. Recrystallisation of **2b** results in a pure product, but the yield is low. However, isolation of the other aminophosphines **2c** and **2f** is not straightforward as the reaction product also contains unreacted anilines which have similar solubilities to aminophosphines in common solvents. It was not possible to isolate any of the diphosphinoamines **3a**, **3b** and **3c** in pure form, and **3b** and **3c** are better prepared by the reaction of the anilines with two equivalents of Ph₂PCl in the presence of two equivalents of triethylamine (see below).

Reaction of $C_6H_4(o-C_6H_5)NH_2$ 1d with Ph_2PCl in the presence of Et_3N in 1:1:1 and 1:2:2 ratio in diethyl ether

Aminolysis is the standard method used to prepare aminophosphines and diphosphinoamines. For example, the ether functionalized aniline $C_6H_4(o$ -OCH₃)NH₂ reacts with Ph₂PCl in the presence of triethylamine to give $C_6H_4(o$ -OCH₃)-NHPPh₂¹⁴ or $C_6H_4(o$ -OCH₃)N(PPh₂)₂¹⁷ in high yield, depending on stoichiometry. However, the method cannot be generalised for all anilines as our earlier results show that iminobiphosphines can be obtained as the major product, if an appropriate functional group is present. Additionally, the choice of solvent is also very important in determining the outcome of the reaction.

In diethyl ether the reaction of the anilines 1(a-f) with Ph_2PCl in the presence of triethylamine (1:1:1 molar ratio) is very slow. The reaction of $C_6F_5NH_2$ **1e** with Ph_2PCl was monitored by ³¹P NMR spectroscopy at room temperature which showed that less than 10% of Ph_2PCl had reacted after one week. The resulting spectrum also showed that apart from the formation of the aminophosphine **2e**, the diphosphinoamine **3e** and iminobiphosphine **4e** were also present. The only synthetically useful reaction is that of **1d** with Ph_2PCl , since this reaction gave the iminobiphosphine **4d** in higher yield in a reasonable time.

If 1d is allowed to react with Ph₂PCl in the presence of triethylamine in a 1 : 1 : 1 ratio in diethyl ether, all three products 2d, 3d and 4d form, as evidenced by two singlet resonances at 29.95 and 67.0 ppm representing 2d and 3d, respectively, and two doublets at 1.60 and -14.00 ppm with a ${}^{1}J(P-P)$ value 260.0 Hz which correspond to 4d. Isolation of 4d is possible. After washing the reaction mixture with a large amount of diethyl ether, 4d can be isolated in ca. 35% yield by washing the remaining solid with thf. When the ratio of 1d : Ph₂PCl : NEt₃ is changed from 1:1:1 to 1:2:2, 4d is obtained in higher yield, ca. 65%, but 3d can also be isolated in about 35% yield. Separation of 3d and 4d is relatively facile since 3d is soluble in diethyl ether whereas 4d is essentially insoluble. After washing the reaction mixture with diethyl ether, the remaining yellow solid contains triethylamine hydrochloride and the iminobiphosphine 4d. The iminobiphosphine 4d could be isolated in pure form following washing with thf. Reactions of other anilines under the same conditions were too slow and not investigated further.

Table 3 Relative ratio of the products from the reaction of the anilines1(a-f) with Ph2PCl and Et3N in 1 : 2 : 2 ratio in dichloromethane basedon ³¹P NMR spectroscopy

1: RNH ₂	3: RN(PPh ₂) ₂ (%)	4 : RN=PPh ₂ –PPh ₂ (%)
1a : $C_{\ell}H_{\ell}(o-CN)NH_{2}$	3a : ~5	4a : 95
1b : $C_6H_4(p-CN)NH_2$	3b : 98	4b : ∼2
1c: $C_6H_4(m-CN)NH_2$	3c : 100	4c : 0
1d: $C_6H_4(o-Ph)NH_2$	3d : 98	4d : ∼2
1e: C ₆ F ₅ NH ₂	3e : 20	4e : 80
1f : $C_6H_4(o-CF_3)NH_2$	3f : 0	4f : 100

Reaction of anilines 1(a-f) with Ph₂PCl in the presence of Et₃N in a 1:1:1 ratio in dichloromethane

In dichloromethane the reaction between the anilines 1(a-f) and Ph₂PCl in the presence of triethylamine is fast and all the reaction products are soluble. Again, the relative percentage of the various products was estimated using ³¹P NMR spectroscopy and the results are summarized in Table 2.

Reaction of 1a with one equivalent of Ph₂PCl in the presence of one equivalent of triethylamine affords the iminophosphine 4a as the main product, although both 2a and 3a are also formed in low yield. Interestingly, with 1b and 1c, formation of iminobiphosphines 4b and 4c was not observed, whereas for 1d, formation of the aminophosphine 2d, is quantitative, and 3d and 4d were not observed. Under the same conditions, 1e gave both 3e and 4e, with 4e being the main product. In the case of 1f, the iminobiphosphine 4f is the only phosphorus containing product, formation of 2f and 3f was not observed. In general, isolation of the products is difficult since the 1 : 1 : 1 reaction does not give high selectivity and some unreacted amine contaminates the reaction mixture. The only synthetically useful reaction is that of 1d which affords 2d in quantitative yield. Although isolation of 4a, 4e and 4f is also possible, they can be prepared in higher yield in a 1:2:2 reaction with Ph₂PCl and Et₃N in dichloromethane (see below).

