EurJIC European Journal of Inorganic Chemistry
ChemPubSoc Europe
FULL PAPER

DOI:10.1002/ejic.201201471

Rational Synthesis and Mutual Conversion of Bis-N-heterocyclic Diphosphanes and Secondary N-Heterocyclic Phosphanes

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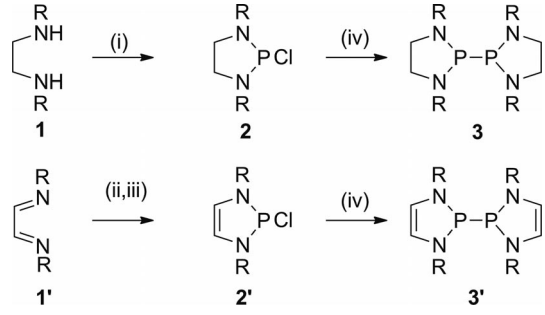
Keywords: Phosphanes / Diphosphanes / Heterocycles / Radicals / Reduction / Reaction mechanisms

Symmetrical N-heterocyclic 1,1′,3,3′-tetrahydro-2,2′-bi-1,3,2-diazaphospholes and 2,2′-bi-1,3,2-diazaphospholidines are prepared by time-saving, sequential "one-pot" syntheses starting from 1,4-diazabutadienes or *N*-alkyl or *N*-aryl-substituted ethane-1,2-diamines. This method offers high selectivity and minimizes the loss of products owing to unwanted hydrolysis, and thus grants high product yields. In some cases, secondary phosphanes were formed together with or instead of diphosphanes. This reaction is explained by a follow-up process involving homolytic fission of diphosphanes to give phosphanyl radicals, which then react with ammonium salts to give a mixture of secondary phosphanes and chlorophosphanes. Even if its synthetic scope is as yet limited, this approach seems promising in offering superior selectivity and higher yields than common synthetic protocols that rely on the use of complex hydrides as reducing agents. In addition to the reductive conversion of diphosphanes into secondary phosphanes, a reverse reaction under exposure of the reactants to light is also reported.

Introduction

Acyclic tetrakis(dialkylamino)diphosphanes of general composition $(R_2N)_2P–P(NR_2)_2$ have sporadically been studied during the past decades.[1,2] The combination of potentially reactive P–N and P–P bonds offers good prospects for various synthetic applications. Lappert et al. reported[2] that sterically encumbered bisphosphanes can undergo reversible homolytic dissociation to give phosphanyl radicals,[3] which may be subsequently employed to generate stable phosphanido metal carbonyls. Crossairt and Cummins recently discussed the possibility to use the unique P–P bond reactivity to activate P_4 or AsP_3,[4] which are starting materials for a variety of P- or As-containing species. Recent studies have particularly focused on derivatives like 2,2′-bi-1,3,2-diazaphospholidines **3**[5,6] or 1,1′,3,3′-tetrahydro-2,2′-bi-1,3,2-diazaphospholes **3′**[7–9] (Scheme 1), in which the $(R_2N)_2P$ moieties form parts of five-membered N-heterocyclic rings.[10] The introduction of bulky *N*-aryl or *N*-alkyl substituents at the rather rigid heterocyclic frameworks of these molecules offers excellent opportunities for the specific tuning of steric interactions and P–P bond reactivity.[8,9] In this respect, heterocycles **3′** received particular attention as the stabilization of diazaphospholenyl radicals



Scheme 1. Synthesis of **3**/**3′** R = *t*Bu (a), *i*Pr (b), Cy (c), 2,6-dimethylphenyl (Dmp, d), 2-methylphenyl (*o*-Tol, e), Mesityl (f), 2,6-diisopropylphenyl (Dipp, g), *o*-$tBuC_6H_4$ (h); reactants and conditions: (i) THF, –78 °C, 1 equiv. PCl_3, 2.5 equiv. NEt_3; (ii) THF, –78 to 0 °C, 2 equiv. Li, 2 equiv. NEt_3HCl; (iii) –78 °C, 1 equiv. PCl_3; (iv) THF, 1.5 equiv. Mg.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201201471.

by cyclic π-electron delocalization enables P–P bond cleavage processes to occur under extremely mild conditions.[8] Quite interestingly, Förster et al.[9] were able to show that, regardless of this disposition, specific substrates like electron-poor alkynes may also address P–N bond reactivity. This apparent dualism offers interesting prospects and stimulates extended studies of the chemical properties of species like **3′**.

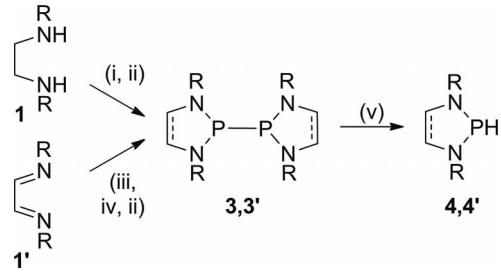
Up to now, only a few heterocyclic diphosphanes of type **3**[5,6,10] or **3′**[7,8] are known, and common synthetic approaches by reductive coupling of 2-chloro-1,3,2-diazaphospholenes **2′** or 2-chloro-1,3,2-diazaphospholidines **2** often give only moderate yields. To improve the synthetic access to diphosphanes **3** and **3′**, we wanted to elaborate a time-saving, sequential "one-pot" synthesis from ethane-1,2-diamines **1** or 1,4-diazabutadienes **1′**. This route should grant high product yields and minimize the effort required for work-up of the reaction mixtures. Surprisingly, we found that some of the reactions studied yielded N-heterocyclic secondary phosphanes rather than the targeted diphosphanes. Therefore, we performed more detailed studies, which allowed us to propose a mechanistic explanation for these at first glance puzzling results and to establish conditions for the mutual conversion between secondary heterocyclic phosphanes and the corresponding diphosphanes.

Results and Discussion

A convenient preparation of bisphosphanes **3** and **3′** proceeds by magnesium reduction of **2**[6] and **2′**, respectively.[8] *P*-Chloro-substituted precursors are typically generated by condensation of ethane-1,2-diamines **1** with PCl_3 or by reduction of 1,4-diazabutadienes **1′** and subsequent condensation with PCl_3 and are isolated prior to the subsequent coupling step.[11–13] Having previously developed a high-yield synthesis of **2′** that combines the reduction and coupling steps into a sequential one-pot procedure,[13] we set out to extend this approach to the preparation of **3** and **3′** by performing all stages of the multistep synthesis in a one-pot manner without purification of the intermediates.

The reactions were carried out by using starting materials **1** and **1′** with *N*-alkyl or *N*-aryl substituents of different steric bulk (Scheme 1). The condensation of diamines **1** with PCl_3 to give **2** was initiated by the addition of Et_3N, whereas **2′** were prepared by the previously described one-pot procedure, which involves quenching of the initially formed diazabutadiene dianion with an ammonium salt and the subsequent base-induced condensation of the α-aminoaldimine intermediate with PCl_3.[13] Even if **2′** is in principle also accessible by direct metathesis of diazabutadiene dianions with PCl_3,[12] the two-step approach used here has been reported to give superior yields.[13] We found that in most cases (**2/2′a**–**f**) the LiCl and NEt_3HCl formed in the previous steps did not interfere with the subsequent reductive coupling step. The removal of tetrahydrofuran (THF) and precipitated salts was thus unnecessary, and the Mg reduction was easily carried out at room temperature in the same reaction vessel. The target diphosphanes were isolated by extraction into a nonpolar solvent, separation of the insoluble side products by filtration, and evaporation of the filtrate. The decision not to purify and crystallize the intermediate products results in substantial time saving and helps to minimize losses caused by hydrolysis upon potential contact with moisture.

In contrast to the cases described so far, the reactions of derivatives of **1** and **1′** with very bulky *N*-aryl substituents (R = Dipp, *o*-*t*BuC_6H_4; **1g**–**h**, **1′g**) took a different course and yielded secondary phosphanes (**4g**, **4′g**)[13] or mixtures of secondary phosphanes and diphosphanes (**3/4h**; Scheme 2). Phosphane **4g** was isolated after a similar work-up as that employed for **3/3′**. Spectroscopic studies allowed us to establish that diphosphanes **3g**–**h/3′g** were the initial reaction products and were later converted into **4g**–**h/4′g** when the reaction went on. This last conversion could be suppressed when the precipitated solids (LiCl, Et_3NHCl), which had been formed as side products with chlorophosphanes **2g**–**h/2′g**, were removed by filtration before the magnesium was added. The pure diphosphanes **3g**,[6] **3′g**[8,9] and **3h** were readily isolated after appropriate work-up when the reaction was conducted under these conditions.



Scheme 2. One-pot synthesis of phosphanes **4g**, **4′g** and **4h**; (i) THF, –78 °C, 1 equiv. PCl_3, 2.5 equiv. Et_3N; (ii) 1.5 equiv. Mg, cat. I_2, room temp. (iii) THF, –78 to 0 °C, 2 equiv. Li, 2 equiv. Et_3NHCl; (iv) –78 °C, 1 equiv. PCl_3; (v) Et_3NHCl/Mg.

