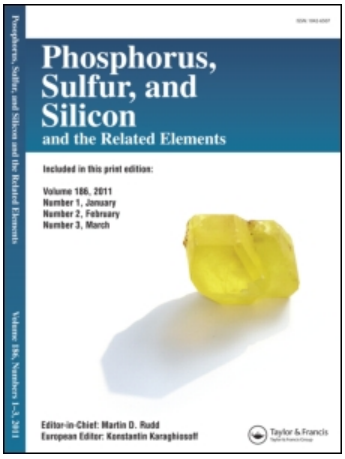

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POLYMERIZABLE DERIVATIVES OF TRIPHENYLPHOSPHINE. ACYLATION OF TRIARYLPHOSPHINES BEARING ALCOHOL OR AMINE SUBSTITUENTS WITH ACRYLOYLCHLORIDE AND METHACRYLOYLCHLORIDE

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POLYMERIZABLE DERIVATIVES OF TRIPHENYLPHOSPHINE. ACYLATION OF TRIARYLPHOSPHINES BEARING ALCOHOL OR AMINE SUBSTITUENTS WITH ACRYLOYLCHLORIDE AND METHACRYLOYLCHLORIDE

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Methods to prepare amino substituted triaryl-phosphines viz. *N*-methyl-2-(diphenylphoshino)benzylamine, *N*-*t*-butyl-2-(diphenylphosphino)benzylamine and α,*N*-dimethyl-4-(diphenylphosphino)benzylamine are presented. The acylation of amino and alcohol substituted triarylphosphines have been studied and the amides *N*-methacryloyl-*N*-methyl-2-(diphenylphophino)benzylamine, *N*-methacryloyl-2-(diphenylphosphino)aniline, *N*-methacryloyl-*N*-methyl-4-(diphenylphosphino)benzylamine, *N*-methyl-*N*-propionyl-4-(diphenylphosphino)benzylamine, *N*-methyl-*N*-propionyl-2-(diphenylphosphino)benzylamine and *N*-acryloyl-*N*-methyl-4-(diphenylphosphino)benzylamine and the ester 2-(diphenylphosphino)benzyl methacrylate have been prepared.

Key words: Phosphine; monomer; acylation; acryloylchloride; methacryloylchloride polymer-bound.

INTRODUCTION

High activity, high selectivity, mild reaction conditions, relative ease of modification are beneficial characteristics often ascribed to homogenous metal complex catalysts.[1] Their applicability in chemical processes are, however, limited by the difficulty of separating such catalysts from the reactants/products. To solve separation problems, the idea of immobilizing metal complexes on an insoluble support was first presented in 1969[2] and for some years this area of research attained a relatively large interest.[3,4] Research in this field has, however, slowed down considerably, mainly because the problems relating to the stability of these hybrid catalysts *i.e.* metal leakage and metal particle formation, have been hard to overcome.[5]

Because of the commercial availability and the relative ease by which crosslinked polystyrene can be functionalized by a desired ligand site this support material has been by far the most studied one.[3] Non-crosslinked polymers are alternative support materials[6,7] but due to the solubility of such materials in organic solvents far less investigated. From purely coordination chemistry considerations soluble polymeric support materials can, however, provide certain advantages: A close resemblance to the dynamic metal-ligand interplay operating in homogeneous metal complex catalysts can most likely be achieved and thereby a more stable catalyst system. Moreover, by virtue of their solubility, such systems are more easily investigated by methods normally applied to complexes in solution. Indeed recent reports[8,9] on the use of ligand functionalized soluble ethylene oligomers provide evidence for a

close resemblance between catalysts bound to this support and their homogeneous counterparts with respect to both catalytic activity and selectivity.

Ligand functionalized linear polymers can be prepared[3] by chemical modification of preformed polymers or alternatively by polymerisation of ligand functionalized monomers provided such can be prepared. Phosphines are the predominant type of ligand in low valent metal complex catalysts[10] but relatively few monomers containing the phosphine moiety have been described.[11–14] As a part of a project aimed at the development of new composite polymer catalyst supports[15,16] in which the advantages of linear polymers i.e. high ligand mobility and flexibility are combined with the advantages of crosslinked polymers *i.e.* mechanical rigidity and separability we have studied the preparation of novel phosphine monomers.

With the particular application in mind the target substances have been triaryl phosphines bearing alcohol or sec-amine substituents on one of the aromatic rings and the subsequent conversion of these to polymerizable molecules via acylation with acryloyl or methacryloyl chloride. Herein the syntheses of various phosphines of the above mentioned type as well as acylated products derived from them are described.

