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

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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*-CF_3)] with Ph_2PCl 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]

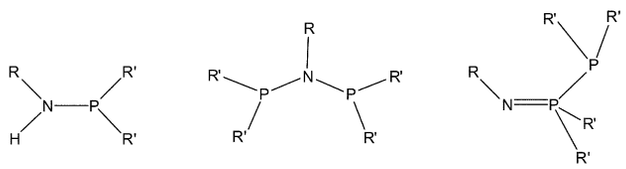

Chart 1

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 Bu^nLi, Na or K, which leads to deprotonation of the amine and formation of an amide anion. The anion can subsequently be converted into an aminophosphine[8] or iminobiphosphine[9] 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 C_6H_4(*o*-CN)NH_2 **1a**, followed by addition of Ph_2PCl, afforded the aminophosphine C_6H_4-(*o*-CN)$NHPPh_2$ **2a** in high yield.[11] During the course of our research, we found in the same reaction the iminobiphosphine C_6H_4(*o*-CN)N=PPh_2PPh_2 **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 Ph_2PCl in the presence of triethylamine which gives the iminobiphosphine **4a** in nearly quantitative yield, instead of the diphosphinoamine C_6H_4(*o*-CN)$N(PPh)_2$ **3a**. The analogous reaction of Ph_2PCl with $PhNHPPh_2$ gave only the diphosphinoamine $PhN(PPh_2)_2$. 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, ^{31}P 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 C_6H_4-(*o*-R)$NHPPh_2$ give rise to singlet resonances between 25 and 35 ppm [*cf.* 29.4 ppm in $PhNH–PPh_2$,[13] 26.4 ppm in $PyNH–PPh_2$ (Py = 2-pyridyl),[1a] 27.2 ppm in C_6H_4(*o*-OCH_3)$NH–PPh_2$,[14] 29.6 ppm in C_6H_4(*o*-PPh_2)$NH–PPh_2$ [15]]. Diphenylphosphinoamines also exhibit a singlet resonance, but at higher frequency, typically around 64–70 ppm [*cf.* 67.7 ppm in $PhN(PPh_2)_2$,[16] 65.6 ppm in C_6H_4(*o*-OCH_3)$N(PPh_2)_2$ [17]]. 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

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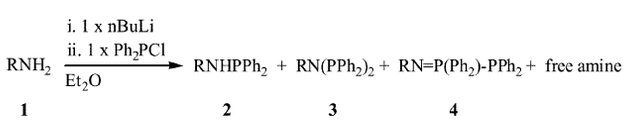
Table 1 Relative ratio of the products from the reaction of the anilines **1(a–f)** with Bu^nLi and Ph_2PCl in 1 : 1 : 1 ratio in diethyl ether based on ^{31}P NMR spectroscopy

1: RNH_2	**2**: $RNHPPh_2$ (%)	**3**: $RN(PPh_2)_2$ (%)	**4**: $RN{=}P(PPh_2){-}PPh_2$ (%)
1a: $C_6H_4(o\text{-}CN)NH_2$	**2a**: 85	**3a**: < 1	**4a**: 15
1b: $C_6H_4(p\text{-}CN)NH_2$	**2b**: 45	**3b**: ~5	**4b**: 50
1c: $C_6H_4(m\text{-}CN)NH_2$	**2c**: 30	**3c**: ~ 5	**4c**: 65
1d: $C_6H_4(o\text{-}Ph)NH_2$	**2d**: 95	**3d**: 0	**4d**: ~5
1e: $C_6F_5NH_2$	**2e**: 0	**3e**: 0	**4e**: 100
1f: $C_6H_4(o\text{-}CF_3)NH_2$	**2f**: 65	**3f**: 0	**4f**: 35