The isolated highly air and moisture sensitive diphosphanes and phosphanes were found to be spectroscopically pure, and their identity was unequivocally confirmed by NMR and MS data. The diphosphanes **3a** and **3h** (Figure 1) and the secondary phosphane **4g** (Figure 2) were also characterized by single-crystal X-ray diffraction studies of crystals obtained by recrystallization from THF/hexane at –20 °C. The molecular structures of **3a** and **3h** exhibit crystallographic C_i symmetry; the five-membered rings feature *transoid* alignment and a twist configuration. The P–P distances are somewhat shorter than those in the acyclic tetraaminodiphosphanes $(iPr_2N)_2P–P(NiPr_2)_2$[1] and (iPr_2N)-$[(Me_3Si)_2N]P–P(NiPr_2)[N(SiMe_3)_2]$[2] (2.29–2.30 Å) but are still far longer than the average P–P distance in diphosphanes (2.217 ± 0.08 Å[14]). The endocyclic bond lengths match those in other bis-N-heterocyclic diphosphanes (Table 1). The P–P distances are equal for **3a** and **3′a** (and likewise for **3g**[6] and **3′g**[9]) and increase in both series of

heterocycles with growing bulk of the *N*-aryl substituents. These parallel trends suggest that the bond lengthening is mainly induced by steric factors.

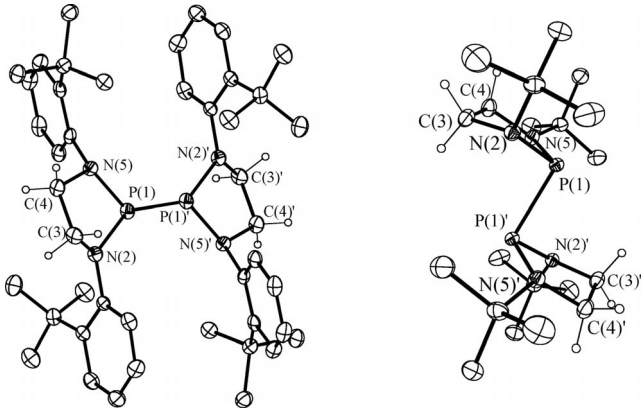


Figure 1. Crystal structure of **3a** and **3h**; H atoms partially omitted for clarity; 50% probability ellipsoids. Both molecules exhibit crystallographic C_i symmetry (symmetry-dependent atoms were generated with the operator $-x + 1, -y + 1, -z + 1$).

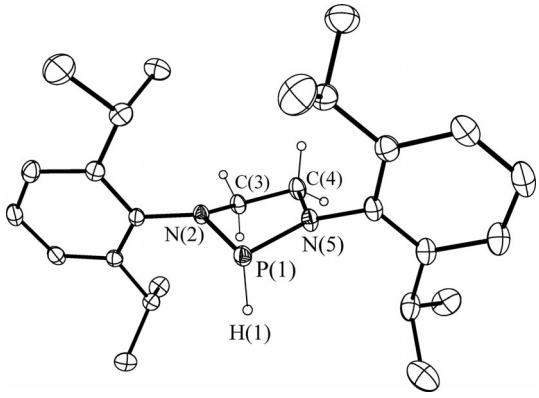


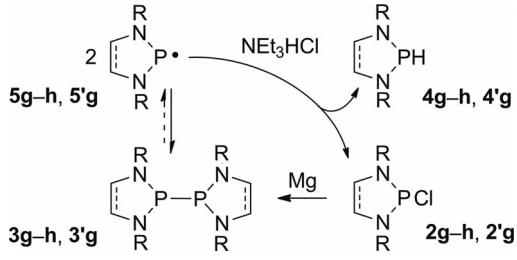
Figure 2. Molecular structure of **4g**; H atoms in the Dipp substituents omitted for clarity; 50% probability ellipsoids. Selected bond lengths [Å]: P(1)–H(1) 1.34(2), P(1)–N(5) 1.688(1), P(1)–N(2) 1.700(1), N(2)–C(3) 1.473(2), N(5)–C(4) 1.466(2), C(3)–C(4) 1.522(2).

Crystalline **4g** contains isolated molecules that display a similar twist conformation of the five-membered ring as that in **3a** and **3h** (Figure 2). The P–N bonds are somewhat shorter but are similar to those in the C–C unsaturated analogue (**4′g**, 1.69–1.71 Å).[13] In contrast, the P–H bond in **4g** [1.34(2) Å] is much shorter than that in **4g′** [1.48(1) Å] and is closer to the "normal" P–H distance in phosphanes (1.288 ± 0.09 Å).[13] The bond lengthening in **4′g** was attributed to the hydride character of the P–H unit and is intimately connected with the possibility of stabilization of a negative formal charge on the hydrogen atom by hyperconjugation between the σ*(PH) orbital with the 6π electrons in the heterocycle (σ* aromaticity).[13,15] In this respect, the relative shortening (with respect to **4′g**) of the P–H distance in **4g** is in accord with the concept that the interruption of the cyclic π delocalization by the C–C saturated backbone renders the hyperconjugative stabilization less efficient and, thus, diminishes the hydride character of the P–H moiety.

Table 1. Selected bond lengths [Å] and angles [°] for **3a**, **3d**, **3f**, **3g**, **3h**, **3′a**, **3′f** and **3′g**.

	R	P1–P1′	P1–N2, P1–N5	C3–C4	N2–P1–N5	Ref.
3a	*t*Bu	2.240(1)	1.716(1), 1.724(1)	1.509(1)	94.93(1)	this work
3d	Dmp	2.301(1)	1.706(1), 1.710(1)	1.512(2)	90.30(6)	[5]
3f	Mes	2.283(1)	1.712(1), 1.716(1)	1.498(2)	90.66(6)	[5]
3g	Dipp	2.321(1)	1.700(2), 1.727(2)	1.525(2)	91.74(9)	[6]
3h	*o*-*t*BuC$_6$H$_4$	2.270(2)	1.716(2), 1.735(2)	1.504(4)	91.35(11)	this work
3′a	*t*Bu	2.244(1)	1.739(1), 1.739(1)	1.338(1)	94.28(4)	[7,8]
3′f	Mes	2.316(2)	1.723(3), 1.726(3)	1.328(4)	89.51(1)	[8]
3′g	Dipp	2.320(1)	1.737(3), 1.718(3)	1.330(5)	90.83(15)	[9]

To understand the reason for the special behaviour of **2g**, **2h** and **2′g** in the one-pot reaction, we attempted to obtain a consistent explanation for the ongoing processes. Both the intermediacy of **3g**, **3h** and **3′g** and the formation of **4g**, **4h** and **4′g** is readily explained by the mechanism displayed in Scheme 3. The in-situ-formed chlorophosphanes **2/2′** react as expected with Mg by reductive coupling to give **3/3′**, which are stable species if the substituents R are small or medium sized. However, sterically demanding groups (R = Dipp, *o*-*t*BuC$_6$H$_4$) induce cleavage of **3g**, **3h** and **3′g** to phosphanyl radicals, which then react with NEt$_3$HCl to give a combination of **4g**, **4h** and **4′g** and **2g**, **2h** and **2′g**. The chlorophosphanes can re-enter the reaction cycle and are eventually transformed into secondary phosphanes **4g**, **4h** and **4′g**.



Scheme 3. Radical-induced formation of phosphanes **4** and **4′** by recursive reductive coupling of **2** and **2′** with Mg.

Support for this mechanistic proposal was gained from further experimental studies, which finally allowed us to confirm the feasibility of each individual step in the proposed reaction sequence. In particular, we found that:

(a) Treatment of chlorophosphanes **2g**, **2h** and **2′g** with magnesium in the absence of Et$_3$NHCl provides isolable quantities of the expected diphosphanes.

(b) The dissociation of the diphosphanes by homolytic P–P bond cleavage had already been established for **3′g**,[8] and electron paramagnetic resonance (EPR) studies also

confirmed the formation of radicals at room temperature for **3g** and **3h** (Scheme 3; generation of radicals from **3g** has recently been discovered by Masuda et al.).[6]

(c) The isolated diphosphanes **3g**, **3h** and **3′g** react with Et_3NHCl in THF or toluene in the absence of Mg to give a 1:1 mixture of **2g**, **2h** and **2′g** and **4g**, **4h** and **4′g**. Monitoring of the reaction by ^{31}P NMR spectroscopy revealed further that i) a mixture of chlorophosphanes **2g** and **2h** and secondary phosphanes **4g** and **4h** also formed after unreacted magnesium was removed from the appropriate one-pot reaction mixtures before the reaction had gone to completion, and ii) the consumption of the chlorophosphane and further formation of secondary phosphane resumed after magnesium was re-added to the mixture.