Reaction of anilines 1(a-f) with Ph₂PCl in the presence of Et₃N in a 1:2:2 ratio in dichloromethane

In dichloromethane, the products from the reaction of the analines 1(a-f) with two equivalents of Ph₂PCl in the presence of two equivalent triethylamine are simpler than in the 1:1:1 reaction. While the formation of aminophosphines 2 can be avoided, there is still competition between the formation of diphosphinoamines 3 and iminobiphosphines 4. In the case of 1a, the iminobiphosphine 4a is formed as the main product, with 3a formed in very low yield. In contrast, 1b and 1d react to form the diphosphinoamines 3b and 3d as the major products, with 4b and 4d observed only in low yield. Starting with 1c under the same condition, diphosphinoamine 3c was obtained in quantitative yield. In the case of 1e, both 3e and 4e are formed, with the 4e being the main product, which can be isolated by recrystallisation. In the case of 1f the iminobiphosphine 4f is obtained in near quantitative yield. These results are summarised in Table 3.

From the above results, it is clear that reaction of aniline with Ph₂PCl using triethylamine as base is very different to that using the inorganic base. Since triethylamine is a much weaker

base than the lithiated aniline, deprotonation of the aminophosphine is less efficient, so that the formation of the diphosphinoamine 3 or iminobiphosphine 4 takes place *via* the aminophosphine 2. However, aminophosphines can undergo prototropism reactions,^{9a,23} so that in solution 2 can exist in equilibrium together with the iminophosphine isomer 2' as shown in Scheme 3. Reaction of 2 with Ph₂PCl gives the diphosphinoamine 3, whereas reaction of 2' with Ph₂PCl affords the iminobiphosphine 4.



Scheme 3 Prototropism of aminophosphine 2.

The aminolysis route is synthetically useful when carried out in dichloromethane, affording diphosphinoamines 3 and iminobiphosphine 4, when the appropriate stoichiometry of reagents is used. The formation of the two different products is determined by the steric and electronic properties of the functional group. Essentially, the greater the steric hindrance and the greater the electron-withdrawing effect of the substituent at the ortho-position of the aniline, the greater the yield of the iminobiphosphine 4. This is clearly demonstrated by the reaction of **1a** and **1f** (both *ortho*-substituted) with two equivalents of Ph₂PCl and triethylamine, which both gave near quantitative yields of iminobiphosphines 4a and 4f, respectively. In contrast, in 1b and 1c, the meta- and para-isomers of 1a, the diphosphinoamines 3b and 3c are the major products. The electronwithdrawing effect of the phenyl group in 1d is comparatively weak, despite the bulky phenyl ring at the ortho-position, and the diphosphinoamine 3d is still the main product. In the case of 1e, although the C_6F_5 is a very strong electron-withdrawing group there is no steric hindrance, so both 3e and 4e are formed. The new bidentate diphosphinoamines 3b, 3c and 3d and the iminobiphosphines 4e and 4f can be isolated in high yield, whereas 3a and 3e are formed in very low yield and are their synthesis is not viable by this route.

Structural characterisation of the diphosphinoamines 3b, 3c, 5 and aminobiphosphines 4b, 4e and 4f

Both **3b** and **3c** form good quality crystals from diethyl ether at room temperature suitable for X-ray determination. In the case of compound **3d** we have been able to determine the connectivity, though the refinement of the structure is of low quality and therefore not reported. Crystals of iminobiphosphines **4b** and **4f** suitable for X-ray determination were obtained from dichloromethane and diethyl ether; the latter crystallised with a CH₂Cl₂ solvate. Crystals of **4e** were obtained by cooling a diethyl ether solution at -22 °C. In addition, the structure of the known diphosphinoamine PhN(PPh₂)₂,¹⁶ the prototype of the series of compounds described herein, is reported for comparison purposes.

There are surprisingly very few X-ray structures of free diphosphinoamines known, compared to their transition metal complexes. Even the structure of the well studied ligand PhN(PPh₂)₂ **5** has not been structurally investigated (Fig. 3). We therefore synthesised this diphosphinoamine according to the literature method,¹⁶ to study the X-ray structure. The solid state structures of **3b**, **3c** and **5** are shown in Figs. 1–3 with key parameters given in the captions. The molecular symmetry for **3b**, **3c** and **5** is different, **3b** shows no symmetry, **3c** lies on a crystallographic mirror plane and it has C_s symmetry, whereas **5** lies on two-fold axis showing then a C_2 symmetry. In **3b**, **3c** and **5** the two lone electron pairs point to the same direction. The P(1)–N(1)–P(2) angles in all the three compounds are slightly different with **5** having the longest C1–N1 distance. The C1–N1



Fig. 1 Molecular structure of **3b** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–N1, 1.732(3); P2–N1, 1.723(3), N1–C1, 1.434(4); N2–C7, 1.151(5); P2–N1–P1, 114.49(14).