converted into the desired product. Lithiation of the functionalised aniline $C_6H_4(o\text{-}CN)NH_2$ **1a** using Bu^nLi in diethyl ether resulted in the precipitation of a solid, which was then reacted with Ph_2PCl. When no further reaction takes place, as evidenced by ^{31}P NMR spectroscopy, the solvent and volatile components were removed under vacuum. The resulting solid was dissolved in thf and analysed by ^{31}P 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 $C_6H_4(o\text{-}CN)NHPPh_2$ **2a**. About 15% of the iminobiphosphine $C_6H_4(o\text{-}CN)N{=}PPh_2{-}PPh_2$ **4a** is present; it gives rise to two sets of doublets at 7.5 ppm and −15.5 ppm with a $^1J_{P-P}$ value of 262 Hz. There are also traces of the diphosphinoamine $C_6H_4(o\text{-}CN)N(PPh_2)_2$ **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 $C_6H_4(p\text{-}CN)NH_2$ **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 $C_6H_4(p\text{-}CN)NHPPh_2$ **2b** is lower (*ca.* 45%), and the formation of the iminobiphosphine $C_6H_4(p\text{-}CN)N{=}PPh_2{-}PPh_2$ **4b** and diphosphinoamine $C_6H_4(p\text{-}CN)N(PPh_2)_2$ **3b** is significantly higher (*ca.* 50 and 5%, respectively). Using the *meta*-isomer $C_6H_4(m\text{-}CN)NH_2$ **1c** as the starting material the amount of the aminophosphine $C_6H_4(m\text{-}CN)NHPPh_2$ **2c** decreased further to about 30% and the quantity of the iminobiphosphine $C_6H_4(m\text{-}CN)N{=}PPh_2{-}PPh_2$ **4c** increased to *ca.* 65% compared to the other isomers. Diphosphinoamine $C_6H_4(p\text{-}CN)N(PPh_2)_2$ **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.

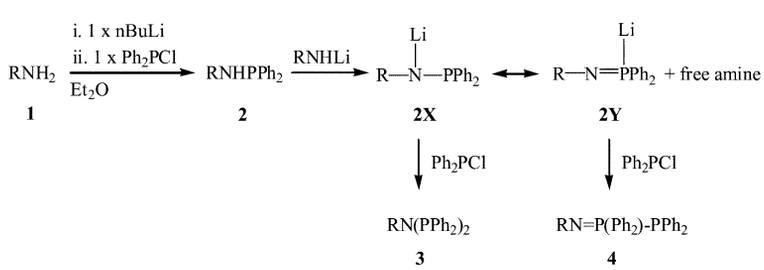


Scheme 1 Reactions of the anilines **1** with Bu^nLi and Ph_2PCl (1:1:1) in diethyl ether.

Replacing the *ortho*-nitrile substituent by a phenyl group in the starting material, *viz*. $C_6H_4(o\text{-}C_6H_5)NH_2$ **1d**, results in the formation of almost exclusively the aminophosphine $C_6H_4(o\text{-}C_6H_5)NHPPh_2$ **2d**, only about 5% of $C_6H_4(o\text{-}C_6H_5)N{=}PPh_2{-}PPh_2$ **4d** is found and the formation of the diphosphinoamine $C_6H_4(o\text{-}C_6H_5)N(PPh_2)_2$ **3d** is not observed. Starting from the aniline **1e** $C_6F_5NH_2$, the iminobiphosphine $C_6F_5N{=}PPh_2{-}PPh_2$ **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 $C_6H_4(o\text{-}CF_3)NH_2$ **1f** the result is similar as from the reaction from **1a**, a high yield of the aminophosphine $C_6H_4(o\text{-}CF_3)NHPPh_2$ **2f** was found, whereas $C_6H_4(o\text{-}CF_3)N{=}PPh_2{-}PPh_2$ **4f** was formed in relatively low yield and the formation of $C_6H_4(o\text{-}CF_3)N(PPh_2)_2$ **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 Ph_2PCl will give the P–N–P product, whereas reaction of the **2Y**-type anion with Ph_2PCl will give the N=P–P product. Based on this hypothesis the ratio of **2X** and **2Y** is clearly dependant 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, $C_6F_5NH_2$ 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 Bu^nLi 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 C_6F_5 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



Scheme 2 Proposed intermediates leading to the formation of **3** and **4**.