(d) Even for diphosphanes such as **3a** and **3′a**, which do not undergo homolytic dissociation at room temperature, formation of secondary phosphanes as side products can be enforced at elevated temperature under conditions for which the formation of small quantities of phosphanyl radicals has been established by EPR studies.[8]

The EPR data of **5g** [g = 2.013, $a(^{31}P)$ = 61.3 G, $a(^{14}N)$ = 3.6 G, $a(^{1}H)$ = 3.1 G; values were obtained from spectral simulations and match the previously reported ones][6] and **5h** (Figure 3) reveal that the hyperfine couplings to phosphorus are some 20 G higher than those reported for the C–C unsaturated diazaphosphanyl radicals **5′a**, **5′f** and **5′g**.[8] This is in accord with the fact that the unpaired electron can no longer be delocalized around the entire heterocycle as it is in **5′**[8] and is more or less confined to the NPN moiety. We further explain the low $a(^{31}P)$ and $a(^{14}N)$ values for **5g** and **5h**, which are both close to the bottom end of the range of known couplings in acyclic diaminophosphanyl radicals [$a(^{31}P)$ = 63–108 G, $a(^{14}N)$ = 3.7–5.1 G[3]], as a consequence of conformational constraints in the heterocyclic structures, which improve NPN π delocalization and, therefore, increase the π character of the unpaired electron.

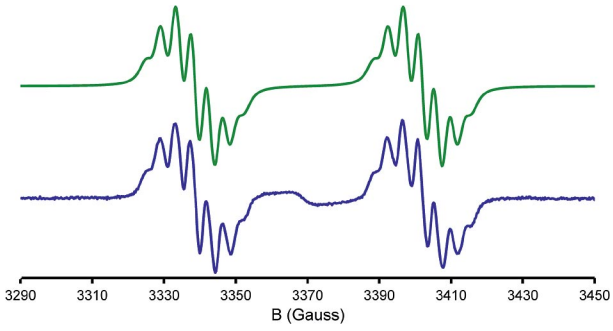


Figure 3. Experimental and simulated EPR spectrum of **5h** at 390 K in toluene. Simulation parameters: g = 2.014, $a(^{31}P)$ = 63.8 G (1 P), $a(^{14}N)$ = 4.3 G (2 N), $a(^{1}H)$ = 3.8 G (2 H).

The most striking deviation between the EPR spectra of **5g** and **5h** concerns the different hyperfine splitting patterns: the signal of **5g** appears as a doublet of nonets owing to coupling with one ^{31}P, two ^{14}N and four equivalent ^{1}H nuclei, whereas that of **5h** is split into a doublet of septets attributable to interaction with one ^{31}P, two ^{14}N and only two ^{1}H nuclei. This, at first glance surprising, finding is conveniently explained in the light of a computational analysis of the hyperfine interactions in **5g**.[6] The computed splitting to protons of axial CH bonds at the twisted ring are clearly larger than those to protons of equatorial CH bonds, and the equivalence of all ring protons was explained as resulting from dynamic averaging owing to rapid ring inversion. If one assumes that **5h** exhibits a similar alignment of *N*-aryl rings and central heterocycle as **3h**, dynamic averaging in this case requires a combination of ring inversion and rotational reorientation of the asymmetrical substituents. As it is reasonable to assume that this process occurs on a much longer time scale, the observed spectrum is considered to represent the hyperfine interactions in a "quasistatic" five-membered ring and is dominated by the two large couplings to the axial protons.

The generation of secondary aminophosphanes **4g**, **4h** and **4′g** during the magnesium reduction of chlorophosphanes in the presence of a weak Brønsted acid can be compared with common synthetic protocols such as the reduction with the complex hydrides $LiAlH_4$[16] or $NaBH_4$[17]. The $LiAlH_4$ reduction frequently suffers from the formation of substantial amounts of side products, which complicate the work-up protocol and lowers the achievable product yields,[15,16] although species such as **4′g**[13] or **4′d** are accessible in reasonable yield. The serendipitous isolation of

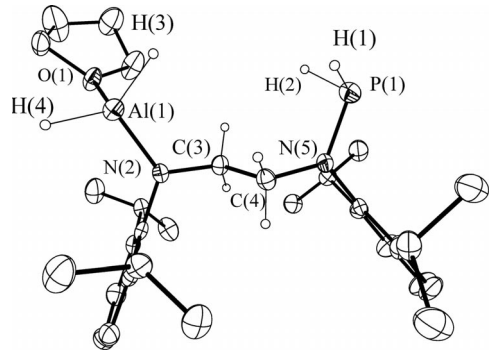
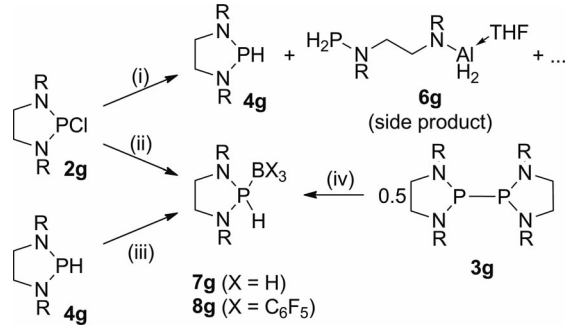


Figure 4. Molecular structure of **6g**·THF; H atoms in the Dipp substituents omitted for clarity; 50% probability ellipsoids. Selected distances [Å]: P(1)–H(1) 1.33(3), P(1)–H(2) 1.36(3), P(1)–N(5) 1.685(2), C(3)–C(4) 1.522(4), N(2)–Al(1) 1.813(2), Al(1)–H(3) 1.51(3), Al(1)–H(4) 1.53(3), Al(1)–O(1) 1.916(2).



Scheme 4. Synthesis of **6g** and phosphane–boranes **7g** and **8g** (R = Dipp): (i) $LiAlH_4$, THF; (ii) $NaBH_4$, THF; (iii) $H_3B{\cdot}SMe_2$, THF; (iv) $H_3B{\cdot}SMe_2$ (**7g**) or $B(C_6F_5)_3$ (**8g**), toluene.

a few crystals of side product **6g** (Figure 4) during the attempted synthesis of **4g** (Scheme 4) confirms that this low selectivity is related to the high chemical activity of the reactant, which is liable to induce over-reduction and ring cleavage. In contrast, the $NaBH_4$ reduction of **2g** smoothly produced phosphane–borane **7g** (Scheme 4), which was isolated in good yield as a stable white solid and characterized by spectroscopic data and a single-crystal X-ray diffraction study (Figure 5). Removal of the coordinated borane is feasible by heating a mixture of **7g** and Et_3N in hexane to reflux for 12 h. Monitoring of the reaction by ^{31}P NMR spectroscopy indicated, however, that this process is not free of side reactions. No attempts to separate Et_3NBH_3 and isolate **4g** were made. The use of super hydride ($Li[BHEt_3]$) as an alternative hydride transfer agent[15] allows for the formation of the secondary aminophosphane **4g** from **2g** without coordination of the borane. From this route, **4g** can be isolated in good yield (80%), and this protocol can thus be considered as an alternative route to the one-pot method outlined in Scheme 2.

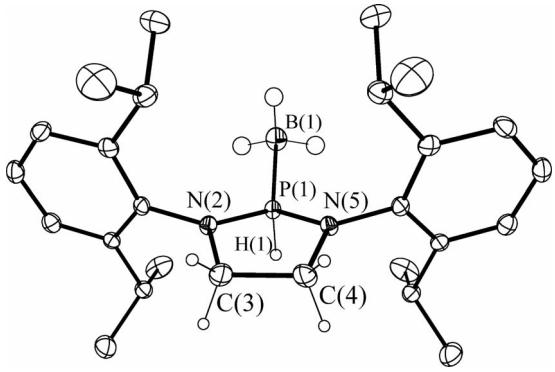


Figure 5. Molecular structure of **7g**; H atoms in the Dipp substituents omitted for clarity; 50% probability ellipsoids. Selected distances [Å] and angles [°]: P(1)–H(1) 1.36(3), P(1)–B(1) 1.884(4), P(1)–N(2) 1.652(2), C(3)–C(3)′ 1.528(4), B(1)–P(1)–H(1) 109(1), N(2)–P(1)–N(2)′ 93.3(1).

Compared to the commonly applied reduction protocols with complex hydrides,[16,17] the magnesium/ammonium salt approach proceeded in our hands with much higher selectivity, facilitated the work-up procedure, and thus granted substantial time-saving and higher product yields. On the other hand, this method currently seems to be limited to the synthesis of a few sterically hindered target species (at least as long as only reactions at room temperature are considered), and one will have to see if the selectivity can be maintained in reductions of substrates with less bulky substituents at elevated temperatures. However, the operational advantages are clearly evident and should stimulate further studies to develop this protocol into a more widely applicable alternative to commonly used reaction schemes.