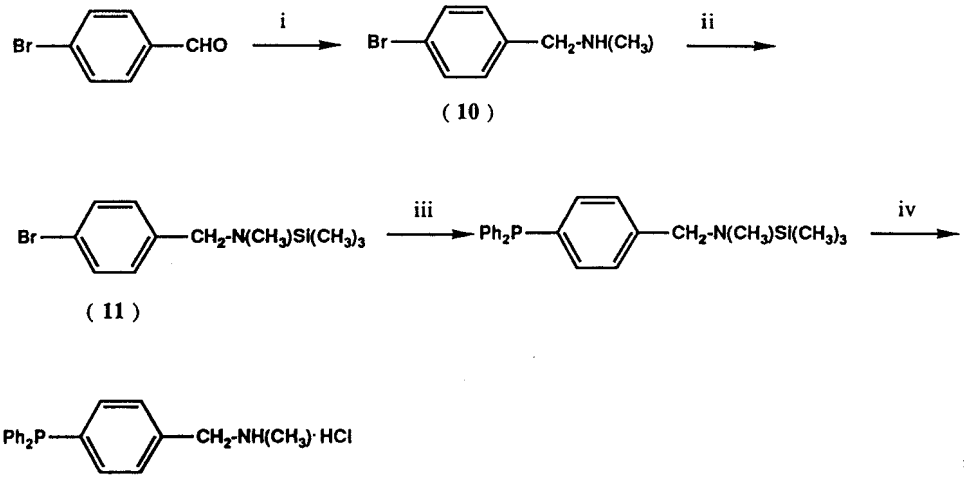
RESULTS AND DISCUSSION

As a consequence of the general interest[10] in functionalized triaryl-phosphines the synthetic methods to obtain substances of this kind are by now well developed[17] and include: i) Friedel-Crafts reactions ii) nucleophilic displacement of aromatic halides or sulfonates by reaction with the diphenylphosphide anion iii) reactions of aryl-Grignard or aryl-lithium reagents with halophosphines iv) the palladium catalyzed coupling of aryl halides with trimethylstannyldiphenylphosphine or trimethylsilyldiphenylphosphine[18] or v) some more special reactions.[19,20] The type of functional group which these methods can tolerate limits their applicability. For the amino substituted phosphines aimed at in the present study the aryl-Grignard or aryl-lithium route was considered the most feasible one provided that the acidic NH hydrogen atoms could be masked by a suitable protective group.[21]

Syntheses of Triphenylphosphines with sec-amine Substituents

The strategy of *N*-protection is illustrated by the synthesis of the methyl amino substituted phosphine (**12**) as outlined in Scheme I. Starting from easily accessible 4-bromobenzaldehyde the amine (**10**) was prepared straightforwardly via condensation with methylamine and subsequent reduction with $NaBH_4$. The amine (**10**) has been synthesized earlier in lower yield using a different method.[22] Further reaction of (**10**) with excess Me_3SiCl using Et_3N as base afforded the silylated amine (**11**). This compound is very moisture sensitive and was therefore not characterized but used in the following step as obtained after distillation. The product of lithiation obtained after reaction with Bu^nLi can be used as a synthon for coupling with many types of reagents and reaction with chlorodiphenylphosphine gave the hydrochloride of the amine (**12**) after work-up under acidic conditions.

This method of preparation works well for 4-bromobenzaldehyde giving a high isolated yield of the amine (**12**). Using the same procedure in the case of 2-bro-

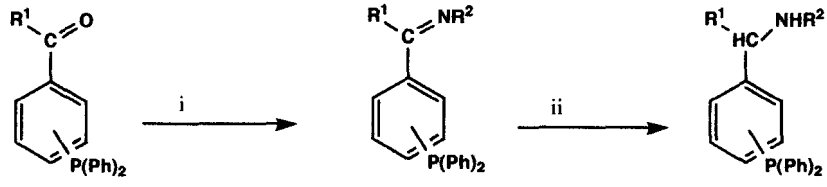


i) a: CH_3 NH_2, thf/MeOH; b: $NaBH_4$ ii) $ClSiMe_3$, NEt_3 in diethylether iii) a: Bu^nLi; b: $ClPPh_2$ in diethylether iv) HCl/H_2O.

Scheme I

mobenzaldehyde gave only products derived from Li—$SiMe_3$ migrations in the lithio-synthon, as evident by combined GLC-MS analysis of the crude reaction mixture. This precludes the synthetic applicability of $SiMe_3$ as a protective group in this case.

In the method given in Scheme I the amino group is introduced before the phosphino group and this has advantages in that extensive chemical transformations on phosphines, with risk of phosphine oxidation, is avoided. The reverse order of reaction *i.e.* to prepare the formyl or acetyl substituted phosphine[23–25] in a first step with subsequent transformations of the carbonyl-group to the amine[26] is, however, a more established method and the syntheses of compounds (**7, 8, 9**) were carried out as given in Scheme II. Thus 2-(diphenylphosphino)benzaldehyd (**1**) was reacted with methyl amine or *t*-butyl amine to give the corresponding imines. The methyl-imine (**6**) was isolated before reduction with $NaBH_4$ giving the phosphinoamine (**7**) while in the case of the *t*-butyl imine the reduction was carried out *in situ* giving the phosphinoamine (**8**). Compared to a recently published method[27] to prepare the phosphinoamine (**7**) we find the method given here more convenient in that it involves fewer reaction steps. The condensation reaction with both amines investigated proceeds smoothly but as methylamine is a gas at room-temperature special experimental procedures are necessary in this case. The condensation of methylamine with 4-(diphenylphosphino) acetophenone (**2**) is a less facile reaction compared to the phosphine-aldehyd (**1**); a 50/50 mixture of the imine and the unreacted carbonyl compound was initially obtained in this case but after careful removal of water from that mixture and on repeated reaction with methylamine an essentially quantitative GC-yield of the imine was obtained. As above this was reduced *in situ* to give the phosphine-amine (**9**).



1: R^1 = H, 2-isomer
2: R^1 = Me, 4-isomer
6: R^1 = H, R^2 = Me, 2-isomer
7: R^1 = H, R^2 = Me, 2-isomer
8: R^1 = H, R^2 = Bu^t, 2-isomer
9: R^1, R^2 = Me, 4-isomer

i) R^2-NH_2, thf/MeOH; ii) $NaBH_4$, thf/MeOH.