Table 2 Relative ratio of the products from the reaction of the anilines **1(a–f)** with Ph_2PCl and Et_3N in 1 : 1 : 1 ratio in dichloromethane based on ^{31}P NMR spectroscopy

1: RNH_2	**2**: $RNHPPh_2$ (%)	**3**: $RN(PPh_2)_2$ (%)	**4**: $RN{=}PPh_2{-}PPh_2$ (%)
1a: $C_6H_4(o\text{-}CN)NH_2$	**2a**: ~5	**3a**: 10	**4a**: 85
1b: $C_6H_4(p\text{-}CN)NH_2$	**2b**: 65	**3b**: 35	**4b**: 0
1c: $C_6H_4(m\text{-}CN)NH_2$	**2e**: 90	**3c**: 10	**4c**: 0
1d: $C_6H_4(o\text{-}Ph)NH_2$	**2d**: 100	**3d**: 0	**4d**: 0
1e: $C_6F_5NH_2$	**2e**: 0	**3e**: 25	**4e**: 75
1f: $C_6H_4(o\text{-}CF_3)NH_2$	**2f**: 0	**3f**: 0	**4f**: 100

could be isolated with CH_2Cl_2, 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 Ph_2PCl in the presence of two equivalents of triethylamine (see below).

Reaction of $C_6H_4(o\text{-}C_6H_5)NH_2$ 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 $C_6H_4(o\text{-}OCH_3)NH_2$ reacts with Ph_2PCl in the presence of triethylamine to give $C_6H_4(o\text{-}OCH_3)NHPPh_2$ [14] or $C_6H_4(o\text{-}OCH_3)N(PPh_2)_2$ [17] 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 ^{31}P 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 Ph_2PCl 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 ^1J(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** : Ph_2PCl : NEt_3 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 anilines **1(a–f)** with Ph_2PCl and Et_3N in 1 : 2 : 2 ratio in dichloromethane based on ^{31}P NMR spectroscopy

1: RNH_2	**3**: $RN(PPh_2)_2$ (%)	**4**: $RN{=}PPh_2{-}PPh_2$ (%)
1a: $C_6H_4(o\text{-}CN)NH_2$	**3a**: ~5	**4a**: 95
1b: $C_6H_4(p\text{-}CN)NH_2$	**3b**: 98	**4b**: ~2
1c: $C_6H_4(m\text{-}CN)NH_2$	**3c**: 100	**4c**: 0
1d: $C_6H_4(o\text{-}Ph)NH_2$	**3d**: 98	**4d**: ~2
1e: $C_6F_5NH_2$	**3e**: 20	**4e**: 80
1f: $C_6H_4(o\text{-}CF_3)NH_2$	**3f**: 0	**4f**: 100

Reaction of anilines 1(a–f) with Ph_2PCl in the presence of Et_3N in a 1 : 1 : 1 ratio in dichloromethane

In dichloromethane the reaction between the anilines **1(a–f)** and Ph_2PCl 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 ^{31}P NMR spectroscopy and the results are summarized in Table 2.

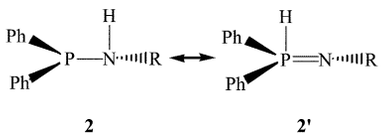
Reaction of **1a** with one equivalent of Ph_2PCl in the presence of one equivalent of triethylamine affords the iminophosphine **4a** as the main product, although both **2a** and **3a** are also formed in low yield. Interestingly, with **1b** and **1c**, formation of iminobiphosphines **4b** and **4c** 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 Ph_2PCl and Et_3N in dichloromethane (see below).

Reaction of anilines 1(a–f) with Ph_2PCl in the presence of Et_3N 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 Ph_2PCl 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 Ph_2PCl 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 Ph_2PCl gives the diphosphinoamine **3**, whereas reaction of **2′** with Ph_2PCl affords the iminobiphosphine **4**.



2 **2'**

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 Ph_2PCl 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 electron-withdrawing 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 CH_2Cl_2 solvate. Crystals of **4e** were obtained by cooling a diethyl ether solution at −22 °C. In addition, the structure of the known diphosphinoamine $PhN(PPh_2)_2$,[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 $PhN(PPh_2)_2$ **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 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.