Based on the proven formation of phosphanyl radicals at room temperature by homolytic cleavage of the P–P bond in **3g**, we desired to further investigate the reaction of this species with boranes. We were interested in the possibility of trapping a phosphanyl radical by forming a Lewis acid–base complex. Thus, the reaction of **3g** with borane–dimethyl sulfide in THF initially gave an NMR silent species when analyzed by ^{31}P NMR spectroscopy. However, after several minutes, the broad doublet of **7g** ($^1J_{P,H}$ = 357 Hz) appeared, which indicated that the addition of a hydrogen atom to the phosphanyl radical to give a P–H bond had occurred. The phosphane–borane **7g** was isolated (Scheme 4) and unambiguously identified by analytical and spectroscopic data and a single-crystal X-ray diffraction study. Similarly, the reaction of **3g** with $B(C_6F_5)_3$ gave the secondary phosphane–borane complex **8g** as revealed by ^{31}P NMR spectroscopy ($^1J_{P,H}$ = 404 Hz) and single-crystal X-ray crystallography (Figure 6). Once again, a hydrogen atom has been added to the phosphanyl to give a closed-shell species. The P–B distance of 2.106(3) Å in **8g** is at the long end of the range for secondary phosphane–$B(C_6F_5)_3$ adducts (2.025–2.098 Å).[18] The P–H distance is similar to those in **4g** and **7g**, which indicates that coordination of $B(C_6F_5)_3$ has little to no structural impact. The gradually increasing ν(PH) vibrational frequencies of **4g** (2025 cm^{-1}), **7g** (2255 cm^{-1}) and **8g** (2314 cm^{-1}) suggest, however, that the P–H bond strengthens perceptibly upon coordination of more and more Lewis acidic boranes.

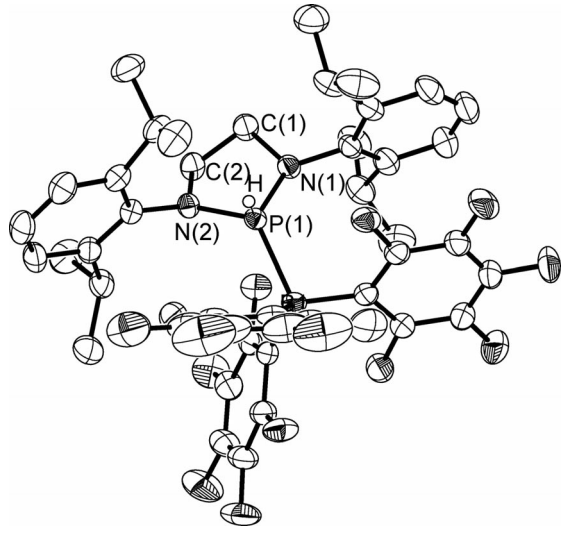


Figure 6. Molecular structure of **8g**; H atoms (other than on the phosphorus atom) omitted for clarity; 50% probability ellipsoids. Selected distances [Å] and angles [°]: P(1)–B(1) 2.106(3), P(1)–H(99) 1.33(2), N(1)–C(1) 1.482(3), N(1)–P(1) 1.671(2), N(2)–C(2) 1.475(3), N(2)–P(1) 1.677(2), P(1)–B(1) 2.106(3), C(1)–C(2) 1.508(4). C(1)–N(1)–P(1) 111.67(17), C(2)–N(2)–P(1) 111.62(16), N(1)–P(1)–N(2) 93.74(11), N(1)–P(1)–B(1) 121.16(12), N(2)–P(1)–B(1) 125.82(12), N(1)–C(1)–C(2) 104.6(2), N(2)–C(2)–C(1) 105.3(2).

Attempts to ascertain the source of the hydrogen atoms for the formation of **6g** and **8g** through a number of experiments proved to be fruitless. The reaction of **3g** with BH_3·THF in THF and BD_3·THF in THF gave inconclusive results, and BH_3·NMe_3 did not react at all. With this in mind, we studied the reaction of **3g** with $B(C_6F_5)_3$ in C_6F_6 as a hydrogen-free solvent, thus eliminating the borane and solvent as hydrogen-atom sources. This reaction resulted likewise in the formation of **8g**. As we see no evidence of

ligand decomposition in the NMR spectra, the hydrogen atom most likely originates from impurities in the reagents and glassware, or in the starting diphosphane **3g**.

The readily occurring conversion of some diphosphanes **3/3′** into appropriate phosphanes **4/4′** raised the question if a reverse transformation might also be feasible. Indeed, during the synthesis of the secondary phosphane **4′d** by $LiAlH_4$ reduction of **2′d**, we noticed that the initially formed product was quantitatively (as monitored by ^{31}P NMR spectroscopy) converted into diphosphane **3′d** when the reaction mixture was stirred for a prolonged time with exposure to daylight. Partial conversion of secondary phosphanes to the corresponding diphosphanes under similar conditions was also observed for **4c** and **3c**, and it had previously been found that prolonged storage of pure **4′a** with exposure to daylight resulted in partial conversion to diphosphane **3′a**, which was isolated in crystalline form and characterized by spectroscopy and a single-crystal X-ray diffraction study.[7] Control experiments confirmed that the phosphane–diphosphane conversion did not take place when the samples were protected from light. The failure to observe any spectroscopically detectable side products suggests that the conversion may be accompanied by the formation of molecular hydrogen, but a positive proof of this hypothesis is still pending.

Conclusions

Symmetrical 2,2′-bi-1,3,2-diazaphospholidines and 1,1′,3,3′-tetrahydro-2,2′-bi-1,3,2-diazaphospholes can be prepared from the appropriate ethane-1,2-diamines or 1,2-diimines in overall yields of 70 to 91% in a short period of time. Most syntheses can be performed as one-pot procedures without isolation of intermediates, but preparation of a few products with sterically demanding *N*-aryl groups requires removal of the ammonium salt (Et_3NHCl), formed as a by-product of a preceding reaction step, prior to the final reductive coupling. In these cases, failure to remove Et_3NHCl results in the reduction of the applied chlorophosphanes to the corresponding secondary phosphanes. Mechanistic studies suggest that this reaction is initiated by homolytic dissociation of the diphosphanes. The phosphanyl radicals formed then react with Et_3NHCl to produce 1:1 mixtures of secondary phosphanes and chlorophosphane starting material, which may then re-enter the reaction sequence. Despite its as yet limited scope, the magnesium/ammonium salt reduction protocol offers some clear advantages over the commonly applied reduction with complex hydrides and, thus, offers interesting prospects for its development into a more generally applicable synthetic method. Preliminary studies reveal that in addition to the reductive conversion of diphosphanes to appropriate secondary phosphanes, a reverse transformation is also feasible upon prolonged exposure of the appropriate secondary phosphanes to daylight. Further studies are needed to establish if these reactions involve the production of molecular hydrogen.

Experimental Section

General Remarks: All preparations were done under an atmosphere of dry, O_2-free N_2 or Ar, by employing both Schlenk-line techniques and an mBraun Labmaster SP inert atmosphere glove box. Solvents were purified by employing a Grubbs type solvent purification system manufactured by Innovative Technology. Hyflo Super Cel (Celite) was purchased from Sigma–Aldrich and dried for 24 h in an oven prior to use. Molecular sieves (4 Å) were purchased from Sigma–Aldrich. and dried overnight at 140 °C under vacuum. EI-MS: Varian MAT 711 instrument, 70 eV. (+)-ESI MS: Bruker Daltonics MicroTOF Q instrument, methanolic solution. Elemental analyses: Perkin–Elmer 2400 Series II CHN/O Analyzer. Some samples could not be prepared under an inert atmosphere, and we explain the rather large deviations between the found and calculated element compositions of some diphosphanes **3/3′** as a consequence of the high oxidation sensitivity of these samples. Melting points were recorded with a Büchi Point B-545 or a Electrothermal MEL-Temp 3.0 apparatus with samples in glass capillaries prepared and sealed under inert conditions. Solution NMR spectra were recorded at 303 K with Bruker Avance 400 (^1H 400.1, ^{13}C 100.5, ^{31}P 161.9, ^{11}B 128.4 MHz), Avance 300 (^1H 300.1, ^{13}C 75.4, ^{31}P 121.4, ^{19}F 282.4, ^{11}B 96.3 MHz) or Avance 250 (^1H 250.1, ^{13}C 62.8, ^{31}P 101.2, ^{11}B, 80.2 MHz) NMR spectrometers. Chemical shifts are referenced to external $Si(CH_3)_4$ (^1H, ^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P), $CFCl_3$ (Ξ = 94.094011, ^{19}F) or $BF_3{\cdot}OEt_2$ (Ξ = 32.083974 MHz, ^{11}B). Coupling constants are given as absolute values; positive chemical shift values denote shifts to lower frequencies, *i*-, *o*-, *m*-, *p*- denote positions in *N*-aryl rings. EPR spectra were measured with a Bruker EMX X-band spectrometer. The EasySpin software[19] was used for spectral simulations. 2-Chloro-1,3,2-diazaphospholidines and 2-chlorodiazaphospholenes were synthesized as described elsewhere. The analytical, spectroscopic and single-crystal X-ray diffraction data of previously unknown **2c** and **2h** are included in the Supporting Information

General Procedure for the Preparation of 2,2′-Bi-1,3,2-diazaphospholidines 3

From Ethane-1,2-diamines (1): The appropriate diamine (5–15 mmol) was added dropwise at –78 °C to a solution of PCl_3 (5–15 mmol, 1 equiv.) and Et_3N (15–40 mmol, 3 equiv.) in THF (50 mL). A white precipitate of Et_3NHCl formed, and the mixture was stirred for 15 min at –78 °C and another 6 h at room temperature to allow complete reaction. Magnesium chips (7.5–22 mmol, 1.5 equiv.) were then added, and the mixture was stirred until completion of the reaction was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy (ca. 24 h; 96 h for **1c**). The volatiles were then removed under reduced pressure, and the residue was suspended in hexane (50 mL). The solids were removed by filtration and washed with hexane or toluene to extract precipitated **3**. The filtrate was evaporated to dryness. The spectroscopically pure products were obtained as white-to-yellow solids or yellow oils (**3b**, **3c**, and **3e**). Crystals of **3a** and **3h** suitable for single-crystal X-ray diffraction studies were obtained by recrystallization from THF/hexane (1:3) at –20 °C.