Fig. 2 Molecular structure of **3c** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–N1, 1.746(2); N1–P1A, 1.746(2), N1–C1, 1.449(6); N2–C7, 1.138(8); P1–N1–P1A, 112.7(2). Letter A indicates the following symmetry transformation: x, -y - 1/2, z.



Fig. 3 Molecular structure of **5** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–N1, 1.7315(15); N1–P1A, 1.7315(15); N1–C1, 1.455(4); P1–N1–P1A, 113.37(14). Letter A indicates the following symmetry transformation: -x, y, -z + 1/2.

distances in **3b** and **3c** are only marginally different to **5** despite the electron-withdrawing effect of CN group at the *para* and *meta* position on the phenyl ring. Although many N=P-P compounds are known, the first structure, **4a**, of this family was published only recently.¹¹ The solid-state structures of **4b**, **4e** and **4f** of are shown in Figs. 4–6



Fig. 4 Molecular structure of **4b** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–P2, 2.2451(16); P1–N1, 1.572(5); N1–C1, 1.382(7); N2–C31, 1.140(7); C4–C31, 1.446(8); N1–P1–C7, 115.1(3); N1–P1–P2, 121.68(17); C1–N1–P1, 131.3(4).



Fig. 5 Molecular structure of **4e** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–P2, 2.2379(16); P1–N1, 1.571(3); N1–C1, 1.371(4); N1–P1–C7, 118.17(14); N1–P1–P2, 117.82(11); C1–N1–P1, 135.2(2).



Fig. 6 Molecular structure of **4f** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–P2, 2.2498(18); P1–N1, 1.578(3); N1–C1, 1.385(5); N1–P1–C7, 113.98(17); N1–P1–P2, 122.49(14); C1–N1–P1, 132.2(3).

together with key parameters listed in the caption. There are close similarities in the solid structures of **4b**, **4e** and **4f** with **4a**. In all cases, the two Ph₂P group bonded to P1 are *trans* to those on P2. All the P1–N1, P1–P2 and N1–C1 distances in **4b**, **4e** and **4f** are very close to that found in **4a**. The difference of the different steric and electron-withdrawing effect seems to have only minimum effect on the structural parameters in the solid state. Additionally, the C1–N1–P1 and N1–P1–P2 angles in **4b** and **4f** are also within the range found in **4a**. However, in **4e**, there is π – π interaction between C₆F₅ ring and one of the phenyl rings bonded to P2 (C19 · · · C24), the distance between the two centroids is 3.628(3) Å. As the result, the C1–N1–P1 angle is larger and the N1–P1–P2 angle is smaller than in **4a**, **4b** and **4f**.

Concluding remarks

We have studied the reaction of a series of functionalised anilines with Ph_2PCl using different bases, stoichiometries and solvents. A series of aminophosphines, diphosphinoamines and iminobiphosphines were isolated. In all the reactions, the outcome of the final products strongly depends on the steric and electronic effect of the functional group attached to the aniline starting material. All the functionalised iminobiphosphine ligands show somewhat unusual properties towards small molecules, such as H_2O , H_2O_2 , S_8 , and transition metal complexes leading to cleavage of the P–P bond or rearrangement from N=P–P to P–NH or P–N–P. These results will be reported in due course.

Experimental

All manipulations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Anilines 1(a-f), BuⁿLi, Ph₂PCl and Et₃N were purchased from Aldrich chemicals and used as received. Solvents were dried using the appropriate reagents and distilled prior to use. NMR spectra were obtained at 20 °C with a Bruker DMX 200 instrument using SiMe₄ for ¹H and 85% H₃PO₄ for ³¹P as external standards. For the ³¹P NMR spectra of the reaction mixture, a C₆D₆ capillary was used as a lock. With the reaction of lithiated anilines with Ph2PCl, the ³¹P NMR spectra were recorded after removal of all the solvents and re-dissolving the resulting solid in a large amount of thf until a clear solution formed. For the final identification, CDCl₃ was used as the NMR solvent. ESI-MS spectra were recorded on a ThermoFinnigan LCQ™ Deca XP Plus quadrupole ion trap instrument.²⁴ Samples were infused directly into the source at 5 $\mu L\ min^{-1}$ using a syringe pump. The spray voltage was set at 5 kV and the capillary temperature at 50 °C. The MS detector was tuned automatically on the base peak, which optimized the remaining parameters. Elemental analysis was carried out by the Institute of Molecular and Biological Chemistry at the EPFL.