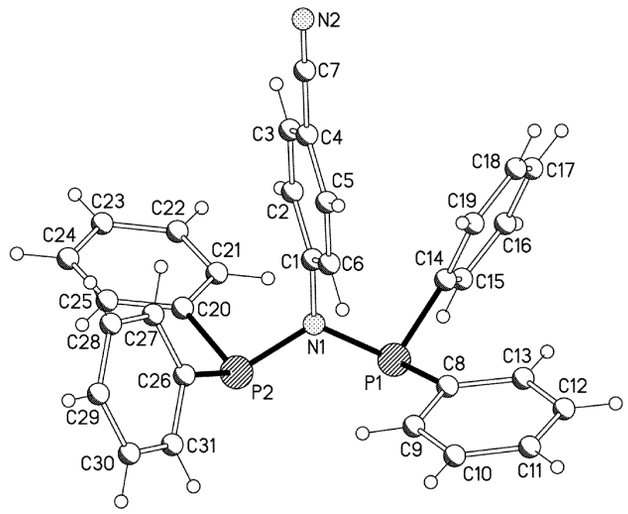


Fig. 1 Molecular structure of **3b** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–N1, 1.732(3); P2–N1, 1.723(3), N1–C1, 1.434(4); N2–C7, 1.151(5); P2–N1–P1, 114.49(14).

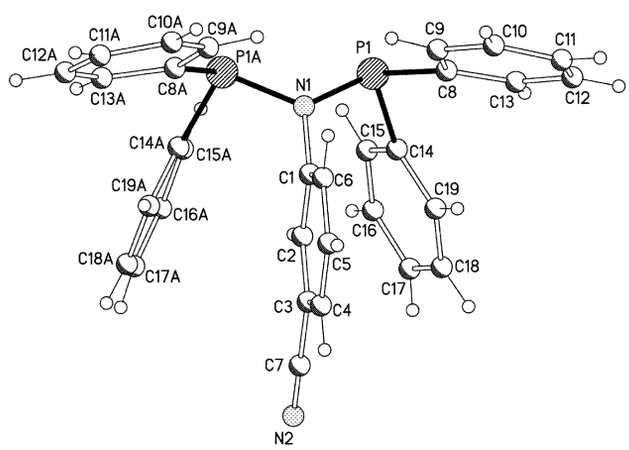


Fig. 2 Molecular structure of **3c** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–N1, 1.746(2); N1–P1A, 1.746(2), N1–C1, 1.449(6); N2–C7, 1.138(8); P1–N1–P1A, 112.7(2). Letter A indicates the following symmetry transformation: x, $-y - 1/2$, z.

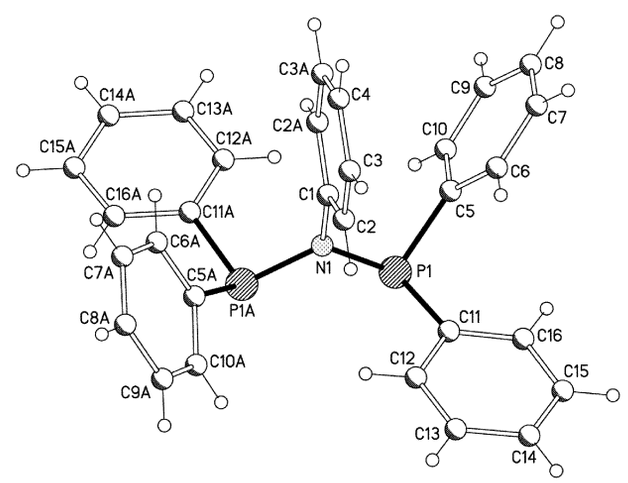


Fig. 3 Molecular structure of **5** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–N1, 1.7315(15); N1–P1A, 1.7315(15); N1–C1, 1.455(4); P1–N1–P1A, 113.37(14). Letter A indicates the following symmetry transformation: $-x$, y, $-z + 1/2$.

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 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 Ph_2P 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 C_6F_5 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**.

