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Solvent-controlled lithiation of P=C–N-heterocycles: Synthesis of mono- and bis(trimethylsilyl)-*tert*-butyl-dihydrobenzazaphospholes – A new type of highly bulky and basic phosphine ligands

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ABSTRACT

The influence of solvents on the lithiation of *N*-methyl-1,3-benzazaphospholes is reported; these are accessible via catalytic phosphonylation of 2-bromoanilines, subsequent reduction to 2-phosphinoanilines and acid-catalysed disproportionative ring closure with excess paraformaldehyde. Reactions with *t*BuLi in polar solvents (THF, Et_2O), particularly in the presence of *t*BuOK, lead to 2-lithiobenzazaphospholes (CH-lithiation) whereas hydrocarbons favour "normal" (hexane) or "inverse" (toluene) addition at the P=C bond. Reactive Li-species were trapped by $ClSiMe_3$, present during the lithiation in hydrocarbons, and give rise to 2- and 3-trimethylsilyl-dihydro-1,3-benzazaphospholes, respectively. In hexane, via preferred lithiation of the primary adduct, the 2,2′-bis(trimethylsilyl)-dihydro-1,3-benzazaphosphole is the main product. 5-Methyl-1,3-benzazaphosphole, with NH function, reacts in toluene in the "normal" mode to 3-*tert*-butyl-1,2-bis(trimethylsilyl)-5-methyl-dihydrobenzazaphosphole. The sterically demanding *tert*-butyl and trimethylsilyl groups are arranged in *anti*-position as shown by crystal structure analyses, the second 2-$SiMe_3$ group in *gauche* position. The *P*-*tert*-butyl-2,2′-bis(trimethylsilyl)-dihydrobenzazaphospholes represent a new type of sterically congested dialkylaryl phosphine ligands with increased basicity by the +I-effect of the silyl groups and +M-effect of the basic nitrogen in *o*-position.

Introduction

Compounds with trivalent phosphorus form a well-known class of ligands with wide variability of electronic and steric properties, ranging from highly basic phosphides and nucleophilic phosphines to more electrophilic phosphites and low-coordinated neutral λ^3-phosphorus species [1]. Whereas phosphine and phosphite ligands find a wide variety of applications in homogenous transition metal coordination catalyses [2], examples of the use of neutral dicoordinated P-ligands in such reactions are rather limited, being restricted to phosphabenzenes and phosphaalkenes [3]. Investigations of various types of 1,3-benzazaphospholes [4–6], which are reasonably stable π-excess aromatic P=C ligands [7], showed formation of kinetically and thermally stable $M(CO)_5$ complexes with zero-valent chromium, molybdenum and tungsten [8]; however, complexes with non-zerovalent transition metals [9] proved to be kinetically labile and, in contrast to phosphabenzene complexes [3a,3b,10], seem to be restricted to electron-rich d^{10} metal species. Labile benzazaphosphole $M(CO)_5$–$AgSbF_6$ complexes are efficient initiators for ring opening polymerization of cyclic ethers [11], but applications as ligands in coordination catalysis are disfavoured by the lability of the relevant complexes. However, an indirect applicability of these P=C compounds with respect to transition metal coordination catalysis might be promising – their transformation towards new types of bulky and basic phosphines as steering ligands. The polymerization of phosphaalkenes to new polyphosphorus materials was recently reported and highlighted [12], and some addition reactions of *t*BuLi at the P=C bond of aromatic P=C heterocycles are also known [13,14]. The 1,3-benzazaphospholes appear particularly useful for the synthesis of sterically demanding and basic phosphine ligands because the addition of *t*BuLi provides *N*-heterocyclic *tert*-butyl-phosphines with high P-basicity, associated with the +M-effect of the *o*-amino group in addition to the inductive (+I) and the steric

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influence of the tertiary alkyl substituent at phosphorus. We observed this addition in the case of bulkier *N*-substituted 1,3-benzazaphospholes as a competing reaction to the 2-CH lithiation by *t*BuLi(pentane) in THF. A closer investigation of the lithiation of *N*-neopentyl-1,3-benzazaphospholes gave evidence that the reaction can be controlled by auxiliaries and the polarity of the solvent. The presence of KO*t*Bu led to clean CH-lithiation, use of non-polar solvents to normal (*t*Bu at phosphorus) and inverse (*t*Bu at C2) addition. The inverse addition was prevented by steric hindrance in the reaction of *N*-adamantyl-1,3-benzazaphosphole with *t*BuLi in hexane [14]. In the case of 1-methyl-1,3-benzazaphosphole, the CH-lithiation was strongly favoured in THF or diethyl ether [15]. The aim of the present study was to find out if controlled addition reactions of *t*BuLi can be achieved for NMe- and NH-1,3-benzazaphospholes by use of less polar solvents.

