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The investigation of the steric hindrance of anilines by means of reactions with PCl_3 and BCl_3†

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Sterically crowded ligands form an integral part of contemporary coordination chemistry. The most common ones include bulky anilines, which are well accessible and modifiable. Ever increasing requirements to primary amines' steric protection leads to reaching the limits of amino-group shielding. In this work, the dissymmetrical aniline $Ar^{t\text{-}Bu}$-NH_2 (**1**) ($Ar^{t\text{-}Bu}$ = 2-C(4-*t*-Bu-C_6H_4)$_3$-4-Me-6-($CHPh_2$)-C_6H_3) is designed and synthesized. Its shielding properties have been evaluated both theoretically and experimentally by the reaction with phosphorus trichloride and a base, giving monomeric chloro(imino)phosphine $Ar^{t\text{-}Bu}$-N=PCl (**3**). The same reactivity of extremely bulky anilines Ar^{H}-NH_2 and Ar^{Me}-NH_2 (Ar^{H} = 2,6-[C(Me)Ph_2]$_2$-C_6H_3; Ar^{Me} = 2,6-[C(Me)(3,5-Me_2-C_6H_3)$_2$]$_2$-C_6H_3) was tested. The products [2,6-R_2-4-PCl_2-C_6H_2]-NH_2 (**4^H**, **4^{Me}**) of C–H activation bearing NH_2 and PCl_2 groups simultaneously on the opposite sides of the central phenyl ring have been isolated alongside the desired products Ar^{H}-NH-PCl_2 (**5^H**) and Ar^{Me}-NH-PCl_2 (**5^{Me}**). Subsequent theoretical and experimental investigation has revealed that the electrophilic substitution by phosphorus trichloride is preferred over the reaction with the sterically encumbered anilide. When the reactions with phosphorus(III) compounds were conducted under forcing conditions, it was possible to isolate several imidophosphines, namely Ar^{H}-N=$PNMe_2$ (**8^H**) and Ar^{Me}-N=$PNMe_2$ (**8^{Me}**), but the steric shielding did not enable direct conversion to the chloro(imino) phosphines Ar^{H}-N=PCl (**9^H**) and Ar^{Me}-N=PCl (**9^{Me}**). For another comparison of steric hindrance, the reactions of Ar^{H}-NH_2, Ar^{Me}-NH_2 and $Ar^{t\text{-}Bu}$-NH_2 with BCl_3 and BH_3 have been carried out. Regardless of the fact that symmetrical anilines with bulkier substituents have given mixtures of unidentified products, the reactions of dissymmetrical aniline yielded the dichloroamidoborane $Ar^{t\text{-}Bu}$-$NHBCl_2$ (**10**) and $Ar^{t\text{-}Bu}$-$NHBH_2$ (**12**) as the first evidence of a terminal $NHBH_2$ group. The substituents in aniline **1** shield the amine group sufficiently, maintaining space for both the synthesis of amides and their subsequent reactivity.

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Introduction

The kinetic stabilization of the reactive metal centers in terms of ligand exchange or oxidation/reduction plays an important role in many branches of coordination and organometallic chemistry.[1] Sterically demanding ligands have accessed new classes of compounds, for example, in main-group chemistry by introducing compounds in unusual oxidation states, which can adopt some properties of transition metals and thus are active in homogeneous catalysis or small-molecule activation.[2–5] A considerable part of the sterically crowded ligands is based on anilines because of their accessibility and modifiability. Their steric and electronic properties can be easily tuned by the substituents at the *ortho*-positions, which can be both aliphatic (Scheme 1A and B) and aromatic (Scheme 1C). These anilines had been prepared years before their potential in coordination chemistry was fully exploited.[6–8] Their steric protection was crucial for the synthesis of many reactive multiply bonded moieties. The heavier analogues of imidazolium salts were supported by the supermesityl group (Mes* = 2,4,6-*t*-Bu_3-C_6H_2).[9,10] The benzhydryl-substituted aniline (Scheme 1B) enabled, for example, the synthesis of chloropnictenium ions.[11] The most suitable aniline for the stabilization of reactive multiple bonds, which was pioneered by the group of Prof. Power, bears a bulky *m*-terphenyl group

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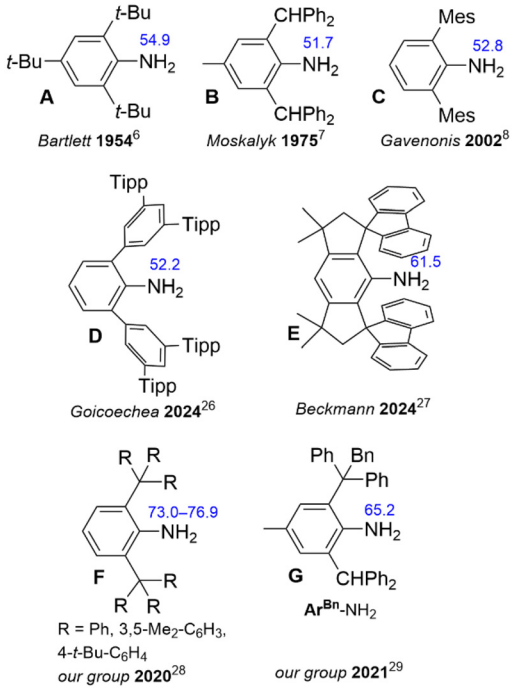
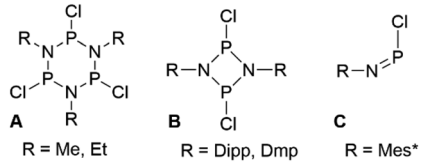
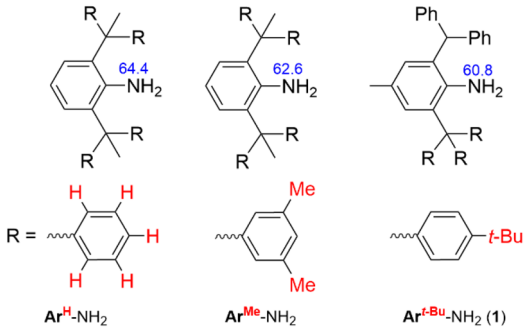


Scheme 1 An overview of sterically demanding anilines and their buried volumes (sphere with a radius of 3.5 Å and nitrogen centre) in blue [%]. Bn = benzyl, Mes = 2,4,6-trimethylphenyl, Tipp = 2,4,6-tri-iso-propylphenyl.



Scheme 2 Examples of chloro(imino)phosphines and their dimers and trimers. Dipp = 2,6-di-iso-propylphenyl, Dmp = 2,6-dimethylphenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl.



Scheme 3 An overview of the sterically demanding anilines Ar^X-NH_2 (X = terminal group of tertiary *ortho*-substituents) used in this work and their buried volumes (sphere with a radius of 3.5 Å and nitrogen centre) in blue [%].[28]

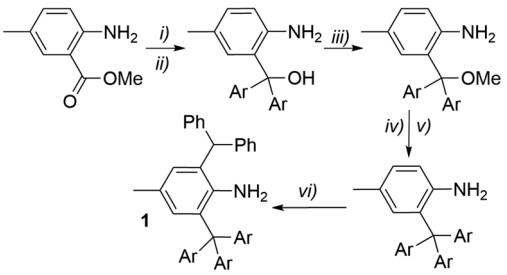
(Scheme 1C).[12–15] The ideal orientation of the mesityl groups facilitated the isolation of many imides of groups 13–15, for instance, two-coordinate gallium(III), indium(III), some transition-metal imides and dimeric heavier analogs of isonitriles. Moreover, the shielding of the terphenyl group enabled the synthesis of many stable radical, biradical and biradicaloid species.[12–25] The research into novel aniline backbones is still proceeding, as evidenced by the recent synthesis of a two-coordinate phosphinidene oxide, which remains stable at ambient temperature when supported by a sterically hindered *m*-terphenyl (Scheme 1D).[26] Beckmann has recently published the first stable nitrene derived from a bulky aniline containing fluorenyl-protecting groups (Scheme 1E).[27] In 2021, our work group published the most sterically hindered anilines (Scheme 1F)[28] considering their buried volumes in proximal space, *i.e.* the percentage of the volume of a sphere centered around the shielded atom with a radius of 3.5 Å, which was occupied by the aryl backbone. There was not much space left for reactivity. Therefore, we continued with the synthesis of a dissymmetrical substituted 2-benzhydryl-4-methyl-6-(1,1-diphenyl-2-phenylethyl)aniline (Scheme 1G, Ar^{Bn}-NH_2),[29] which proved that a proper combination of steric parameters could provide shielding of the reactive center while maintaining space for reactivity. However, its synthesis has been time-consuming and low-yielding, and could not be upscaled.

The steric parameters of amines can be evaluated based on their chemical properties. For example, chloro(imino)phosphines are ideal reactivity targets. Depending on the shielding of the organic group, they form dimeric or trimeric units (Scheme 2A and B), because the trivalent phosphorus atom in the formal N=P double bond is prone to share its electron density in sp^3 hybridized orbitals.[30,31] Substantial steric protection is required for the stabilization of the monomeric chloro(imino)phosphines (Scheme 2C). So far, only Mes*,[9] Ar^{Bn} and the above-mentioned extremely bulky *m*-terphenyl have been able to provide it.[26,29] As published earlier, neither benzhydryl- nor mesityl-substituted anilines were able to prevent the dimerization.[29]

This work presents the synthesis of a novel dissymmetrical aniline (Scheme 3), which is expected to have the ideal steric parameters for the stabilization of reactive amides. It also demonstrates its subsequent reactivity in contrast to the most sterically crowded anilines.

Results and discussion

The four-step process that we have designed begins with the reduction of methyl 2-amino-5-methylbenzoate with a Grignard reagent and methylation of the new hydroxy group (Scheme 4). Step three is performed by non-catalyzed C–C coupling, resembling the reaction that has facilitated the synthesis of the most sterically demanding anilines.[28] The only difference is the change of the solvent from THF to toluene. During the optimization of the reaction conditions, we found out that the presence of the excess THF lowers the yield. We



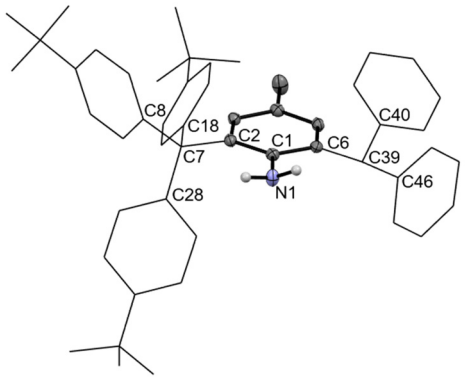
Scheme 4 The synthesis of $Ar^{t\text{-}Bu}$-NH_2 (**1**). (i) 4-*t*-Bu-C_6H_4MgBr; (ii) NH_4Cl; (iii) $CH(OMe)_3/H_2SO_4$; (iv) 4-*t*-Bu-C_6H_4MgBr; (v) NH_4Cl; and (vi) $Ph_2CH(OH)/ZnCl_2/HCl$.

tested other solvents such as Et_2O, CPME and 2-Me-THF with the same result. The last step is Friedel–Crafts alkylation, which requires heating to 180 °C because of the high melting point of the parent aniline. The whole procedure can be completed smoothly within two weeks on a multigram scale, achieving an overall yield of 15%. In order to evaluate the steric properties of aniline **1** ($Ar^{t\text{-}Bu}$-NH_2), we calculated its buried volume (60.9%), which can be compared with those of the anilines Ar^{H}-NH_2 and Ar^{Me}-NH_2 as well as the above-mentioned fluorenyl-substituted aniline (Scheme 1E and F; 61.5–64.4%) despite the 'small' benzhydryl group (for more information, see the ESI). The efficiency of the shielding provided by the substituted trityl group is clearly illustrated in the steric map of **1** (Fig. 1). The buried volumes of **1**, Ar^{H}-NH_2 and Ar^{Me}-NH_2 decrease with increasing spherical radius from 2.5 to 6.0 Å (Fig. S45†), which is consistent with the fact that the tertiary organic groups provide the most efficient shielding to the nitrogen atom preventing potential oligomerizations. This is in contrast with anilines bearing terphenyl groups, which have lower buried volume in the region close to the nitrogen atom but provide better long-range shielding owing to their geometry.[32]

The molecular structure of $Ar^{t\text{-}Bu}$-NH_2 (**1**) has revealed no intermolecular contacts between the amino groups (Fig. 1). Both shielding groups exhibit a similar orientation relative to the corresponding symmetrical anilines.[28] The ^1H and ^{13}C NMR spectra of **1** and its precursors strongly resemble those of previously published sterically demanding anilines prepared by uncatalyzed C–C coupling.