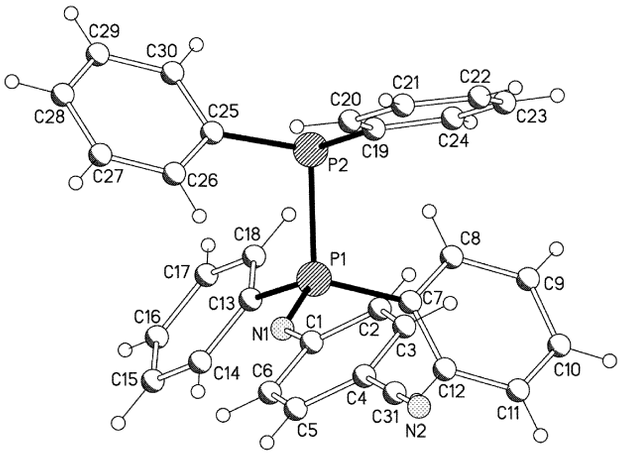


Fig. 4 Molecular structure of **4b** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–P2, 2.2451(16); P1–N1, 1.572(5); N1–C1, 1.382(7); N2–C31, 1.140(7); C4–C31, 1.446(8); N1–P1–C7, 115.1(3); N1–P1–P2, 121.68(17); C1–N1–P1, 131.3(4).

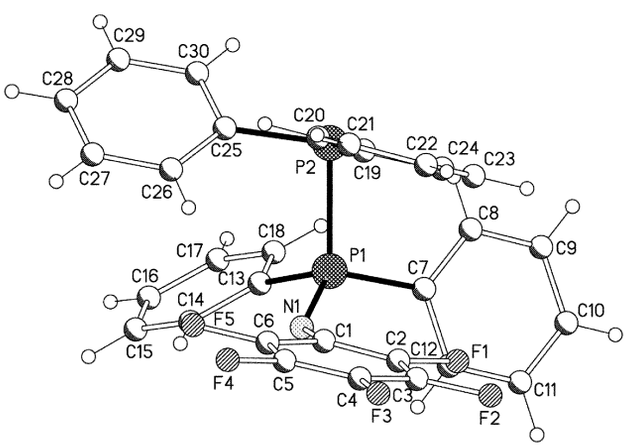


Fig. 5 Molecular structure of **4e** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–P2, 2.2379(16); P1–N1, 1.571(3); N1–C1, 1.371(4); N1–P1–C7, 118.17(14); N1–P1–P2, 117.82(11); C1–N1–P1, 135.2(2).

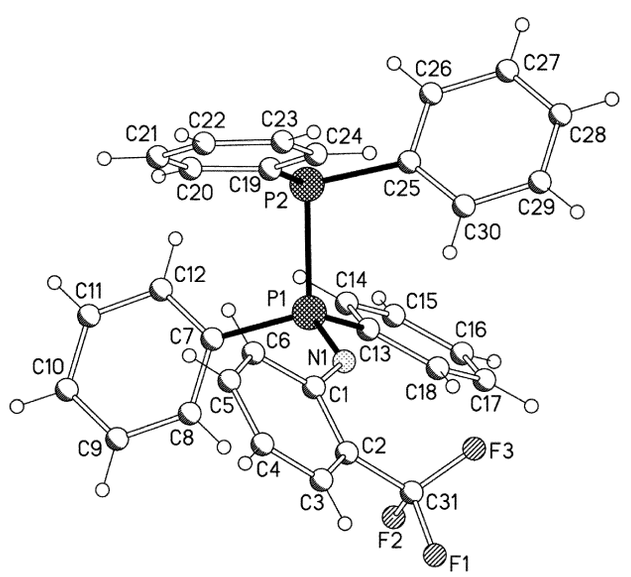


Fig. 6 Molecular structure of **4f** in the solid-state. Key bond lengths (Å) and angles (°) include: P1–P2, 2.2498(18); P1–N1, 1.578(3); N1–C1, 1.385(5); N1–P1–C7, 113.98(17); N1–P1–P2, 122.49(14); C1–N1–P1, 132.2(3).

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)**, Bu^nLi, Ph_2PCl and Et_3N 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 $SiMe_4$ for ^1H and 85% H_3PO_4 for ^{31}P as external standards. For the ^{31}P NMR spectra of the reaction mixture, a C_6D_6 capillary was used as a lock. With the reaction of lithiated anilines with Ph_2PCl, the ^{31}P 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, $CDCl_3$ 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 μL 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 Bu^nLi and Ph_2PCl, synthesis of 2a and 4a

The reagent Bu^nLi (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 Ph_2PCl (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 Ph_2PCl). For spectroscopic chracterisation of **1a** and **4a** see ref. 11.