Reaction of aniline $C_6H_4(o-CN)NH_2$ 1a with BuⁿLi and Ph₂PCl, synthesis of 2a and 4a

The reagent BuⁿLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was added slowly to a solution of $C_6H_4(o-CN)NH_2$ **1a** (2.36 g, 20.0 mmol) in 50 ml of diethyl ether at -78 °C. The resulting suspension was allowed to warm to -20 °C over 30 min and Ph₂PCl (4.41 g, 20.0 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then filtered and washed with diethyl ether (3 × 20 ml). From the diethyl ether filtrate large crystals of **2a** were obtained on cooling to -22 °C. The solid was washed with dichloromethane (3 × 30 ml). The dichloromethane filtrates were collected and the solvent was removed in vacuum. The resulting solid was recrystallised from dichloromethane and diethyl ether to give the product **4a**. Yield: 0.24 g, 5% (based on Ph₂PCl). For spectroscopic chracterisation of **1a** and **4a** see ref. 11.

Reaction of aniline $C_6H_4(p-CN)NH_2$ 1b with BuⁿLi and Ph₂PCl, synthesis of 2b and 4b

The reagent BuⁿLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was slowly added to a solution of $C_6H_4(p-CN)NH_2$ 1b (2.36 g, 20.0 mmol) in 50 ml of diethyl ether at -78 °C. The resulting suspension was allowed to warm to -20 °C over 30 min and Ph2PCl (4.41 g, 20.0 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then filtered and washed with diethyl ether (3 \times 20 ml). From the diethyl ether filtrates 2b was obtained on repeated recrystallisation in diethyl ether (three times). Yield: 0.60 g, 10%. Mp 142 °C. ¹H NMR: δ 8.00–6.90 (m, 14H, aromatic H), 4.90 (br signal, 1H, NH), ppm. ³¹P NMR: δ 29.30 (s) ppm. ESI-MS⁺: m/z 303 [M + H]⁺. Anal. Calc. for C₁₉H₁₅N₂P: H, 5.00; C 75.49; N, 9.27. Found: H, 5.09, C, 75.58, N, 9.25%. The remaining solid was then washed with dichloromethane $(3 \times 30 \text{ ml})$. The dichloromethane filtrates were collected and solvent was removed in vacuum. The solid was recrystallised from dichloromethane and diethyl ether to give the product 4b as colourless crystals. Yield: 1.70 g, 35%. ¹H NMR: δ 8.05–6.85 (m, aromatic H) ppm; ³¹P NMR: δ 7.50 (d), -15.65 (d, ¹J_{P-P} = 264.0 Hz) ppm ESI-MS⁺: m/z 487 [M + H]⁺. Anal. Calc. for C31H24N2P2: H 4.97, C 76.54, N 5.76. Found H 5.01, C 76.60, N 5.61%.

Reaction of aniline $C_6H_4(m$ -CN)NH₂ 1c with BuⁿLi and Ph₂PCl, synthesis of 4c

The reagent BuⁿLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was slowly added to a solution of $C_6H_4(m$ -CN)NH₂ 1c (2.36 g, 20.0 mmol) in 50 ml of diethyl ether at -78 °C. The resulting suspension was allowed to warm to -20 °C over 30 min and Ph₂PCl (4.41 g, 20.0 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then filtered and washed with diethyl ether (3 × 20 ml). The remaining solid was washed with dichloromethane (3 × 30 ml). The dichloromethane filtrates were collected and solvent was removed in vacuum. The resulting solid was recrystallised from dichloromethane and thf to give the product 4c. Yield: 2.48 g, 51%. Mp 143 °C. ¹H NMR: δ 8.10–6.80 (m, aromatic H) ppm; ³¹P NMR: δ 7.50 (d), -15.00 (d, ¹ J_{P-P} = 263.0 Hz) ppm. ESI-MS⁺: m/z 487 [M + H]⁺. Anal. Calc. for C₃₁H₂₄N₂P₂: H 4.97, C 76.54, N 5.76. Found: H 5.03, C 76.62, N 5.55%.

Reaction of aniline $C_6H_4(o-C_6H_5)NH_2$ 1d with BuⁿLi and Ph₂PCl, synthesis of 2d and 4d

The reagent BuⁿLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was slowly added to a solution of $C_6H_4(o-C_6H_5)NH_2$ 1d (3.38 g, 20.0 mmol) in 50 ml of diethyl ether at -78 °C. The resulting suspension was allowed to warm to -20 °C over 30 min and Ph₂PCl (4.41 g, 20.0 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then filtered and washed with diethyl ether $(3 \times 20 \text{ ml})$. The diethyl ether filtrates were collected and the solvent was removed in vacuum. The resulting oil was washed with cold diethyl ether $(3 \times 5 \text{ ml})$ at -22° C to give the product of 2d as an off-white oil. Yield: 5.30 g, 75%. ¹H NMR: δ 5.80 (br signal, 1H, NH), 8.00-7.40 (m, aromatic H) ppm. ³¹P NMR: δ 30.5(s) ppm. ESI-MS⁺: m/z 354 [M + H]⁺. Anal. Calc. for C₂₄H₂₀NP: H 5.70; C 81.57; N 3.96. Found: H 5.75, C 81.68, N 3.91%. The remaining solid was washed with dichloromethane (3 \times 10 ml). The dichloromethane filtrates were collected and solvent was removed in vacuum to give a yellow solid. Washing this solid with diethyl ether $(2 \times 5 \text{ ml})$ gave the product **4d**. Yield: 0.10 g, 2%. Mp 148 °C. ¹H NMR: δ 8.15–7.40 (m, aromatic H) ppm; ³¹P NMR: δ 1.60 (d), -14.00 (d, ${}^{1}J_{P-P} = 261.0$) ppm. ESI-MS⁺: m/z 538 [M + H]⁺. Anal. Calc. for C36H29NP2: H 5.44, C 80.43, N 2.61. Found: H 5.45, C 80.51, N 2.59%.