The reaction of **1** with an excess of PCl_3 and triethylamine smoothly yields chloro(imino)phosphine **3** within one day (Scheme 5). Intermediate **2** (observed in the ^1H and ^{31}P NMR spectra) can be prepared directly by reacting **1** with *n*-BuLi and subsequently with PCl_3, or alternatively with a mixture of pyridine and PCl_3.

In contrast, the anilines Ar^{H}-NH_2 and Ar^{Me}-NH_2 (Scheme 1) fail to react with a mixture of PCl_3 and a base (triethylamine, DBU or pyridine) even at elevated temperatures and with an excess of the base. Therefore, the parent anilines were reacted with *n*-BuLi and subsequently with PCl_3 (Scheme 6). Surprisingly, this resulted in a mixture of the *para*-substituted anilines $\mathbf{4}^{H}$ and $\mathbf{4}^{Me}$ alongside the desired products $\mathbf{5}^{H}$ and $\mathbf{5}^{Me}$



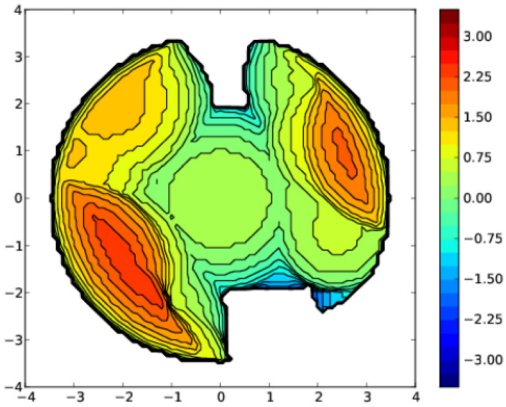
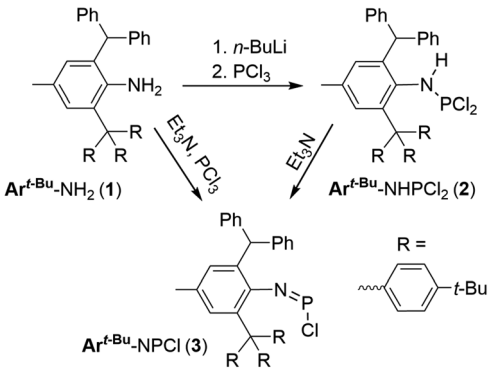
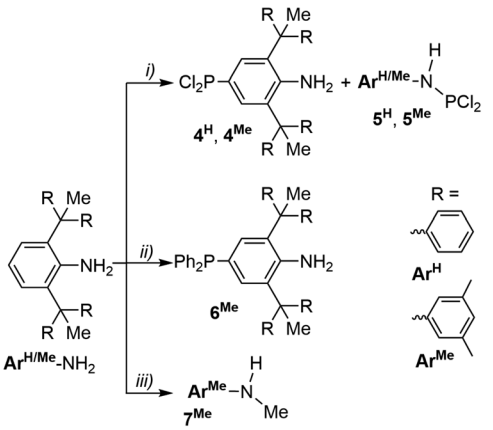


Fig. 1 The molecular structure (above) and the steric map[33] (below) of **1**. An ORTEP diagram, 40% probability level. The shielding groups are displayed as wireframes for clarity. Selected interatomic distances [Å] and angles [°]: C1–N1 1.4031(19), C2–C7 1.5561(18), C7–C28 1.546(2), C6–C39 1.5295(19), C39–C40 1.531(2).

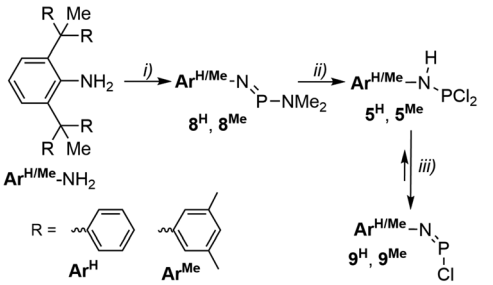


Scheme 5 The reactivity of the dissymmetrical aniline **1**.

in a ratio of approximately 9 : 1, as determined by the ^1H NMR spectra. Neither the optimization of the reaction conditions nor the use of various deprotonation agents (*n*-BuLi, LDA, MeMgBr, Me_2Mg, $NaNH_2$, LiHMDS, NaphNa, BnK, KC_8, or a mixture of *n*-BuLi and TMEDA) shifted the ratio in favor of the amidophosphines $\mathbf{5}^{H}$ and $\mathbf{5}^{Me}$, which were instead synthesized using an alternative approach (see Scheme 7). To the best of our knowledge, this is the first reported example of such C–H



Scheme 6 The deprotonation of symmetrical anilines and subsequent reactivity of the anilides. (i) 1. *n*-BuLi, 2. PCl_3; (ii) 1. *n*-BuLi, 2. Ph_2PCl; and (iii) 1. *n*-BuLi, 2. MeOTf.



Scheme 7 The reactivity of symmetrical anilines. (i) $(Me_2N)_2PCl$; (ii) PCl_3/HCl; and (iii) Et_3N.

activation in an anilide to date. This appears to be a consequence of the steric shielding around the central amino group. The only example of a similar C–H substitution was performed at tertiary *N*,*N*-dimethylaniline, where overnight heating at 115 °C and the presence of pyridine were necessary.[34] In order to shed further light on the mechanism of the C–H activation, we considered several reaction pathways for the starting aniline $\mathbf{Ar^{Me}}$-NH_2. First, we excluded the possibility of deprotonation of the C–H group by *n*-BuLi or the anilide $\mathbf{Ar^{Me}}$-NHLi, which is most likely formed in the first step. This was experimentally confirmed by quenching the reaction mixture with D_2O, which revealed a decrease exclusively in the integral intensity of the NH_2 group in the ^{1}H NMR spectrum, while no reduction in the *p*-C–H signal was observed, even after repeated deprotonation and quenching. The DFT calculations support both possible ways (see Fig. S46†). The lithiation of the NH_2 group is more thermodynamically preferable (ΔG_r = −44.96 kcal mol^{-1}) compared to the *para*-position (ΔG_r = −19.25 kcal mol^{-1}). The anilide $\mathbf{Ar^{Me}}$-NHLi is unexpectedly labile, decomposing slowly even in non-coordinating solvents. However, the addition of a base (Et_2O, THF, and TMEDA) significantly accelerates this decomposition. The subsequent reaction with phosphorus trichloride can then proceed as a conversion with the anilide group, which has been observed numerous times in the literature,[35,36] or electrophilic substitution at the *para*-position. The DFT-estimated Gibbs free energies of both reactions are comparable (−25.62 ($\mathbf{4^{Me}}$) and −22.10 ($\mathbf{5^{Me}}$) kcal mol^{-1}). The theoretical mechanism of the conversion (Fig. S47†) proceeds without thermodynamic barriers. In contrast, the activation energy for the attack at the *para*-position is 12.53 kcal mol^{-1} (TS-1) (Fig. S48†). The electrophilic substitution starts with the formation of a Menshutkin-type complex[37] of phosphorus trichloride followed by coordination to the *para*-position, eliminating hydrogen chloride in the end. Despite the thermodynamic barrier, this is the preferred reaction pathway due to the steric factors. To prove this experimentally, we conducted the reaction with Ph_2PCl (Scheme 6), which yields exclusively $\mathbf{6^{Me}}$ as the product of *para*-substitution. We also tested the reactions of $\mathbf{Ar^{Me}}$-NH_2 and $\mathbf{Ar^{Me}}$-NHLi with MeOTf and $MeNTf_2$. The reactions with the parent aniline do not proceed even with an excess of the methylating agents at elevated temperature. However, the anilide reacted with MeOTf yielding $\mathbf{Ar^{Me}}$-N(H)Me ($\mathbf{7^{Me}}$) because the lithium atom could be removed smoothly by the triflate unlike the hydrogen atom in the aniline $\mathbf{Ar^{Me}}$-NH_2. In contrast, the reaction of the anilide $\mathbf{Ar^{Me}}$-NHLi with the sterically more crowded bis(triflimide) did not proceed most probably because of the steric shielding of the *ortho*-substituents.

The dichlorophosphines $\mathbf{4^H}$ and $\mathbf{4^{Me}}$ are the first compounds simultaneously bearing the groups PCl_2 and NH_2, which would normally undergo spontaneous condensation with the elimination of hydrogen chloride. This is prevented by the steric protection of the *ortho*-substituents. The phosphines $\mathbf{4^H}$, $\mathbf{4^{Me}}$, $\mathbf{5^H}$ and $\mathbf{5^{Me}}$ exhibit distinct differences in their NMR spectra. The replacement of the hydrogen atom by the PCl_2 group in $\mathbf{4^H}$ and $\mathbf{4^{Me}}$ is reflected in both the ^{1}H NMR spectra (by the absence of the *para-H* signal) and the $^{13}C\{^1H\}$ NMR spectra (through the high coupling constant $^1J(^{13}C, ^{31}P)$ = 36.8 Hz). Compounds **2**, $\mathbf{5^H}$ and $\mathbf{5^{Me}}$ exhibited the expected downfield-shifted N*H* signals at 4.22 (**2**), 4.81 ($\mathbf{5^H}$) and 5.37 ($\mathbf{5^{Me}}$) ppm. There are only negligible differences between the chemical shifts of the prepared dichlorophosphines in the ^{31}P NMR spectra (**2**: $\delta(^{31}P)$ = 157 ppm; $\mathbf{4^H}$/$\mathbf{5^H}$: $\delta(^{31}P)$ = 167/160 ppm; $\mathbf{4^{Me}}$/$\mathbf{5^{Me}}$: $\delta(^{31}P)$ = 168/162 ppm). These values are comparable to those of analogous published compounds, such as 4-PCl_2-C_6H_4-NMe_2 ($\delta(^{31}P)$ = 165 ppm)[34] and Dipp-N(H)PCl_2 ($\delta(^{31}P)$ = 155 ppm).[35] The signal of chloro(imino)phosphine **3** ($\delta(^{31}P)$ = 124 ppm) is slightly upfield-shifted compared to Mes*-N=PCl and $\mathbf{Ar^{Bn}}$-N=PCl ($\delta(^{31}P)$ = 136 and 137 ppm, respectively).[9,35]

The molecular structures of **2**, $\mathbf{4^H}$ and $\mathbf{5^H}$ were confirmed by X-ray diffraction analysis (Fig. 2–4). The molecular structures of $\mathbf{Ar^{t\text{-}Bu}}$-$NHPCl_2$ (**2**) and $\mathbf{Ar^H}$-$NHPCl_2$ ($\mathbf{5^H}$) (Fig. 2 and 3) revealed significant differences in the orientation of the $NHPCl_2$ group (Fig. 3). In both cases, the geometry around the phosphorus atom is best described as a distorted trigonal pyramid, with different orientations of the N1–Cl1–Cl2 plane relative to the central ring of the aniline backbone (**2**: 30.87°;

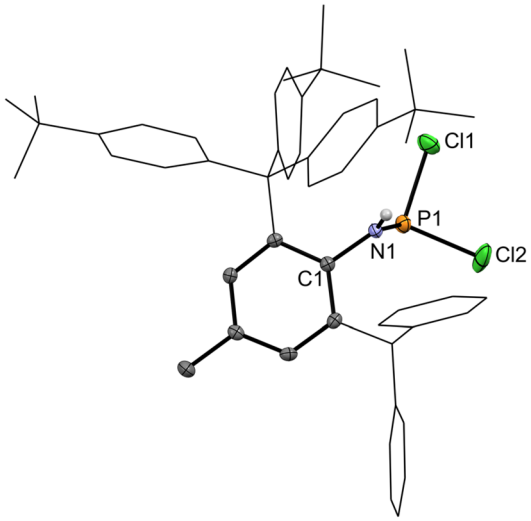


Fig. 2 The molecular structure of **2**. An ORTEP diagram, 40% probability level. The shielding groups are displayed as wireframes for clarity. Selected interatomic distances [Å] and angles [°]: C1–N1 1.444(3), N1–P1 1.6481(19), P1–Cl1 2.0500(9), P1–Cl2 2.1072(9), C1–N1–P1 120.41(15), N1–P1–Cl1 100.84(7), N1–P1–Cl2 105.53(7), Cl1–P1–Cl2 95.35(4).