Scheme II

Attempts to Prepare Primary Amines

To our knowledge, the only known triarylphosphine bearing a primary amine substituent is (2-aminophenyl) diphenylphosphine which has been prepared by some rather special reactions[19,20] not applicable to other amines than the 2-isomer of aniline. Although not essential for the purpose of obtaining phosphines which can be acylated with acryl or methacryloyl chloride to give polymerizable phosphines some methods with prospects to be more generally applicable in the synthesis of primary amine substituted tri-arylphosphines were investigated.

The reduction of aldoximes is a possible entry into primary amines[28] and for that purpose the aldoxime (**5**) was prepared by condensation of the aldehyde (**1**) with hydroxylaminehydrochloride. Once the optimal reaction conditions were found this reaction gave the aldoxime in high isolated yield but the subsequent reduction to the corresponding amine has not been possible to achieve. Reduction using Raney-Nickel[29] or catalytic hydrogenations[30] with Pd/C as catalysts resulted in complete recovery of the starting aldoxime. One possible explanation for this lack of reactivity in these reactions is the phosphine-group present in the molecule; a poisoning effect by absorption on the metal surface via the phosphine-group of the reacting molecule is not unlikely. Chemical reductions using reducing agents as e.g. aluminumhydrides,[31] borohydrides[32] or Na/ethanol[33] were also unsuccessful because of extensive carbon-phosphorus bond cleavage in these cases. Primary amines can be protected as their 2,5 dimethyl pyrrole derivatives giving synthons which are compatible with Grignard or lithium reagents.[34,35] Following this line 4-bromoaniline was reacted with hexane-2,5-dione to give the corresponding dimethylpyrrole derivative. Further reaction with Bu^{n}Li and chlorodiphenylphosphine gave 1-(4-(diphenylphosphino) phenyl-2,5 dimethylpyrrol in high yield as indicated by GC-MS of the crude reaction mixture. All attempts to remove the protective group by extensive variations of the literature procedures were, however, unsuccessful giving intractable tary residues. A likely cause of this failure is the nucleophilicity of the phosphine group which effectively can compete with the deprotecting agent, hydroxylamine,[36] in the attack on the 2 and 5 carbon atoms of the pyrrole ring. This line of syntheses was therefore not persued further.

Primary amines can also be protected as their stabase (cyclic disilazane) adducts

by reaction with 1,1,4,4-tetramethyl-1,4-dichlorodisilethylene, also in this case giving synthons compatible with Grignard and lithium reagents.[37,38] This protective group is more easily removed than the 2,5 dimethylpyrrol group and hence should not give problems in the cleavage step. Reaction of the stabase protected 4-bromobenzylamine with Bu^{n}Li and chlorodiphenylphosphine did, however, not give the expected product. Instead a rather complex mixture of other products was observed. In separate NMR tube experiments chlorodiphenylphosphine was therefore reacted at room temperature with the stabase protected 4-bromo benzylamine giving three separate ^{31}P resonances at δ = 81.9, 61.3 and 43.2 ppm.

These resonance frequencies correspond to that of chlorodiphenylphosphine δ = 82.0 ppm and to those observed[39] for the phosphine $(C_6H_5)_2P—N(Et)_2$ δ = 61.4 ppm and the phosphonium salt $[(C_6H_5)_3P^+—N(Et)_2]Br^-$ δ = 46.4 ppm. Thus the observed ^{31}P resonances indicate a preponderance for chlorodiphenylphosphine to attack at the nitrogen atom of the protective group to give ring-opening and formation of a P—N and a Si—Cl bonds. These problems observed for the stabase protected amine preclude the use of this protective group in phosphine synthesis. Until now we have not found any simple high yield method applicable to the syntheses of triarylphosphines bearing a primary amine substituent, but efforts in this direction are continuing.

Reaction of Amine and Alcohol Functionalized Triarylphosphines with Acyl Halides

Our approach[15,16] to obtain polymer-bound phosphines are based on the preparation of phosphine monomers from the alcohol and amine functionalized molecules (**3, 4, 7, 9, 12**) described above via acylation with easily accessible vinylic acyl halides viz. acryloylchloride, methacryloylchloride. Reference compounds resembling a segment of the polymer chain from such monomers are also of value in order to make a just comparison of the catalytic activity of homogeneous and polymer-bound metal complexes and acylations with propionylchloride have been applied for that purpose.

The acylation of the amino-phosphine (**3**) with benzoylchloride[40,41] and acetylchloride[42] have been described as has the reaction of the bidentate bis[2-(diphenylphosphino)ethyl] amine with a wide range of acylating agents.[43,44] Using similar procedures in the reaction of the amines (**7**) and (**12**) with propionylchloride gave the amides (**17**) and (**18**) straightforwardly as white crystals. No competing side reactions as e.g. acylation at phosphorus were observed despite the presence of the phosphine group in the reacting molecules.

The tendency of vinylic acylhalides like e.g. acryloylchloride or methacryloylchloride to undergo anionic polymerisations initiated by strong nucleophiles like tertiary phosphines[45–47] complicates the acylation of the functionalized phosphines using these acylating agents. The polymerisation reaction is in the case of phosphine initiators dependent on an initial attack of the nucleophilic phosphorus atom on the electrophilic terminal carbon atom of the vinylic compound leading to the formation of a zwitterion viz. $R_3P^+—CH—CH^-—C(O)—X$ in which the negatively charged carbon atom can attack yet another monomer to give chain-growth.

