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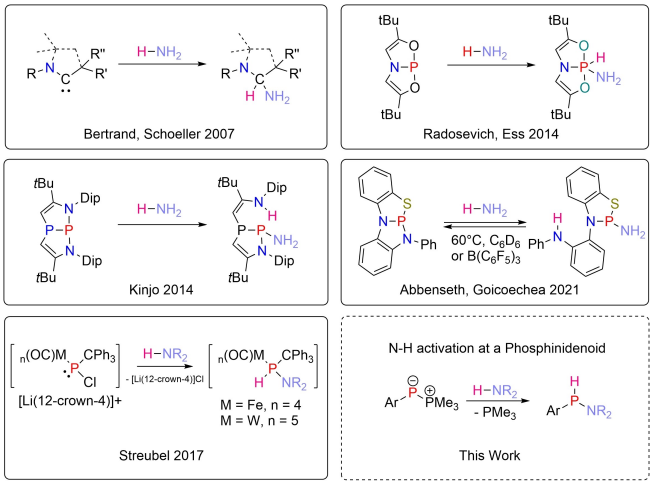
Phosphorus

Metal-Free N–H Bond Activation by Phospha-Wittig Reagents**

Fabian Dankert, Jan-Erik Siewert, Priyanka Gupta, Florian Weigend, and Christian Hering-Junghans**

Dedicated to Professor Holger Braunschweig on the occasion of his 60th birthday

Abstract: N-containing molecules are mostly derived from ammonia (NH_3). Ammonia activation has been demonstrated for single transition metal centers as well as for low-valent main group species. Phosphinidenes, mono-valent phosphorus species, can be stabilized by phosphines, giving so-called phosphanylidenephosphoranes of the type $RP(PR'_3)$. We demonstrate the facile, metal-free NH_3 activation using $ArP(PMe_3)$, affording for the first time isolable secondary aminophosphines $ArP(H)NH_2$. DFT studies reveal that two molecules of NH_3 act in concert to facilitate an NH_3 for PMe_3 exchange. Furthermore, H_2NR and HNR_2 activation is demonstrated.



Scheme 1. Key examples of NH_3-activation. At a single carbon center, at geometrically constrained P-atoms, at Li/Cl phosphinidenoid metal complexes and outline of this study.

Ammonia (NH_3) is the most ubiquitously used source of nitrogen in the synthesis of N-containing molecules. However, NH_3 activation is challenging and oxidative addition at a single metal center using Ir-pincer complexes was first shown in 2005 by Hartwig et al. and by Turculet and co-workers in 2009.[1] This challenge stems from the N–H bond dissociation enthalpy (106.12(6) kcal mol^{-1})[2] and from the formation of unreactive Werner-type complexes with NH_3.[3] Strictly metal-free NH_3 activation was reported by Bertrand, Schoeller et al. using (alkyl)(amino) carbenes (AACs), resulting in the oxidative addition at a dicoordinate carbon center (Scheme 1, top).[4] Since this report a variety of low valent group 13[5] and 14[6] compounds have been shown to oxidatively add NH_3. In 1987 Arduengo and co-workers described the addition of ECl_3 to $HN(CH_2CH_2C(O)R)$ to give planar T-shaped pnictogen species, which in case of E = P oxidatively activated CH_3OH as well as facilitated the coupling of alkynes.[7] Radosevich and Ess revisited these geometrically constrained P-species and used them in the activation of RNH_2 (R = H, alkyl, aryl), affording N-functionalized P^V compounds (Scheme 1, top).[8] The application of P^{III} species in unusual non-trigonal coordination environments in NH_3 activation has since attracted considerable interest,[9] and was recently reviewed.[10] Moreover, reversible NH_3-activation using NNS-type ligands on P^{III} was reported in 2021 (Scheme 1, middle right).[11] In this regard the reversible H_2 activation and NH_3 activation to give azadiphosphiridines by the neutral biradicaloid $[P(\mu\text{-}N^{Mes}Ter)]_2$ (^{Mes}Ter = 2,6-(2,4,6-Me_3-C_6H_2)$_2$$C_6H_3$) is noteworthy.[12] In contrast to geometrically constrained P^{III} compounds the activation of NH_3 at a metal-free P^I center has not been reported to date.