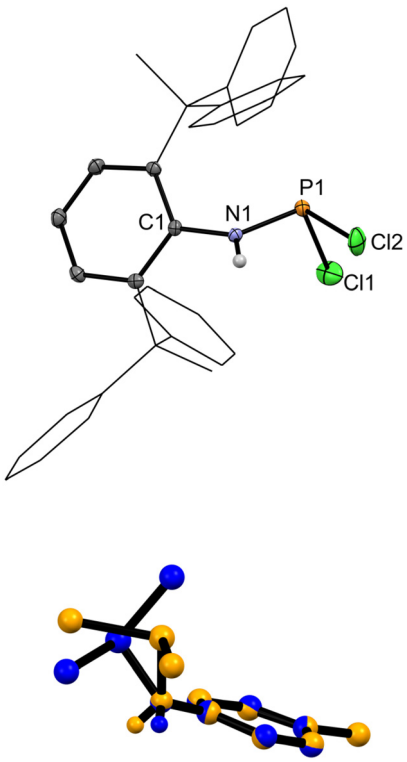


Fig. 3 The molecular structure of 5^{H} (above). An ORTEP diagram, 40% probability level. Selected interatomic distances [Å] and angles [°]: C1–N1 1.427(2), N1–P1 1.6628(13), P1–Cl1 2.1321(6), P1–Cl2 2.0565(6), C1–N1–P1 126.88(11), N1–P1–Cl1 105.16(5), N1–P1–Cl2 95.85(5), Cl1–P1–Cl2 97.62(3). The overlapping molecular structures (below) of **2** (orange) and 5^{H} (blue). The *ortho*-substituents have been omitted for clarity.

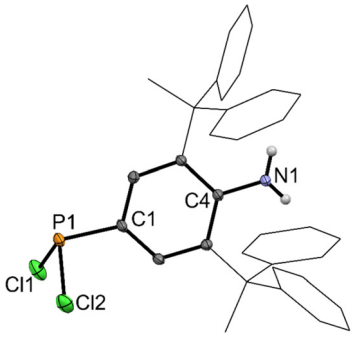


Fig. 4 The molecular structure of 4^{H}. An ORTEP diagram, 40% probability level. The shielding groups are displayed as wireframes for clarity. Selected interatomic distances [Å] and angles [°]: C4–N1 1.368(2), C1–P1 1.792(2), P1–Cl1 2.0694(6), P1–Cl2 2.0706(6), C1–P1–Cl1 103.24(5), C1–P1–Cl2 101.14(5), Cl1–P1–Cl2 97.73(2).

5^{H}: 85.81°). The difference is most likely a consequence of the high steric repulsion of the trityl group in **2**, where one of the chlorine atoms is oriented directly between two of the aromatic rings. This is also evident from the values observed in the structures of analogous compounds bearing anilines with lower buried volumes (Dipp-$NHPCl_2$: 40.62°; 2,6-Mes_2-C_6H_3-$NHPCl_2$: 47.12°).[35,36] The shielding of the amino group in 4^{H} is further demonstrated by the absence of any intermolecular interactions with the chlorine atoms.

The molecular structure of 4^{H} (Fig. 4) has revealed no intermolecular interactions between the NH_2 and PCl_2 groups, which reflects the steric shielding of the tertiary organic groups. The geometry around the phosphorus atom is best described as a slightly distorted trigonal pyramidal structure resembling that of other similar compounds, such as 2,6-Mes_2-C_6H_3-PCl_2.[38]

In order to avoid deprotonation by strong nucleophiles, we treated the anilines $\mathbf{Ar^{H}}$-NH_2 and $\mathbf{Ar^{Me}}$-NH_2 with phosphorus amides ($(Me_2N)_3P$, $(Me_2N)_2PCl$ and Me_2NPCl_2). Using an excess of $(Me_2N)_2PCl$ and high temperature (160 °C) yielded the corresponding imides $\mathbf{8^{H}}$ and $\mathbf{8^{Me}}$ (Scheme 7), whereas the other reagents left the anilines intact. Their molecular structures were confirmed by X-ray diffraction analysis (see the ESI†) in the solid state and by multinuclear NMR spectroscopy. For example, $\delta(^{31}P)$ = 266 ($\mathbf{8^{H}}$) and 271 ($\mathbf{8^{Me}}$) ppm were nearly identical to $\delta(^{31}P)$ = 268 ppm for Mes*-N=PN(i-Pr)$_2$.[39] The desired chloro(imino)phosphine was prepared by reacting $\mathbf{8^{H}}$ and $\mathbf{8^{Me}}$ with one equivalent of hydrogen chloride, which yielded a mixture of the corresponding anilines $\mathbf{Ar^{H}}$-NH_2($\mathbf{Ar^{Me}}$-NH_2), $\mathbf{8^{H}}$ ($\mathbf{8^{Me}}$), $\mathbf{5^{H}}$ ($\mathbf{5^{Me}}$), and $\mathbf{Ar^{R}}$-N(H)P(Cl)NMe_2 (as determined from ^{1}H and ^{31}P NMR spectra). Since some phosphorus (III) amides can undergo ligand-scrambling reactions (for instance, the synthesis of the above-mentioned amides from $(Me_2N)_3P$ and PCl_3),[40] the same reaction was performed in the presence of excess PCl_3 to yield compounds $\mathbf{5^{H}}$ and $\mathbf{5^{Me}}$. Subsequent treatment with triethylamine surprisingly led to the establishment of an equilibrium between $\mathbf{5^{H}}$ ($\mathbf{5^{Me}}$) and $\mathbf{9^{H}}$ ($\mathbf{9^{Me}}$), which could not be shifted by an excess of the base, a

change of solvent, or variation in temperature. A similar situation was observed in the synthesis of chloro(imino)phosphine derived from bulky *m*-terphenyl aniline (Scheme 1E).[26] Consequently, mixtures of $\mathbf{5^H}$ ($\mathbf{5^{Me}}$), $\mathbf{9^H}$ ($\mathbf{9^{Me}}$) and triethylammonium chloride were consistently obtained. The ^{31}P NMR shifts of $\mathbf{9^H}$ and $\mathbf{9^{Me}}$ ($\delta(^{31}P)$ = 128 and 129 ppm, respectively) were nearly identical to that of **3**.

The molecular structures of $\mathbf{8^H}$, $\mathbf{8^{Me}}$, $\mathbf{9^H}$ and $\mathbf{9^{Me}}$ (Fig. 5 and 6) confirmed the presence of a phosphorus–nitrogen multiple bond. The P–N separations ($\mathbf{8^H}$, $\mathbf{8^{Me}}$: 1.545(2)–1.557(2) Å, $\mathbf{9^H}$, $\mathbf{9^{Me}}$: 1.414(2)–1.485(2) Å) were significantly shortened in the case of compounds $\mathbf{9^H}$ and $\mathbf{9^{Me}}$, which corresponds to the sum of covalent radii for a triple bond (Σr_{cov}(P≡N) = 1.48 Å).[41] This is most likely caused by the inductive effect of the chlorine atom, which polarizes the P–N bond. The polarization is weaker in $\mathbf{8^H}$ and $\mathbf{8^{Me}}$, but the bond lengths still lie between the sums of covalent radii for double and triple bonds (Σr_{cov}(P=N) = 1.62 Å). Similar interatomic distances have been observed in analogous compounds, for example, in Mes*-N=PNMe$_2$ (1.539(3) Å)[38] and Mes*-N=PCl (1.508(4) Å).[9] In $\mathbf{8^H}$ and $\mathbf{8^{Me}}$, the NMe$_2$ group adopts the *anti*-position relative to the central ring (both arrangements are documented in the literature).[42] The chlorine atom in $\mathbf{9^H}$ and $\mathbf{9^{Me}}$ occupies the *syn*-position, similar to other published chloroiminophosphines.[9,26,29] The most striking difference between the chloroiminophosphines $\mathbf{9^H}$ and $\mathbf{9^{Me}}$ and the published compounds is the C–N–P angle, which is significantly wider (170.9(17)° for $\mathbf{9^H}$ and 174.1(2)° for $\mathbf{9^{Me}}$, compared to 141.1(2)–147.1(2)° for the published phosphines). This is most likely caused by the higher steric repulsion of the aniline backbone.

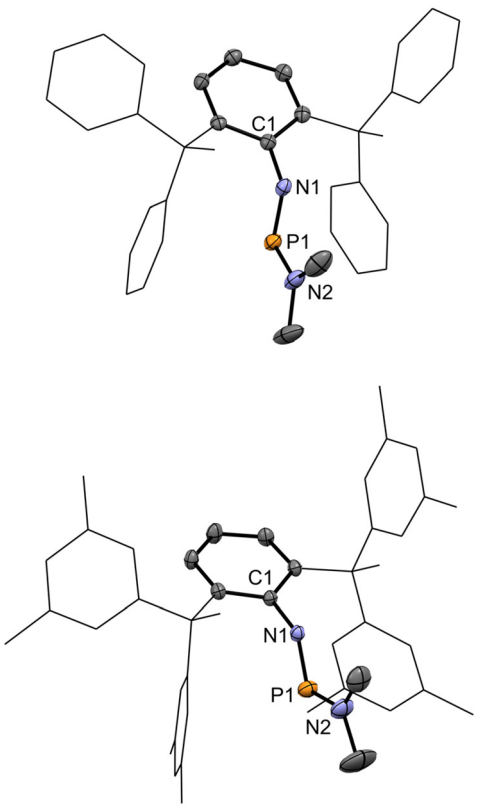


Fig. 5 The molecular structures of $\mathbf{8^H}$ (above) and $\mathbf{8^{Me}}$ (below). An ORTEP diagram, 40% probability level. The shielding groups are displayed as wireframes for clarity. Selected interatomic distances [Å] and angles [°]: $\mathbf{8^H}$: C1–N1 1.401(2), N1–P1 1.5562(16), P1–N2 1.6502(19), C1–N1–P1 125.67(12), N1–P1–N2 104.34(9); $\mathbf{8^{Me}}$: C1–N1 1.399(3), N1–P1 1.545(2), P1–N2 1.653(3), C1–N1–P1 129.54(17), N1–P1–N2 104.86(12).