Electron donating substituents, X, on the carbonyl carbon atom reduces the electron with-drawing tendency of the carbonyl group thus making the terminal

vinylic carbon atom less electrophilic. The propensity for different acrylic derivatives to undergo anionic polymerization can therefore be arranged as follows: X = Cl > OR > NH(Ar) > NR_2. Moreover, by virtue of the electron donating properties of the methyl group, methacrylic derivatives are less reactive in anionic polymerization than the corresponding acrylic derivatives.

Initial attempts to acylate the alcoholphosphine (**4**) with acryloylchloride, varying reaction conditions extensively, gave only white insoluble products, not fully characterized but supposed to be the outcome of a polymerization of the vinylic compound. In contrast to the extensive polymerization observed in the reaction of the alcoholphosphine (**4**) reports describing the successful acylation of the bidentate bis[2-(diphenylphosphino)ethyl] amine[44] and the chiral phosphine (2S,4S)-(−)-diphenylphosphino-2-diphenylphosphinomethyl-pyrrolidine[13] using acryloylchloride have been published. This indicates that the nucleophilicity of the substituent on the phosphine is of importance and that kinetic effects are involved. In the reacting acryloylchloride there are two electrophilic centres viz. the carbonyl carbon atom and the terminal vinylic carbon atom. Likewise in the reacting phosphine there are two nucleophilic centres viz. the phosphorus atom and the alcohol or the amine substituent. As observed in the preparation of the propionyl derivatives discussed above the attack of phosphorus at the carbonyl carbon can be neglected and the alcohol and amine substituents are not prone to induce anionic polymerization.[48] This leaves phosphorus attack at the terminal carbon atom leading to polymerization or alcohol/amine attack at the carbonyl carbon atom leading to the desired substitution as two competing reaction paths. For good nucleophiles like in the case with bis[2-(diphenylphosphino)ethyl] amine the product from nucleophilic substitution will be the kinetic product and once formed the amide is substantially more stable towards anionic polymerization than the corresponding acyl halide. Substituents of lower nucleophilicity like the alcohol group of phosphine (**4**) will react slower in the acylation reaction and at the same time will the ester stabilize the double bond to a lesser extent. Thus phosphines with substituents of low nucleophilicity tend to give mainly polymers in reactions with acryloylchloride.

The importance of the nature of the nucleophilic substituents is clearly born out by comparing the acylation of the alcoholphosphine (**4**) and the aminophosphine (**12**); the amide (**19**) was obtained in high yield from the amine (**12**) and acryloyl chloride while the alcohol (**4**) gave only polymers under similar reaction conditions. Because of the tendency of anionic polymerization we have concentrated on the less reactive methacryloyl chloride in the preparation of phosphine monomers. Using this acyl halide the ester (**16**) and the amides (**13, 14** and **15**) were obtained in good (**13, 14** and **15**) to fair (**16**) yields by standard acylation procedures.

In this context it is interesting to note that while the amides (**13, 14** and **15**) are stable in solution showing no tendency for spontaneous polymerization the ester (**16**) slowly polymerizes in solution. This demonstrates the difference in stability toward anionic polymerization due to better electron donation of the amide group compared to the ester group. This is also reflected in the position of the C=O stretching vibration of the different monomers at 1710 cm^{-1} (**16**) and 1620 cm^{-1} (**15**) and in the chemical shifts of the highest olefinic protons at 5.9 ppm (**16**) and 5.2 ppm (**15**).

Concerning the ^1H NMR observed for the acylated compound some comments might be of value. In the case of the amides hindered rotation around the amide

bond give rise to two rotamers in solution which are observed as separate set of signals. The ester (**16**) also gives a complicated ^1H spectrum at room temperature which simplifies at higher temperatures. Full account for this observation can not be given yet but most likely this is a result of hindered inversion at phosphorus due to the substituent in the 2-position of one of the phenyls at phosphorus.

EXPERIMENTAL

Chemicals and general procedures. $NH_2OH \cdot HCl$, $NaBH_4$, CH_3NH_2 (anhydrous), Bu^{n}Li 1.6M (hexane), acryloylchloride, methacryloylchloride, propionylchloride and 4-bromobenzaldehyde were from commercial sources and used as received. Et_3N and *t*-$BuNH_2$ were distilled over KOH under argon before use, chlorodiphenylphosphine was distilled at reduced pressure and chlorotrimethylsilane was distilled over calcium hydride under argon. All distilled substances were kept in Schlenk-tubes under argon until use.

2-(diphenylphosphino) benzaldehyde (**1**),[24] 4-(diphenylphosphino) acetophenone (**2**)[25] 2-(diphenylphosphino) aniline (**3**)[19] and 2-(diphenylphosphino) benzylalcohol (**4**)[49] were prepared as described earlier.

Solvents were dried using activated 3Å moleculare sieves and kept under argon until use. All reactions were routinely performed with magnetic stirring under an atmosphere of dried argon in glassware dried at 130°C. Gas-chromatographic analyses were performed on a 10 ft BP1 capillary column using a Varian 3300 gas-chromatograph equipped with a Varian 4290 electronic integrator. NMR spectra were recorded on a Varian XL 300 spectrometer in $CDCl_3$ solution, ^1H at 300 MHz and ^{31}P at 121 MHz. Positive ^{31}P shifts are taken as ppm downfield of 85% H_3PO_4 and ^1H shifts are given relative to Me_4Si (δ = 0 ppm). IR spectra were recorded on a Nicolet 20SXC FTIR spectrometer as Nujol mulls between CsI plates or as CsI pellets. Elemental analyses were performed at Mikrokemi AB, Uppsala, Sweden or at Analytische Laboratorium, Gummersbach, Germany.