Results and discussion

Starting materials

For the preparation of the starting materials we used a new three step route (Scheme 1), in part communicated recently [6c]. The first step is the synthesis of **1a**,**b** by phosphonylation of 2-bromo (methyl)anilines with diethyl phosphite in toluene in the presence of $Pd(PPh_3)_4$ (2 mol%)/triethylamine using a protocol of Hirao et al. [16]. The coupling gave good yields and is more convenient to handle than the original synthesis of **1a** by Issleib and Vollmer [17] by means of photoinduced Michaelis-Becker coupling of 2-iodoaniline with $KOP(OEt)_2$ in liquid ammonia. Steps two and three comprise the reduction of the 2-phosphonoaniline with $LiAlH_4$ to **2a**,**b** and the conversion to **3a**,**b** by subsequent heating (24 h) with excess paraformaldehyde (4-5 equivalents CH_2O) in the presence of *p*-toluenesulfonic acid (15 mol%). The latter reaction combines the condensation of the 2-phosphinoaniline with two molecules of formaldehyde with concomitant cyclization and reductive *N*-methylation. The driving force for the internal transfer of hydrogen is the gain in energy by aromatization of a dihydrobenzazaphosphole intermediate.

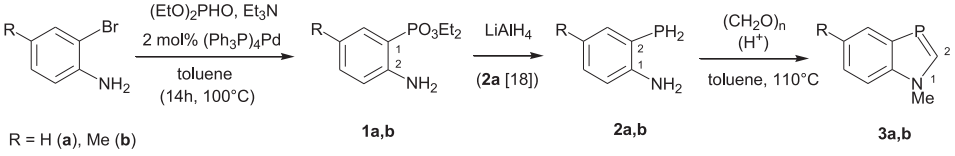
Lithiation and substitution reactions

The lithiation of **3a** with *t*BuLi (1.7 M in pentane) in diethyl ether at −78 °C led to 2-lithio-1-methyl-1,3-benzazaphosphole **4a**, which crystallized from THF/hexane as a μ-Li-bridging dimeric bis-THF solvate. This was stable at room temperature at least one day and allowed coupling with a variety of electrophilic element halides or carbonyl compounds to form benzazaphospholes with functional groups in the 2-position [15]. When the reaction of **3a** with *t*BuLi (1.6 M) was carried out in a mixture of diethyl ether with the less polar hexane (1:1 v/v) and a slight excess of chlorotrimethylsilane, added before *t*BuLi (at −70 °C) to trap reactive organolithium species, the previously observed 2-trimethylsilylbenzazaphosphole **5a** [15] was not obtained. Instead, a complex mixture of the addition products **6a**, **7a** and **8a** was formed in a molar ratio of 17:68:15% (based on 1H NMR integration) (Scheme 2). Sufficiently different and characteristic ^{31}P, ^{13}C and ^{1}H NMR data of the different compound types and comparison with related species (see below) allowed their unambiguous identification. *t*BuLi itself did not react significantly with $ClSiMe_3$ under these conditions. The formation of mainly **7a** can be rationalized in terms of rapid silylation of the primarily formed *normal* addition product and preferential lithiation of the resulting **6a**, with the second silylation affording **7a**. The *inverse* addition is a minor side reaction leading to small amounts of **8a**, formed by desilylation at phosphorus with MeOH. CH-lithiation was not observed under the above conditions.