Phosphinidenes, the isovalent analogues of carbenes, are in most cases transient species and possess two lone pairs of electrons (LP), along with one unoccupied valence (singlet state) or two unpaired electrons (triplet state).[13] Using a combination of electronic and kinetic stabilization, a singlet phosphinidene was recently isolated.[14] Most phosphinidenes are either stabilized by coordination to a transition metal fragment,[15] or by cycloaddition reactions to (conjugated) multiple bond systems, releasing the R–P fragment via

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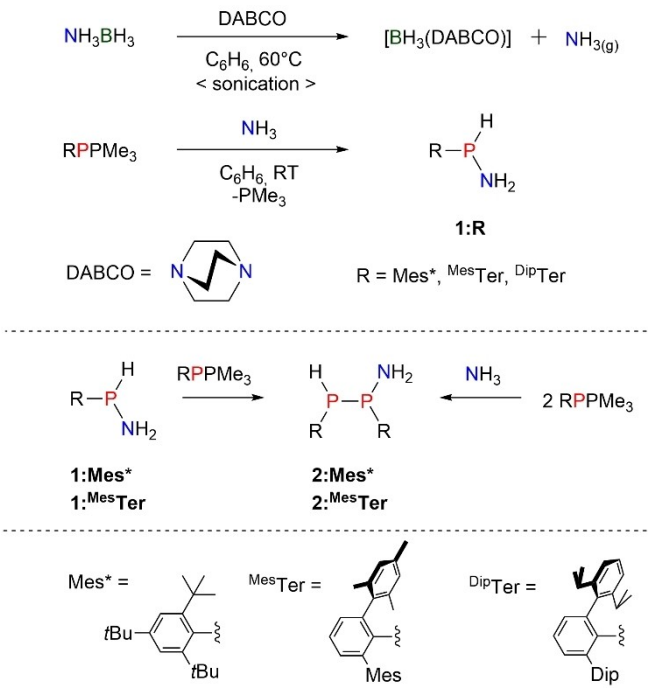
cyclo-reversion.[16] With the emergence of Na(dioxane)$_x$-(PCO),[17] elementyl phosphaketenes [E]-PCO became feasible and thermal or photochemical CO liberation was shown to unlock phosphinidene-type reactivity.[18] Phosphanylidenephosphoranes, Lewis base stabilized phosphinidenes, often referred to as Phospha-Wittig reagents,[19] of the type ArP(PMe$_3$), have been shown to be phosphinidene transfer reagents.[20]

A PMe$_3$ for NHO (NHO = N-heterocyclic olefin) exchange followed by C(sp^2)-H-activation was demonstrated.[21] The activation of strong E–H bonds with metal-free phoshinidenes remains largely elusive, though. For example, it has been a long-standing challenge to isolate secondary aminophosphines RP(H)–NR$_2$ as α-elimination of the amine results in the formation of the phosphinidene [R–P].[22] Stabilization by coordination of the phosphorus to a transition metal fragment (M) has been shown to render [R–P(H)NR$_2$]M stable.[23] Using phosphanorbornadiene Cr and W complexes, Mathey and co-workers showed that upon diene cleavage amines, water and methanol can be activated at phosphorus.[24] Streubel and co-workers have shown that complexes of the type [(CO)$_n$M–P(Cl)R][Li(12-crown-4)(thf)$_n$] (M = Fe, W) unlock phosphinidenoid reactivity upon LiCl elimination and the functionalization of E–H bonds (E = N, O) at the metal-coordinated phosphorus atom has been documented (Scheme 1, bottom left).[25] Herein we report the facile N–H bond activation in NH$_3$ and amines using simple, metal-free ArP(PMe$_3$), affording isolable Ar–P(H)NH$_2$ for the first time (Scheme 1, bottom right).