Reaction of aniline $C_6F_5NH_2$ 1e with BuⁿLi and Ph₂PCl, synthesis of 4e

The reagent BuⁿLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was slowly added to a solution of C₆F₅NH₂ **1e** (3.66 g, 20.0 mmol) in 50 ml of diethyl ether at -78 °C. The resulting solution was allowed to warm to -20 °C over 30 min and Ph₂PCl (4.41 g, 20.0 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then filtered and washed with diethyl ether (3 × 20 ml). The combined ether filtrates were concentrated to about its ¹/₄ volume and cooled at -22 °C overnight. Crystals formed from the solution and were collected by filtration to give the product **4e**. Yield: 3.03 g, 55%. Mp 122 °C. ¹H NMR: δ 8.25–7.15 (m, aromatic H) ppm; ³¹P NMR: δ 10.05 (d), -14.50 (d, ¹J_{P-P} = 266.5 Hz) ppm. ESI-MS⁺: *mlz* 552 [M + H]⁺. Anal. Calc. for C₃₀H₂₀F₅NP₂: H 3.66, C 65.34, N 2.54. Found H 3.68, C 65.42, N 2.53%.

Reaction of aniline $C_6H_4(o-CF_3)NH_2$ 1f with BuⁿLi and Ph₂PCl, synthesis of 4f

The reagent BuⁿLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was slowly added to a solution of $C_6H_4(o-CF_3)NH_2$ 1f (3.22 g, 20.0 mmol) in 50 ml of diethyl ether at -78 °C. The resulting suspension was allowed to warm to -20 °C over 30 min and Ph2PCl (4.41 g, 20.0 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then filtered and washed with diethyl ether $(3 \times 10 \text{ ml})$. The remaining solid was washed with dichloromethane $(3 \times 30 \text{ ml})$. The dichloromethane filtrates were collected and solvent was removed in vacuum The solid was washed again with diethyl ether (3 \times 10 ml) and then recrystallised from dichloromethane and diethyl ether to give the product 4f. Yield: 2.38 g, 45%. Mp 126 °C. ¹H NMR: δ 8.05–6.65 (m, aromatic H) ppm; ³¹P NMR: δ 5.35 (d), -17.20 (d, ${}^{1}J_{P-P}$ = 265.5 Hz) ppm. ESI-MS⁺: *m*/*z* 530 $[M + H]^+$. Anal. Calc. for $C_{31}H_{24}F_3NP_2$: H 4.57, C 70.32, N 2.65. Found H 4.59, C 70.43, N 2.64%.

The 1 : 1 : 1 reaction of aniline 1d with Ph_2PCI/Et_3N in diethyl ether, synthesis of 4d

To a solution of $C_6H_4(o-C_6H_5)NH_2$ 1d (1.69 g, 10.0 mmol) and triethylamine (1.02 g, 10.0 mmol) in 50 ml diethyl ether Ph₂PCl (2.21 g, 10.0 mmol) was added at room temperature in one portion. The reaction mixture was stirred 4 days and then filtered. The yellow solid was washed firstly with diethyl ether (3 × 20 ml) and then thf (3 × 20 ml). The thf filtrates were collected. Removal of the solvent gave the compound 4d. Yield: 0.94 g, 35% (based on Ph₂PCl).

Under the same condition, the 1 : 1 : 1 reaction of **1a**, **1b**, **1c**, **1e** and **1f** with Ph₂PCl/Et₃N in diethyl ether is too slow and was not investigated further.

The 1 : 2 : 2 reaction of aniline 1d with Ph_2PCI/Et_3N in diethyl ether, synthesis of 3d and 4d

To a solution of $C_6H_4(o-C_6H_5)NH_2$ **1d** (1.69 g, 10.0 mmol) and triethylamine (2.03 g, 20.0 mmol) in 50 ml diethyl ether Ph₂PCl (4.42 g, 20.0 mmol) was added at room temperature in one portion. The reaction mixture was stirred one week and then filtered. The yellow solid was washed firstly with diethyl ether (3 × 20 ml) and then thf (3 × 20 ml). From the diethyl ether filtrates **3d** was obtained after removal of the solvent. Yield: 1.86 g, 35%. Mp 158 °C. ¹H NMR: δ 8.35–7.35 (m, aromatic H) ppm; ³¹P NMR: δ 68.20 (s) ppm. ESI-MS⁺: m/z 538 [M + H]⁺. Anal. Calc. for $C_{36}H_{29}NP_2$: H 5.44, C 80.43, N 2.61. Found H 5.48, C 80.47, N 2.59%. From the thf filtrate the compound **4d** was obtained after removal of the solvent. Yield: 3.48 g, 65%.