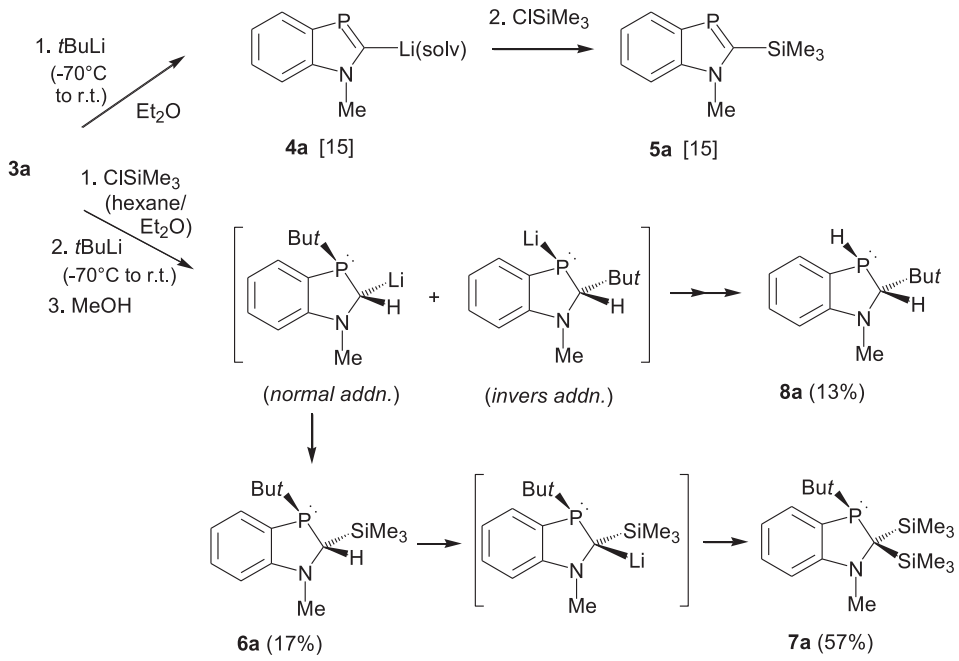
For further experiments **3b** was used, because the additional 5-methyl group facilitates interpretation of the proton NMR spectra, which is helpful in the analysis of product mixtures. The lithiation of **3b** in THF with *t*BuLi (pentane) in the presence of $ClSiMe_3$ did not provide the expected clean 2-trimethylsilyl-benzazaphosphole **5b** but instead a mixture with the addition-bis(silylation) product **7b** in a molar ratio of 33:67%. The ratio of **5b**/**7b** in Et_2O, determined by integration of $SiMe_3$ proton signals, was 25:75% under the same conditions, and was similar in Et_2O/hexane (1:1) (23:77%). Exclusive CH-lithiation and formation of **5b** required reaction with *t*BuLi (pentane) and KO*t*Bu in THF (−70 to −30 °C) and subsequent trimethylsilylation. This shows that the presence of $ClSiMe_3$ favours addition of *t*BuLi at the P=C bond, whereas KO*t*Bu, which coordinates alkyllithium compounds to form highly polar Lochmann–Schlosser-bases [18], strongly supports CH-lithiation, as known already for various other compound types [19]. *Inverse* addition was not observed in these experiments but became the major reaction if the conversion of **3b** with *t*BuLi (pentane) was carried out in toluene (−70 °C) in the presence of $ClSiMe_3$; the *inverse* P-silylation product **9b** was obtained in ca. 70% yield along with a trace amount of the *normal* isomer **6b** (Scheme 3).

Reaction of the NH-benzazaphosphole **3c** with 1.5 equivalents *t*BuLi (pentane) in toluene in the presence of $ClSiMe_3$ (1.5 equiv.) resulted in N-silylation and *normal* addition and furnished the 1,2-bis(silylated) 3-*tert*-butyl-dihydrobenzazaphosphole **10c** (Scheme 4) in good yield. This, together with lack of even a weak phosphorus resonance for the corresponding N-trimethylsilyl-1,3-benzazaphosphole, which like 2-methyl-N-trimethylsilyl-benzazaphospholes should appear downfield shifted [20], suggests rapid addition of *t*BuLi at either the primarily formed NLi-species or the $NSiMe_3$ compound formed therefrom.

To introduce functional groups via reagents that themselves react with *t*BuLi, the lithiated species must be generated at first and be sufficiently persistent towards the solvent to allow defined substitution reactions. This is possible for the relatively stable 2-lithio-benzazaphospholes, as shown earlier for **4a** [15] and for **4b** by reaction with CO_2 and workup to the carboxylic acid **11b**. The latter was recently communicated, including a characterization by crystal structure analysis [6c]. Benzazaphosphole-2-carboxylic acids are stable compounds and form η^1-P pentacarbonyl tungsten complexes, as shown for **12a**, without interference by the acidic COOH-group (Chart 1). Attempts to synthesize *N*-methyl-3-*tert*-butyl-dihydrobenzazaphosphole-2-carboxylic acids, however, have so far failed to give defined products, although this was possible in the case of bulkier *N*-neopentyl, *N*-adamantyl and asymmetric *N*-(1-aryl)ethyl substituted dihydrobenzazaphosphole-2-carboxylic



Scheme 1. Synthesis of *N*-methyl-1,3-benzazaphospholes **3a**,**b**.