First, we found that treating H$_3$BNH$_3$ with DABCO in a 1:1 ratio in benzene under sonication at 60 °C gave NH$_3$ in stoichiometric fashion. Next Mes*P(PMe$_3$) (Mes* = 2,4,6-tBu$_3$-C$_6$H$_2$) was treated with 10 equiv NH$_3$ in benzene for 3 h giving Mes*P(H)NH$_2$ (**1:Mes***) (Scheme 2).

1:Mes* showed a doublet of triplets in the ^{31}P NMR spectrum at −24.35 ppm ($^1J_{PH}$ = 240.0, $^2J_{PH}$ = 8.5 Hz), collapsing into a singlet upon proton decoupling. In the ^{1}H NMR spectrum the PH proton is detected as a doublet of triplets at 6.52 ppm. IR spectroscopy revealed N–H and P–H bands at 3432 and 2387 cm^{-1}, respectively. **1:Mes*** is formed quantitatively and was isolated as a colourless crystalline powder. Next, ^{Mes}TerP(PMe$_3$) and ^{Dip}TerP(PMe$_3$) (^{Dip}Ter = 2,6-(2,6-iPr_2-C$_6$H$_3$)$_2$C$_6$H$_3$) were exposed to an excess of NH$_3$ and the quantitative formation of **1:^{Mes}Ter** and **1:^{Dip}Ter**, was observed (Scheme 2). Compounds **1:R** represent the first isolable secondary aminophosphines of the type R–P(H)NH$_2$. Aminophosphines of the type R-PH(NR$_2$) have been postulated to be prone to eliminate HNR$_2$. The first free secondary aminophosphine (Me$_3$Si)$_2$N–P(H)–N(H)SiMe$_3$ was shown to be thermally stable with respect to an α-elimination of H$_2$NSiMe$_3$.[26] Attempting to crystallize **1:Mes*** or **1:^{Mes}Ter** from concentrated benzene solutions yielded minimal amounts of colourless crystals for single crystal X-Ray diffraction (SC-XRD) experiments.[27] These were identified as the diphosphines RP(H)P(NH$_2$)R (**2:R**; R = Mes*, ^{Mes}Ter) (Figure 1). **2:R** were then rationally synthesized by either treatment of RP(PMe$_3$) with 0.5 equiv of NH$_3$ or by addition of a second eq. of RP(PMe$_3$) to a benzene solution of **1:R** (see Supporting Information). **1:Mes*** and **1:^{Mes}Ter** are stable and undergo α-elimination, which was found to be energetically feasible by theoretical means (Table S9), to afford **2:R** only in highly concentrated solutions over an extended period of time. Moreover, **2:Mes*** was exposed to NH$_3$ and the formation of **1:Mes*** was not detected, excluding **2:Mes*** as possible intermediate in the formation of **1:Mes***. **2:^{Dip}Ter** could not be synthesized, thus indicating the steric protection of the ^{Dip}Ter-substituent.

2:Mes* shows two doublets ($^1J_{PP}$ = 238.5 Hz) in the ^{31}P{^{1}H} NMR spectrum at 30.82 (*P*NH$_2$) and at −30.92 ppm (*P*H), indicating a P–P single bond and a single diastereomer in solution. Interestingly, in the ^{31}P{^{1}H} NMR spec-



Scheme 2. Synthesis of RP(H)NH$_2$ (**1:R**) and formation of diphosphines **2:R**.