The 1:1:1 reaction of aniline 1d with Ph_2PCI/Et_3N in dichloromethane, synthesis of 2d

To a solution of **1d** (1.69 g, 10.0 mmol) and triethylamine (1.01 g, 10.0 mmol) in 50 ml dichloromethane Ph₂PCl (2.21 g,

Table 4Crystal data and details of the structure determination for 3b, 3c, 4b, 4e, 4f and 5

	3b	3c	4b	4 e	4f	5
Chemical formula	$C_{31}H_{24}N_2P_2$	$C_{31}H_{24}N_2P_2$	C ₃₁ H ₂₄ N ₂ P ₂	C ₃₀ H ₂₀ F ₅ NP ₂	C ₃₂ H ₂₆ Cl ₂ F ₃ NP ₂	C ₃₀ H ₂₅ NP ₂
Formula weight	486.46	486.46	486.46	551.41	614.38	461.45
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	Pnma	Cc	$P\bar{1}$	$P\overline{1}$	C2/c
aĺÅ	11.397(4)	16.8591(16)	15.778(3)	10.322(6)	10.087(2)	18.5448(16)
b/Å	11.702(4)	17.3905(12)	11.6783(16)	10.871(4)	10.647(5)	12.7369(11)
c/Å	18.829(3)	8.7547(7)	15.070(2)	13.079(6)	15.187(7)	10.4063(8)
a/°	90	90	90	108.49(4)	82.05(4)	90
βl°	91.048(19)	90	112.375(15)	95.79(4)	74.46(3)	100.092(7)
γl°	90	90	90	110.44(4)	67.64(3)	90
V/Å ³	2510.7(12)	2566.8(4)	2567.8(7)	1266.7(10)	1452.0(10)	2420.0(3)
Ζ	4	4	4	2	2	4
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.287	1.259	1.258	1.446	1.405	1.267
F(000)	1016	1016	1016	564	632	968
μ/mm^{-1}	0.196	0.192	0.192	0.230	0.377	0.198
T/K	140	140	140	140	140	140
λ/Å	0.71070	0.71073	0.71073	0.71070	0.71070	0.71073
Measured reflections	13933	14985	7264	7700	9435	6712
Unique reflections	4318	2343	3951	4197	4805	2017
Unique reflections $[I > 2\sigma(I)]$	3263	1999	2905	2862	3330	1745
Data/parameters	4318/317	2343/172	3951/317	4197/344	4805/390	2017/151
$R^{a}[I \ge 2\sigma(I)]$	0.0708	0.0784	0.0663	0.0477	0.0748	0.0391
$wR2^a$ (all data)	0.2181	0.1488	0.1787	0.1373	0.2295	0.0959
GoF ^b	1.165	1.292	0.973	1.004	1.096	1.147
$^{a}R = \Sigma F_{0} - F_{c} / \Sigma F_{0} , wR2 = \{\Sigma \}$	$\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[$	$w(F_o^2)^2$] $^{1/2}$. ^b GoF = {	$\sum [w(F_o^2 - F_c^2)^2]/(n)$	(n-p) ^{1/2} where <i>n</i> is t	he number of data and	<i>p</i> is the number

 $K = 2||T_0| = |T_c||/2|T_0|, WK2 = \{2|W|T_0|, of parameters refined.$

10.0 mmol) was added at 0 °C within 15 min. The reaction mixture was then stirred for 30 min at r.t. and examined by ³¹P NMR spectroscopy which shows that the signals of Ph₂PCl disappeared and only one singlet at 30.20 ppm indicating **2d** had formed. After removal of the solvent the residue was washed with diethyl ether (3 × 20 ml). Removal of the diethyl ether gave the product **2d** as greyish oil in pure form. Yield 3.47 g, 98%.

Under the same condition, the 1 : 1 : 1 reaction of **1a**, **1b**, **1c**, **1e** and **1f** with Ph₂PCl/Et₃N in dichloromethane gave mixtures and only investigated by ³¹P NMR spectra. Attempts to isolate a pure product were not made.

The 1 : 2 : 2 reaction of anilines 1b, 1c and 1d with Ph_2PCI/Et_3N in dichloromethane, synthesis of 3b, 3c and 3d

To a solution of $C_6H_4(p-CN)NH_2$ **1b** (1.18 g, 10.0 mmol) and triethylamine (2.02 g, 20.0 mmol) in dichloromethane (50 ml), Ph₂PCl (4.42 g, 20.0 mmol) was added at 0 °C within 15 min. The reaction mixture was stirred 30 min at r.t.. After removal of the dichloromethane solvents the residue was washed with diethyl ether (4 × 30 ml). Removal of the solvent gave the product **3b** as colourless solid. Yield 4.69 g. 96%. Mp 109 °C. ¹H NMR: δ 8.0–6.6 (m, aromatic H) ppm; ³¹P NMR: δ 68.50 (s) ppm ESI-MS⁺: *m*/*z* 487 [M + H]⁺. Anal. Calc. for C₃₁H₂₄N₂P₂: H 4.97, C 76.54, N 5.76. Found H 4.99, C 76.58, N 5.61%.

