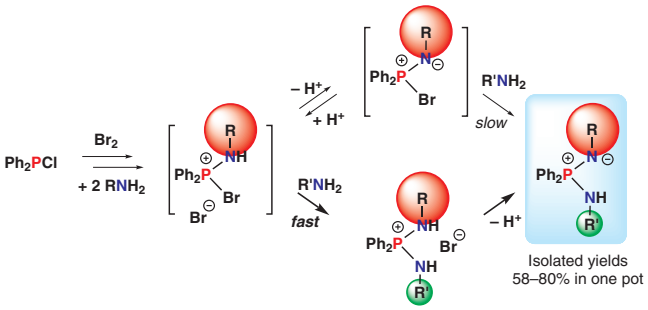
Synthesis T. A. Peganova, A. M. Kalsin Paper

Synthesis of Nonsymmetric Iminophosphonamines by Kirsanov Condensation

Tat'yana A. Peganova
Alexander M. Kalsin*

Russian Academy of Sciences, A. N. Nesmeyanov Institute of Organoelement Compounds, Vavilov Str. 28, 119991 Moscow, Russian Federation
kalsin@ineos.ac.ru



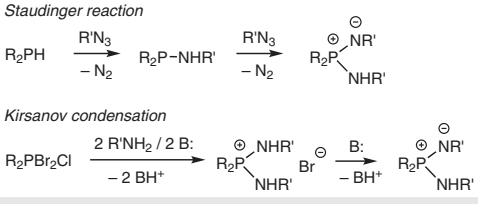
Received: 17.09.2019
Accepted after revision: 17.10.2019
Published online: 31.10.2019
DOI: 10.1055/s-0039-1690242; Art ID: ss-2019-c0535-op

Abstract Despite the growing interest in iminophosphonamines $R_2P(NHR')(NR')$, nonsymmetric examples bearing different N,N′-substituents are quite rare and have been prepared exclusively by the Staudinger reaction. We report here the synthesis of a series of new iminophosphonamines $Ph_2P(NHR)(NR')$ (R = Me, *t*-Bu, *o*-Tol; R′ = *p*-Tol, *o*-Tol, 2,6-Xyl, 2,6-Diip, *p*-Ts) showing that the Kirsanov condensation is a viable and simpler approach, although with some limitations. This method allows the synthesis to be accomplished in a one-pot manner via stepwise double amination of a trihalophosphorane and permits the introduction of at least one sterically bulky N-substituent. The second amination step is shown to be highly sensitive to: (a) the steric bulk of the amine, and (b) the acidity of the aminohalophosphonium intermediate.

Key words Kirsanov condensation, nonsymmetric iminophosphonamines, steric effects, aminohalophosphonium

The interest in iminophosphonamines $Ph_2P(NR)(NHR')$ has been constantly growing due to their potential use as superbases in asymmetric Brønsted base organocatalysis[1] and as κ^2-*N*,*N* chelate ligands for the synthesis of transition metal iminophosphonamides. The latter have been reported as active catalysts for alkene polymerization,[2] 3,4-selective polymerization of isoprene,[3] alkene oligomerization,[4] ethene dimerization,[2c] cyclopropanation,[5] and aziridination,[6] as well as for Tsuji–Trost cross-coupling[7] and acetophenone transfer hydrogenation.[8] Nonsymmetric iminophosphonamines bearing different N,N′-substituents have been efficiently utilized in the Kumada cross-coupling of aryl Grignard reagents with aryl chlorides and fluorides[9] and in controlling regio- and stereoselectivity in the polymerization of isoprene.[10]

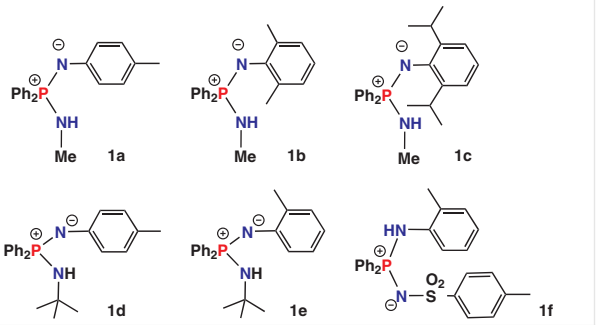
Generally, there are two major approaches to the synthesis of iminophosphonamines, i.e. the Staudinger reaction of secondary phosphanes[11] and aminophosphanes[12] with organoazides and the Kirsanov condensation of bromophosphonium salts with primary amines[13] followed by deprotonation of diaminophosphonium salts formed in the first step (Scheme 1). The Staudinger reaction is more versatile and allows nonsymmetric iminophosphonamines having sterically hindered N,N′-substituents to be obtained.[3,9,10,14] The Kirsanov reaction is simpler to implement as it does not require dangerous disubstituted phosphanes and azides. However, its drawback is typical to nucleophilic substitution reactions. In particular the yields are very low for amines with electron-withdrawing or sterically bulky substituents. Thus, even bis(*o*-tolylamino)phosphonium[13c] and bis(*tert*-butylamino)phosphonium[13a] salts can be obtained only after prolonged heating in moderate-to-low yields. Furthermore, no reports on the synthesis of nonsymmetric iminophosphonamines by this reaction can be found in the literature; some authors even claim this approach to be not viable.[15]



Scheme 1 Synthetic approaches to iminophosphonamines

Here we report on the synthesis of a series of new nonsymmetric iminophosphonamines obtained by double amination of trihalodiphenylphosphorane with primary aryl/alkyl amines (Scheme 2) and discuss the limitations of this method. Although the substitution of halogen in the highly polar P–Hal bond at the phosphorus atom with good nucleophiles is generally thought to be a fast process, our

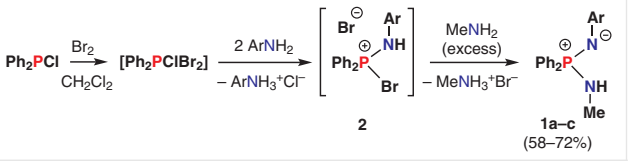
Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany



Scheme 2 Nonsymmetric iminophosphonamines reported in this article

results show that it is possible to carry out double amination in a controllable stepwise way.

Nonsymmetric iminophosphonamines **1a–c** were readily synthesized in a straightforward manner by one-pot stepwise amination with $ArNH_2$ [Ar = *p*-Tol; 2,6-$Me_2C_6H_3$ (Xyl); 2,6-$^i Pr_2C_6H_3$ (Diip)] and methylamine of trihalophosphorane prepared in situ from chlorodiphenylphosphane and bromine in dichloromethane (Scheme 3).