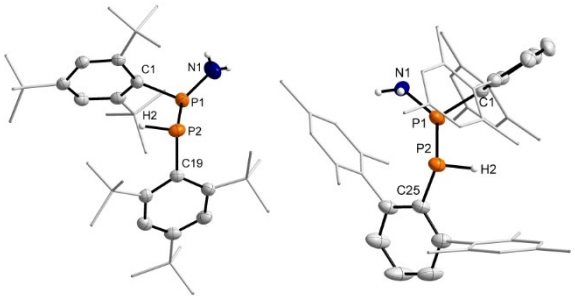
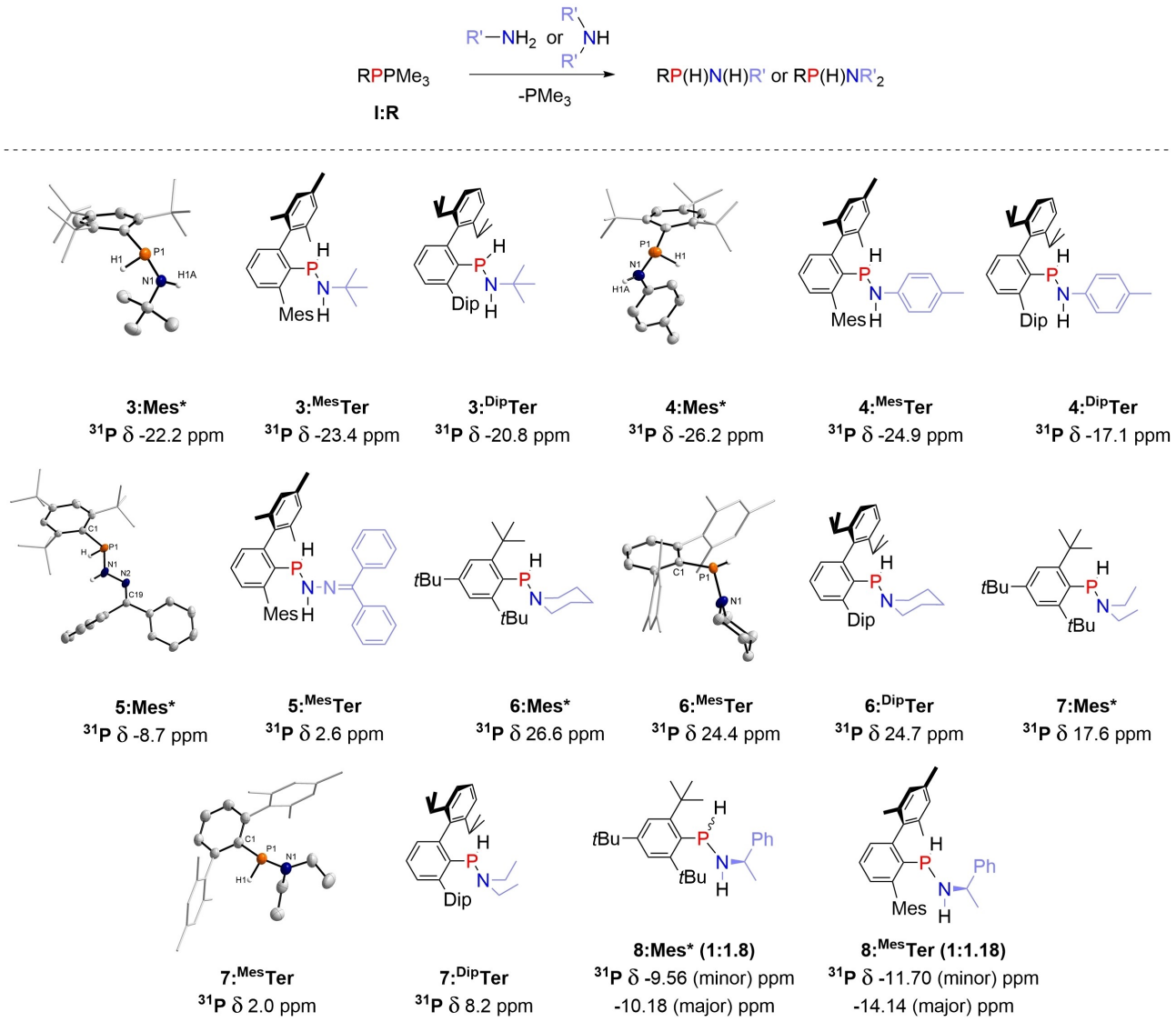


Figure 1. Molecular structures of **2:Mes*** (left) and **2:^{Mes}Ter** (right). Ellipsoids drawn at 50% probability with C-*H*-atoms omitted, *t*Bu- and Mes-groups rendered as wire-frame for clarity. Selected bond lengths [Å] and angles [°] (**2:Mes***): N1-P1 1.6587(30), P1-P2 2.2498(10); C1-P1-P2 101.80(7), N1-P1-P2 105.08(10), P1-P2-C19 99.37(7); **2:^{Mes}Ter**: N1-P1 169.35(35), P1-P2 222.8(8); N1-P1-P2 103.21(10), P1-P2-C25 103.56 (65), C1-P1-P2 104.067(63).