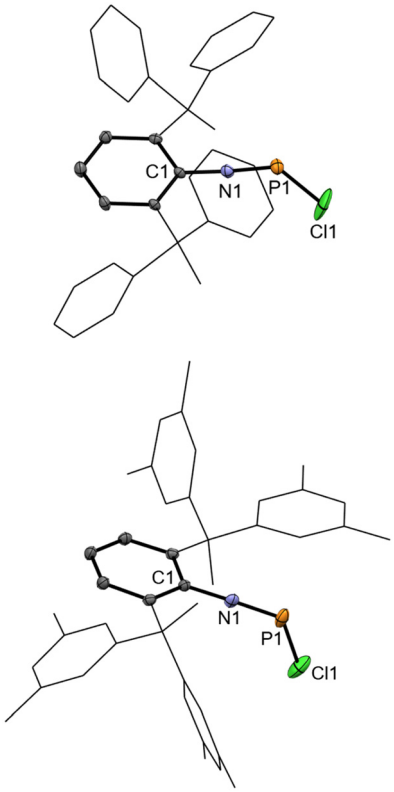
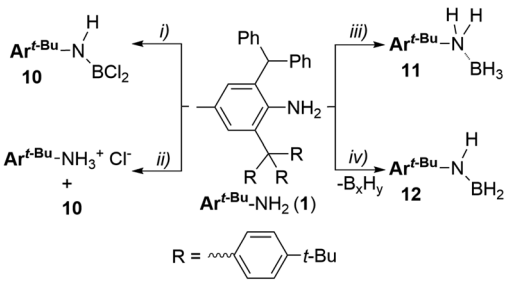


Fig. 6 The molecular structures of $\mathbf{9^H}$ (above) and $\mathbf{9^{Me}}$ (below). An ORTEP diagram, 40% probability level. The shielding groups are displayed as wireframes for clarity. Selected interatomic distances [Å] and angles [°]: $\mathbf{9^H}$: C1–N1 1.41(3), N1–P1 1.414(19), P1–Cl1 1.892(9), C1–N1–P1 170.9(17), N1–P1–Cl1 121.9(8); $\mathbf{9^{Me}}$: C1–N1 1.394(3), N1–P1 1.485(2), P1–Cl1 2.1618(8), C1–N1–P1 174.1(2), N1–P1–Cl1 114.23(8).

The presented results clearly demonstrate that the dissymmetrical aniline **1** can shield the reactive P=N double bond more efficiently than symmetrical anilines. Consequently, we decided to react it with boron compounds to investigate whether it could stabilize Lewis-acidic boron amides in their monomeric form. The reaction with BCl_3 produced a 1 : 1 mixture of the aminoborane $\mathbf{Ar^{t\text{-}Bu}}$-NHBCl$_2$ (**10**) and the corresponding anilinium salt $\mathbf{Ar^{t\text{-}Bu}}$-NH$_3$Cl (Scheme 8). Due to their very similar solubility, compound **10** was instead prepared directly through the reaction of *n*-BuLi and BCl_3. The reactions of primary amines with BCl_3 typically proceed *via* condensation,[43–45] yielding trimeric borazines (RNBCl)$_3$. The intermediate RNHBCl$_2$ has been observed by ^{11}B NMR spectroscopy;[46,47] however, to the best of our knowledge, it has never been fully characterized.



Scheme 8 The reactivity of aniline **1** with BCl_3, BH_3·THF and B_2H_6. (i) 1. *n*-BuLi, 2. BCl_3; (ii) BCl_3; (iii) BH_3·THF; and (iv) BnCl, Bu_4NBH_4.

The ^{11}B NMR shift ($\delta(^{11}B)$ = 32.3 ppm) of the BCl_2 group in **10** is similar to those observed in other structurally characterized monomeric amidoboranes of the type R_2NBCl_2. For instance, Dmp-N(BCl_2)CH=CHN(BCl_2)-Dmp exhibits a shift of $\delta(^{11}B)$ = 31.0 ppm (ref. 48) and the mentioned intermediates of the type $RNHBCl_2$ show shifts of 32.0 and 32.8 ppm. Surprisingly, the reaction of the anilines **Ar^{H}**-NH_2 and **Ar^{Me}**-NH_2 with BCl_3 yields complicated mixtures of products.

The N1–B1 separation (1.378(6) Å) in the molecular structure of **10** (Fig. 7) is closer to the sum of the covalent radii for a double bond (Σr_{cov}(B=N) = 1.38 Å) than for a single bond (Σr_{cov}(B–N) = 1.56 Å),[49] which is consistent with the strong electron donation from nitrogen to the vacant orbital of boron. This bond length slightly exceeds those observed in other monomeric dichloroamides, such as Ph_2NBCl_2: 1379(7) Å[50] and Dmp-N(BCl_2)CH=CHN(BCl_2)-Dmp: 1.395(2) Å[48].

Following the successful synthesis of **10**, we aimed to explore an analogous synthesis of the terminal $NHBH_2$ group, which had remained elusive to date due to its tendency to undergo various condensation reactions.[51,52] Consequently, **1** was treated with THF·BH_3 in hexane, which resulted in the smooth precipitation of the Lewis adduct **Ar$^{t\text{-Bu}}$**-NH_2·BH_3 (**11**). However, the dissolution of **11** led to a partial release of borane even at room temperature, most likely caused by the steric repulsion with the aniline backbone. This is further supported by the molecular structure of **11** in the solid state (Fig. 8). The separation of the N1–B1 bond is the longest among the published complexes $ArNH_2$·BH_3, where it decreases in length with the reduced bulk of the aryl backbone (**Ar$^{t\text{-Bu}}$** > Ar* > Dipp > Ph (1.687(3)–1.619(3) Å)).[50,52] The same trend has been observed for the angle C1–N1–B1 (119.2(2)–115.03(1)°). Therefore, aniline **1** was treated with an excess of *in situ* generated borane,[53] and the reaction mixture was heated in a sealed tube at 90 °C. This led to the formation of the desired compound, displaying the expected signals in both the ^1H NMR (N*H*, $\delta(^1H)$ = 6.11 ppm; BH_2, $\delta(^1H)$ = 5.42 ppm) and ^{11}B NMR spectra ($\delta(^{11}H)$ = −23.5 ppm, dt, $^1J(^{11}B, ^1H)$ = 135.8 Hz, $^2J(^{11}B, ^1H)$ = 40.5 Hz). However, products of borane thermal decomposition, such as pentaborane,[54] were also detected, and their similar solubility hindered the isolation of borane **12**. Nevertheless, this is the first evidence of the $NHBH_2$ terminal group.

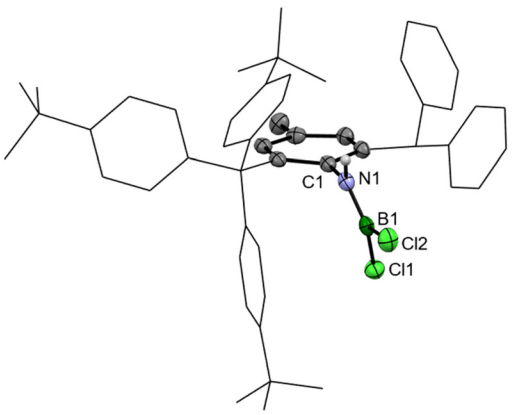


Fig. 7 The molecular structure of **10**. An ORTEP diagram, 40% probability level. The shielding groups are displayed as wireframes for clarity. Selected interatomic distances [Å] and angles [°]: C1–N1 1.432(5), N1–B1 1.378(6), B1–Cl1 1.760(5), B1–Cl2 1.761(5), C1–N1–B1 127.3(3), N1–B1–Cl1 122.0(3), N1–B1–Cl2 119.8(3), Cl1–B1–Cl2 118.1(3).

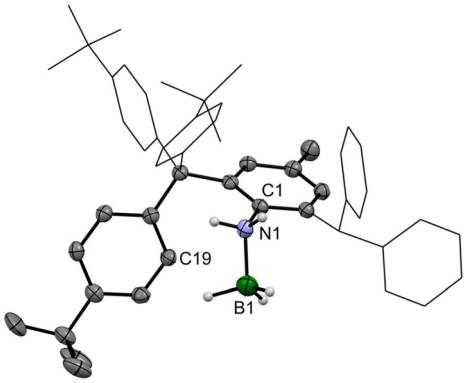


Fig. 8 The molecular structure of **11**. An ORTEP diagram, 40% probability level. The shielding groups are displayed as wireframes for clarity. Selected interatomic distances [Å] and angles [°]: C1–N1 1.460(2), N1–B1 1.687(3), B1–C19 3.316(3), C1–N1–B1 119.3(2).

Experimental section

Materials and methods

All air- and moisture-sensitive manipulations were performed under an argon atmosphere using standard Schlenk-tube techniques. The solvents were dried with PureSolv–Innovative Technology equipment under an argon atmosphere. Deuterated benzene was sourced from Euriso-Top GmbH. Chloro-*N*,*N*-bis(dimethylamino)phosphine was prepared according to the published procedure.[38] *n*-BuLi (1.6 M solution in *n*-hexane, Merck), phosphorus trichloride (Abcr), hydrogen chloride (4 M solution in CPME, Merck), hydrochloric acid (35%, Penta), magnesium (Merck), 1-bromo-4-*t*-butylbenzene (Merck), methyl 2-amino-5-methylbenzoate (Apollo Scientific), trimethyl orthoformate (Merck), diphenylmethanol (Merck), trimethylsilyl chloride (Merck), benzyl chloride (Merck) and *n*-tetrabutylammonium borohydride (Merck) were used as received.

Synthetic procedures

The synthesis of 1-NH_2-2-[C(OH)(4-*t*-Bu-C_6H_4)$_2$]-4-Me-C_6H_3. A solution of 1-bromo-4-*t*-butylbenzene (81.4 g, 382 mmol) in THF (150 mL) was added dropwise to a stirred suspension of magnesium (10.2 g, 420 mmol) in THF (550 mL) at 0 °C. The mixture was then gradually heated to 40 °C and stirred for one day. Afterward, the solution was decanted and added to a solution of methyl 2-amino-5-methylbenzoate (15.8 g, 95 mmol) in THF (300 mL) at 0 °C. The reaction mixture was stirred for one day and then carefully quenched with a saturated solution of NH_4Cl. The organic phase was separated, dried over $MgSO_4$ and filtered. The resulting yellow solution was dried *in vacuo*, and the solid residue was washed with a small amount of *n*-hexane, yielding 1-NH_2-2-[C(OH)(4-*t*-Bu-C_6H_4)$_2$]-4-Me-C_6H_3 as a white powder. Yield: 30.75 g, 85%. **Mp:** 173 °C. Anal. calc. for $C_{28}H_{35}NO$ (401.27): C 83.7, H 8.8, N 3.5; found: C 83.8, H 8.7, N 3.5. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.20 (s, 18H, CH_3), 1.92 (s, 3H, CH_3), 2.95 (s, 2H, NH_2), 5.75 (s, 1H, O*H*), 6.21 (d, ^3J(^{1}H, ^{1}H) = 7.8 Hz, 1H, *m*-C_6H_3), 6.77 (s, 1H, *m*-C_6H_3), 6.81 (d, ^3J(^{1}H, ^{1}H) = 7.8 Hz, 1H, *o*-C_6H_3), 7.24 (d, ^3J(^{1}H, ^{1}H) = 8.3 Hz, 4H, *m*-C_6H_4), 7.54 (d, ^3J(^{1}H, ^{1}H) = 8.4 Hz, 4H, *o*-C_6H_4) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 20.4 (s, *C*H_3), 31.1 (s, C(*C*H_3)$_3$), 34.1 (s, *C*(CH$_3$)$_3$), 82.0 (s, *C*OH), 119.5 (s, *m*-C_6H_3), 124.9 (s, *m*-C_6H_4), 127.9 (s, *o*-C_6H_4), 128.5 (s, *o*-C_6H_3), 128.8 (s, *o*-C_6H_3), 130.4 (s, *m*-C_6H_3), 134.9 (s, *ipso*-C_6H_3), 141.4 (s, *m*-C_6H_3), 143.9 (s, *ipso*-C_6H_4), 149.5 (s, *p*-C_6H_4) ppm.