From 2-Chloro-1,3,2-diazaphospholidines 2: The appropriate chlorodiazaphospholidine (**2d** 500 mg, 1.5 mmol; **2e** 1.00 g, 3.2 mmol; **2g** 4.40 g, 10 mmol) was dissolved in THF (20–50 mL). Magnesium turnings (1.5 equiv.) and a crystal of I_2 (**2e**: no I_2 added) were added to the solution. The mixture was stirred until completion of the reaction was confirmed by ^{31}P NMR spectroscopy (approx. 24 h). The work-up was carried out as described above.

1,1′,3,3′-Tetra-*tert*-butyl-2,2′-bi-1,3,2-diazaphospholidine (3a): Yield 2.50 g (81%); m.p. 127 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 91.7

ppm. ^{1}H NMR (C_6D_6): δ = 1.26 (s, 36 H, CH_3), 2.86 (m, 4 H, NCH_2), 3.23 (m, 4 H, NCH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 30.3 (pseudo-t, $^{3/4}J_{P,C}$ = 4.7 Hz, CH_3), 48.5 (s, NCH_2), 53.5 [pseudo-t, $^{2/3}J_{P,C}$ = 9.3 Hz, *N*C(*t*Bu)] ppm. EI-MS (70 eV, 415 K): *m*/*z* (%) = 201.1 (100) $[M/2]^+$, 402.3 (20) $[M]^+$. $C_{20}H_{44}N_4P_2$ (402.54): calcd. C 59.67, H 11.02, N 13.92; found C 57.12, H 10.4, N 12.53.

1,1′,3,3′-Tetraisopropyl-2,2′-bi-1,3,2-diazaphospholidine (3b): Yield 2.06 g (79%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 97.4 ppm. ^{1}H NMR (C_6D_6): δ = 1.18 (d, $^3J_{H,H}$ = 6.3 Hz, 12 H, CH_3), 1.21 (d, $^3J_{H,H}$ = 6.5 Hz, 12 H, CH_3), 2.75 (m, 2 H, NCH_2), 3.21 (m, 4 H, CH), 3.31 (m, 2 H, NCH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 23.15 (pseudo-t, $^{3/4}J_{P,C}$ = 3.8 Hz, CH_3), 23.4 (pseudo-t, $^{3/4}J_{P,C}$ = 6.4 Hz, CH_3), 50.2 (pseudo-t, $^{2/3}J_{P,C}$ = 0.7 Hz, NCH_2), 52.2 (pseudo-t, $^{2/3}J_{P,C}$ = 10.5 Hz, CH) ppm. EI-MS (70 eV): *m*/*z* (%) = 333.28 (100) $[M - CH_3]^+$.

1,1′,3,3′-Tetracyclohexyl-2,2′-bi-1,3,2-diazaphospholidine (3c): Yield 920 mg (91%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 96.1 ppm. ^{1}H NMR (C_6D_6): δ = 0.90–1.57 (m, 20 H, C_6H_{11}), 1.63–1.80 (m, 12 H, C_6H_{11}), 2.03–2.19 (m, 8 H, C_6H_{11}), 2.83 (m, 4 H, C_6H_{11}), 2.90 (m, 4 H, NCH_2), 3.40 (m, 4 H, NCH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 26.0 (br. s, C_6H_{11}), 26.4 (br. s, C_6H_{11}), 33.8 (pseudo-t, $J_{P,C}$ = 3.8 Hz, C_6H_{11}), 34.2 (pseudo-t, $J_{P,C}$ = 6.4 Hz, C_6H_{11}), 50.4 (br. s, NCH_2), 60.8 (pseudo-t, $^{2/3}J_{P,C}$ = 9.6 Hz, NCH) ppm. MS (ESI+): *m*/*z* (%) = 539.36 (80) $[MHO_2]^+$, 372.33 (30) $[M - 2(C_6H_{11})\text{-}HOCH_3]^+$.

1,1′,3,3′-Tetrakis(2,6-dimethylphenyl)-2,2′-bi-1,3,2-diazaphospholidine (3d): Yield 340 mg (77%); m.p 155 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 98.6 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.44 (s, 12 H, *o*-CH_3), 2.50 (s, 12 H, *o*-CH_3), 2.90 (m, 4 H, NCH_2) 3.63 (m, 4 H, NCH_2), 6.56 (d, $^3J_{H,H}$ = 7 Hz, 4 H, *m*-CH), 6.89 (t, $^3J_{H,H}$ = 7 Hz, 4 H, *p*-CH), 6.98 (d, $^3J_{H,H}$ = 7 Hz, 4 H, *m*-CH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.6 (pseudo-t, $^{4/5}J_{P,C}$ = 2.9 Hz, CH_3), 20.7 (pseudo-t, $^{4/5}J_{P,C}$ = 5.9 Hz, CH_3), 53.1 (pseudo-t, $^{2/3}J_{P,C}$ = 2.3 Hz, NCH_2), 124.3 (br. s, *p*-C), 128.2 (br. s, *m*-C), 129.6 (br. s, *m*-C), 135.0 (pseudo-t, $^{3/4}J_{P,C}$ = 1.1 Hz, *o*-C), 137.3 (pseudo-t, $^{3/4}J_{P,C}$ = 1.6 Hz, *o*-C), 141.9 (pseudo-t, $^{2/3}J_{P,C}$ = 5.8 Hz, *i*-C) ppm. EI-MS (70 eV, 415 K): *m*/*z* (%) = 297.1 (50) $[M/2]^+$, 121.1 (100) $[NH_2 - Dmp]^+$, 314.1 (20) $[M/2 + OH]^+$.

1,1′,3,3′-Tetra-*o*-tolyl-2,2′-bi-1,3,2-diazaphospholidine (3e): Yield 1.02 g (76%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 101.2 ppm. ^{1}H NMR (C_6D_6): δ = 2.01 (br. s, 12 H, *o*-CH_3), 2.79 (m, 4 H, NCH_2), 3.70 (m, 4 H, NCH_2), 6.85–7.00 (m, 12 H, C_6H_4), 7.24–7.29 (m, 4 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 19.0 (pseudo-t, $^{4/5}J_{P,C}$ = 2.8 Hz, CH_3), 54.0 (br. s, NCH_2), 123.5 (pseudo-t, $J_{P,C}$ = 1 Hz, C_6H_4), 124.5 (pseudo-t, $J_{P,C}$ = 6.4 Hz, C_6H_4), 126.6 (br. s, C_6H_4), 131.2 (br. s, C_6H_4), 133.5 (pseudo-t, $J_{P,C}$ = 1.6 Hz, C_6H_4), 146.8 (pseudo-t, $J_{P,C}$ = 7.2 Hz, C_6H_4) ppm. EI-MS (70 eV, 415 K): *m*/*z* (%) = 269.1 (70) $[M/2]^+$, 120.1 (100) $[C_8H_{10}N]^+$, 121.1 (55) $[C_8H_{11}N]^+$.

1,1′,3,3′-Tetramesityl-2,2′-bi-1,3,2-diazaphospholidine (3f): Yield 2.6 g (80%); m.p. 255 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 99.4 ppm. ^{1}H NMR (C_6D_6): δ = 1.65 (s, 12 H, *p*-CH_3), 2.26 (s, 12 H, *o*-CH_3), 2.57 (m, 4 H, NCH_2), 2.62 (s, 12 H, *o*-CH_3), 3.44 (m, 4 H, NCH_2), 6.50 (br. s, 8 H, *m*-CH), 6.67 (br. s, 8 H, *m*-CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 19.2 (br. s, CH_3), 20.7 (dd, $^4J_{P,C}$ = 1.3 Hz, $^5J_{P,C}$ = 0.8 Hz, *o*-CH_3), 20.8 (br. s, CH_3), 53.3 (pseudo-t, $^{2/3}J_{P,C}$ = 2.4 Hz, NCH_2), 129.2 (br. s, *m*-C), 130.4 (pseudo-t, $^{4/5}J_{P,C}$ = 1.4 Hz, *m*-C), 134.7 (pseudo-t, $^{3/4}J_{P,C}$ = 0.5 Hz, *o*-C), 137.1 (br. s, *o*-C), 139.9 (pseudo-t, $^{2/3}J_{P,C}$ = 5.9 Hz, *i*-C) ppm. EI-MS (70 eV, 420 K): *m*/*z* (%) = 325.2 (100), $[M/2]^+$, 650.4 (5) $[M]^+$.