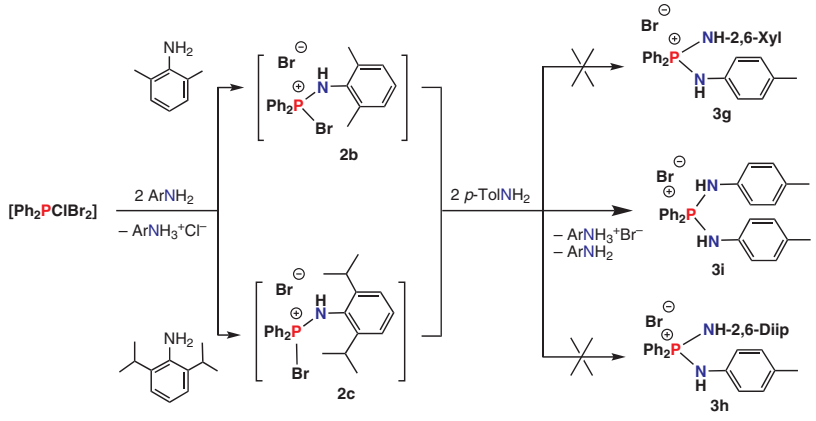
Scheme 3 One-pot synthesis of **1a–c**

The compounds **1a–c** were fully characterized by ^{31}P, ^{13}C, ^1H NMR and elemental analysis. In the ^{31}P NMR spectra the phosphorus resonance of **1a–c** is observed at δ = +7.3 to –7.6 similar to δ_P = –3.5 reported earlier for Ph_2P(N-*p*-Tol)(NH-*p*-Tol) (**1i**).[16] In the ^1H NMR the NH resonances are significantly upfield shifted in comparison to δ = 5.55 for **1i**, reflecting the decrease of NH acidity due to the introduction of strongly donating N-alkyl substituent. Their chemical shifts [δ = 2.94 (**1a**), 2.73 (**1b**), 2.10 (**1c**)] depend on the electron-donor properties of aryl groups (Ar = *p*-Tol, Xyl, Diip, respectively). The IR spectra of **1a–c** in the solid state feature a characteristic band of NH stretching vibrations ν_{NH} at 3354–3356 cm^{-1}. The iminophosphonamines **1a–c** were isolated in good yields 58–72%, the only side products were the corresponding aminophosphine oxides $Ph_2P(O)(NHAr)$ **5a–c** and $Ph_2P(O)(NHMe)$ formed as a result of hydrolysis of the monoaminophoshonium intermediate[13c] or the target product by adventitious traces of water during the work-up procedures.

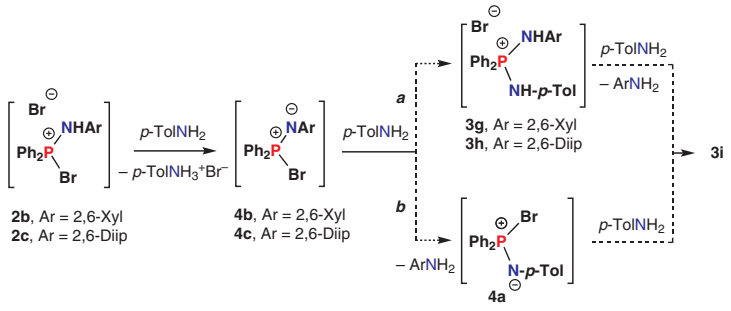
The first amination step proceeds smoothly with the arylamines used, including sterically congested examples. The ^{31}P NMR monitoring showed that even with the bulkiest 2,6-DiipNH_2 the amination is accomplished within 2 h at room temperature forming aminobromophosphonium salt [Ph_2PBr(NHAr)]Br (**2c**; δ_P = 57.7, Figure S1(a) in the Supporting Information) in more than 90% yield. The second amination step with highly nucleophilic methylamine is also fast and the corresponding iminophosphonamine is formed within 1 h.

However, replacing methylamine with sterically more demanding and less nucleophilic *p*-toluidine did not result in the formation of nonsymmetric diaminophosphonium salts **3g** and **3h** bearing bulky 2,6-Xyl and 2,6-Diip substituents, respectively; instead, both reactions produced exclusively symmetric di-*p*-tolylaminophosphonium salt **3i** (Scheme 4).

The ^{31}P NMR monitoring of this reaction (Figure S1, in the Supporting Information) shows that the addition of *p*-toluidine to the in situ generated **2c** resulted in precipitation of *p*-Tol$NH_3^+Br^-$ and formation of a new compound with the phosphorus resonance significantly upfield shifted to δ_P = –1.6, which is a typical region for iminophosphonamines. It appeared that the first equivalent of *p*-toluidine rapidly deprotonates **2b**, **2c** to form bromo(imino)phosphoranes **4b**, **4c** (Scheme 5). The latter can further



Scheme 4 Attempted synthesis of **3g** and **3h**

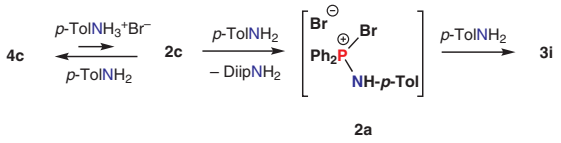


Scheme 5 Possible reaction pathways to **3i**

react stepwise with 2 equiv of *p*-toluidine by S_N2 substitution reaction of bromide and of the bulky amine via either unstable nonsymmetric diaminophosphonium salts **3g**, **3h** (path a), or bromo(imino)phosphorane **4a** (path b).

To investigate further this mechanism, we synthesized compound **4c** by the reaction of Ph_2PClBr_2, generated in situ, with 3 equiv of 2,6-DiipNH$_2$. Although the isolated product **4c** (δ_P = –3.2 in C_6D_6) contained cumulatively 15–20% of impurities (Figure S2a in the Supporting Information) and cannot be purified further due to its high solubility even in hexane, the major impurity (ca. 10%) observed at δ_P = –1.0 is tentatively the related chloro(imino)phosphorane Ph_2PCl(N-2,6-Diip) (**4c'**) that gives further the same diaminophosphonium salt but with Cl^- counterion (see below). It is worth mentioning that a similarly small downfield shift of ^{31}P resonances have been reported for Ph_2PCl(N-SiMe$_3$)[17] and Ph_2PBr(N-SiMe$_3$).[18] The ^1H (Figure S2b) and ^{13}C NMR (Figure S2c) spectra correspond well to the formula of **4c** with the resonances observed close to the related iminophosphonamine **1c**, and show no resonance that can be attributed to the NH group. The mass spectrum (Figure S2d) of the solid sample showed molecular peaks with *m*/*z* 439 (**4c**), 395 (**4c'**) and 377, the latter being attributed to the corresponding aminophosphine oxide **5c** formed due to hydrolysis.

Surprisingly, **4c** does not react with *p*-toluidine even under reflux for 4 h in CH_2Cl_2. Among the alkylamines tested (MeNH$_2$ and *t*-BuNH$_2$), only methylamine reacted with **4c** to give expectedly **1c**. On the other hand, **4c** does react with *p*-toluidine in the presence of *p*-TolNH$_3^+$Br$^-$ to give **3i** (Scheme 6). This implies that the first step in Scheme 3 is partially reversible and, in fact, *p*-toluidine reacts with a residual amount of **2c**, as amine is much better leaving group in S_N2 substitution reactions than a negatively charged amide. Apparently, the reaction proceeds via aminobromophosphonium salt **2a** (Scheme 6) rather than via sterically congested aminodiarylphosphonium intermediate **3h** (Scheme 5, path a).



Scheme 6 The mechanism of **3i** formation

Indeed, we have shown that *p*-toluidine cannot substitute bulky 2,6-DiipNH$_2$ even in the sterically more accessible diaminophosphonium salt [Ph_2P(NH-2,6-Diip)(NHMe)]Br (**3c**) generated in situ. Thus, the reaction of **1c** with *p*-TolNH$_3^+$Br$^-$ in CH_2Cl_2 results in the quick dissolution of the ammonium salt and upfield shift of the ^{31}P NMR resonance from δ_P = –3.1 to δ_P = 39.8 due to the formation of **3c**, while no further reaction occurred with *p*-toluidine released even after heating for 2 days (Figure S3 in the Supporting Information). Hence, if the formation of diaminophosphonium salt **3** is hampered due to steric reasons, the bulkier amino group at the phosphorus atom can be substituted with the sterically less hindered one exclusively via the intermediate **2**.