2-(diphenylphosphino) benzaldoxime (**5**). A deoxygenated solution of hydroxylamine hydrochloride (1.0 g, 14.4 mmol) and $NaHCO_3$ (0.08 g, 0.9 mmol) in a 1/1 mixture of ethanol/water (30 cm^3) was added to a suspension of the aldehyd **1** (1.1 g, 3, 8 mmol) in ethanol (70 cm^3). The reaction is conveniently monitored by the disappearance of the yellow colour of the aldehyde. Reaction for two hours at room-temperature, cooling to 0°C and addition of water (100 cm^3) afforded 2-(diphenylphosphino) benzaldoxime (**5**) as white crystals. The crystals were collected, washed with ethanol/water (1/1) and finally dried in vacuo at 50°C for four hours. Yield 1.0 g, 86%

Anal. Calcd. for $C_{19}H_{16}NOP$: 74.4% C, 5.3% H, 4.6% N, 10.1% P.
Found: 75.0% C, 5.6% H, 4.6% N, 9.8% P.

m.p. (°C): 162–165
^1H NMR δ: 0.9 (1 H, s, N—O**H**), 7.8–6.9 (14 H, m, Ar—**H**), 8.83 (1 H, d, N=C**H**—).
^{31}P NMR δ: −13.78 (s), −13.82 (s).
IR cm^{-1}: 3246 (br) (O—H), 1635 (vw) (C=N)
Raman cm^{-1}: 1623 (s) (C=N)

N-methyl-2-(diphenylphosphino) benzylimine (**6**). A three-necked flask (1 l) equipped with a paraffin pressure relief valve and a gas inlet tube was charged with 2-(diphenylphosphino) benzaldehyde (**1**) (10.6 g, 36.5 mmol), methanol (200 cm^3) and thf (300 cm^3). After cooling to −20°C methylamine (3 g, 97 mmol) was bubbled into the solution. The temperature was raised to 0°C and the reaction was continued at that temperature while maintaining a slow stream of methylamine through the solution. The cooling bath was removed after one hour and as the temperature increased the colour of the solution gradually changed to finally reach a tint yellowish colour at 15°C. At that temperature the reaction was stopped and the product isolated by evaporation of the solvent at a bath temperature not exceeding 30°C. The white crystals were collected and washed with cold cyclohexane (2 × 50 cm^3). Isolated yield 10.4 g, 94% essentially pure product according to GLC. The product can be further purified by dissolving it in a minimum amount of boiling methanol followed by cooling to −30°C overnight in which case the product is isolated as colourless crystals.

Anal. Calcd. for $C_{20}H_{18}NP$: 79.2% C, 6.0% H, 4.6% N, 10.2% P.
Found: 79.1% C, 6.1% H, 4.7% N, 10.2% P.

m.p. (°C): 104–108
^1H NMR δ: 3.39 (3 H, d, N—C**H**$_3$), 6.9–8.0 (14 H, m, Ar—**H**), 8.95 (1 H, d, N=C**H**—).
^{31}P NMR δ: −13.79 (s), −13.84 (s).
IR cm^{-1}: 1640 (s) (C=N)

N-methyl-2-(diphenylphosphino) benzylamine (**7**). The imine (**2**) (10.2 g, 33.7 mmol) and methylamine (0.5 g, 16.1 mmol) were dissolved in a mixture of thf (100 cm^3) and methanol (100 cm^3). The mixture was stirred half an hour at room temperature, cooled to 0°C followed by addition of powdered $NaBH_4$ (1.38 g, 34.4 mmol). Stirring overnight and evaporation of the solvent afforded an oil to which diethylether (120 cm^3) and 5M HCl (25 cm^3) was added. The suspension was cooled to 0°C under continuous stirring and thereafter phase separated. The water phase containing the amine hydrochloride was washed with diethylether (2 × 50 cm^3) and the product amine taken up in diethylether by neutralizing the aqueous phase with Na_2CO_3 in small portions and extracting with diethylether (2 × 70 cm^3). The combined ether extract was washed with water (5 × 50 cm^3), brine (2 × 50 cm^3) and dried over Na_2SO_4. Filtration and solvent removal by evaporation afforded a colourless oil which was dried in vacuo. After cooling overnight at −30°C 9.8 g (95%) of white crystals were obtained.

Anal. Calcd. for $C_{20}H_{20}NP$: 78.7% C, 6.6% H, 4.6% N, 10.1% P.
Found: 78.6% C, 6.7% H, 4.6% N, 10.2% P.

m.p. (°C): 53–59
^{1}H NMR δ: 2.34 (3 H, s, N—**CH_3**), 3.92 (2 H, d, Ar—**CH_2**), 6.9–7.7 (14 H, m, Ar—**H**)
^{31}P NMR δ: −15.16 (s), −15.18 (s).
IR cm^{-1}: 3322 (w, br) (NH)
Raman cm^{-1}: 3320 (w)(NH)

N-t-butyl-2-(diphenylphosphino) benzylamine (**8**). *t*-butylamine (18.8 g, 250 mmol) was added to a solution of the aldehyde (**1**) (10.1 g, 34,8 mmol) in thf/methanol (1/1) (400 cm^3) held at 0°C. The reaction was continued for half an hour at 0°C and three hours at room temperature before the mixture was cooled to 0°C and $NaBH_4$ (1.8 g, 47.6 mmol) added. Reaction overnight and work-up as described for the methylamin (**7**) afforded the title compound as a pale yellow oil (10.3 g, 85%).