1,1′,3,3′-Tetradiisopropylphenyl-2,2′-bi-1,3,2-diazaphospholidine (3g): Yield 2.95 g (72%); m.p. 215 °C. $^{31}P\{^1H\}$ NMR ([D_8]THF): δ = 145.2 ppm. ^{1}H NMR ([D_8]THF): δ = 0.5 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 0.91 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 0.99 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 0.98 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 1.05 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 1.38 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 1.22 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 1.29 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 2.60 (sept, $^3J_{H,H}$ = 6.5 Hz, 2 H, CH), 3.16 (m, 4 H, NCH_2), 3.36 (m, 4 H, NCH_2), 3.34 (m, 2 H, CH), 4.02 (sept, $^3J_{H,H}$ = 6.5 Hz, 2 H, CH), 4.08 (sept, $^3J_{H,H}$ = 6.5 Hz, 2 H, CH), 6.72 (m, 2 H, *m*-CH), 6.78 (m, 2 H, *m*-CH), 6.8–6.87 (m, 6 H, *m*/*p*-CH), 7.15 (m, 2 H, *m*-CH) ppm. EI-MS (70 eV, 430 K): *m*/*z* (%) = 409.3 (100) $[M/2]^+$, 367.3 (70) $[C_{25}H_{38}N_2]^+$. $C_{52}H_{76}N_4P_2$ (819.13): calcd. C 76.25, H 9.35, N 6.84; found C 73.91, H 9.43, N 6.25.

1,1′,3,3′-Tetra-2-*tert*-butylphenyl-2,2′-bi-1,3,2-diazaphospholidine (3h): Yield 3.07 g (87%); m.p. >180 °C (decomp.). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 120.8 ppm. ^{1}H NMR (C_6D_6): δ = 1.39 (s, 36 H, *t*Bu), 3.08 (m, 4 H, NCH_2), 3.77 (m, 4 H, NCH_2), 6.82 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, C_6H_4), 6.94 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, C_6H_4), 7.35 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, C_6H_4), 7.67 (d, $^3J_{H,H}$ = 7.5 Hz, 4 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.8 (pseudo-t, $J_{P,C}$ = 1.5 Hz, CH_3), 36.0 (s, *i*-C), 58.0 (s, NCH_2), 125.2 (s, C_6H_4), 126.8 (s, C_6H_4), 128.7 (s, C_6H_4), 130.8 (pseudo-t, $J_{P,C}$ = 8.5 Hz, C_6H_4), 146.2 (pseudo-t, $J_{P,C}$ = 2.5 Hz, C_6H_4), 147.0 (pseudo-t, $J_{P,C}$ = 5.3 Hz, C_6H_4) ppm. $C_{44}H_{60}N_4P_2$ (706.92): calcd. C 74.76, H 8.55, N 7.93; found C 72.60, H 8.30, N 7.24.

1,1′,3,3′-Tetrahydro-2,2′-bi-1,3,2-diazaphospholes 3′

From Diazabutadienes 1′: Lithium turnings (69 mg, 10 mmol) were added to a solution of the appropriate diazabutadiene **1′a**–**1′f** (5 mmol) in THF (50 mL). The mixture was stirred for 24 h, and the excess Li was removed by filtration. The red solution was cooled to –78 °C, NEt_3HCl (1.38 g, 10 mmol) was added, and the stirred solution slowly warmed until the reaction was complete. The mixture was again cooled to –78 °C, and PCl_3 (690 mg, 5 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for another 2 h. Magnesium turnings (182 mg, 7.5 mmol) and a few crystals of I_2 were added, and the solution was irradiated in an ultrasonic bath for 2 h. The volatiles were then removed under reduced pressure, the residue was extracted with hexane, and the filtrate was evaporated to dryness. The spectroscopically pure products were obtained as yellow to light rose solids. Performing the same reaction sequence with **1′g** as starting material resulted in quantitative (by ^{31}P NMR spectroscopy) formation of **4′g**. No attempts were made to isolate this product.

From 2-Chloro-2,3-dihydro-1*H*-diazaphospholes 2′: The appropriate chlorodiazaphospholene (**2′a** 1.17 g, 5 mmol; **2′f** 940 mg, 2.6 mmol; **2′g** 2.00 g, 4.5 mmol) was dissolved in THF (10–20 mL). Magnesium turnings (1.5 equiv.) and a crystal of I_2 were added. The mixture was irradiated in an ultrasonic bath for approx. 2 h. The work-up was carried out as described above.

From Diazaphospholene 4′d: Compound **4′d** was prepared in situ by the addition of $LiAlH_4$ (1.25 mmol, 1.25 mL, 1 M in THF) to a cooled (–78 °C) solution of **2′d** (5 mmol, 1.65 g) in THF (50 mL); the mixture was stirred for 1 h. The quantitative formation of **4′d** was established by ^{31}P NMR spectroscopy. The mixture was stirred for 72 h with exposure to daylight and then evaporated to dryness. The residue was extracted with toluene (50 mL), the resulting suspension was filtered, and the filtrate was concentrated under reduced pressure to a total volume of 10 mL. The ^{31}P NMR spectrum of the filtrate revealed the presence of **3′d** as the only phosphorus-containing species. Crystallization at –20 °C produced a

moderate yield of orange crystals, which were isolated by filtration and dried under vacuum.

1,1′,3,3′-Tetra-*tert*-butyl-1,1′,3,3′-tetrahydro-2,2′-bi-1,3,2-diazaphosphole (3′a): Yield 920 mg (92%), m.p. 117 °C. $C_{20}H_{40}N_4P_2$ (398.51): calcd. C 60.28, H 10.12, N 14.06; found C 59.85, H 10.07, N 14.05. The spectroscopic data are identical to those reported elsewhere.[8]

1,1′,3,3′-Tetrakis(2,6-dimethylphenyl)-1,1′,3,3′-tetrahydro-2,2′-bi-1,3,2-diazaphosphole (3′d): Yield 540 mg (37%), m.p. 140 °C. ^{1}H NMR (C_6D_6): δ = 6.99 (s, 8 H, *m*-CH), 6.73 (m, 4 H, *p*-CH), 5.68 (m, 2 H, NCH), 2.39 (s, 12 H, *o*-CH_3), 1.88 (m, 12 H, *o*-CH_3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 87.8 ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 141.1 (m, *o*-C), 139.9 (m, *i*-C), 136.7 (m, *o*-C), 131.4 (m, *m*-CH), 126.3 (m, *m*-CH), 123.1 (m, *p*-CH), 114.6 (m, NCH), 20.2 (m, *o*-CH_3), 19.7 (s, *o*-CH_3) ppm.

1,1′,3,3′-Tetramesityl-1,1′,3,3′-tetrahydro-2,2′-bi-1,3,2-diazaphosphole (3′f): Yield 640 mg (76%), m. p. >200 °C (decomp.). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 74.1 ppm. ^{1}H NMR ($CDCl_3$): δ = 2.27 (br. s, 12 H, *p*-CH_3), 2.38 (br. s, 24 H, *o*-CH_3), 5.83 (br. d, $^3J_{P,H}$ = 2.4 Hz, 4 H, NCH), 6.90 (s, 8 H, *m*-CH) ppm. $C_{40}H_{48}N_4P_2$ (646.78): calcd. C 74.28, H 7.48, N 8.66; found C 73.69, H 7.47, N 8.62.

1,1′,3,3′-Tetradiisopropylphenyl-1,1′,3,3′-tetrahydro-2,2′-bi-1,3,2-diazaphosphole (3′g): Yield 1.30 g (72%), m.p. 157 °C. $C_{52}H_{72}N_4P_2$ (805.12): calcd. C 76.62, H 8.90, N 6.87; found C 75.90, H 8.67, N 6.78. The spectroscopic data are identical with those reported elsewhere.[9]

1,3-Bis(2,6-dimethylphenyl)-2,3-dihydro-1*H*-1,3,2-diazaphosphole (4′d): Compound **4′d** was prepared as described above by the addition of $LiAlH_4$ (1.25 mmol, 1.25 mL, 1 M in THF) to a cooled (–78 °C) solution of **2′d** (5 mmol, 1.65 g) in THF (50 mL). The mixture was warmed to ambient temperature and stirred for 1 h. During this time, the reaction flask was wrapped with aluminium foil to protect the reaction mixture from light. The solids were removed by filtration and washed with hexane. The filtrates were evaporated to dryness, and the residue was recrystallized from MeCN. Yield 830 mg (56%); m.p. 38 °C. ^{31}P NMR (C_6D_6): δ = 64.3 (d, $^1J_{P,H}$ = 138 Hz) ppm. ^{1}H NMR (C_6D_6): δ = 2.29 (br. s, 18 H, *o*-CH_3), 5.74 (d, $^3J_{P,H}$ = 2.0 Hz, 2 H, NCH), 6.92 (s, 6 H, *m*/*p*-CH), 7.12 (d, $^1J_{P,H}$ = 138 Hz, 1 H, PH) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 19.2 (br. s, *o*-CH_3), 121.3 (d, $^2J_{P,C}$ = 6.3 Hz, NCH), 126.3 (d, $^4J_{P,C}$ = 1.8 Hz, *m*-CH), 128.8 (d, $^5J_{P,C}$ = 1.0 Hz, *p*-CH), 137.3 (br. s, *o*-C), 140.6 (d, $^2J_{P,C}$ = 13.8 Hz, *i*-C) ppm. $C_{18}H_{21}N_2P$ (296.35): calcd. C 72.95, H 7.14, N 9.45; found C 72.86, H 7.31, N 9.41.