The synthesis of 1-NH_2-2-[C(OMe)(4-*t*-Bu-C_6H_4)$_2$]-4-Me-C_6H_3. Sulfuric acid (15.1 mL, 268 mmol, 96%) was added dropwise to a solution of trimethyl orthoformate (135 mL, 1.23 mol) and 1-NH_2-2-[C(OH)(4-*t*-Bu-C_6H_4)$_2$]-4-Me-C_6H_3 (30.8 g, 76.6 mmol) in a 1 : 1 mixture of dichloromethane and methanol while stirring at room temperature. The resulting reaction mixture was stirred for three days, and a small portion (0.5 mL) was taken to check the conversion to the desired product. If any starting material was detected, another portion of sulfuric acid (7.5 mL, 134 mmol, 96%) and trimethyl orthoformate (135 mL, 1.23 mol) was added and stirred for one more day. Otherwise, the reaction mixture was neutralized with a saturated sodium bicarbonate solution. The organic phase was separated, dried over $MgSO_4$, and the volatiles were removed *in vacuo*. The solid residue was washed with a small amount of methanol, yielding 1-NH_2-2-[C(OMe)(4-*t*-Bu-C_6H_4)$_2$]-4-Me-C_6H_3 as a white powder. Yield: 22.75 g, 72%. **Mp**: 144 °C. Anal. calc. for $C_{29}H_{37}NO$ (415.29): C 83.8, H 9.0, N 3.4; found: C 83.5, H 8.9, N 3.5. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.16 (s, 18H, C(CH_3)$_3$), 2.09 (s, 3H, ArCH_3), 3.3 (s, 3H, OCH_3), 3.82 (s, 2H, NH_2), 6.31 (d, ^3J(^{1}H, ^{1}H) = 8 Hz, 1H, *m*-C_6H_3), 6.92 (d, ^3J(^{1}H, ^{1}H) = 8 Hz, 1H, *o*-C_6H_3), 7.23 (d, ^3J(^{1}H, ^{1}H) = 8.4 Hz, 4H, *m*-C_6H_4), 7.38 (s, 1H, *o*-C_6H_3), 7.54 (d, ^3J(^{1}H, ^{1}H) = 8.4 Hz, 4H, *o*-C_6H_4) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 20.5 (s, *C*H$_3$), 31.1 (s, C(*C*H$_3$)), 34.0 (s, *C*(CH$_3$)), 52.2 (s, OCH$_3$), 87.8 (s, Ar$_2$*C*OCH$_3$), 116.9 (s, *m*-C_6H_3), 124.2 (s, *o*-C_6H_3), 124.7 (s, *m*-C_6H_4), 127.8 (s, *o*-C_6H_4), 129.6 (s, *o*-C_6H_3), 132.1 (*m*-C_6H_3), 141.6 (s, *ipso*-C_6H_4), 141.8 (s, *ipso*-C_6H_3), 144.8 (s, *o*-C_6H_3), 149.0 (s, *p*-C_6H_4).

The synthesis of 1-NH_2-2-C(4-*t*-Bu-C_6H_4)$_3$-4-Me-C_6H_3. A solution of 1-bromo-4-*t*-butylbenzene (46.7 g, 219 mmol) in THF (150 mL) was added dropwise to a stirred suspension of magnesium (5.85 g, 240 mmol) in THF (400 mL) at 0 °C. The mixture was gradually heated to 40 °C and stirred for one day. The solution was then decanted and concentrated to 150 mL (viscous oil), and toluene (400 mL) was added. The resulting solution was added dropwise to a solution of 1-NH_2-2-[C(OMe)(4-*t*-Bu-C_6H_4)$_2$]-4-Me-C_6H_3 (15.8 g, 95 mmol) in toluene (300 mL) at 0 °C. The reaction mixture was slowly heated to 50 °C and stirred for one day. The reaction was carefully quenched with a saturated solution of NH_4Cl. The organic phase was separated, dried over $MgSO_4$, and filtered. The resulting yellow solution was dried *in vacuo*, and the solid residue was washed with a small amount of *n*-hexane, yielding 1-NH_2-2-C(4-*t*-Bu-C_6H_4)$_3$-4-Me-C_6H_3 as a white powder. Yield: 11.32 g, 40%. **Mp**: 252 °C. Anal. calc. for $C_{38}H_{47}N$ (517.80): C 88.2, H 9.2, N 2.7; found: C 88.3, H 9.1, N 2.6. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.21 (s, 27H, CH_3), 2.09 (s, 3H, CH_3), 2.93 (s, 2H, NH_2), 6.30 (d, ^3J(^{1}H, ^{1}H) = 7.8 Hz, 1H, *o*-C_6H_3), 6.94 (d, ^3J(^{1}H, ^{1}H) = 7.8 Hz, 1H, *m*-C_6H_3), 7.17 (d, ^3J(^{1}H, ^{1}H) = 8.1 Hz, 6H, *o*-C_6H_4), 7.30 (s, 1H, *m*-C_6H_3), 7.46 (d, ^3J(^{1}H, ^{1}H) = 8.2 Hz, 6H, *o*-C_6H_4) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 21.4 (s, *C*H$_3$), 31.8 (s, C(*C*H$_3$)$_3$), 34.7 (s, *C*(CH$_3$)$_3$), 63.3 (s, *C*Ar$_3$), 118.2 (s, *o*-C_6H_3), 125.1 (s, *m*-C_6H_4), 126.6 (s, *ipso*-C_6H_3), 129.2 (s, *m*-C_6H_3), 126.2 (s, *m*-C_6H_3), 132.0 (s, *m*-C_6H_4), 132.3 (s, *m*-C_6H_3), 132.5 (s, *ipso*-C_6H_3), 143.1 (s, *ipso*-C_6H_4), 144.4 (s, *p*-C_6H_3), 149.1 (s, *p*-C_6H_4) ppm.

The synthesis of Ar$^{t\text{-Bu}}$-NH_2 (1). A mixture of 1-NH_2-2-C(4-*t*-Bu-C_6H_4)$_3$-4-Me-C_6H_3 (2 g, 3.9 mmol) and diphenylmethanol (1.07 g, 5.8 mmol) was heated to 120 °C. It is better to homogenize the mixture as much as possible prior to the heating, because the formation of **1** will solidify the reaction mixture and stop stirring. A solution of zinc chloride (0.53 g, 3.9 mmol) in hydrochloric acid (0.55 mL, 5.8 mmol) was then added dropwise. The resulting mixture was heated to 180 °C for three hours, slowly cooled to room temperature, and extracted with dichloromethane. The organic layer was separated, dried over $MgSO_4$, and filtered. The volatiles were removed *in vacuo*, and the resulting yellow powder was washed twice with a small amount of *n*-pentane (5 mL), yielding **1** as a white powder. Yield: 1.6 g, 61%. **Mp**: 152 °C. Anal. calc. for $C_{51}H_{57}N$ (683.02): C 89.6, H 8.4, N 2.1; found: C 89.5, H 8.2, N 2.0. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.21 (s, 27H, CH_3), 1.97 (s, 3H, CH_3), 3.07 (s, 2H, NH_2), 5.37 (s, 1H, Ph$_2$C*H*), 6.80 (s, 1H, *m*-C_6H_2), 7.02–7.11 (m, 10H, C_6H_5), 7.17 (d, ^3J(^{1}H, ^{1}H) = 8.5 Hz, 6H, *m*-C_6H_4), 7.25 (d, ^3J(^{1}H, ^{1}H) = 8.3 Hz, 1H, *m*-C_6H_2), 7.44 (d, ^3J(^{1}H, ^{1}H) = 8.5 Hz, 6H, *o*-C_6H_4) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 21.7 (s, *C*H$_3$), 31.8 (s, C(*C*H$_3$)$_3$), 34.7 (s, *C*(CH$_3$)$_3$), 53.2 (s, PhCH), 63.6, (s, *C*Ar$_3$), 125.1 (s, *m*-C_6H_4), 126.3 (s, *p*-C_6H_5), 127.0 (s, *p*-C_6H_5), 129.0 (s, *m*-C_6H_5), 130.3 (s, *m*-C_6H_2), 130.4 (s, *o*-C_6H_5), 131.0 (s, *m*-C_6H_2), 131.4 (s, *o*-C_6H_2), 132.0 (s, *o*-C_6H_4), 133.6 (s, *o*-C_6H_2), 142.0 (s, *ipso*-C_6H_2), 143.2 (s, *ipso*-C_6H_4), 143.9 (s, *ipso*-C_6H_5), 149.1 (s, *p*-C_6H_4) ppm.

The synthesis of Ar$^{t\text{-Bu}}$-NHPCl$_2$ (2). Path A. Phosphorus trichloride (0.01 mL, 0.11 mmol) was added to a solution of **1** (0.07 g, 0.1 mmol) in pyridine (2 mL) at room temperature. The resulting yellowish mixture was stirred for two hours. The reaction mixture was filtered, and the volatiles were removed *in vacuo.* The solid residue was washed with a small amount of *n*-hexane, yielding **2** as a yellowish powder. Yield: 0.052 g, 65%. **Path B**. *n*-BuLi (0.38 mL, 0.61 mmol, 1.6 M solution in *n*-hexane) was added to a solution of **1** (0.38 g, 0.57 mmol) in toluene (5 mL) at room temperature. The resulting orange solution was stirred for one hour. Phosphorus trichloride (0.049 mL, 0.57 mmol) was then added to the red solution at −80 °C. The reaction mixture was gradually warmed to room temperature and stirred for one day. The suspension was filtered, and the volatiles were removed *in vacuo*, yielding **2** as a yellowish powder. Yield: 0.375, 86%. **Mp**: 288 °C. Anal. calc. for $C_{51}H_{56}Cl_2NP$ (784.09): C 78.0, H 7.2, N 1.8; found: C 77.9, H 7.1, N 1.6. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.22 (s, 27H, C(CH_3)$_3$), 1.83 (s, 3H, CH_3), 4.27 (s, 1H, NHPCl$_2$), 6.56 (s, 1H, CHPh$_2$), 7.08 (t, ^3J(^{1}H, ^{1}H) = 7.36 Hz, 4H, *m*-C$_6H_5$), 7.15 (t, ^3J(^{1}H, ^{1}H) = 7.36 Hz, 4H, *p*-C$_6H_5$), 7.17–7.22 (m, 11H, *m*-C$_6H_4$ + *o*-C$_6H_5$ + *m*-C$_6H_2$), 7.36 (s broad, 1H, *m*-C$_6H_2$), 7.40 (d, ^3J(^{1}H, ^{1}H) = 8.42 Hz, 6H, *o*-C$_6$H$_4$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 21.6 (s, *C*H$_3$) 31.7 (s, C(*C*H$_3$)$_3$), 34.7 (s, *C*(CH$_3$)$_3$), 53.0 (s, C*H*Ph$_2$), 63.9 (s, *C*Ar$_3$), 125.7 (s, *o*-*C*$_6$H$_4$), 127.6 (s, *p*-*C*$_6$H$_5$), 129.5 (s, *o*-C$_6$H$_5$) 130.8 (s, *o*-*C*$_6$H$_5$), 131.8 (s, *m*-*C*$_6$H$_2$), 131.9 (s, *m*-*C*$_6$H$_2$), 132.1 (s, *m*-*C*$_6$H$_5$), 136.6 (d, ^2J(^{13}C, ^{31}P) = 15.4 Hz, *ipso*-*C*$_6$H$_2$), 136.9 (*p*-*C*$_6$H$_2$), 143.0 (s, *ipso*- *C*$_6$H$_4$), 144.0 (s, *ipso*-*C*$_6$H$_5$), 147.0 (*o*-C$_6$H$_2$) 149.9 (*m*-*C*$_6$H$_4$) ppm. **^{31}P{^{1}H} NMR** (25 °C, C_6D_6, 202.52 MHz): δ = 157.4 (s) ppm.