For elemental analysis purpose part of the oil was dissolved in diethylether and treated with HCl gas to afford the hydrochloride of the amin as white crystals.

Anal. Calcd. for $C_{23}H_{27}$ ClNP: 72.0% C, 7.1% H, 3.6% N, 8.1% P.
Found: 71.1% C, 7.1% H, 3.4% N, 8.0% P.

m.p. (°C): 225 (decomp.)
^{1}H NMR δ: 1.42 (9 H, s, N—**$C(CH_3)_3$**), 4.17 (2 H, s, br, Ar—**CH_2**),
8.1–6.8 (14 H, m, Ar—**H**), 9.46 (2 H, s, br, —**NH_2**+).
^{31}P NMR δ: −16.69 (s), −16.75 (s).
IR cm^{-1} 3310 (w, br) (NH).

α, N-dimethyl-4-(diphenylphosphino) benzylamine (**9**). $MeNH_2$ (2.0 g, 64.4 mmol) was condensed into a heavy-walled teflon valve equipped Schlenk-flask containing acetophenonephosphine (**2**) (0.77 g, 2.5 mmol) in thf (50 cm^3) and methanol (50 cm^3). The teflon valve was closed and the flask heated for 48 h in an oil-bath held at 50°C. The flask was opened after cooling to room-temperature and the solution evaporated to dryness to give a solid residue composed of the starting compound and the product imine. The residue was carefully dried in vacuo for one hour at 50°C to remove traces of water before addition of $MeNH_2$, thf and methanol to repeat the above given reaction. As determined by GLC this second reaction gave the imine in 98% yield which without isolation was converted to the corresponding amine by addition of $NaBH_4$ (0.19 g, 3.0 mmol) letting the reduction continue overnight at room temperature. Work-up as described for (**7**) gave an oil which after some days crystallized to give 0.59 g (73%) of white crystals.

Anal. Calcd. for $C_{21}H_{22}NP$: 79.0% C, 6.9% H, 4.4% N, 9.7% P.
Found: 79.4% C, 7.0% H, 4.4% N, 9.4% P.

m.p. (°C): 53–59
^{1}H NMR δ: 1.36 (3 H, d, C—**CH_3**), 2.31 (3 H, s, N—**CH_3**), 3.64 (1 H, q, Ar—**CH**—),
7.4–7.2 (14 H, m, Ar—**H**).
^{31}P NMR δ: −5.26 (s).
IR cm^{-1}: 3308 (w, br) (NH)
Raman cm^{-1}: 3320 (br) (NH)

N-methyl-4-bromobenzylamine (**10**). Over a period of 1 hour methylamine (9 g, 290 mmol) was bubbled into a solution of 4-bromobenzaldehyde (25 g, 135 mmol) in thf (100 cm^3) and methanol (300 cm^3) at 0°C. The reaction mixture was stirred for one additional hour at room temperature whereafter it was cooled to 0°C and reacted with $NaBH_4$ (8.7 g, 230 mmol) in small portions not letting the temperature exceed 0°C. The reduction reaction was continued overnight at room temperature. After evaporation of the solvent, the residue was dissolved in ether and the ether solution washed with water (5 × 40

cm^3), brine (2 × 50 cm^3) and dried over Na_2SO_4. Solvent removal and destillation at reduced pressure collecting the fraction boiling at 60–70°C/0.05–0.1 mbar afforded 23 g, 85% of the title compound.

The purity and identity of the compound was checked by ^1H NMR: 7.5–7.1 (4 H, m, Ar—**H**), 3.7 (2 H, s, Ar—$\mathbf{CH_2}$), 2.4 (3 H, s, N—$\mathbf{CH_3}$), 1.4 (1 H, broad s, N—**H**).

N-methyl-4-(diphenylphosphino) benzylamine (**12**). Trimethylchlorosilane (24.1 g, 220 mmol) in diethylether (300 cm^3) was added dropwise over 40 min. to a solution of *N*-methyl-4-bromobenzylamine (**10**) (33 g, 165 mmol) and triethylamine (25.3 g, 250 mmol) in diethylether (300 cm^3) at 0°C. As the reaction proceeded an abundant precipitation of triethylamine hydrochloride occurred making stirring difficult if not an efficient stirrer was used. After the addition was completed the reaction mixture was stirred additionally for three hours at room temperature. Schlenk-filtration under inert atmosphere and washing of the precipitate on the filter with diethylether (2 × 70 cm^3) gave a colourless solution which was transferred under inert atmosphere to a distillation flask. Solvent removal by distillation at normal pressure followed by distillation at reduced pressure (bp. 67–70°C at 0.05 mbar) afforded *N*-methyl-*N*-trimethylsilyl-4-bromobenzylamine (**11**) as a colourless oil. Because of the extreme moisture sensitivity of the product this was not characterized but used directly in the following reaction.