trum of **2:^{Mes}Ter** two sets of doublets in close proximity are detected in a 2:3 ratio, indicating two diastereomers in solution, which might arise from the sterically more flexible environment provided by the ^{Mes}Ter-substituent. While the P*H* proton of **2:Mes*** at 5.01 ppm gives a doublet of doublets in the ^{1}H NMR spectrum, two P*H* resonances are detected for **2:^{Mes}Ter** at 3.88 and 3.49 ppm in a 2:3 ratio. **2:Mes*** crystallizes as its *R*,*R*-diastereomer with the Mes*-substituents being located on the same side of the P1–P2 axis (2.2498(10) Å) with a dihedral angle (C1–P1–P2–C19) of 106.36° (Figure 1), agreeing with the structure of the related diphosphine Mes*P(H)P(CN···B(C_6F_5)$_3$)Mes* (cf. d(P–P) = 2.2461(8) Å, >(C1–P1–P2–C19) = 106.65°).[20c] Whereas in solution two diastereomers of **2:^{Mes}Ter** prevail, only the *S*,*S*-diastereomer is detected in the solid state with NH_2 and H being disordered (Figure S2). The dihedral angle (C1–P1–P2–C25) of 138.54° is considerably wider compared to **2:Mes***, which can be attributed to the 2,6-substituents of the ^{Mes}Ter groups, see above. Next, RP(PMe_3) and the primary amine H_2N*t*Bu were combined to give RP(H)N(H)*t*Bu (**3:R**; R = Mes*, ^{Mes}Ter, ^{Dip}Ter). **3:Mes*** shows a doublet of doublets in the ^{1}H NMR spectrum at 6.39 ppm (P*H*: $^{1}J_{PH}$ = 211.1; $^{3}J_{HH}$ = 3.5 Hz) as well as a doublet of doublets at 1.12 ppm (N*H*: $^{2}J_{PH}$ = 5.2; $^{3}J_{HH}$ = 3.5 Hz). **3:^{Mes}Ter** contained trace amounts of the diphosphene (^{Mes}TerP)$_2$ (ca. 10 %).[20c] The clean formation of **3:^{Dip}Ter** was achieved in benzene at 80 °C and the characteristic ^{31}P NMR data of compounds **3:R** are summarized in Scheme 3. The molecular structures of **3:Mes*** and **3:^{Dip}Ter** revealed both enantiomers represented by disorder of the whole –P(H)N(H)R unit, with P1–N1 distances (**3:Mes*** 1.6917(13), **3:^{Dip}Ter** 1.6646 (48) Å) in the range of contracted single bonds (Σr_{cov}(P–N) = 1.82 Å),[28] a trigonal pyramidal P and planar N atoms. To further expand the scope to aniline derivatives, *p*-toluidine was combined in benzene with the respective phospha-Wittig reagents. After sonication overnight at 60 °C or



Scheme 3. NH-activation of primary and secondary amines at ArP(PMe_3).

stirring at room temperature, Mes*P(H)N(H)Tol (**4:Mes***) and ^{Mes}TerP(H)N(H)Tol (**4:^{Mes}Ter**) were obtained as beige powders. With $Ph_2C{=}N{-}NH_2$ Mes*P(PMe_3) cleanly reacted to give Mes*P(H)N(H)NCPh_2 (**5:Mes***) in 58 % isolated yield. **5:Mes*** is a colorless crystalline solid, with a characteristic doublet of doublets at 7.02 ppm (P*H*), a pseudo-triplett at 5.88 ppm (N*H*) in the ^{1}H NMR spectrum and a singlet in the ^{31}P{^{1}H} NMR spectrum at −8.8 ppm. **5:Mes*** shows short P1–N1 (1.709(1) Å) and N1–N2 (1.360(18)Å) as well as N2–C19 (1.2900(13) Å) distances in the expected range for a hydrazone derivative (*cf.* $Ph_2C{=}NN(H)PPh_2$ P–N 1.697(2), N–N 1.373(2), C=N 1.292(2) Å).[29] The PH and NH protons reside on the same side according to SC-XRD experiments.