Reaction of aniline $C_6H_4(p\text{-}CN)NH_2$ 1b with Bu^nLi and Ph_2PCl, synthesis of 2b and 4b

The reagent Bu^nLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was slowly added to a solution of $C_6H_4(p\text{-}CN)NH_2$ **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 Ph_2PCl (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 filtrates **2b** was obtained on repeated recrystallisation in diethyl ether (three times). Yield: 0.60 g, 10%. Mp 142 °C. ^{1}H NMR: δ 8.00–6.90 (m, 14H, aromatic H), 4.90 (br signal, 1H, NH), ppm. ^{31}P NMR: δ 29.30 (s) ppm. ESI-MS$^+$: *m*/*z* 303 $[M + H]^+$. Anal. Calc. for $C_{19}H_{15}N_2P$: 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 × 30 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%. ^{1}H NMR: δ 8.05–6.85 (m, aromatic H) ppm; ^{31}P 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 $C_{31}H_{24}N_2P_2$: H 4.97, C 76.54, N 5.76. Found H 5.01, C 76.60, N 5.61%.

Reaction of aniline $C_6H_4(m\text{-}CN)NH_2$ 1c with Bu^nLi and Ph_2PCl, synthesis of 4c

The reagent Bu^nLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was slowly added to a solution of $C_6H_4(m\text{-}CN)NH_2$ **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 Ph_2PCl (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. ^{1}H NMR: δ 8.10–6.80 (m, aromatic H) ppm; ^{31}P NMR: δ 7.50 (d), −15.00 (d, $^1J_{P-P}$ = 263.0 Hz) ppm. ESI-MS$^+$: *m*/*z* 487 $[M + H]^+$. Anal. Calc. for $C_{31}H_{24}N_2P_2$: H 4.97, C 76.54, N 5.76. Found: H 5.03, C 76.62, N 5.55%.

Reaction of aniline $C_6H_4(o\text{-}C_6H_5)NH_2$ 1d with Bu^nLi and Ph_2PCl, synthesis of 2d and 4d

The reagent Bu^nLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was slowly added to a solution of $C_6H_4(o\text{-}C_6H_5)NH_2$ **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 Ph_2PCl (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 diethyl ether filtrates were collected and the solvent was removed in vacuum. The resulting oil was washed with cold diethyl ether (3 × 5 ml) at −22 °C to give the product of **2d** as an off-white oil. Yield: 5.30 g, 75%. ^{1}H NMR: δ 5.80 (br signal, 1H, NH), 8.00–7.40 (m, aromatic H) ppm. ^{31}P NMR: δ 30.5(s) ppm. ESI-MS$^+$: *m*/*z* 354 $[M + H]^+$. Anal. Calc. for $C_{24}H_{20}NP$: 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 × 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 × 5 ml) gave the product **4d**. Yield: 0.10 g, 2%. Mp 148 °C. ^{1}H NMR: δ 8.15–7.40 (m, aromatic H) ppm; ^{31}P NMR: δ 1.60 (d), −14.00 (d, $^1J_{P-P}$ = 261.0) 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 5.45, C 80.51, N 2.59%.

Reaction of aniline $C_6F_5NH_2$ 1e with Bu^nLi and Ph_2PCl, synthesis of 4e

The reagent Bu^nLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was slowly added to a solution of $C_6F_5NH_2$ **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 Ph_2PCl (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 ¼ 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. ^{1}H NMR: δ 8.25–7.15 (m, aromatic H) ppm; ^{31}P NMR: δ 10.05 (d), −14.50 (d, $^1J_{P-P}$ = 266.5 Hz) ppm. ESI-MS$^+$: *m*/*z* 552 $[M + H]^+$. Anal. Calc. for $C_{30}H_{20}F_5NP_2$: H 3.66, C 65.34, N 2.54. Found H 3.68, C 65.42, N 2.53%.