A 1 liter three-necked flask equipped with a pressure-equalizing funnel was charged with the silylated amine (**11**) (43.6 g, 16 mmol) and diethylether (300 cm^3). The flask was cooled to 0°C and BuLi (1.6 M in hexan, 16.8 mmol) was added drop-wise over 40 minutes followed by reaction at 0–5°C for 3.5 hours. Chlorodiphenylphosphine (24.1 g, 22 mmol) in diethylether was then added dropwise over 1 hour. After continued reaction at room-temperature overnight the ether solution was cooled to 0°C and treated with Na_2CO_3 (50 cm^3, 1 M solution) and further extracted with water (3 × 50 cm^3) and HCl (3 × 50 cm^3, 0.01 M solution). The organic phase was collected, cooled to 0°C and on addition of HCl (60 cm^3, 2 M solution) an yellow oil separated which after some minutes stirring started to crystallize. The crystals were collected and air-dried before washing with acetone (50 cm^3), diethylether (2 × 50 cm^3) giving 39.5 g (72%) of the white title compound as its hydrochloride. Elemental analysis was carried out on the hydrochloride, while NMR spectra were run on the free amine.

Anal. Calcd. for $C_{20}H_{21}ClNP$: 70.3% C, 6.2% H, 4.1% N, 9.1% P.
Found: 70.2% C, 6.3% H, 4.2% N, 8.8% P.

m.p. (°C): 185–189
^1H NMR δ: 2.5 (3 H, s, N—$\mathbf{CH_3}$), 3.8 (2 H, s, Ar—$\mathbf{CH_2}$—), 7.4–7.3 (14 H, m, Ar—**H**).
^{31}P NMR δ: −5.38 (s).

Acylated compounds. The acylated compounds **13–19** were prepared using the following general procedures in the acylation reaction. The scale of the reaction and the work-up procedures are specified for each substance: The substituted phosphine (1 equiv.) and triethylamine (2 equiv.) were dissolved in diethylether and reacted with the appropriate acylchloride (1.1 equiv.) at 0°C for 1 hour followed by reaction over night at room temperature. The resulting suspension was filtered to remove precipitated triethylaminehydrochloride. The precipitate was washed with diethylether and the combined ether solution was washed with water, brine and finally dried over Na_2SO_4 before isolation as specified below.

N-methacryloyl-N-methyl-2-(diphenylphosphino) benzylamine (**13**). The solvent was removed by evaporation and the crude product obtained was purified by chromatography on silica (40–60 μm) using toluene: ethylacetate (85:15) as the eluent. Solvent removal from the fractions containing the product afforded an oil. Crystallization was accomplished by suspending the oil in a mixture of ethylacetate: pentane (1:1) and cooling at −30°C. 0.8 g, 47% white crystals of the title compound was obtained starting from 1.4 g of the amine (**7**).

Anal. Calcd. for $C_{24}H_{24}NOP$: 77.0% C, 6.7% H, 3.7% N, 8.3% P.
Found: 77.0% C, 6.6% H, 3.9% N, 8.1% P.

m.p. (°C): 77–85
^1H NMR δ: 1.98 (s) and 1.78 (s) (3 H, C—$\mathbf{CH_3}$), 2.88 (3 H, s, N—$\mathbf{CH_3}$),
4.84 (s) and 4.68 (s) (2 H, Ar—$\mathbf{CH_2}$), 5.20 (s), 5.03 (s) and 4.90–4.85 (d)
(2 H, C=$\mathbf{CH_2}$), 7.37–6.87 (14 H, m, Ar—**H**).
^{31}P NMR δ: −14.80 (s).
IR cm^{-1}: 1621 (s), 1648 (m) (C=O).

N-methacryloyl-2-(diphenylphosphino) aniline (**14**). The crude product from the acylation reaction was purified and crystallized as for compound (**13**) giving 0.38 g, 40% of white crystals from 0.75 g of the amine (**3**).

Anal. Calcd. for $C_{22}H_{20}NOP$: 76.5% C, 5.8% H, 4.1% N, 9.0% P.
Found: 76.3% C, 5.9% H, 3.9% N, 9.0% P.

m.p. (°C): 93–99
^{1}H NMR δ: 1.9 (3 H, m, C**H**$_3$), 5.6 and 5.3 (2 H, m, C=C**H**$_2$), 8.43 (1 H, d, N—**H**), 8.5–6.9 (14 H, m, Ar—**H**)
^{31}P NMR δ: −19.80 (s), −19.82 (s)
IR cm^{-1}: 1682 (s), 1676 (s), (C=O), 1629 (m) (C=C).

N-methacryloyl-N-methyl-4-(diphenylphosphino) benzylamine (**15**). The free amine was obtained by treatment of the hydrochloride of the amine (**12**) with Na_2CO_3 in water/diethylether suspension. The oil obtained after phase separation and evaporation of the organic solvent was carefully dried under high vacuo before the acylation reaction. The crude product from the acylation reaction was purified by chromatography and crystallized as for compound (**13**). 11 g, 56% white crystals of the title compound was obtained starting from 16 g of the amine (**12**).

Anal. Calcd. for $C_{24}H_{24}NOP$: 77.0% C, 6.7% H, 3.7% N, 8.3% P.
Found: 77.0% C, 6.7% H, 3.7% N, 8.1% P.

m.p. (°C): 99–101
^{1}H NMR δ: 2.0 (3 H, s, C—**H**$_3$), 2.9 (3 H, br. s, N—**H**$_3$), 4.6 (2 H, s, Ar—**H**$_2$), 5.1 (1 H, s, C=**H**$_2$), 5.2 (1 H, br. s, C=**H**$_2$), 7.4–71 (14 H, m, Ar—**H**),
^{31}P NMR δ: −5.33 (s), −5.38 (s)
IR cm^{-1}: 1649 (s) and 1621 (s), (C=O).