Then we investigated whether piperidine or $HNEt_2$ could be NH-activated, as secondary amine activation was previously only reported for NNS-substituted P^{III} system in dipolar fashion.[11] RP(PMe_3) reacted cleanly with piperidine in C_6H_6 under sonication for 4 h at elevated temperatures, to give RP(H)N(C_5H_{10}) (**6:R**, R = Mes*, ^{Mes}Ter, ^{Dip}Ter) quantitatively as colorless solids. **6:R** show characteristic ^{31}P{^{1}H} NMR signals at ca. 25 ppm, deshielded compared to **3:R** and **4:R**. RP(PMe_3) also reacted cleanly with $HNEt_2$ under the same conditions outlined above to give RP(H)NEt_2 (**7:R**, R = Mes*, ^{Mes}Ter, ^{Dip}Ter), with ^{31}P{^{1}H}NMR shifts between 17.6 ppm (**7:Mes***) and 1.97 ppm (**7:^{Mes}Ter**), which is shielded significantly compared to ^{Mes}TerP(NEt_2)$_2$ (cf. δ(^{31}P) = 100.2 ppm).[30] X-Ray quality crystals of **6:R** and **7:R** (except for **6:Mes***) were grown and their molecular structures show trigonal pyramidal P atoms with P–N bond lengths of ca. 1.68 Å. The value agrees well with that within the metal complex [$(CO)_5$W](P(H)(CPh_3)NBn_2) (cf. *d*-(P–N) = 1.6877(19) Å).[25a] Using (*R*)-(+)-1-phenylethylamine we succeeded in the synthesis of a diastereomeric mixture of the chiral phosphines *R,R*-**8:Mes*** and *R,S*-**8:Mes***, with one of the diastereomers being formed preferentially (1:1.8 ratio). Using ^{Mes}TerP(PMe_3) a 1:1.2 mixture of both isomers was obtained. This clearly shows the potential of rapidly accessing a new class of chiral phosphines through NH-activation at phospha-Wittig reagents.

We next investigated the underlying reaction mechanism for the metal-free N–H activation at ArP(PMe_3). Reaction pathways were identified with a chain-of-states method under the sole constraint of equally spaced structures[31] at the PBE/def2-TZVP DFT level, followed by full optimization of the stationary points (see Supporting Information for computational details).[32] Mes*P(PMe_3) was used as the phosphanylidenephosphorane and akin to the NH-bond activation mechanism proposed by Streubel and Espinosa for [$(CO)_4$Fe](P(NH_3)Me) in which four NH_3 molecules facilitate the NH transfer,[25b] we employed two NH_3 molecules in our calculations (Figure 2).