The synthesis of Ar$^{t\text{-Bu}}$-NPCl (3). Phosphorus trichloride (0.044 mL, 0.5 mmol) was added to a solution of **1** (0.295 g, 0.4 mmol) in triethylamine (5 mL) at room temperature. The resulting yellow suspension was stirred for 16 hours. The volatiles were removed *in vacuo*, and the solid was extracted with benzene. The suspension was filtered, and the volatiles were removed *in vacuo*, yielding **3** as an orange powder. Yield: 0.261 g, 80%. **Mp**: 183 °C. Anal. calc. for $C_{51}H_{55}ClNP$ (748.43): C 81.9, H 7.4, N 1.9; found: C 82.0, H 7.3, N 1.8. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.19 (s, 27H, C(CH_3)$_3$), 1.78 (s, 3H, CH_3), 6.35 (s, 1H, Ph$_2$C*H*), 6.69 (s, 2H, *m*-C$_6H_2$), 6.93 (s, 1H, *m*-C$_6H_2$), 7.0 (t, ^3J(^{1}H, ^{1}H) = 7.3 Hz, 2H, *p*-C$_6H_5$), 7.08 (t, ^3J(^{1}H, ^{1}H) = 7.4 Hz, 4H, *m*-C$_6H_5$), 7.12 (d, ^3J(^{1}H, ^{1}H) = 8.6 Hz, 6H, *m*-C$_6H_4$), 7.17 (d, ^3J(^{1}H, ^{1}H) = 7.4 Hz, 4H, *o*-C$_6H_5$), 7.28 (s, 1H, *m*-C$_6H_2$), 7.30 (d, ^3J(^{1}H,^{1}H) = 8.5 Hz, 6H, *o*-C$_6H_4$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 21.3 (s, *C*H$_3$), 31.3 (s, C(*C*H$_3$)$_3$), 34.2 (s, *C*(CH$_3$)$_3$), 52.7 (s, Ph$_2$*C*H), 63.9 (s, *C*Ar$_3$), 124.5 (s, *m*-*C*$_6$H$_4$), 126.5 (s, *p*-*C*$_6$H$_5$), 128.5 (s, *m*-*C*$_6$H$_5$), 129.9 (s, *m*-*C*$_6$H$_2$) 130.0 (s, *o*-*C*$_6$H$_5$), 130.5 (s, *m*-*C*$_6$H$_2$) 131.8 (s, *o*-*C*$_6$H$_4$), 135.0 (s, *p*-*C*$_6$H$_2$), 136.7 (d, ^3J(^{13}C, ^{31}P) = 9.55 Hz, *o*-*C*$_6$H$_2$), 139.8 (d, ^2J(^{13}C, ^{31}P) = 13.19 Hz, *ipso*-*C*$_6$H$_2$), 139.9 (s, *ipso*-*C*$_6$H$_2$), 142.9 (s, *ipso*-*C*$_6$H$_4$), 143.1 (s, *ipso*-*C*$_6$H$_5$), 148.6 (s, *ipso*-*C*$_6$H$_4$) ppm. **^{31}P{^{1}H} NMR** (25 °C, C_6D_6, 202.52 MHz): δ = 123.6 (s) ppm.

The synthesis of [2,6-(C(Me)Ph$_2$)$_2$-4-NH$_2$-C$_6$H$_2$]PCl$_2$ (4^{H}). *n*-BuLi (0.747 mL, 1.2 mmol, 1.6 M solution in *n*-hexane) was added to a stirred suspension of **Ar^{H}**-NH$_2$ (0.417 g, 0.9 mmol) in *n*-hexane (2 mL) at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred for one day. The suspension was filtered, and *n*-hexane (2 mL) was added. Phosphorus trichloride (0.08 mL, 0.9 mmol) was then added dropwise to the stirred suspension at −80 °C. The reaction mixture was gradually warmed to room temperature and stirred for one day. The suspension was filtered, and the solid was extracted and recrystallized from boiling benzene, yielding **4^{H}** as colorless single crystals. Due to their similar solubility, a small amount (*ca.* 5%) of **5^{H}** could not be separated from the product. Yield: 0.143 g, 29%. **Mp**: 215 °C. Anal. calc. for $C_{34}H_{30}Cl_2NP$ (553.15): C 73.7, H 5.5, N 2.5; found: C 73.5, H 5.4, N 2.4. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.99 (s, 6H, CH_3), 3.67 (s, 2H, NH_2), 6.99–7.11 (m, 20H, Ar*H*), 7.72 (d, ^3J(^{1}H, ^{31}P) = 10.1 Hz, 2H, *m*-C$_6H_2$) ppm. **^{31}P{^{1}H} NMR** (25 °C, C_6D_6, 202.52 MHz): δ = 166.5 (s) ppm.

The synthesis of [2,6-(C(Me)(3,5-Me$_2$-C$_6$H$_3$)$_2$-4-NH$_2$-C$_6$H$_2$]PCl$_2$ (4^{Me}). *n*-BuLi (0.560 mL, 0.9 mmol, 1.6 M solution in *n*-hexane) was added to a stirred suspension of **Ar^{Me}**-NH$_2$ (0.393 g, 0.69 mmol) in *n*-hexane (2 mL) at 0 °C. The mixture was gradually warmed to room temperature and stirred for one day. The reaction mixture was filtered, and *n*-hexane (2 mL) was added. Phosphorus trichloride (0.08 mL, 0.9 mmol) was then added dropwise to the stirred suspension at −80 °C. The reaction mixture was gradually warmed to room temperature and stirred for one day. The suspension was filtered, and the solid was dried *in vacuo*. The solid was extracted and recrystallized from boiling benzene, yielding **4^{Me}** as colorless single crystals. Yield: 0.108 g, 23%. **Mp**: 232 °C. Anal. calc. for $C_{34}H_{30}Cl_2NP$ (681.31): C 75.7, H 7.4, N 2.1; found: C 75.5, H 7.5, N 2.0. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 2.07 (s, 24H, ArCH_3), 2.21 (s, 6H, Ar$_2$C(CH_3)), 3.94 (s, 2H, NH_2), 6.69 (s, 4H, *p*-C$_6H_3^{Me}$), 7.01 (s, 8H, *o*-C$_6H_3^{Me}$), 7.80 (d, ^3J(^{31}P, ^{1}H) = 9.9 Hz, 2H, *m*-C$_6$H$_3$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 22.0 (s, Ar*C*H$_3$), 28.2 (s, Ar$_2$C(*C*H$_3$)), 52.9 (s, Ar$_2$*C*(CH$_3$)), 127.1 (s, *o*-C$_6$H$_3^{Me}$), 129.1 (s, *p*-*C*$_6$H$_3^{Me}$), 132.2 (d, ^1J(^{31}P, ^{13}C) = 36.8 Hz *m*-*C*$_6$H$_2$), 134.4 (s, *p*-*C*$_6$H$_2$), 134.7 (s, *o*-*C*$_6$H$_2$), 138.3 (*m*-*C*$_6$H$_3^{Me}$), 147.0 (*ipso*-*C*$_6$H$_3^{Me}$), 149.3 (s, *ipso*-*C*$_6$H$_2$) ppm. **^{31}P NMR** (25 °C, C_6D_6, 202.52 MHz): δ = 167.6 (t, ^3J(^{31}P, ^{1}H) = 9.9 Hz, Ar*P*Cl$_2$) ppm.

The synthesis of Ar^{H}-NHPCl$_2$ (5^{H}). A solution of phosphorus trichloride (0.23 mL, 2.7 mmol) and hydrogen chloride (0.18 mL, 0.5 mmol, 3 M solution in CPME) in toluene (20 mL) was added dropwise to a stirred solution of **8^{H}** (0.28 g, 0.5 mmol) in toluene (10 mL) at −80 °C. The reaction mixture was gradually warmed to room temperature and stirred for one hour. The volatiles were removed *in vacuo*, and the resulting solid was washed with petroleum ether and dried under reduced pressure, yielding **5^{H}** as a white powder. Yield: 0.262 g, 89%. **Mp**: 171 °C. Anal. calc. for $C_{34}H_{30}Cl_2NP$ (553.15): C 73.7, H 5.5, N 2.5; found: C 73.2, H 5.6, N 2.3. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 2.25 (s, 6H, CCH_3), 4.81 (d, ^2J(^{1}H, ^{31}P) = 1.8 Hz, 1H, N*H*PCl$_2$), 6.70 (t, ^3J(^{1}H, ^{1}H) = 7.9 Hz, 1H, *p*-C$_6H_3$), 7.00 (t, ^3J(^{1}H, ^{1}H) = 7.24 Hz, 4H, *p*-C$_6H_5$), 7.02 (s, 2H, *m*-C$_6H_3$), 7.08 (t, ^3J(^{1}H, ^{1}H) = 7.8 Hz, 8H, *m*-C$_6H_5$), 7.20 (t, ^3J(^{1}H, ^{1}H) = 7.6 Hz, 8H, *o*-C$_6H_5$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 32.3 (s, Ar$_2$C*C*H$_3$), 53.7 (s, Ar$_2$*C*CH$_3$),

124.8 (s, *p*-C_6H_3), 127.2 (s, *p*-C_6H_5), 129.0 (s, *m*-C_6H_3), 129.2 (s, *o*-C_6H_5), 131.6 (s, *m*-C_6H_3), 138.2 (s, $^2J(^{31}P, ^{13}C)$ = 11.8 Hz, *ipso*-C_6H_3), 146.3 (s, *o*-C_6H_3), 148.3 (s, *ipso*-C_6H_5) ppm. **$^{31}P\{^1H\}$ NMR** (25 °C, C_6D_6, 202.52 MHz): δ = 159.6 (s) ppm.

The synthesis of Ar^{Me}-$NHPCl_2$ (5^{Me}). A solution of phosphorus trichloride (0.24 mL, 2.8 mmol) and hydrogen chloride (0.19 mL, 0.6 mmol, 3 M solution in CPME) in toluene (20 mL) was added dropwise to a stirred solution of 8^{Me} (0.36 g, 0.6 mmol) in toluene (10 mL) at −80 °C. The reaction mixture was gradually warmed to room temperature and stirred for one hour. The volatiles were removed *in vacuo*, and the resulting solid was washed with petroleum ether and dried under reduced pressure, yielding 5^{Me} as a white powder. Yield: 0.314 g, 85%. **Mp**: 172 °C. Anal. calc. for $C_{42}H_{46}Cl_2NP$ (665.27): C 76.0, H 7.0, N 2.1; found: C 75.9, H 7.1, N 2.0. **^1H NMR** (25 °C, C_6D_6, 500 MHz): δ = 2.11 (s, 24H, ArCH_3), 2.45 (s, 6H, $Ar_2C(CH_3)$), 5.27 (d, $^2J(^{31}P, ^1H)$ = 2.6 Hz, 1H, N*H*PCl_2), 6.72 (s, 4H, *p*-$C_6H_3^{Me}$), 6.78 (t, $^3J(^1H, ^1H)$ = 7.7 Hz, 1H, *p*-C_6H_3), 7.07 (s, 8H, *o*-$C_6H_3^{Me}$), 7.18 (d, $^3J(^1H, ^1H)$ = 7.9 Hz, 2H, *m*-C_6H_3) ppm. **$^{13}C\{^1H\}$ NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 22.0 (s, Ar*C*H_3), 31.5 (s, $Ar_2C(CH_3)$), 53.7 (s, $Ar_2C(CH_3)$), 124.8 (s, *p*-C_6H_3), 127.7 (s, *p*-$C_6H_3^{Me}$), 129.0 (s, *o*-$C_6H_3^{Me}$), 129.3 (s, *o*-C_6H_3), 131.6 (s, *m*-C_6H_3), 138.6 (s, $^2J(^{31}P, ^{13}C)$ = 11.2 Hz, *ipso*-C_6H_3), 146.3 (s, *o*-C_6H_3), 148.9 (s, *ipso*-$C_6H_3^{Me}$) ppm. **$^{31}P\{^1H\}$ NMR** (25 °C, C_6D_6, 202.52 MHz): δ = 162.2 (s) ppm.