2-(diphenylphosphino)-benzyl methacrylate (**16**). Toluene (70 cm^3) was added to the etheral solution from the acylation reaction. The ether was evaporated not letting the temperature exceed 25°C and the residual toluene phase filtered through Celite to remove traces of unsoluble material from the turbid solution. Addition of pentane (350 cm^3) and cooling over night at −30°C afforded white crystals. Starting from 19.6 g of the alcohol (**4**) 11.5 g, 47% of the title compound was obtained. The compound is prone to undergo spontaneous polymerisation in solutions above room temperature and solutions must therefore be handled at low temperature.

Anal. Calcd. for $C_{23}H_{21}O_2P$: 76.6% C, 5.9% H, 8.6% P.
Found: 76.4% C, 6.0% H, 8.4% P.

m.p. (°C): 67–72
^{1}H NMR δ: 1.83 and 1.76 (3 H, m, C—**H**$_3$), 5.44 (2 H, d, Ar—**H**$_2$), 5.89, 5.58, 5.36 and 5.53 (2 H, m, C=**H**$_2$), 7.8–6.8 (14 H, m, Ar—**H**),
^{31}P NMR δ: −16.2 (s), IR cm^{-1}: 1710 (s), (C=O).

N-methyl-N-propionyl-4-(diphenylphosphino) benzylamine (**17**). The free amine was isolated as in the preparation of compound (**15**). Evaporation of the ether solution obtained in the acylation reaction afforded a colourless oil. White crystals were obtained by suspending the oil in ethylacetat:pentane (1:1) and cooling at −30°C overnight. The crystals were isolated by filtration of the cold solution. Yield 2.5 g, 81% from 2.6 g of the amine (**12**).

Anal. Calcd. for $C_{23}H_{24}NOP$: 76.4% C, 6.7% H, 3.9% N, 8.6% P.
Found: 76.6% C, 6.7% H, 4.0% N, 8.3% P.

m.p. (°C): 81–85
^{1}H NMR δ: 1.24–1.13 (3 H, m, C—**H**$_3$), 2.44–2.35 (2 H, m, C(O)—**H**$_2$), 2.95 (s) and 2.93 (s) (3 H, N—**H**$_3$), 4.50 (s) and 4.53 (s) (2 H, Ar—**H**$_2$), 7.4–7.1 (14 H, m, Ar—**H**).
^{31}P NMR δ: −5.43 (s), −5.49 (s).
IR cm^{-1}: 1643 (s), (C=O).

N-methyl-N-propionyl-2-(diphenylphosphino) benzylamine (**18**). This was prepared from the amine (**7**) in a manner strictly analogous to that used to prepare compound (**17**). Isolated yield 3.4 g, 95% of white crystals starting from 3.0 g of the amine.

Anal. Calcd. for $C_{23}H_{24}NOP$: 76.4% C, 6.7% H, 3.9% N, 8.6% P.
Found: 76.3% C, 6.7% H, 4.0% N, 8.5% P.

^{1}H NMR δ: 1.15 (t) and 1.02 (t) (3 H, C—**H**$_3$), 2.28 (q) and 2.11 (q) (2 H, C(O)—**H**$_2$), 2.85 (3 H, d, N—**H**$_3$), 4.81 (d) and 4.60 (br., s) (2 H, Ar—**H**$_2$), 7.7–6.8 (14 H, m, Ar—**H**),
m.p. (°C): 79–83
^{31}P NMR δ: −14.7 (s), −14.9 (s)
IR cm^{-1}: 1655 (s) and 1643 (sh) (C=O)

N-acryloyl-N-methyl-4-(diphenylphosphino) benzylamine (**19**). The hydrochloride of the amine (**12**) (3.4 g, 9.97 mmol) was dissolved in a mixture of toluene (100 cm^3) and 2 M $NaOH/H_2O$ (100 cm^3) and reacted with acryloylchloride (1.18 g, 13.0 mmol) as described earlier.[13] The crude product (2.7 g, colourless oil) from the acylation reaction was purified by chromatography as for compound (**13**). 1.5 g, 41% of the title compound was obtained as a colourless oil. According to NMR this contains traces of acetone from the work up procedure despite drying for four hours in vacuo (0.1 mbar) giving a somewhat erratic elemental analysis.

Anal. Calcd. for $C_{23}H_{22}NOP$: 76.9% C, 6.2% H, 3.9% N, 8.6% P.
Found: 75.9% C, 6.2% H, 3.8% N, 8.1% P.

Abbreviations for the olefinic protons —$COCH_a$=CH_bH_c, (H_b=cis, H_c=trans) to H_a
^{1}H NMR (δ ppm): 3.0 (3 H, s, N—$\mathbf{CH_3}$), 4.1 (2 H, d, Ar—$\mathbf{CH_2}$—),
5.68 and 5.74 (1 H, 2 q, C=$\mathbf{CH_b}$, J_{ba} = 10.4 Hz, J_{bc} = 2.1 Hz),
6.37 and 6.42 (1 H, 2 q, C=$\mathbf{CH_c}$, J_{ca} = 16.7 Hz, J_{cb} = 2.0 Hz),
6.57 and 6.64 (1 H, 2 q, C=$\mathbf{CH}$—, J_{ac} = 16.8 Hz, J_{ab} = 10.5 Hz), 7.1–7.4 (14 H, m, Ar—$\mathbf{H}$).
^{31}P NMR δ: −5.33 (s), −5.37 (s)
IR cm^{-1}: 1652 (s, C=O), 1619 (s, C=C).

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