1,3-Bis(2,6-diisopropylphenyl)-1,3,2-diazaphospholidine 4g

From 1g in a One-Pot Procedure: Compound **1g** (761 mg, 2 mmol) in THF (10mL) was added dropwise to a cooled (–78 °C) solution of PCl_3 (275 mg, 2 mmol) and Et_3N (607 mg, 6 mmol) in THF (50 mL). A precipitate of Et_3NHCl formed, and the mixture was stirred for 15 min at –78 °C and then for 6 h at room temperature. Magnesium turnings (73 mg, 3 mmol) were added, and the mixture was stirred for 24 h at room temperature and then for 60 h at 50 °C. Completion of the reaction was confirmed by ^{31}P{^{1}H} NMR spectroscopy. The volatiles were then removed under reduced pressure, and the residue was suspended in hexane (20 mL). The solids were removed by filtration and washed with hexane. The filtrates were evaporated to dryness to give spectroscopically pure **4g** as a pale yellow solid. Analytically pure single crystals were obtained by recrystallization from hexane. Yield 640 mg (78%), m.p. 138 °C. $C_{26}H_{39}N_2P$ (410.58): calcd. C 76.06, H 9.57, N 6.82; found C 75.89, H 9.85, N 6.79.

From 2g and Super Hydride: Compound **2g** (3.00 g, 6.7 mmol) was dissolved in THF (25 mL). With rapid stirring, $Li[BHEt_3]$ (6.75 mL, 1.0 M in THF, 6.7 mmol) was added dropwise over 10 min. The reaction was allowed to stir for 30 min and remained colourless throughout. The volatiles were removed in vacuo, and the resulting white solid was dissolved in pentane (50 mL). The suspension was filtered through a pad of diatomaceous earth. The resulting colourless solution was evaporated to dryness to produce **4g** as a white powder. Colourless crystals were grown from slow evaporation of a concentrated toluene solution at ambient temperature. Yield 2.20 g (80%), m.p. 139–140 °C. $C_{26}H_{39}N_2P$ (410.58): calcd. C 76.06, H 9.57, N 6.82; found C 76.10, H 9.57, N 6.75. ^{31}P NMR (C_6D_6): δ = 71.0 (d, $^1J_{P,H}$ = 141 Hz) ppm. ^{1}H NMR (C_6D_6): δ = 1.18 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH_3), 1.22 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH_3), 1.3 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 1.32 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 3.32 (m, 4 H, NCH_2), 3.41 (m, 2 H, CH), 3.69 (sept, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH), 6.98–7.22 (m, 6 H, *m*/*p*-C_6H_3), 7.04 (d, $J_{P,H}$ = 141 Hz, 1 H, PH) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.1 (s, CH_3), 24.7 (d, $J_{P,C}$ = 2 Hz, CH_3), 24.9 (s, CH_3), 25.6 (d, $J_{P,C}$ = 1.3 Hz, CH_3), 28.6 (d, $J_{P,C}$ = 1.5 Hz, CH_3), 29.0 (s, CH_3), 56.0 (d, $^2J_{P,C}$ = 8.0 Hz, NCH_2), 124.0 (d, $J_{P,C}$ = 1.5 Hz, C_6H_3), 124.3 (s, C_6H_3), 128.1 (s, C_6H_3), 139.2 (d, $J_{P,C}$ = 14.7 Hz, C_6H_3), 148.9 (d, $J_{P,C}$ = 2.9 Hz, C_6H_3), 150.7, (d, $J_{P,C}$ = 2.8 Hz, C_6H_3) ppm. IR (KBr): $\tilde{\nu}$ = 2958 (s), 2924 (m), 2967 (m), 2025 (m, PH), 1464 (m), 1441 (m), 1381 (m), 1360 (m), 1321 (m), 1265 (m), 1205 (m), 1107 (w), 1063 (m), 1040 (m) cm^{-1}. IR (solution in heptane): $\tilde{\nu}$ = 2047 (PH) cm^{-1}.

((2,6-Diisopropylphenyl){2-[(2,6-diisopropylphenyl)(phosphanyl)-amino]ethyl}amino)aluminum Dihydride (6g): $LiAlH_4$ (171 mg, 4.5 mmol) was added to a cooled (–78 °C) solution of **2g** (1.33 g, 3 mmol) in THF (50 mL). The mixture was warmed to room temperature and stirred for 15 min. The volatiles were removed under reduced pressure, hexane (50 mL) was added, and the solids were separated by filtration. The ^{31}P NMR spectrum of the solution showed the presence of a mixture of **4g** (75%) and **6g** (25%). Storage at –20 °C for 2 d produced a few colourless crystals of **6g**, which were manually picked and found to be suitable for a single-crystal X-ray diffraction study. ^{31}P{^{1}H} NMR (C_6D_6): δ = –26.3 (s) ppm. ^{31}P NMR (C_6D_6): δ = –26.3 (tt, $^1J_{P,H}$ = 197, $^3J_{P,H}$ = 6 Hz) ppm. ^{1}H NMR (C_6D_6): δ = 1.06 (m, 4 H, THF), 1.13 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CH_3), 1.17 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CH_3), 1.28 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CH_3), 1.23 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CH_3), 3.43 (m, 4 H, NCH_2) 3.47–3.61 (m, 4 H, CH), 3.52 (m, 4 H, THF), 5.44 (d, $^1J_{P,H}$ = 197 Hz, 2 H, PH), 7.0–7.22 (m, 6 H, *m*/*p*-C_6H_3) ppm. The ^{1}H NMR signal of the protons attached to the aluminium atom could not be detected, and further analytical data are not available as macroscopic samples could not be obtained free from contamination by **4g** and other species.

1,3-Bis(2,6-diisopropylphenyl)-1,3,2-diazaphospholidine–Borane (7g)

From 2g and $NaBH_4$: $NaBH_4$ (38 mg, 1 mmol) was added to a solution of **2g** (450 mg, 1 mmol) in THF (50 mL). The mixture was stirred for 48 h at room temperature, the solvent was removed under reduced pressure, and the residue was extracted with warm hexane. Pure **7g** was obtained from the extract after recrystallization from THF/hexane at –20 °C. Yield 420 mg (93%), m.p. 163.5 °C. $C_{26}H_{43}BN_2P$ (425.42): calcd. C 73.58, H 9.97, N 6.60; found C 71.21, H 9.80, N 6.27.

From 3g and BH_3·SMe_2: In a 20 mL scintillation vial, **3g** (100 mg, 122 μmol) was dissolved in toluene (5 mL) and BH_3·SMe_2 (122 μL 2.0 M soln. in THF, 244 μmol) was added with rapid stirring. The orange solution was allowed to stir for 30 min, at which point it transitioned to yellow. The solution was filtered through a pad of

diatomaceous earth. Crystallization by slow evaporation of the solvent at ambient temperature yielded X-ray quality, colourless crystals of a solvate of composition **7g**·THF [m.p. 156–159 °C. $C_{26}H_{42}BN_2P{\cdot}C_4H_8O$ (496.52): calcd. C 72.57, H 10.15, N 5.64; found C 72.18, H 10.17, N 6.24]. Complete removal of the solvent yielded 90 mg (yield 87%) of an off-white solid. ^{31}P NMR (C_6D_6): δ = 81.7 (br. m, $^1J_{P,H}$ = 355 Hz) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ = –40.2 (br. d, $^1J_{P,B}$ = 70 Hz) ppm. ^1H NMR (C_6D_6): δ = 7.45 (br. d, $^1J_{P,H}$ = 355 Hz, PH), 7.10–7.17 (m, 4 H, *m*-CH), 6.96–7.06 (m, 2 H, *p*-CH), 3.73 (sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, CH), 3.12–3.38 (m, 6 H, NCH_2 and CH), 1.45 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH_3), 1.23 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH), 1.21 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH), 1.17 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 24.0 (s, CH_3), 24.4 (s, CH_3), 25.0 (s, CH_3), 25.7 (s, CH_3), 28.5 (s, CH), 29.3 (s, CH), 52.1 (s, NCH_2), 124.1 (d, $J_{P,C}$ = 1.3 Hz, C_6H_3), 124.8 (d, $J_{P,C}$ = 0.5 Hz, C_6H_3), 128.6 (d, $J_{P,C}$ = 1.5 Hz, C_6H_3), 135.0 (d, $J_{P,C}$ = 6.8 Hz, C_6H_3), 149.2 (d, $J_{P,C}$ = 1.6 Hz, C_6H_3), 149.8 (d, $J_{P,C}$ = 2.7 Hz, C_6H_3) ppm. IR (KBr): $\tilde{\nu}$ = 2429, 2373, 2346 (BH_3), 2255 (PH) cm^{-1}.