The synthesis of [2,6-(C(Me)(3,5-Me_2-C_6H_3)$_2$-4-NH_2-C_6H_2] PPh_2 (6^{Me}). *n*-BuLi (0.48 mL, 0.76 mmol, 1.6 M solution in *n*-hexane) was added to a stirred suspension of Ar^{Me}-NH_2 (0.29 g, 0.51 mmol) in *n*-hexane (2 mL) at room temperature. The reaction mixture was stirred for 30 minutes and filtered, and *n*-hexane (2 mL) was added. Diphenyl(chloro)phosphine (0.18 mL, 1.0 mmol) was then added dropwise to the stirred suspension at −80 °C. The reaction mixture was gradually warmed to room temperature and stirred for one day. The suspension was filtered and the solid was dried *in vacuo*. The solid was washed with hexane (3 mL) and diethyl ether (3 mL). The colorless solid was extracted with benzene (3 mL) to give 6^{Me} in the form of a colorless powder. Yield 0.140 g, 37%. **Mp.** 237 °C. Anal. calc. for $C_{54}H_{56}NP$ (750.02): C 86.5, H 7.5, N 1.9; found: C 86.4, H 7.3, N 1.8. **^1H NMR** (25 °C, C_6D_6, 500 MHz): δ = 2.06 (s, 24H, Ar-CH_3), 2,27 (s, 6H, CCH_3), 3.62 (s, 2H, NH_2), 6.64 (s, 4H, *p*-$C_6H_3^{Me}$), 6.97–7.04 (m, 8 + 2 + 4H, *o*-$C_6H_3^{Me}$, *m*-C_6H_5, *p*-C_6H_5), 7.28 (d, $^3J(^{31}P, ^1H)$ = 8.22 Hz, 2H, *m*-C_6H_3), 7.33 (t, $^3J(^{31}P, ^1H)$ = 7.65 Hz, *o*-C_6H_5) ppm.**$^{13}C\{^1H\}$ NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 21.69 (s, Ar-*C*H_3), 28.5 (s, C*C*H_3), 52.6 (s, *C*CH_3), 122.9 (d, $^1J(^{31}P, ^{13}C)$ = 6.1 Hz, *ipso*-C_6H_5), 127.2 (s, *o*-$C_6H_3^{Me}$), 128,7, 128.7 (s, *m*-C_6H_5 *p*-C_6H_5), 134.2 (d, $^2J(^{31}P, ^{13}C)$ = 19.21 Hz, *o*-C_6H_5), 135.1 (d, $^3J(^{31}P, ^{13}C)$ = 8.56 Hz, *o*-C_6H_3), 135.8 (d, $^2J(^{31}P, ^{13}C)$ = 22.78 Hz, *m*-C_6H_3), 137.9 (s, *m*-$C_6H_3^{Me}$), 140.3 (d, $^1J(^{31}P, ^{13}C)$ = 11.88 Hz, *p*-C_6H_3), 145.8 (s, *ipso*-C_6H_3), 147.8 (s, *ipso*-$C_6H_3^{Me}$) ppm. **$^{31}P\{^1H\}$ NMR** (25 °C, C_6D_6, 20 252 MHz): δ = −5.8 (s) ppm.

The synthesis of Ar^{Me}-N(H)Me (7^{Me}). *n*-BuLi (0.09 mL, 0.13 mmol, 1.6 M solution in *n*-hexane) was added to a stirred suspension of Ar^{Me}-NH_2 (0.05 g, 0.09 mmol) in *n*-hexane (2 mL) at room temperature. The reaction mixture was stirred for 30 minutes. Methyl trifluoromethanesulfonate (0.02 mL, 0.18 mmol) was added dropwise to the stirred suspension at room temperature and stirred for one day. The suspension was filtered, and the solid was dried *in vacuo*. The solid was extracted with benzene to give 7^{Me} in the form of a colorless powder. Yield 0.03 g, 59%. **Mp.** 169 °C. Anal. calc. for $C_{54}H_{56}NP$ (579.39): C 89.1, H 8.5, N 2.5; found: C 89.0, H 8.6, N 2.5. **^1H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.64 (d, $^3J(^1H, ^1H)$ = 5.76 Hz, 3H, NHCH_3), 2.09 (s, 24H, Ar-CH_3), 2,45 (s, 6H, CCH_3), 3.06 (d broad, $^3J(^1H, ^1H)$ = 5.84 Hz, 1H, N*H*CH_3), 6.71 (s, 4H, *p*-$C_6H_3^{Me}$), 6.79 (t, $^3J(^1H, ^1H)$ = 7.83 Hz, 1H, *p*-C_6H_3), 7.11 (s, 8H, *o*-$C_6H_3^{Me}$), 7.19 (d, $^3J(^1H, ^1H)$ = 7.78 Hz, 2H, *m*-C_6H_3) ppm. **$^{13}C\{^1H\}$ NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 21.9 (s, Ar-*C*H_3), 31.7 (s, C*C*H_3), 36.6 (NH*C*H_3), 54.0 (s, *C*CH_3), 120.8 (s, *p*-C_6H_3), 127.4 (s, *o*-$C_6H_3^{Me}$), 128.4 (s, *p*-$C_6H_3^{Me}$), 132.0 (s, *m*-C_6H_3), 137.7 (s, *m*-$C_6H_3^{Me}$), 143.3 (s, *o*-C_6H_3), 150.5 (s, *ipso*-C_6H_3), 150.6 (s, *ipso*-$C_6H_3^{Me}$) ppm.

The synthesis of Ar^H-N=$PNMe_2$ (8^H). A suspension of Ar^H-NH_2 (1.0 g, 2.6 mmol) and bis-(*N*,*N*-dimethylamino)chlorophosphine (1 mL, 6.9 mmol) was heated to 160 °C and stirred for 16 hours. The reaction mixture was gradually cooled to 85 °C, and *n*-hexane (30 mL) was added. The suspension was filtered and left to crystallize for one day. The resulting yellowish crystals of 8^H were decanted and dried *in vacuo*. Yield: 0.758 g, 64%. **Mp**: 232 °C. Anal. calc. for $C_{36}H_{35}N_2P$ (526.25): C 82.1, H 6.7, N 5.3; found: C 82.0, H 6.5, N 5.32. **^1H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.93 (d, $^3J(^{31}P, ^1H)$ = 10.9 Hz, 3H, N=PN(CH_3)$_2$), 2.33 (s, 6H, Ar_2CCH_3), 2.35 (s, 3H, N=PN(CH_3)$_2$), 6.66 (t, $^3J(^1H, ^1H)$ = 7.9 Hz, 1H, *p*-C_6H_3), 7.00 (t, $^3J(^1H, ^1H)$ = 7.3 Hz, 4H, *p*-C_6H_5), 7.07 (t, $^3J(^1H, ^1H)$ = 7.3 Hz, 8H, *m*-C_6H_5), 7.13 (d, $^3J(^1H, ^1H)$ = 7.9 Hz 2H, *m*-C_6H_3), 7.25 (d, $^3J(^1H, ^1H)$ = 7.9 Hz, 8H, *o*-C_6H_5) ppm. **$^{13}C\{^1H\}$ NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 29.0 (s, Ar_2CCH_3), 33.7 (d, $^2J(^{31}P, ^{13}C)$ = 9.3 Hz, N=PN*C*H_3), 35.3 (d, $^2J(^{31}P, ^{13}C)$ = 41.5 Hz, N=PN*C*H_3), 53.6 (s, Ar_2CCH_3), 118.4 (s, *p*-C_6H_3), 126.23 (s, *p*-C_6H_5), 128.4 (s, *m*-C_6H_5), 129.6 (s, *o*-C_6H_5), 129.9 (s, *m*-C_6H_3), 137.7 (d, $^2J(^{31}P, ^{13}C)$ = 16.8 Hz, *ipso*-C_6H_3), 147.7 (s, *ipso*-C_6H_3), 150.8 (s, *ipso*-C_6H_5) ppm. **$^{31}P\{^1H\}$ NMR** (25 °C, C_6D_6, 202.52 MHz): δ = 265.9 (s) ppm.

The synthesis of Ar^{Me}-N=$PNMe_2$ (8^{Me}). A suspension of Ar^{Me}-NH_2 (1.0 g, 1.8 mmol) and bis-(*N*,*N*-dimethylamino)chlorophosphine (1 mL, 6.9 mmol) was heated to 160 °C and stirred for 16 hours. The reaction mixture was gradually cooled to 85 °C, and *n*-hexane (30 mL) was added. The suspension was filtered and left to crystallize for one day. The resulting yellowish crystals of 8^{Me} were decanted and dried *in vacuo*. Yield: 0.678 g, 60%. **Mp**: 250 °C. Anal. calc. for $C_{44}H_{51}N_2P$ (638.88): C 82.7, H 8.1, N 4.4; found: C 82.5, H 8.0, N 4.2. **^1H NMR** (25 °C, C_6D_6, 500 MHz): δ = 2.03 (s broad, 3H, N(CH_3)$_2$), 2.10 (s, 24H, Ar-CH_3), 2.53 (s, 6H, CCH_3), 2.57 (s, 3H, N(CH_3)$_2$), 6.69 (t, $^3J(^1H, ^1H)$ = 7.8 Hz, 1H, *p*-C_6H_3), 6.71 (s, 4H, *p*-$C_6H_3^{Me}$), 7.07 (s, 8H, *o*-$C_6H_3^{Me}$), 7.23 (d, $^3J(^1H, ^1H)$ = 7.8 Hz, 2H, *m*-C_6H_3) ppm. **$^{13}C\{^1H\}$ NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 22.0 (s, Ar*C*H_3), 28.4 (s, Ar_2CCH_3), 33.7 (s, N=PN(*C*H_3)$_2$), 35.4 (s, N=PN(*C*H_3)$_2$), 53.5 (s, Ar_2CCH_3), 118.3 (s, *p*-C_6H_3), 127.9 (s, *o*-$C_6H_3^{Me}$), 127.9 (s, *p*-$C_6H_3^{Me}$), 130.1 (s, *m*-C_6H_3), 137.6 (s, *ipso*-$C_6H_3^{Me}$), 138.7 (d, $^2J(^{31}P, ^{13}C)$ = 17.0 Hz, *ipso*-C_6H_3), 148.1 (s,

ipso-C_6H_3), 151.3 (s, *ipso*-$C_6H_3^{Me}$) ppm. **$^{31}P\{^1H\}$ NMR** (25 °C, C_6D_6, 20 252 MHz): δ = 271.3 (s) ppm.

An attempted synthesis of Ar^H-N=PCl (9^H). Triethylamine (0.72 mL, 5.2 mmol) was added dropwise to a stirred solution of 5^H (0.87 g, 1.3 mmol) in benzene at room temperature. The suspension was stirred for three days and filtered. Another portion of triethylamine (0.18 mL, 1.3 mmol) was then added, and the resulting suspension was filtered again. Crystallization at 4 °C for seven days yielded a mixture of single crystals: colorless crystals of 5^H and triethylammonium chloride and red crystals of 9^H.

An attempted synthesis of Ar^{Me}-N=PCl (9^{Me}). Triethylamine (0.49 mL, 3.5 mmol) was added dropwise to a stirred solution of 5^{Me} (0.58 g, 0.9 mmol) in benzene at room temperature. The suspension was stirred for three days and filtered. Another portion of triethylamine (0.12 mL, 0.9 mmol) was then added, and the resulting suspension was filtered again. Crystallization at 4 °C for seven days yielded a mixture of single crystals: colorless crystals of 5^{Me} and triethylammonium chloride and red crystals of 9^{Me}.