Reaction of aniline $C_6H_4(o\text{-}CF_3)NH_2$ 1f with Bu^nLi and Ph_2PCl, synthesis of 4f

The reagent Bu^nLi (12.5 ml, 1.6 M in hexane, 20.0 mmol) was slowly added to a solution of $C_6H_4(o\text{-}CF_3)NH_2$ **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 Ph_2PCl (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 × 10 ml). The remaining solid was washed with dichloromethane (3 × 30 ml). The dichloromethane filtrates were collected and solvent was removed in vacuum The solid was washed again with diethyl ether (3 × 10 ml) and then recrystallised from dichloromethane and diethyl ether to give the product **4f**. Yield: 2.38 g, 45%. Mp 126 °C. ^{1}H NMR: δ 8.05–6.65 (m, aromatic H) ppm; ^{31}P NMR: δ 5.35 (d), −17.20 (d, $^1J_{P-P}$ = 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_2PCl/Et_3N in diethyl ether, synthesis of 4d

To a solution of $C_6H_4(o\text{-}C_6H_5)NH_2$ **1d** (1.69 g, 10.0 mmol) and triethylamine (1.02 g, 10.0 mmol) in 50 ml diethyl ether Ph_2PCl (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 Ph_2PCl).

Under the same condition, the 1 : 1 : 1 reaction of **1a**, **1b**, **1c**, **1e** and **1f** with Ph_2PCl/Et_3N in diethyl ether is too slow and was not investigated further.

The 1 : 2 : 2 reaction of aniline 1d with Ph_2PCl/Et_3N in diethyl ether, synthesis of 3d and 4d

To a solution of $C_6H_4(o\text{-}C_6H_5)NH_2$ **1d** (1.69 g, 10.0 mmol) and triethylamine (2.03 g, 20.0 mmol) in 50 ml diethyl ether Ph_2PCl (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. ^{1}H NMR: δ 8.35–7.35 (m, aromatic H) ppm; ^{31}P 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_2PCl/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 Ph_2PCl (2.21 g,

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

	3b	**3c**	**4b**	**4e**	**4f**	**5**
Chemical formula	$C_{31}H_{24}N_2P_2$	$C_{31}H_{24}N_2P_2$	$C_{31}H_{24}N_2P_2$	$C_{30}H_{20}F_5NP_2$	$C_{32}H_{26}Cl_2F_3NP_2$	$C_{30}H_{25}NP_2$
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*	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	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)
α/°	90	90	90	108.49(4)	82.05(4)	90
β/°	91.048(19)	90	112.375(15)	95.79(4)	74.46(3)	100.092(7)
γ/°	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)
Z	4	4	4	2	2	4
D_c/g 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 [$I > 2\sigma(I)$]	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} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. ^{b} GoF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where n is the number of data and p is the number 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 ^{31}P NMR spectroscopy which shows that the signals of Ph_2PCl 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 Ph_2PCl/Et_3N in dichloromethane gave mixtures and only investigated by ^{31}P NMR spectra. Attempts to isolate a pure product were not made.

The 1 : 2 : 2 reaction of anilines 1b, 1c and 1d with Ph_2PCl/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), Ph_2PCl (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. ^{1}H NMR: δ 8.0–6.6 (m, aromatic H) ppm; ^{31}P NMR: δ 68.50 (s) ppm ESI-MS$^+$: *m*/*z* 487 [M + H]$^+$. Anal. Calc. for $C_{31}H_{24}N_2P_2$: 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 Ph_2PCl (4.42 g, 20.0 mmol) in 50 ml dichloromethane yielded **3c**. Yield: 4.81 g, 99%. Mp 99 °C. ^{1}H NMR: δ 8.05–6.60 (m, aromatic H) ppm; ^{31}P NMR: δ 69.50 (s) ppm ESI-MS$^+$: *m*/*z* 487 [M + H]$^+$. Anal. Calc. for $C_{31}H_{24}N_2P_2$: 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 Ph_2PCl (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 Ph_2PCl/Et_3N 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 Ph_2PCl (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 ¼ 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 Ph_2PCl/Et_3N 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), Ph_2PCl (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 Ph_2PCl (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 correction[26] 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 CH_2Cl_2 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.

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