Nevertheless, bromide substitution in **4c** with *p*-toluidine can be initiated by replacing dichloromethane with polar aprotic acetonitrile, although in this solvent concurrent transamination occurs as a side reaction. Thus, the reflux of **4c** and 1 equiv *p*-toluidine in acetonitrile for 8 h resulted in about 60% conversion into mostly diaminophosphonium salts **3i** and **3h** (7:1), showing ^{31}P NMR resonances at δ_P = 24.7 and 26.7, respectively (Figure S4a, in the Supporting Information). This assignment was further supported by the ESI-HRMS spectrum recorded for the reaction solution, in which the molecular peaks at *m*/*z* 397.1797, 467.2573 and 378.1949 correspond to the [M + H$^+$] of **3i** (calcd *m*/*z* 397.1834), **3h** (calcd *m*/*z* 467.2616) and **5c** (calcd *m*/*z* 378.1987), respectively, with the latter two peaks being significantly less intensive (Figure S4b). Unfortunately, we were not able to isolate pure **3h** from the reaction mixture due to its low content. Thus, this method does not appear to be a convenient route to nonsymmetric sterically hindered aminodiarylphosphonium salts, as polar aprotic solvent accelerates substitution of both bromide and bulky amino substituents giving rise to a mixture of diaminophosphonium salts that are difficult to separate.

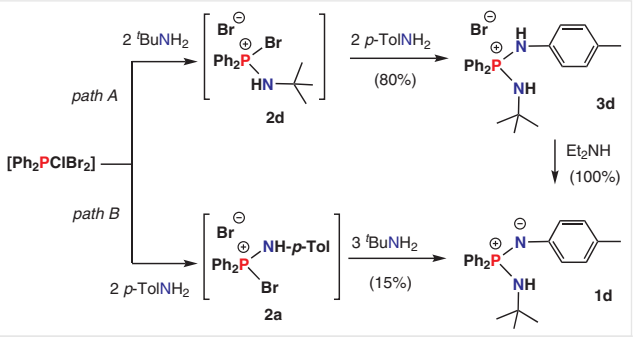
(Alkylamino)bromophosphonium salts [$Ph_2PBr(NHR)$]Br **2** have lower acidity than their arylamino analogues and are not deprotonated to **4** by primary amines, similarly to what has been observed earlier for diaminophosphonium salts **3**.[16] This was successfully employed in the synthesis of nonsymmetric iminophosphonamine [$Ph_2P(NH^tBu)$(N-*p*-Tol)] (**1d**). Thus, the amination of the intermediate **2d**, which does not undergo deprotonation, with *p*-toluidine readily gives the corresponding nonsymmetric diaminophosphonium salt [$Ph_2P(NH^tBu)$(NH-*p*-Tol)]Br (**3d**) in 80% yield after 18 h at room temperature (Scheme 7, path A). This salt can be quantitatively deprotonated with Et_2NH to give **1d**. Alternatively, the amination of the intermediate **2a** with *tert*-butylamine is very slow due to its fast deprotonation to the less electrophilic **4a**, and the product **1d** was obtained in only 15% yield after 70 h of reflux (Scheme 7, path B).

Expectedly, increasing the bulk of the arylamines involved in the amination of *tert*-butylamino-substituted salt **2d** retards the reaction. Thus, *o*-toluidine slowly reacts with the in situ prepared **2d** to give **3e** in 77% yield after 3 days at room temperature, while no reaction was observed with bulkier 2,6-$XylNH_2$ even under reflux for several days (Scheme 8). Further deprotonation of diaminophosphonium salt **3e** with Et_2NH yields quantitatively iminophosphonamine **1e**. The reported earlier low yield of 23% for the corresponding symmetric diaminophosphonium salt [Ph_2P(NH-*o*-Tol)$_2$]Br (**3j**)[13c] can now be explained by the reduced reactivity of bromo(imino)phosphorane [Ph_2PBr(N-*o*-Tol)] (**4e**) formed by deprotonation of [Ph_2PBr(NH-*o*-Tol)]Br intermediate (**2e**).

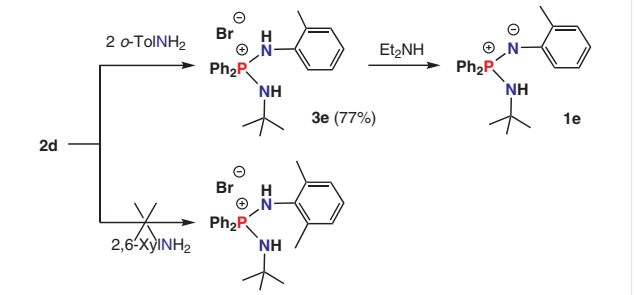
It has to be noted that the satisfactory elemental analysis for diaminophosphonium salt **3d** can be obtained considering it to be a mixed salt Br^-/Cl^- (85–90/15–10%) meaning that in the intermediate **2d** bromide is partially substituted with chloride, either in the counterion or in the P–Hal moiety, similarly to the impurity of **4c′** observed in the synthesis of **4c**.

As the final example, the nonsymmetric iminophosphonamine **1f** bearing bulky *o*-tolyl and electron-withdrawing *p*-tosyl groups was synthesized by the reaction of the in situ prepared **2e** with 2 equiv of TsNHNa in THF (Scheme 9). Despite the relatively small bulkiness and high nucleophilicity of *p*-$TsNH^-$[19] relative to amines,[20] the reduced electrophilicity of the intermediate **4e** is responsible for slowing down this reaction; the product was isolated in 61% yield after prolonged reflux for 1.5 days in THF.

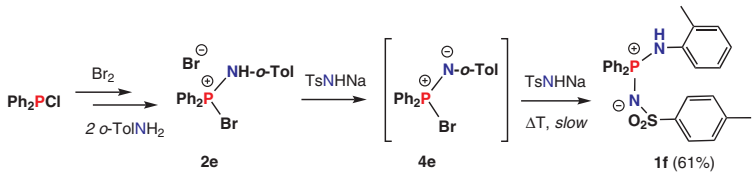
In summary, with this study we have shown that the synthesis of nonsymmetric diaminophosphonium salts and the corresponding iminophosphonamines by Kirsanov condensation is possible because the rates of the two consecutive amination steps differ significantly. Typically to S_N2 reactions, the bulkiness of the first amino-substituent introduced retards the second amination step, allowing to avoid undesirable double amination with the same amine that would lead to symmetric product. However, such steric effects limit the scope of the reaction to iminophosphonamines containing no more than one bulky amino group. When two bulky amines are used, the reaction either stops at the formation of aminobromophosphonium salt after the first amination step or yields symmetric diaminophosphonium salt bearing two least sterically encumbered amino moieties as a result of the concurrent substitution of the bulkier amine. One complication that has to be considered, is facile deprotonation of acidic (arylamino)bromophosphonium intermediates with the excess of



Scheme 7 Two synthetic pathways to **1d**



Scheme 8 Reaction of **2d** with bulky arylamines



Scheme 9 Synthesis of **1f**

amine to less reactive zwitterionic bromophosphonimines. Therefore, nonsymmetric N-alkyl/N-aryl iminophosphonamines can be obtained much faster and with higher yields, when alkylamine is used at the first amination step. Although the Staudinger reaction is more versatile and can deal with wider variety of amines, including sterically encumbered and poorly nucleophilic ones, the Kirsanov condensation can offer effective simpler one-pot route from commercially more accessible compounds to iminophosphonamines having one sterically bulky N-substituent, and thus deserves its place in the chemists' toolbox.