A synthesis of $Ar^{t\text{-}Bu}$-$NHBCl_2$ (10). *n*-BuLi (0.48 mL, 0.76 mmol, 1.6 M solution in *n*-hexane) was added dropwise to a stirred solution of **1** (0.52 g, 0.76 mmol) in toluene (5 mL) at room temperature. The reaction mixture was stirred for one hour. Boron trichloride (0.77 mL, 0.77 mmol) was then added dropwise to the stirred solution at room temperature. After ten minutes, the reaction mixture was filtered, the volatiles were removed *in vacuo*, and the resulting solid was washed with *n*-hexane (10 mL), yielding **10** as a colorless powder. Yield: 0.327 g, 56%. **Mp**: 289 °C. **^1H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.18 (s, 27H, $C(CH_3)_3$), 1.85 (s, 3H, CH_3), 5.10 (s, 1H, NH_2), 6.0 (s, 1H, $CHPh_2$), 6.94–7.12 (m, 11H, C_6H_5 + *m*-C_6H_2), 7.15 (d, $^3J(^1H,^1H)$ = 8.72 Hz), 6H, (*m*-C_6H_4), 7.32 (d, $^3J(^1H,^1H)$ = 8.70 Hz), 6H, (*o*-C_6H_4) ppm. **$^{13}C\{^1H\}$ NMR** (25 °C, C_6D_6, 125.76 MHz): δ = 21.8 (s, CH_3) 31.3 (s, $C(CH_3)_3$), 34.2 (s, $C(CH_3)_3$), 53.4 (s, $CHPh_2$), 63.4 (s, CAr_3), 125.1 (s, *o*-C_6H_4), 128.9 (s, *m*-C_6H_5), 130.2 (s, *m*-C_6H_2), 130.3 (s, *o*-C_6H_5), 130.5 (s, *p*-C_6H_5), 130.9 (s, *p*-C_6H_5), 131.3 (s, *m*-C_6H_4), 136.4 (s, *p*-C_6H_2), 136.5 (s, *m*-C_6H_5), 142.5 (s, *ipso*-C_6H_4), 143.7 (s, *ipso*-C_6H_5), 143.5 (s, *p*-C_6H_2), 144.6 (s, *o*-C_6H_2), 144.8 (s, *o*-C_6H_2), 149.2 (s, *m*-C_6H_4) ppm. **$^{11}B\{^1H\}$** (25 °C, C_6D_6, 160 MHz): 32.3 (s broad) ppm.

A synthesis of $Ar^{t\text{-}Bu}$-NH_2·BH_3 (11). A solution of the tetrahydrofuran complex of borane (0.19 mL, 0.19 mmol, 1 M solution in THF) was added dropwise to a stirred solution of **1** (0.064 g, 0.94 mmol) in petroleum ether (2 mL). The reaction mixture was stirred for two hours. The resulting suspension was filtered, and the solid was dried at −20 °C, yielding **11** as a white powder. Yield: 0.32, 49%.

An attempted synthesis of $Ar^{t\text{-}Bu}$-$NHBH_2$ (12). Benzyl chloride (6.9 μL, 0.06 mmol) was added to a solution of **1** (0.04 g, 0.06 mmol) and tetrabutylammonium borohydride (0.015 g, 0.12 mmol) in deuterated benzene (0.5 mL). The reaction mixture was sealed in an NMR tube and heated to 90 °C. NMR spectra were recorded immediately and subsequently after 20, 90 and 240 minutes.

Conclusions

In conclusion, we have developed a novel dissymmetrically substituted aniline **1**, which combines high buried volume with retained space for reactivity. This has been exemplified through the successful synthesis of chloro(imino)phosphane **3** and the monomeric dichloroamidoborane **10**. For comparison, we have tested the reactivity of the most sterically demanding anilines, which exhibited unprecedented C–H activation at the *para*-position of the aniline. This reaction facilitated the synthesis of the first compounds, 4^H and 4^{Me}, simultaneously bearing PCl_2 and NH_2 groups. It is thus evident that it is not necessary to have extremely crowded substituents at both *ortho*-positions of the aniline.

Author contributions

The manuscript was prepared with contributions from all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†

Crystallographic data for structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 2404684 (**1**); 2404683 (**2**); 2404678 (4^H); 2404677 (5^H); 2404685 (8^H); 2404676 (8^{Me}); 2404680 (9^H); 2404679 (9^{Me}); 2404681 (**10**); and 2404682 (**11**).

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References

1 P. P. Power, *Nature*, 2010, **463**(7278), 171–177.
2 M. E. Evans and C. Jones, *Chem. Soc. Rev.*, 2024, **53**, 5054–5082.
3 T. Chu and G. I. Nikonov, *Chem. Rev.*, 2018, **118**, 3608–3680.
4 A. J. Boutland, D. Dange, A. Stasch, L. Maron and C. Jones, *Angew. Chem., Int. Ed.*, 2016, **55**, 9239–9243.
5 T. J. Hadlington, M. Driess and C. Jones, *Chem. Soc. Rev.*, 2018, **47**, 4176–4197.

6 P. D. Bartlett, M. Roha and R. M. Stiles, *J. Am. Chem. Soc.*, 1954, **76**, 2349–2353.
7 R. E. Moskalyk and J. L. Malicky, *J. Pharm. Sci.*, 1975, **64**, 292–294.
8 J. Gavenonis and T. D. Tilley, *J. Am. Chem. Soc.*, 2002, **124**, 8536–8537.
9 E. Niecke, M. Nieger and F. Reichert, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1715–1716.
10 M. Kuprat, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2013, **52**, 7126–7130.
11 C. Hering-Junghans, M. Thomas, A. Villinger and A. Schulz, *Chem. – Eur. J.*, 2015, **21**, 6713–6717.
12 R. J. Wright, A. D. Phillips, T. L. Allen, W. H. Fink and P. P. Power, *J. Am. Chem. Soc.*, 2003, **125**, 1694–1695.
13 N. J. Hardman, C. Cui, H. W. Roesky, W. H. Fink and P. P. Power, *Angew. Chem., Int. Ed.*, 2001, **40**, 2172–2174.
14 R. J. Wright, M. Brynda, J. C. Fettinger, A. R. Betzer and P. P. Power, *J. Am. Chem. Soc.*, 2006, **128**, 12498–12509.
15 S. R. Baird, E. Hupf, I. C. Watson, M. J. Ferguson and E. Rivard, *Chem. Commun.*, 2023, **59**, 2903–2906.
16 W. A. Merrill, R. J. Wright, C. S. Stanciu, M. M. Olmstead, J. C. Fettinger and P. P. Power, *Inorg. Chem.*, 2010, **49**, 7097–7105.
17 R. S. Ghadwal, H. W. Roesky, K. Pröpper, B. Dittrich, S. Klein and G. A. Frenking, *Angew. Chem., Int. Ed.*, 2011, **50**, 5374–5378.
18 L. Kong and C. Cui, *Organometallics*, 2010, **29**, 5738–5740.
19 D. Dhara, L. Endres, I. Krummenacher, M. Arrowsmith, R. D. Dewhurst, B. Engels, R. Bertermann, M. Finze, S. Demeshko, F. Meyer, F. Fantuzzi and H. Braunschweig, *Angew. Chem., Int. Ed.*, 2024, **63**, e202401052.
20 J. Bresien, D. Michalik, A. Schulz, A. Villinger and E. Zander, *Angew. Chem., Int. Ed.*, 2021, **60**, 1507–1512.
21 A. Hinz, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2015, **54**, 668–672.
22 J. Cheng, J. Liu, X. Leng, T. Lohmiller, A. Schnegg, E. Bill, S. Ye and L. Deng, *Inorg. Chem.*, 2019, **58**, 7634–7644.
23 X.-N. Yao, J.-Z. Du, Y.-Q. Zhang, X.-B. Leng, M.-W. Yang, S.-D. Jiang, Z.-X. Wang, Z.-W. Ouyang, L. Deng, B.-W. Wang and S. Gao, *J. Am. Chem. Soc.*, 2017, **139**, 373–380.
24 J. Du, L. Wang, M. Xie and L. Deng, *Angew. Chem., Int. Ed.*, 2015, **54**, 12640–12644.
25 C. A. Laskowski, A. J. M. Miller, G. L. Hillhouse and T. R. Cundari, *J. Am. Chem. Soc.*, 2011, **133**, 771–773.
26 C. Hu, N. H. Rees, P. Pink and J. M. Goicoechea, *Nat. Chem.*, 2024, **16**, 1855–1860.
27 M. Jenssen, T. Frederichs, M. Olaru, E. Lork, E. Hupf and J. Beckmann, *Science*, 2024, **385**, 318–321.
28 J. Vrána, M. A. Samsonov, V. Němec and A. Růžička, *Chem. Commun.*, 2020, **56**, 2487–2490.
29 J. Vrána, V. Němec, M. A. Samsonov and A. Růžička, *Dalton Trans.*, 2021, **50**, 14352–14361.
30 M. S. Balakrishna, D. L. Eisler and T. Chivers, *Chem. Soc. Rev.*, 2007, **36**, 650–664.
31 F. García, R. A. Kowenicki, L. Riera and D. S. Wright, *Dalton Trans.*, 2005, 2495–2496.
32 E. Zander, J. Bresien, V. V. Zhivonitko, J. Fessler, A. Villinger, D. Michalik and A. Schulz, *J. Am. Chem. Soc.*, 2023, **145**, 14484–14497.
33 A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano and L. Cavallo, *Eur. J. Inorg. Chem.*, 2009, 1759–1766.
34 H. Jansen, M. C. Samuels, E. P. A. Couzijn, J. C. Slootweg, A. W. Ehlers, P. Chen and K. Lammertsma, *Chem. – Eur. J.*, 2010, **16**, 1454–1458.
35 N. Burford, T. S. Cameron, K. D. Conroy, B. Ellis, C. L. B. Macdonald, R. Ovans, A. D. Phillips, P. J. Ragogna and D. Walsh, *Can. J. Chem.*, 2002, **80**, 1404–1409.
36 F. Reiß, A. Schulz, A. Villinger and N. Weding, *Dalton Trans.*, 2010, **39**, 9962–9972.
37 F. H. Herbstein, *Cryst. Growth Des.*, 2005, **5**, 2362–2368.
38 B. Buster, A. A. Diaz, T. Graham, R. Khan, M. A. Khan, D. R. Powell and R. J. Wehmschulte, *Inorg. Chim. Acta*, 2009, **362**, 3465–3474.
39 D. Gudat, W. Hoffbauer, A. B. Rozhenko, W. W. Schoeller and M. I. Povolotskii, *Magn. Reson. Chem.*, 2000, **38**, 861–866.
40 U. Berens, U. Englert, S. Geyser, J. Runsink and A. Salzer, *Eur. J. Org. Chem.*, 2006, 2100–2109.
41 P. Pyykkö, S. Riedel and M. Patzschke, *Chem. – Eur. J.*, 2005, **11**, 3511–3520.
42 A. N. Chernega, M. Y. Antipin, Y. T. Struchkov, A. B. Drapailo and V. D. Romanenko, *J. Struct. Chem.*, 1990, **31**, 292–300.
43 A. N. Khodadadi, E. Cela, D. Marchionni, F. Huang, F. Ferlin and L. Vaccaro, *Green Chem.*, 2024, **26**, 7059–7066.
44 M. Maier, J. Klopf, C. Glasmacher, F. Fantuzzi, J. Bachmann, O. Ayhan, A. Koner, B. Engels and H. Helten, *Chem. Commun.*, 2022, **58**, 4464–4467.
45 S. J. Groszos and S. F. Stafiej, *J. Am. Chem. Soc.*, 1958, **80**, 1357–1360.
46 J. Hahn, M. Krieg, C. Keck, C. Maichle-Mössmer, R. F. Finkc and H. F. Bettinger, *Dalton Trans.*, 2018, **47**, 17304–17316.
47 P. B. Hitchcock, H. A. Jasim, M. F. Lappert and H. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1984, 662–664.
48 L. Weber, J. Förster, H. G. Stammler and B. Neumann, *Eur. J. Inorg. Chem.*, 2006, 5048–5056.
49 (*a*) P. Pyykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 186–197; (*b*) P. Pyykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 12770–12779.
50 F. Zettler and H. Hess, *Chem. Ber.*, 1975, **108**, 2269–2273.
51 H. Helten, A. P. M. Robertson, A. Staubitz, J. R. Vance, M. F. Haddow and I. Manners, *Chem. – Eur. J.*, 2012, **18**, 4665–4680.
52 K. J. Sabourin, A. C. Malcolm, R. McDonald, M. F. Fergusona and E. Rivard, *Dalton Trans.*, 2013, **43**, 4625–4632.
53 M. Periasamy, G. P. Muthukumaragopal and N. Sanjeevakumar, *Tetrahedron Lett.*, 2007, **48**, 6966–6969.
54 S. Heřmánek, *Chem. Rev.*, 1992, **92**, 325–362.