Using the same procedure as described above, $C_6H_4(m-CN)NH_2$ **1c** (1.18 g, 10.0 mmol), triethylamine (2.02 g, 20.0 mmol) and Ph₂PCl (4.42 g, 20.0 mmol) in 50 ml dichloromethane yielded **3c**. Yield: 4.81 g, 99%. Mp 99 °C. ¹H NMR: δ 8.05–6.60 (m, aromatic H) ppm; ³¹P NMR: δ 69.50 (s) ppm ESI-MS⁺: *m/z* 487 [M + H]⁺. Anal. Calc. for C₃₁H₂₄N₂P₂: H 4.97, C 76.54, N 5.76. Found H 4.98, C 76.59, N 5.59%.

Using the same procedure as described above, $C_6H_4(o-C_6H_5)-NH_2$ **1d** (1.69 g, 10.0 mmol), triethylamine (2.02 g, 20.0 mmol) and Ph₂PC1 (4.42 g, 20.0 mmol) in 50 ml dichloromethane yielded **3d**. Yield: 5.10 g, 95%.

The 1 : 2 : 2 reaction of aniline 1e with Ph₂PCl/Et₃N in dichloromethane, synthesis of 4e

To a solution of $C_6F_5NH_2$ **1e** (1.83 g, 10.0 mmol) and triethylamine (2.02 g, 20.0 mmol) in 50 ml dichloromethane added Ph₂PCl (4.42 g, 20.0 mmol) at 0 °C within 15 min. The reaction mixture was then stirred at room temperature for 30 min. After removal of the dichloromethane solvents the remaining solid was washed with diethyl ether (4 × 30 ml). All the filtrates were collected and concentrated to about its ¹/₄ volume. At -22° , crystals formed and collected by filtration to give the product **4e**. Yield: 2.75 g, 50%.

The 1 : 2 : 2 reactions of 1a and 1f with Ph₂PCI/Et₃N in dichloromethane, synthesis of 4a and 4f

To a solution of $C_6H_4(o-CN)NH_2$ **1a** (1.18 g, 10.0 mmol) and triethylamine (2.02 g, 20.0 mmol) in dichloromethane (50 ml), Ph₂PCl (4.42 g, 20.0 mmol) was added at 0 °C over 15 min. The reaction mixture was then stirred at room temperature for 30 min. After removal of the dichloromethane solvents the resulting solid was washed with diethyl ether (3 × 10 ml). The remaining solid was washed again with thf (4 × 30 ml). The thf filtrates were collected. Removal of the thf gave the product **4a**. Yield: 4.52 g, 93%.

Starting from **1f** $C_6H_4(o-CF_3)NH_2$ (1.61 g, 10.0 mmol) and triethylamine (2.02 g, 20.0 mmol) and Ph₂PCl (4.42 g, 20.0 mmol) in 50 ml dichloromethane following the same procedure as described above, **4f** was obtained. Yield: 5.24 g, 99%.

Structural characterisation

X-Ray measurements were performed on a 4-circle kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD (3c, 4b, 5) and on a marresearch mar345 IPDS (3b, 4e, 4f) at 140 K. A summary of the crystallographic data and the structure refinements is listed in Table 4 and relevant geometrical parameters, including bond lengths and angles are included into the figure captions. Data reduction was carried out with CrysAlis RED, release 1.6.9.25 Absorption correction²⁶ was applied to all data sets except for 3c. Structure solution and refinement as well as molecular graphics and geometrical calculations were performed for all structures with the SHELXTL software package, release 5.1.27 The structures were refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. H atoms were placed in calculated positions using the "riding model". Some disorder problems have been encountered during the refinement of 4f. In this

case a disordered CH₂Cl₂ has been solved using the split model [occupancy factor for site A = 0.763(5)] and fixing geometrical parameters.

CCDC reference numbers 207371-207376.

See http://www.rsc.org/suppdata/dt/b3/b303645f/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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