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry argon. Absolute solvents were used for the synthesis; solvents were purified by standard methods and distilled under argon prior to use. The ^{1}H, ^{31}P, and ^{13}C NMR spectra were obtained on Bruker Avance 600 or Bruker Avance 400 spectrometers and referenced to the residual signals of deuterated solvent (^{1}H and ^{13}C), and to 85% H_3PO_4 (^{31}P, external standard). IR spectra for were recorded on a Shimadzu IR Prestige21 FTIR spectrophotometer equipped with an MCT detector cooled with liquid N_2, ATR accessory (MIRacle with a Diamond/ZnSe Crystal Plate Pike®) or in KBr pellets. The original NMR and IR spectra are given in the Supporting Information in Figures S5–S12. The EI mass spectrum for **4c** was obtained on a Finnigan MAT Incos 50 mass spectrometer with direct sample inlet into the ion source at 70 eV ionization energy. HRMS of the reaction sample (**4c** + *p*-toluidine) were registered on Bruker micrOTOF Q instrument equipped with electrospray ionization (ESI) ion source. The measurements were performed in positive mode with HV capillary at 4.5 kV, spray shield offset at –0.5 kV, and scan range of *m*/*z* 50–3000. The elemental analyses were carried out on a Carlo Erba 1106 CHN analyzer.

$Ph_2P(NHMe)(N\text{-}p\text{-}Tol)$ (1a); Typical Procedure for $Ph_2P(NHMe)(NAr)$ 1a–c

To a solution of Ph_2PCl (3.60 mL, 4.42 g, 20 mmol) in CH_2Cl_2 (15 mL), a solution of Br_2 (1.0 mL, 3.2 g, 20 mmol) in CH_2Cl_2 (15 mL) was added dropwise with stirring at r.t., and the mixture was stirred for 1.5 h. Then a solution of *p*-toluidine (4.28 g, 40 mmol) in CH_2Cl_2 (40 mL) was added dropwise to the suspension of Ph_2PClBr_2. The mixture was stirred overnight. The precipitated $p\text{-TolNH}_3^+Cl^-$ was filtered off under argon and washed with CH_2Cl_2 (3 × 20 mL). The filtrate was transferred to another flask, cooled down to –30 °C, and to it was added dropwise a cold freshly prepared 2.7 M $MeNH_2$ in CH_2Cl_2 solution (30 mL, 80 mmol). The mixture was allowed to warm to r.t. and stirred overnight. The precipitate of $MeNH_3^+Br^-$ was filtered off and washed with CH_2Cl_2 (3 × 10 mL). The combined filtrate was concentrated to ~7 mL, the white precipitate was filtered off and washed with cold CH_2Cl_2 (3 × 2 mL) and dried under vacuum to give $Ph_2P(NHMe)(N\text{-}p\text{-Tol})$ (**1a**) (3.94 g). The mother liquor was evaporated to dryness, then extracted with warm Et_2O (3 × 10 mL) and filtered off. The filtrate was concentrated to 10 mL, the precipitate was filtered off and washed with Et_2O (2 × 2 mL) and dried under vacuum to give a second crop of 0.69 g. Total yield: 4.63 g (72%).

IR (KBr): 3056, 2913, 2810, 1607, 1502, 1436, 1294, 1273, 1117, 1099, 1025 cm^{-1}.

IR (ATR): 3356 cm^{-1} (NH).

^{1}H NMR ($CDCl_3$): δ = 7.91 (dd, $^{3}J_{HH}$ = 7.2 Hz, $^{3}J_{HP}$ = 12.0 Hz, 4 H, *o*-H_{Ph}), 7.46 (td, $^{3}J_{HH}$ = 7.2 Hz, $^{5}J_{HP}$ = 1.6 Hz, 2 H, *p*-H_{Ph}), 7.37 (td, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HP}$ = 3.2 Hz, 4 H, *m*-H_{Ph}), 6.92 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H, C_6H_4), 6.88 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H, C_6H_4), 2.94 (br s, 1 H, NH), 2.68 (d, $^{3}J_{HP}$ = 12.0 Hz, 3 H, NH*Me*), 2.24 (s, 3 H, Me_{Tol}).

^{13}C NMR ($CDCl_3$): δ = 148.3 (d, $^{2}J_{CP}$ = 3.7 Hz, *i*-*C*-N_{Tol}), 132.2 (d, $^{2}J_{CP}$ = 9.2 Hz, *o*-CH_{Ph}), 131.7 (d, $^{1}J_{CP}$ = 126 Hz, *i*-C_{Ph}), 131.5 (d, $^{4}J_{CP}$ = 2.7 Hz, *p*-CH_{Ph}), 129.5 (s, β-CH_{Tol}), 128.7 (d, $^{3}J_{CP}$ = 12.3 Hz, *m*-CH_{Ph}), 126.8 (s, *i*-C-Me_{Tol}), 123.3 (d, $^{3}J_{CP}$ = 17.9 Hz, α-CH_{Tol}), 26.9 (s, NH*Me*), 20.7 (s, *Me*$_{Tol}$).

^{31}P NMR ($CDCl_3$): δ = 7.3.

Anal. Calcd for $C_{20}H_{21}N_2P$: C, 74.98; H, 6.61; N, 8.74. Found: C, 74.85; H, 6.69; N, 8.58.

$Ph_2P(NHMe)(N\text{-}2,6\text{-}Me_2C_6H_3)$ (1b)

Synthesized analogously from 2,6-dimethylaniline (2.50 mL, 2.45 g, 20 mmol). After filtering off the $MeNH_3Br$ salt, the filtrate was evaporated to dryness. Most impurities were removed by washing the residue with Et_2O (3 × 10 mL). Finally, it was extracted with warm benzene (~60 mL), the filtrate was concentrated to 7–10 mL to result in precipitation. The precipitate was filtered off, washed with benzene (2 × 2 mL) and dried under vacuum to give **1b** (2.70 g). Second crop of **1b** (1.16 g) was precipitated by treating the filtrate with 3 volumes of Et_2O. Total yield: 3.86 g (58%).

IR (KBr): 3357, 3076, 3058, 2956, 2919, 2820, 1589, 1475, 1467, 1436, 1428, 1291, 1274, 1116, 1096, 1035, 1027 cm^{-1}.

IR (ATR): 3355 cm^{-1} (NH).

^{1}H NMR ($CDCl_3$): δ = 7.74 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HP}$ = 10.6 Hz, 4 H, *o*-H_{Ph}), 7.47 (br t, $^{3}J_{HH}$ ~ 7 Hz, 2 H, *p*-H_{Ph}), 7.40 (m, 4 H, *m*-H_{Ph}), 6.94 (d, $^{3}J_{HH}$ = 7.2 Hz, 2 H, *m*-C_6H_3), 6.88 (t, $^{3}J_{HH}$ = 7.2 Hz, 1 H, *p*-C_6H_3), 2.72 (d, $^{3}J_{HP}$ = 11.2 Hz, 3 H, NH*Me*), 2.73 (overlap, 1 H, NH), 2.19 (s, 6 H, Me_{Xyl}).