1,3-Bis(2,6-diisopropylphenyl)-1,3,2-diazaphospholidine Tris(pentafluorophenyl)borane (8g): In a 20 mL scintillation vial, **3g** (30 mg, 37 µmol) was dissolved in toluene (5 mL). With rapid stirring, a solution of $B(C_6F_5)_3$ (37.5 mg, 73 µmol) in toluene (5 mL) was added dropwise over 5 min. The orange solution was allowed to stir for 30 min, at which point it transitioned to colourless. The solution was filtered through a pad of diatomaceous earth, and crystallization by slow evaporation of the solvent at ambient temperature yielded X-ray quality, colourless crystals. Yield: 55 mg (49%); m.p. 145–148 °C. ^{31}P NMR (C_6D_6): δ = 66.8 (br. d, $^1J_{P,H}$ = 404 Hz) ppm. ^1H NMR (C_6D_6): δ = 8.35 (br. s, 0.5 H, PH) 7.13–6.80 (br. m, 6 H, Ar-H), 3.54–2.86 (br. m, 8 H, CH/NCH_2), 1.16–0.84 (br. m, 24 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 150.30, 149.24, 147.34, 146.48, 139.02, 135.82, 129.06, 124.88, 54.68, 52.36, 29.63, 28.54, 28.38, 26.50, 24.17, 22.32 ppm. ^{11}B NMR (C_6D_6): δ = 74.3 (br. s) ppm. ^{19}F NMR (C_6D_6): the signals were prohibitively broad at ambient temperature. IR (KBr): $\tilde{\nu}$ = 2314 (PH) cm^{-1}. $C_{44}H_{39}BF_{15}N_2P$ (922.57): calcd. C 57.28, H 4.26, N 3.04; found C 57.13, H 4.53, N 2.99.

Crystal Structure Determinations: Diffraction studies on **3a**, **3h**, **4g**, **6g** and **7g** were carried out with a Nonius Kappa-CCD diffractometer at 100(2) K with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97[20]) and refined with a full-matrix least-squares scheme on F^2 (SHELXL-97[20]). Semi-empirical absorption corrections were applied for **3a**, **3h** and **4g**. Non-hydrogen atoms were refined anisotropically, H atoms on phosphorus, boron, or aluminium atoms in **4g**, **6g**, and **7g** were refined isotropically, and H atoms in CH bonds were refined with a riding model on F^2. The hydrogen atoms attached to the phosphorus atoms in **4g** and **7g** were located and refined freely using isotropic thermal displacement parameters.

Crystals of **4g**, **7g** and **8g** were mounted from Paratone-N oil in a nylon cryoloop or on a MiTeGen MicroMount. The data were collected at 130(2) K (**7g**) or 150(2) K (**4g**, **8g**) with a Siemens/Bruker diffractometer equipped with an APEX II CCD-detector and a KRYO-FLEX cooling device with Mo-K_α radiation (λ = 0.71073 A). A hemisphere of data was collected with ω scans and with frame exposures of 5 to 30 seconds and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled with the APEX II software.[21] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out with the SAINT+ software.[21] The data were corrected for absorption by using the SADABS program.[21] The structure was solved (direct methods and difference Fourier techniques) and refined by using SHELXL.[20] All hydrogen-atom positions were idealized and were allowed to ride on the atom to which they were attached. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. The results of the additional studies on **4g** and **7g** are given in the Supporting Information

3a: Yellow crystals, $C_{20}H_{44}N_4P_2$, M: 402.53 g mol^{-1}, crystal size: 0.31 × 0.30 × 0.14 mm, triclinic, space group $P\bar{1}$, a = 6.2158(6) Å, b = 9.9562(9) Å, c = 10.3690(8) Å, α = 104.970(4)°, β = 107.243(4)°, γ = 94.332(5)°, V = 583.95(9) A^3, Z = 1, ρ_{calcd} = 1.145 Mg m^{-3}, $F(000)$ = 222, θ_{max} = 28.28°, μ = 0.198 mm^{-1}, 9622 reflections measured, 2879 unique reflections [R_{int} = 0.035] for structure solution and refinement with 118 parameters, $R1$ [$I > 2\sigma(I)$] = 0.038, $wR2$ = 0.082, largest diff. peak and hole: 0.502 and –0.246 e Å^{-3}.

3h: Light yellow crystals, $C_{44}H_{60}N_4P_2$, M = 706.90 g mol^{-1}, crystal size: 0.21 × 0.12 × 0.08 mm, monoclinic, space group $C2/c$, a = 29.019(5) Å, b = 7.0404(15) Å, c = 22.511(4) Å, β = 122.750(5)°, V = 3868.0(13) Å^3, Z = 4, ρ_{calcd} = 1.214 Mg m^{-3}, $F(000)$ = 1528, θ_{max} = 28.28°, μ = 0.149 mm^{-1}, 15184 reflections measured, 4755 unique reflections [R_{int} = 0.110] for structure solution and refinement with 227 parameters, $R1$ [$I > 2\sigma(I)$] = 0.062, $wR2$ = 0.115, largest diff. peak and hole: 0.335 and –0.351 e Å^{-3}.

4g: Colourless crystals, $C_{26}H_{39}N_2P$ M = 410.56 g mol^{-1}, crystal size: 0.49 × 0.26 × 0.25 mm, monoclinic, space group $P2_1/n$, a = 19.6355(13) Å, b = 6.4031(4) Å, c = 20.3670(14) Å, β = 107.602(3)°, V = 2440.8(3) A^3, Z = 4, ρ_{calcd} = 1.117 Mg m^{-3}, $F(000)$ = 896, θ_{max} = 28.28°, μ = 0.127 mm^{-1}, 38687 reflections measured, 5991 unique reflections [R_{int} = 0.039] for structure solution and refinement with 256 parameters, $R1$ [$I > 2\sigma(I)$] = 0.043, $wR2$ = 0.102, largest diff. peak and hole 0.406 and –0.309 e Å^{-3}.

6g: Colourless crystals, $C_{30}H_{50}AlN_2OP$, M = 512.35 g mol^{-1}, crystal size: 0.25 × 0.21 × 0.13 mm, monoclinic, space group $P2_1/c$, a = 11.4877(14) Å, b = 16.524(2) Å, c = 16.392(2) Å, β = 97.247(5)°, V = 3086.8(7) A^3, Z = 4, ρ_{calcd} = 1.103 Mg m^{-3}, $F(000)$ = 1120, θ_{max} = 26.35°, μ = 0.141 mm^{-1}, 23075 reflections measured, 6279 unique reflections [R_{int} = 0.092] for structure solution and refinement with 328 parameters, $R1$ [$I > 2\sigma(I)$] = 0.060, $wR2$ = 0.108, largest diff. peak and hole: 0.734 and –0.357 e Å^{-3}.

7g: Colourless crystals, $C_{26}H_{42}N_2PB$, M = 424.4 g mol^{-1}, crystal size: 0.46 × 0.22 × 0.19 mm, orthorhombic, space group $Pnma$, a = 11.9870(13) Å, b = 20.809(2) Å, c = 10.5990(9) Å, V = 2643.7(5) A^3, Z = 4, ρ_{calcd} = 1.066 Mg m^{-3}, $F(000)$ = 928, θ_{max} = 26.38, μ = 0.118 mm^{-1}, 17895 reflections measured, 2775 unique reflections [R_{int} = 0.0795] for structure solution and refinement with 149 parameters, $R1$ [$I > 2\sigma(I)$] = 0.046, $wR2$ = 0.091, largest diff. peak and hole: 0.223 and –0.265 e Å^{-3}.

8g: Colourless crystals, $C_{44}H_{39}BF_{15}N_2P$, M = 922.55 g mol^{-1}, crystal size: 0.33 × 0.31 × 0.15 mm, monoclinic, space group $P2_1/c$, a = 11.410(3) Å, b = 17.962(5) Å, c = 20.961(6) Å, β = 99.656(4)°, V = 4235(2) A^3, Z = 4, ρ_{calcd} = 1.447 Mg m^{-3}, $F(000)$ = 1888, θ_{max} = 28.15°, μ = 0.166 mm^{-1}, 41000 reflections measured, 7462 unique reflections [R_{int} = 0.037] for structure solution and refinement with 706 parameters (906 restraints), $R1$ [$I > 2\sigma(I)$] = 0.044, $wR2$ = 0.113, largest diff. peak and hole: 0.470 and –0.331 e Å^{-3}.

CCDC-913787 (for **3a**), -913803 (for **3h**), -913802 (for **4g**), -913789 (for **6g**), -913868 (for **7g**), and -912900 (for **8g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Synthetic procedures and crystallographic and spectroscopic data for **2c**,**h**; spectroscopic data for **4h**; additional crystallographic data for **4g** and **7g**, crystallographic data for an oxidation product of **8g**.

Acknowledgments

Financial support by Deutsche Forschungsgemeinschaft (DFG), Deutscher Akademischer Austauschdienst (DAAD) (to D. F.) and the Academy of Finland (to M. N.) is gratefully acknowledged. The authors thank Dr. Wolfgang Frey (Institut für Organische Chemie, University of Stuttgart) for measuring X-ray diffraction data sets and J. Trinkner and K. Wohlbold (Institut für Organische Chemie, University of Stuttgart) for recording the mass spectra.

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Received: December 5, 2012
Published Online: February 11, 2013