References

- 1 For the most recent reports on aminophophines: (a) S. M. Aucott, A. M. Z. Slawin and J. D. Woollins, J. Chem. Soc., Dalton Trans., 2000, 2559; (b) S. M. Aucott, M. L. Clarke, A. M. Z. Slawin and J. D. Woollins, J. Chem. Soc., Dalton Trans., 2001, 972; (c) M. L. Clarke, A. M. Z. Slawin, M. V. Wheatley and J. D. Woollins, J. Chem. Soc., Dalton Trans., 2001, 3421.
- 2 For the recent reports on diphosphinoamines: (a) K. G. Gaw, M. B. Smith and J. W. Steed, J. Organomet. Chem., 2002, 664, 294; (b) I. Bachert, P. Braunstein, M. K. McCart, F. Fabrizi de Biani, F. Lashi, P. Zanello, G. Kickelbick and U. Schubert, J. Organomet. Chem., 1999, 573, 47; (c) I. Bachert, I. Bartussek, P. Braunstein, E. Guillon, J. Rose and G. Kickelbick, J. Organomet. Chem., 1999, 580, 257; (d) I. Bachert, P. Braunstein and R. Hasselbring, New J. Chem., 1996, 20, 993.
- 3 M. S. Balakrishna, V. Sreenivasa Reddy, S. S. Krishnamurthy, J. F. Nixon and J. C. T. R. Burckett St. Laurent, Coord. Chem. Rev., 1994. 129. 1.
- 4 T. Appleby and J. D. Woollins, Coord. Chem. Rev., 2002, 235, 121.
- 5 (a) V. L. Foss, Yu. A. Veits, T. E. Tretyakova and I. F. Lutsenko, Zh. Obshch. Khim., 1977, 47, 954; (b) V. L. Foss, Yu. A. Veits, T. E. Ghernykh and I. F. Lutsenko, Zh. Obshch. Khim., 1984, 54, 2670; (c) Yu. A. Veits, E. G. Neganova, A. A. Borisenko, V. L. Foss and I. F. Lutsenko, Zh. Obshch. Khim., 1989, 59, 1733.
- 6 O. Scherer and W. M. Janssen, J. Organomet. Chem., 1969, 20, 111.

- 7 (a) G. Ewart, A. P. Lane, J. McKechnie and D. S. Payne, J. Chem. Soc. A, 1964, 1543; (b) A. P. Lane, D. A. Morton-Blake and D. S. Payne, J. Chem. Soc. A, 1967, 1492.
- 8 D. Fenske, B. Maczek and K. Maczek, Z. Anorg. Allg. Chem., 1997, **623**, 1113.
- 9 (a) H. Rossknecht and A. Schmidtpeter, Z. Naturforsch., Teil B, 1971, 26, 81; (b) H. Rossknecht, W. P. Lehman and A. Schmidtpeter, Phosphorus, 1975, 5, 195.
- 10 For X-ray structures of aminophosphines in the solid state see ref. 1 and: (a) T. G. Wetzel, S. Dehnen and P. W. Roesky, Angew. Chem., Int. Ed., 1999, 38, 1086; (b) B. Eichhorn, H. Nöth and T. Seifert, Eur. J. Inorg. Chem., 1999, 12, 2355.
- 11 Z. Fei, R. Scopelliti and P. J. Dyson, Inorg. Chem., 2003, 42, 2125.
- 12 S. Berger, S. Braun and H.-O. Kalinowski, NMR-Spektroskopie von Nichtmetallen, Band 3, ³¹P-NMR-Spektroskopie, Georg Thieme Verlag, Stuttgart, New York, 1993.
- 13 W. Wiegräbe and H. Bock, Chem. Ber., 1968, 101, 1414.
- 14 A. D. Burrows, M. F. Mahon and M. T. Palmer, J. Chem. Soc., Dalton Trans., 2000, 1669.
- 15 S. M. Aucott, A. M. Z. Slawin and J. D. Woollins, J. Organomet. Chem., 1999, 583, 83.
- 16 W. Seidel and M. Alexiev, Z. Anorg. Allg. Chem., 1978, 438, 68.
- 17 K. G. Gaw, M. B. Smith and A. M. Z. Slawin, New J. Chem., 2000, 24, 429.
- 18 (a) D. R. Armstrong, A. C. Carstairs and K. W. Henderson, Organometallics, 1999, 18, 3589; (b) K. W. Henderson and P. G. Williard, Organometallics, 1999, 18, 5620.
- 19 F. T. Edelmann, F. Pauer, M. Wedler and D. Stalke, Inorg. Chem., 1992, 31, 4143.
- 20 P. P. Power, Acc. Chem. Res., 1988, 21, 147.
- 21 (a) M. T. Ashby and Z. Li, Inorg. Chem., 1992, 31, 1321; (b) N. Poetschke, M. Nieger, M. A. Khan, E. Niecke and M. T. Ashby, *Inorg. Chem.*, 1997, 36, 4087.22 O. Kühl, T. Koch, F. B. Jr. Somoza, P. C. Junk, E. Hey-Hawkins,
- D. Plat and M. S. Eisen, J. Organomet. Chem., 2000, 604, 116. 23 O. I. Kolodyazhnyi and N. Prinada, Zh. Obshch. Khim., 2001, 71,
- 691. 24 W. Henderson, J. S. McIndoe, B. K. Nicholson and P. J. Dyson,
- J. Chem. Soc., Dalton Trans., 1998, 519.
- 25 Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, 2002.
- 26 N. Walker and D. Stuart, Acta Crystallogr., Sect A, 1983, 39, 158.
- 27 G. M. Sheldrick, University of Göttingen, Germany, 1997, Bruker AXS, Inc., Madison, WI, 53719, USA, 1997.