^{13}C NMR ($CDCl_3$): δ = 147.2 (d, $^{2}J_{CP}$ = 1.0 Hz, *i*-C-N_{Xyl}), 133.4 (s, *i*-C-Me_{Xyl}), 132.1 (d, $^{2}J_{CP}$ = 9.0 Hz, *o*-CH_{Ph}), 131.3 (d, $^{4}J_{CP}$ = 2.6 Hz, *p*-CH_{Ph}), 128.5 (d, $^{3}J_{CP}$ = 12.4 Hz, *m*-CH_{Ph}), 127.8 (d, $^{4}J_{CP}$ = 1.8 Hz, *m*-CH_{Xyl}), 118.6 (d, $^{5}J_{CP}$ = 3.0 Hz, *p*-CH_{Xyl}), 27.4 (d, $^{2}J_{CP}$ = 1.3 Hz, NH*Me*), 20.9 (s, Me_{Xyl}).

^{31}P NMR ($CDCl_3$): δ = –3.6.

Anal. Calcd for $C_{21}H_{23}N_2P$: C, 75.43; H, 6.93; N, 8.38. Found: C, 75.24; H, 7.01; N, 8.26.

$Ph_2P(NHMe)(N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)$ (1c)

Synthesized analogously from 2,6-diisopropylaniline (3.75 mL, 3.54 g, 20 mmol). After filtering off the $MeNH_3Br$ salt, the filtrate was evaporated to dryness and the residue was extracted with benzene (~40 mL). The benzene suspension was filtered to remove residual ammonium salts and was concentrated to 3 mL followed by treating with Et_2O (10 mL). The solution was left to crystallize in the fridge overnight. The crystalline solid obtained was filtered off, washed with cold Et_2O (2 × 3 mL) and dried under vacuum; yield: 2.32 g (59%).

IR (KBr): 3356, 3076, 3051, 2978, 2956, 2860, 1585, 1462, 1432, 1380, 1339, 1290, 1119, 1097, 1028 cm^{-1}.

IR (ATR): 3354 cm^{-1} (NH).

^{1}H NMR ($CDCl_3$): δ = 7.76 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HP}$ = 12.0 Hz, 4 H, *o*-H_{Ph}), 7.35 (d, $^{3}J_{HH}$ = 7.6 Hz, 2 H, *m*-C_6H_3), 7.19 (overlap. m, 2 H, *p*-H_{Ph}), 7.14 (overlap m, 4 H, *m*-H_{Ph}), 6.88 (overlap, 1 H, *p*-C_6H_3), 3.78 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2 H, *CH*Me_2), 2.40 (dd, $^{3}J_{HP}$ = 11.6 Hz, $^{3}J_{HH}$ = 6.0 Hz, 3 H, NH*Me*), 2.10 (dq, $^{3}J_{HP}$ = 9.6 Hz, $^{3}J_{HH}$ = 5.6 Hz, 1 H, NH), 1.36 (d, $^{3}J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$).

^{13}C NMR ($CDCl_3$): δ = 144.1 (d, $^2J_{CP}$ = 1.8 Hz, *i*-C-N_{Diip}), 142.3 (d, $^3J_{CP}$ = 6.3 Hz, *i*-C-$^iPr_{Diip}$), 132.2 (d, $^1J_{CP}$ = 127 Hz, *i*-C_{Ph}), 132.1 (d, $^2J_{CP}$ = 9.2 Hz, *o*-CH_{Ph}), 131.3 (d, $^4J_{CP}$ = 2.7 Hz, *p*-CH_{Ph}), 128.5 (d, $^3J_{CP}$ = 12.4 Hz, *m*-CH_{Ph}), 122.6 (d, $^4J_{CP}$ = 2.2 Hz, *m*-CH_{Diip}), 119.2 (d, $^5J_{CP}$ = 3.2 Hz, *p*-CH_{Diip}), 28.2 (s, *C*HMe$_2$), 27.4 (d, $^2J_{CP}$ = 1.7 Hz, NHMe), 23.9 (s, CH*Me*$_2$).

^{31}P NMR ($CDCl_3$): δ = –7.6.

Anal. Calcd for $C_{25}H_{31}N_2P$: C, 76.89; H, 8.00; N, 7.17. Found: C, 76.94; H, 8.04; N, 7.11.

Synthesis of $Ph_2P(NH^tBu)(N$-*p*-Tol) (1d); Method A

The monoaminophosphorane [Ph_2PBr(NH-*p*-Tol)]Br (20 mmol) was prepared in situ and separated from *p*-Tol$NH_3^+Cl^-$ precipitate, as described above. To this solution an excess of *t*-BuNH_2 (8.4 mL, 5.85 g, 80 mmol) was added and the mixture was refluxed for 70 h. The precipitate of *t*-BuNH_3Br was filtered off and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was evaporated to dryness, the residue was extracted with Et_2O (3 × 20 mL) and the resulting solution was kept in the fridge overnight. The precipitate was filtered off and discarded, the filtrate was concentrated to 20 mL and left in the fridge overnight again to give crude product, which was then recrystallized twice (Et_2O) and dried under vacuum to give pure $Ph_2P(NH^tBu)$(*N*-*p*-Tol); yield: 1.05 g (15%).

IR (KBr): 3340, 3072, 3052, 2978, 2960, 2920, 1605, 1505, 1440, 1381, 1336, 1219, 1111, 1052, 985 cm^{-1}.

IR (ATR): 3338 cm^{-1} (NH).

^{1}H NMR ($CDCl_3$): δ = 8.01 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 10.8 Hz, 4 H, *o*-H_{Ph}), 7.37–7.46 (m, 6 H, *m*-H_{Ph}, *p*-H_{Ph}), 6.92 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, C_6H_4), 6.86 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, C_6H_4), 2.95 (d, $^2J_{HP}$ = 6.4 Hz, 1 H, NH), 2.24 (s, 3 H, Me_{Tol}), 1.21 (s, 9 H, C*Me*$_3$).

^{13}C NMR ($CDCl_3$): δ = 148.6 (s, *i*-*C*-N_{Tol}), 134.5 (d, $^1J_{CP}$ = 128 Hz, *i*-C_{Ph}), 132.1 (d, $^2J_{CP}$ = 9.0 Hz, *o*-CH_{Ph}), 131.1 (d, $^4J_{CP}$ = 1.9 Hz, *p*-CH_{Ph}), 129.3 (s, β-CH_{Tol}), 128.5 (d, $^3J_{CP}$ = 12.3 Hz, *m*-CH_{Ph}), 126.2 (s, *i*-*C*-Me_{Tol}), 123.7 (d, $^3J_{CP}$ = 20.0 Hz, α-CH_{Tol}), 52.8 (s, *C*Me$_3$), 32.2 (s, C*Me*$_3$), 20.7 (s, NH*Me*).

^{31}P NMR ($CDCl_3$): δ = –3.7.

Anal. Calcd for $C_{23}H_{27}N_2P$: C, 76.22; H, 7.51; N, 7.73. Found: C, 76.09; H, 7.41; N, 7.51.