The reaction pathway from Mes*P(PMe_3) + 2 NH_3 to Mes*P(H)NH_2 + PMe_3 + NH_3 is shown in Figure 2. The two NH_3 molecules form a dimer, which is adsorbed by a hydrogen bridge (H2···P1), coming with an overall gain of 14 kJ mol^{-1} (LM1). It is followed by a transition state (TS1) where the P–P bond is weakened and the P···H contact is released in favour of a P···N contact with the N atom of the other NH_3 unit of the dimer (P1···N1), which requires 77 kJ mol^{-1}. Next, the P–P bond is cleaved in favour of the P–N bond (LM2, gain 2 kJ mol^{-1}). LM2 features a hydrogen bridge N1–H1···N2. The formation of favourable Mes*P(H)NH_2 with weakly adsorbed NH_3 and PMe_3 (LM3) is achieved via a second transition state, TS2, which is higher in enthalpy than LM2 by 35 kJ mol^{-1}. This transition state differs from LM2 in two respects: It consists of rather an $NH_2^{(-)}$ and an $NH_4^{(+)}$ unit (NBO charges −0.31 and +0.53) connected by a H bond (N1···H1–N2), and a second H bond from the NH_4 unit to the P atom. The latter becomes the P–H bond in LM3 (energy gain 134 kJ mol^{-1} with respect to TS2). Final removal of PMe_3 and NH_3 requires 11 kJ mol^{-1}. Thus, the overall gain is 27 kJ mol^{-1}, and with barrier heights of 77 and 36 kJ mol^{-1} the reaction is feasible under ambient conditions. Matters are completely different for the reaction with a single NH_3 molecule. Here, the transition state for an intramolecular direct H-shift from N to P was found to be 172 kJ mol^{-1} above the initial state; further, the analogue to LM2 shows vibration modes close to zero (7 and 9 cm^{-1}, see Supporting Information for details) and converges to the analogue of LM1 if only weakly distorted. Also, all attempts to optimize a transition state between these two local minima ended in the analogue of LM1. These features are not in line with the reaction going to completion at room temperature (see Supporting Information for details). It is thus evident, that smooth changes from N–H···N to N···H–N (and similarly for P) make this reaction feasible at room temperature. Based on these theoretical studies it would be expected that the formation of secondary aminophosphines is generally dependent on the amine concentration. In order to probe this the 1:1 reaction of Mes*P(PMe_3) and *p*-toluidine was followed by ^{1}H NMR spectroscopy at different concentrations at room temperature. This clearly showed that the reaction is faster at higher amine concentrations (Figure S95). In addition, we found that a Mes*P(PMe_3) to *p*-toluidine ratio of 1:2 resulted in full conversion to give **4:Mes*** in less than 5 min at room temperature. Even though the conversion time plots did not allow to extract the reaction order, the amine concentration clearly affects the outcome of the reaction.

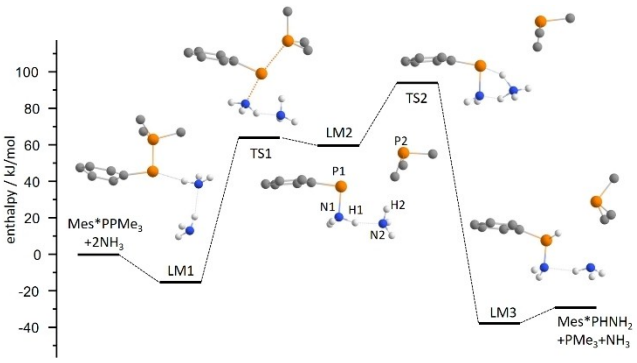


Figure 2. Enthalpy profile for the proposed reaction pathway from Mes*P(PMe_3) and 2 NH_3 (Mes* represented by central C_6) at the PBE/def2-TZVP DFT level.

It has been shown earlier that the transamination of $P(NEt_2)_3$ with primary aromatic di- and polyamines gave rise to the formation of a variety of structurally stabilized aminophosphines, with the concomitant formation of $HNEt_2$.[33] We thus tested whether **6:Mes*** would undergo transamination in the presence of an excess of *p*-toluidine. Heating a mixture of **6:Mes*** and *p*-toluidene (1:3 ratio) over a period of 2 weeks at 80 °C gave rise to the formation **4:Mes*** and piperidene, with a conversion of ca. 75 % based on ^{31}P NMR spectroscopy (Figure S96). This clearly illustrates the synthetic potential of secondary aminophosphines.[34]

In summary, the facile activation of NH_3 with the aid of phospha-Wittig reagents of the type $ArP(PMe_3)$ has been demonstrated to give for the first time secondary aminophoshanes of the type $ArP(H)NH_2$ (**1:R**). The activation of primary and secondary amines was likewise achieved. This novel reactivity of phospha-Wittig reagents is a straightforward way towards P–N-bonds from a variety of substrates, including chiral amines. Efforts to utilize this concept in the design of new P-containing materials are currently underway. For example, we strive to construct multidentate ligand architectures and to explore the synthesis of chiral phosphine ligands.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Amines · Bond Cleavage · N–H Activation · Phosphorus · Small Molecule Activation

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