Synthesis of $Ph_2P(NH^tBu)(N$-*p*-Tol) (1d); Typical Procedure for the Synthesis of $Ph_2P(NH^tBu)$(NAr) (1d, Ar = *p*-Tol; 1e, Ar = *o*-Tol) by Method B

[$Ph_2P(NH^tBu)$(NH*p*-Tol)]Br (3d); Typical Procedure

To a solution of Ph_2PCl (3.6 mL, 4.42 g, 20 mmol) in CH_2Cl_2 (15 mL), a solution of Br_2 (1.0 mL, 3.2 g, 20 mmol) in CH_2Cl_2 (15 mL) was added dropwise. The mixture was stirred for 1.5 h at r.t. to give a suspension, to which a solution of *t*-BuNH_2 (4.2 mL, 2.93 g, 40 mmol) in CH_2Cl_2 (15 mL) was added over 30 min. The mixture was stirred overnight, then the precipitate was filtered off and washed with CH_2Cl_2 (2 × 5 mL). A solution of *p*-toluidine (4.28 g, 40 mmol) in CH_2Cl_2 (30 mL) was added dropwise to the combined filtrate at r.t. and the suspension formed was left overnight. The precipitate was filtered off, washed with CH_2Cl_2 (3 × 10 mL) and discarded. The filtrate was evaporated to dryness, the residue was dissolved in acetone (40 mL) and left for overnight in the fridge. The white crystalline formed was filtered off, washed with acetone (3 × 7 mL) and dried under vacuum to give acetone solvate **3d**·0.5Me_2CO. The solvent-free product was then obtained by precipitating it from CH_2Cl_2 solution with excess Et_2O and successive drying under vacuum; yield: 7.1 g (80%). The elemental analysis well corresponds to a 85:15 mixture of bromide and chloride salts.

IR (KBr): 3025, 2974, 2804, 1710, 1612, 1515, 1439, 1422, 1391, 1356, 1278, 1223, 1193, 1116, 1067, 1053, 1026, 952 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 9.38 (d, $^2J_{HP}$ = 12.8 Hz, 1 H, N*H*Tol), 8.19 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 13.2 Hz, 4 H, *o*-H_{Ph}), 7.55 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *p*-H_{Ph}), 7.46 (td, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 3.6 Hz, 4 H, *m*-H_{Ph}), 7.25 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, C_6H_4), 6.83 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, C_6H_4), 5.79 (d, $^2J_{HP}$ = 10.8 Hz, 1 H, N*H*Bu^t), 2.28 (s, 3 H, Me_{Tol}), 1.25 (s, 9 H, ^{t}Bu).

^{13}C NMR ($CDCl_3$): δ = 135.6 (d, $^2J_{CP}$ = 1.5 Hz, *i*-*C*-N_{Tol}), 133.8 (d, $^4J_{CP}$ = 2.7 Hz, *p*-CH_{Ph}), 132.8 (d, $^2J_{CP}$ = 11.6 Hz, *o*-CH_{Ph}), 132.7 (s, *i*-*C*-Me_{Tol}), 129.6 (s, β-C_{Tol}), 129.4 (d, $^3J_{CP}$ = 14.0 Hz, *m*-CH_{Ph}), 125.1 (d, $^1J_{CP}$ = 128 Hz, *i*-C_{Ph}), 121.3 (d, $^3J_{CP}$ = 7.3 Hz, α-C_{Tol}), 55.9 (d, $^2J_{CP}$ = 3.8 Hz, *C*Me$_3$), 31.5 (d, $^3J_{CP}$ = 4.4 Hz, C*Me*$_3$), 20.7 (s, Me_{Tol}).

^{31}P NMR ($CDCl_3$): δ = 27.0.

Anal. Calcd for $C_{23}H_{28}Br_{0.85}Cl_{0.15}N_2P$: C, 63.26; H, 6.46; N, 6.41; Br, 15.55. Found: C, 63.39; H, 6.49; N, 6.46; Br, 15.5.

[$Ph_2P(NH^tBu)$(NH-*o*-Tol)]Br (3e)

Synthesized analogously from *o*-toluidine (4.4 mL, 4.44 g, 41.2 mmol). The work up procedure was the same except that the crystallization from CH_2Cl_2 gave a solvate, from which the solvent molecule cannot be removed even after drying under vacuum for 2 d at 50 °C; yield: 7.8 g (77%).

IR (KBr): 3054, 2970, 2762, 1606, 1588, 1495, 1439, 1397, 1374, 1288, 1268, 1243, 1229, 1188, 1114, 1052, 1025, 964 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.73 (d, $^2J_{HP}$ = 9.6 Hz, 1 H, N*H*Tol), 8.03 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 13.2 Hz, 4 H, *o*-H_{Ph}), 7.64 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *p*-H_{Ph}), 7.53 (td, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 3.6 Hz, 4 H, *m*-H_{Ph}), 7.05 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 6.94 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 6.86 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 6.76 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 6.11 (s, 1 H, N*H*Bu^t), 2.37 (s, 3 H, Me_{Tol}), 1.20 (s, 9 H, ^{t}Bu).

^{13}C NMR ($CDCl_3$): δ = 135.5 (s, *i*-*C*-Me_{Tol}), 134.3 (d, $^4J_{CP}$ = 1.7 Hz, *p*-CH_{Ph}), 134.0 (d, $^2J_{CP}$ = 7.2 Hz, *i*-*C*-N_{Tol}), 133.2 (d, $^2J_{CP}$ = 11.4 Hz, *o*-CH_{Ph}), 131.3 (s, *m*-CH_{Tol}), 129.4 (d, $^3J_{CP}$ = 13.7 Hz, *m*-CH_{Ph}), 125.9 (d, $^1J_{CP}$ = 124 Hz, *i*-C_{Ph}), 125.5 (s, *m*′-CH_{Tol}), 124.7 (s, *p*-CH_{Tol}), 124.4 (d, $^3J_{CP}$ = 3.1 Hz, *o*-CH_{Tol}), 55.5 (d, $^2J_{CP}$ = 3.0 Hz, *C*Me$_3$), 31.6 (d, $^3J_{CP}$ = 4.1 Hz, C*Me*$_3$), 19.4 (s, Me_{Tol}).

^{31}P NMR ($CDCl_3$): δ = 29.7.

Anal. Calcd for $C_{23}H_{28}BrN_2P$·0.8CH_2Cl_2: C, 55.91; H, 5.84; N, 5.48. Found: C, 55.94; H, 5.91; N, 5.41.

$Ph_2P(NH^tBu)(N$-*p*-Tol) (1d) by Deprotonation of 3d; Typical Procedure for 1d,e

To a suspension of **3d** (0.88 g, 2.0 mmol) in benzene (40 mL) neat Et_2NH (0.22 mL, 0.155 g, 2.1 mmol) was added, and the mixture was stirred at r.t. for 2 h. The precipitate of Et_2NH_2Br was filtered off and washed with benzene (3 × 3 mL). The filtrate was evaporated and the residue was dried in vacuo; yield: 0.72 g (~100%).

$Ph_2P(NH^tBu)(N$-*o*-Tol) (1e)

Obtained analogously from **3e** (0.88 g, 2.0 mmol); yield: 0.70 g (98%).

IR (KBr): 3317, 3076, 3058, 2972, 2960, 2921, 1590, 1484, 1437, 1339, 1220, 1121, 1059, 990 cm^{-1}.

IR (ATR): 3315 cm^{-1} (NH).

^{1}H NMR (C_6D_6): δ = 8.07 (ddd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 11.6 Hz, $^4J_{HH}$ = 2.0 Hz, 4 H, *o*-H_{Ph}), 7.43 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 7.12 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 7.00–7.06 (m, 6 H, *m*-H_{Ph}, *p*-H_{Ph}), 6.92 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 6.88 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 2.88 (s, 3 H, Me_{Tol}), 2.62 (d, $^2J_{HP}$ = 6.8 Hz, 1 H, NH), 1.01 (s, 9 H, ^{t}Bu).

^{13}C NMR (C_6D_6): δ = 149.8 (s, *i*-*C*-N_{Tol}), 135.3 (d, $^1J_{CP}$ = 127 Hz, *i*-C_{Ph}), 132.9 (d, $^3J_{CP}$ = 24.8 Hz, *i*-*C*-Me_{Tol}), 132.1 (d, $^2J_{CP}$ = 9.0 Hz, *o*-CH_{Ph}), 131.7 (s, *m*′-CH_{Tol}), 130.4 (d, $^4J_{CP}$ = 1.8 Hz, *p*-CH_{Ph}), 128.3 (d, $^3J_{CP}$ = 12.3 Hz, *m*-CH_{Ph}), 125.9 (s, *m*-CH_{Tol}), 122.1 (d, $^3J_{CP}$ = 11.4 Hz, *o*-CH_{Tol}), 117.7 (s, *p*-CH_{Tol}), 52.4 (s, *C*Me_3), 31.6 (d, $^3J_{CP}$ = 3.6 Hz, C*Me*$_3$), 20.0 (s, Me_{Tol}).

^{31}P NMR (C_6D_6): δ = –6.5.

Anal. Calcd for $C_{23}H_{27}N_2P$: C, 76.22; H, 7.51; N, 7.73. Found: C, 76.29; H, 7.54; N, 7.43.

Ph_2P(NH-*o*-Tol)(N-*p*-Ts) (1f)

To a solution of Ph_2PCl (1.80 mL, 2.21 g, 10 mmol) in CH_2Cl_2 (10 mL), a solution of Br_2 (0.5 mL, 1.56 g, 10 mmol) in CH_2Cl_2 (10 mL) was added dropwise with stirring at r.t., and the mixture was stirred for 1.5 h. Then the suspension of Ph_2PClBr_2 formed was cooled down to 0 °C and a solution of *o*-toluidine (2.13 mL, 2.14 g, 20 mmol) in CH_2Cl_2 (15 mL) was added dropwise over 0.5 h. The mixture was allowed to warm up to r.t. and stirred overnight. The precipitated *o*-$TolNH_3^+Cl^-$ was filtered off under argon and washed with CH_2Cl_2 (3 × 10 mL); the filtrate was reacted further with suspension of *p*-TsNHNa in THF prepared in situ by treating *p*-$TsNH_2$ (3.42 g, 20 mmol) with NaH (0.80 g, 60% suspension in oil, 20 mmol) in THF (100 mL) at r.t. overnight. The suspension was refluxed for ~35 h, then hot mixture was filtered through a G4 fritted glass filter, and the solid was washed with hot THF (3 × 20 mL). The filtrate was concentrated to ~10 mL and was left in the fridge overnight. The precipitate was filtered off, washed with cold THF (3 × 3 mL) and dried under vacuum to give the product (1.9 g). An additional crop of the product was obtained by treating the mother liquor solution with Et_2O (10 mL). The product was recrystallized (THF) to give pure **1** as off-white microcrystalline; yield: 2.81 g (61%).

IR (KBr): 3378, 3240, 3056, 2917, 1602, 1584, 1496, 1442, 1388, 1375, 1268, 1242, 1191, 1141, 1119, 1110, 1086, 949 cm^{-1}.

IR (ATR): 3250 cm^{-1} (NH).

^{1}H NMR ($CDCl_3$): δ = 7.92 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 13.6 Hz, 4 H, *o*-H_{Ph}), 7.57 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, $SO_2C_6H_4$), 7.54 (td, $^3J_{HH}$ = 7.6 Hz, $^5J_{HP}$ = 1.6 Hz, 2 H, *p*-H_{Ph}), 7.44 (td, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 4.0 Hz, 4 H, *m*-H_{Ph}), 7.10 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, *o*-H_{Tol}), 6.97 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, $SO_2C_6H_4$), 6.82 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, *p*-H_{Tol}), 6.68 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, *m*-H_{Tol}), 6.57 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, *m*′-H_{Tol}), 5.74 (d, $^2J_{HP}$ = 5.2 Hz, 1 H), 2.36 (s, 3 H, Me_{Ts}), 2.28 (s, 3 H, Me_{Tol}).

^{13}C NMR ($CDCl_3$): δ = 142.6 (s, *i*-*C*-S_{Ts}), 140.8 (s, *i*-*C*-Me_{Ts}), 135.6 (d, $^2J_{CP}$ = 1.5 Hz, *i*-*C*-N_{Tol}), 133.1 (d, $^4J_{CP}$ = 2.8 Hz, *p*-CH_{Ph}), 132.4 (d, $^2J_{CP}$ = 10.8 Hz, *o*-CH_{Ph}), 130.7 (s, *p*-CH_{Tol}), 129.1 (d, $^3J_{CP}$ = 13.7 Hz, *m*-CH_{Ph}), 128.1 (d, $^1J_{CP}$ = 132 Hz, *i*-C_{Ph}), 128.7 (s, CH_{Ts}), 127.7 (d, $^3J_{CP}$ = 8.1 Hz, *i*-*C*-Me), 126.6 (s, *m*′-CH_{Tol}), 125.9 (s, CH_{Ts}), 122.9 (s, *m*-CH_{Tol}), 119.5 (d, $^3J_{CP}$ = 4.2 Hz, *o*-CH_{Tol}), 21.4 (s, Me_{Ts}), 18.0 (s, Me_{Tol}).

^{31}P NMR ($CDCl_3$): δ = 12.1.

Anal. Calcd for $C_{26}H_{25}N_2O_2PS$: C, 67.81; H, 5.47; N, 6.08. Found: C, 67.81; H, 5.53; N, 6.11.

Ph_2PBr(N-2,6-^{i}Pr$_2$C$_6$H$_3$) (4c)

To a solution of Ph_2PCl (3.60 mL, 4.42 g, 20 mmol) in CH_2Cl_2 (15 mL), a solution of Br_2 (1.0 mL, 3.2 g, 20 mmol) in CH_2Cl_2 (15 mL) was added dropwise with stirring at r.t., and the mixture was stirred for 1.5 h. Then a solution of 2,6-diisopropylaniline (11.3 mL, 10.62 g, 60 mmol) in CH_2Cl_2 (40 mL) was added dropwise to the suspension of Ph_2PClBr_2, and the mixture was stirred overnight. The precipitated ammonium salt was filtered off and washed with CH_2Cl_2 (3 × 20 mL). The filtrate was evaporated to dryness and the residue was dissolved in hexane (30 mL). The precipitate of residual ammonium salt and aminophosphine oxide Ph_2P(O)(NH-2,6-Diip) was filtered off and discarded, the filtrate was evaporated and the oily residue was dried under vacuum; yield: 8.4 g (80–85% purity) (out of 8.8 g in theory).

^{1}H NMR (C_6D_6): δ = 7.77 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 14.4 Hz, 4 H, *o*-H_{Ph}), 7.20 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, *m*-C_6H_3), 7.09 (td, $^3J_{HH}$ = 7.8 Hz, $^5J_{HP}$ = 1.2 Hz, 1 H, *p*-C_6H_3), 6.97 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *p*-H_{Ph}), 6.92 (td, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 4.8 Hz, 4 H, *m*-H_{Ph}), 3.68 (sept, $^3J_{HH}$ = 6.6 Hz, 2 H, C*H*Me_2), 1.22 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$).

^{13}C NMR (C_6D_6): δ = 141.6 (br d, $^3J_{CP}$ = 10.0 Hz, *i*-C-^{i}Pr_{Diip}), 140.3 (s, *i*-C-N_{Diip}), 133.6 (d, $^1J_{CP}$ = 126 Hz, *i*-C_{Ph}), 132.0 (s, *p*-CH_{Ph}), 131.5 (d, $^2J_{CP}$ = 11.1 Hz, *o*-C_{Ph}), 128.5 (d, $^3J_{CP}$ = 14.6 Hz, *m*-C_{Ph}), 123.3 (d, $^4J_{CP}$ = 3.0 Hz, *m*-CH_{Diip}), 121.9 (br s, *p*-CH_{Diip}), 28.7 (s, C*H*Me_2), 23.9 (s, CH*Me*$_2$).

^{31}P NMR (C_6D_6): δ = –3.1.

MS (EI, 70 eV): *m*/*z* (%) = 439 (10) [M] (**4c**), 395 (60) [M′] (**4c′**), 377 (40) [M – Br + OH], 359 (100) [M – HBr].

Funding Information

This work was supported by the Russian Science Foundation (grant No. 19-13-00459). NMR studies, spectral characterization, elemental analysis were performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690242.

References

(1) (a) Kögel, J. F.; Kneusels, N.-J.; Sundermeyer, J. *Chem. Commun.* **2014**, *50*, 4319. (b) Gao, X.; Han, J.; Wang, L. *Org. Lett.* **2015**, *17*, 4596.

(2) (a) Keim, W.; Appel, R.; Storeck, A.; Krüger, C.; Goddard, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 116; *Angew. Chem.* **1981**, *93*, 11191. (b) Schubbe, R.; Angermund, K.; Fink, G.; Goddard, R. *Macromol. Chem. Phys.* **1995**, *196*, 467. (c) Stapleton, R. L.; Chai, J.; Taylor, N. J.; Collins, S. *Organometallics* **2006**, *25*, 2514. (d) Collins, S.; Ziegler, T. *Organometallics* **2007**, *26*, 6612. (e) Stapleton, R. A.; Chai, J.; Nuanthanom, A.; Flisak, Z.; Nele, M.; Ziegler, T.; Rinaldi, P. L.; Soares, J. B. P.; Collins, S. *Macromolecules* **2007**, *40*, 2993. (f) Vollmerhaus, R.; Shao, P.; Taylor, N. J.; Collins, S. *Organometallics* **1999**, *18*, 2731. (g) Tomaszewski, R.; Vollmerhaus, R.; Al-Humydi, A.; Wang, Q.; Taylor, N. J.; Collins, S. *Can. J. Chem.* **2006**, *84*, 214.

(3) Li, S.; Miao, W.; Tang, T.; Dong, W.; Zhang, X.; Cui, D. *Organometallics* **2008**, *27*, 718.

(4) (a) Albahily, K.; Fomitcheva, V.; Gambarotta, S.; Korobkov, I.; Murugesu, M.; Gorelsky, S. I. *J. Am. Chem. Soc.* **2011**, *133*, 6380. (b) Albahily, K.; Fomitcheva, V.; Shaikh, Y.; Sebastiao, E.; Gorelsky, S. I.; Gambarotta, S.; Korobkov, I.; Duchateau, R.

Organometallics **2011**, *30*, 4201. (c) Albahily, K.; Licciulli, S.; Gambarotta, S.; Korobkov, I.; Chevalier, R.; Schuhen, K.; Duchateau, R. *Organometallics* **2011**, *30*, 3346.

(5) (a) Straub, B. F.; Hofmann, P. *Angew. Chem. Int. Ed.* **2001**, *40*, 1288; *Angew. Chem.* **2001**, *113*, 1328. (b) Straub, B. F.; Gruber, I.; Rominger, F.; Hofmann, P. *J. Organomet. Chem.* **2003**, *684*, 124. (c) Shishkov, I. V.; Rominger, F.; Hofmann, P. *Organometallics* **2009**, *28*, 1049.

(6) Nebra, N.; Lescot, C.; Dauban, P.; Mallet-Ladeira, S.; Martin-Vaca, B.; Bourissou, D. *Eur. J. Org. Chem.* **2013**, 984.

(7) Peganova, T. A.; Kalsin, A. M.; Ustynyuk, N. A.; Vasil'ev, A. A. *Russ. Chem. Bull.* **2014**, *63*, 2305.

(8) Sinopalnikova, I. S.; Peganova, T. A.; Belkova, N. V.; Deydier, E.; Daran, J.-C.; Shubina, E. S.; Kalsin, A. M.; Poli, R. *Eur. J. Inorg. Chem.* **2018**, 2285.

(9) Yang, Y.; Lv, K.; Wang, L.; Wang, Y.; Cui, D. *Chem. Commun.* **2010**, *46*, 6150.

(10) Guo, W.-J.; Wang, Z.-X. *J. Org. Chem.* **2013**, *78*, 1054.

(11) (a) Paciorek, K. L.; Kratzer, R. H. *J. Org. Chem.* **1966**, *31*, 2426. (b) Wingerter, S.; Pfeiffer, M.; Murso, A.; Lustig, C.; Stey, T.; Chandrasekhar, V.; Stalke, D. *J. Am. Chem. Soc.* **2001**, *123*, 1381. (c) Vollmerhaus, R.; Tomaszewski, R.; Shao, P.; Taylor, N. J.; Wiacek, K. J.; Lewis, S. P.; Al-Humydi, A.; Collins, S. *Organometallics* **2005**, *24*, 494. (d) Cristau, H.-J.; Tailefer, M.; Jouanin, I. *Synthesis* **2001**, 69.

(12) (a) Scherer, O. J.; Klusmann, P. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 541; *Angew. Chem.* **1968**, *80*, 560. (b) Scherer, O. J.; Schieder, G. *Chem. Ber.* **1968**, *101*, 4184. (c) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353.

(13) (a) Cristau, H.-J.; Garcia, C. *Synthesis* **1990**, 315. (b) Cristau, H.-J.; Garcia, C.; Kadoura, J.; Torreilles, E. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1990**, *49–50*, 151. (c) Gusev, O. V.; Peganova, T. A.; Gonchar, A. V.; Petrovskii, P. V.; Lyssenko, K. A.; Ustynyuk, N. A. *Phosphorus, Sulfur, Silicon Relat. Elem.* **2009**, *184*, 322.

(14) (a) Li, S.; Cui, D.; Li, D.; Hou, Z. *Organometallics* **2009**, *28*, 4814. (b) Qi, C.; Zhang, S. *Appl. Organomet. Chem.* **2006**, *20*, 70. (c) Prashanth, B.; Singh, S. *Dalton Trans.* **2014**, *43*, 168808. (d) Scherer, O. J.; Schieder, G. *J. Organomet. Chem.* **1969**, *19*, 315.

(15) Rufanov, K. A.; Titov, I. Y.; Petrov, A. R.; Harms, K.; Sundermeyer, J. *Z. Anorg. Allg. Chem.* **2019**, *645*, 559.

(16) Peganova, T. A.; Sinopalnikova, I. S.; Peregudov, A. S.; Fedyanin, I. V.; Demonceau, A.; Ustynyuk, N. A.; Kalsin, A. M. *Dalton Trans.* **2016**, *45*, 170301.

(17) Ford, R. R.; Goodman, M. A.; Neilson, R. H.; Roy, A. K.; Wettermark, U. G.; Wisian-Neilson, P. *Inorg. Chem.* **1984**, *23*, 2063.

(18) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875.

(19) Breugst, M.; Tokuyasu, T.; Mayr, H. *J. Org. Chem.* **2010**, *75*, 5250.

(20) (a) Brotzel, F.; Chu, Y. C.; Mayr, H. *J. Org. Chem.* **2007**, *72*, 3679. (b) Kanzian, T.; Nigst, T. A.; Maier, A.; Pichl, S.; Mayr, H. *Eur. J. Org. Chem.* **2009**, 6379.