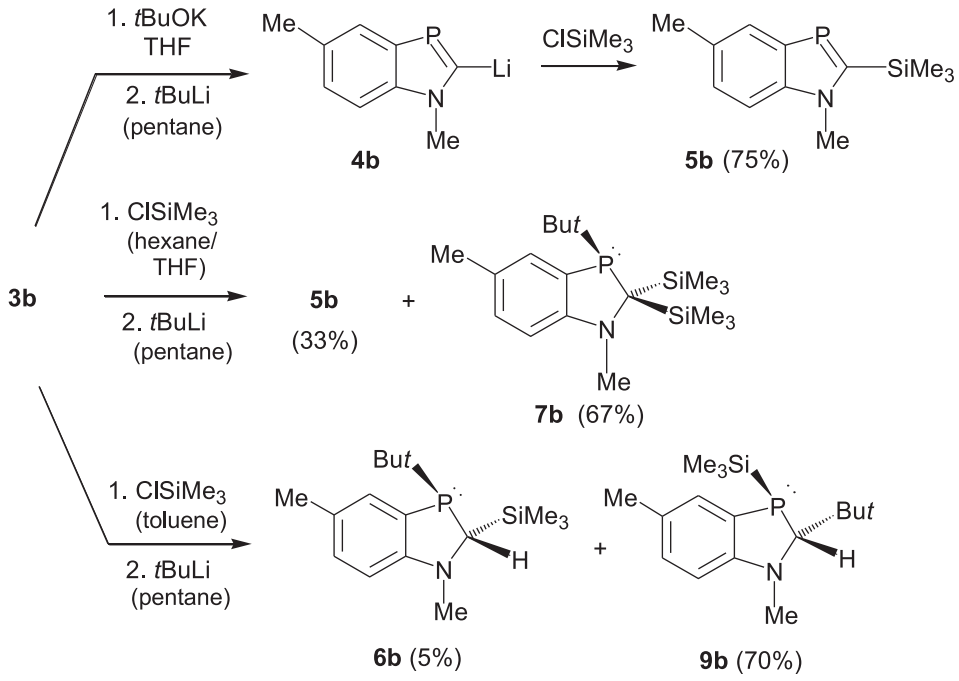


Scheme 2. Reactions of **3a** with *t*BuLi and $ClSiMe_3$ under varied conditions with assumed intermediates (the double arrow before **8a** symbolizes P-silylation and desilylation by MeOH).

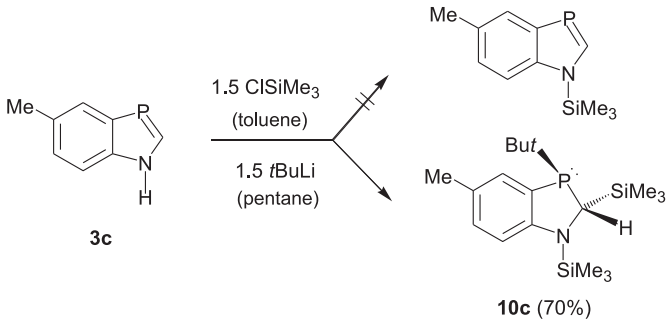
acids, which all proved to form efficient ethylene oligomerization catalyst systems with $Ni(COD)_2$ [14].

Structural aspects

The structure of the products was elucidated by conclusive ^{31}P, ^{1}H and ^{13}C solution NMR and high resolution mass spectra. The assignment of the proton and ^{13}C resonances was facilitated by typical shift ranges and coupling constants to phosphorus, known from related, independently synthesized compounds [14]. Particular features of the novel bulkily substituted 3-*tert*-butyl-2,2′-bis(trimethylsilyl)-dihydrobenzazaphospholes **7a**,**b** are significant downfield shifts and signal broadenings of the second $SiMe_3$ signal in the proton and ^{13}C NMR spectra, and significantly increased $^{1}J_{PC}$ coupling constants for $PCMe_3$ (ΔJ ca. 10 Hz) and P—*C*—N (ΔJ ca. 15 Hz) compared to **6a** and **10c**, whereas $^{1}J_{PC3a}$ become smaller (by 3—6 Hz). Detailed information on the structure, the arrangement of the substituents and distortions of P3 and C2 from the ring plane is provided by crystal structure analyses of **7b** and **10c** (Figs. 1 and 2). Both compounds crystallize in the space group



Scheme 3. Reactions of **3b** with *t*BuLi (−70 °C to r.t.) and $ClSiMe_3$ in various solvents.



Scheme 4. Reaction of the NH-benzazaphosphole **3c** with *t*BuLi and $ClSiMe_3$.

$P2_1/c$ with four molecules in the unit cell. N1 lies effectively within the plane of the six-membered ring [**7b** displaced by −0.002(2) Å; **10c** by −0.026(1) Å], P3 is only slightly displaced [**7b** by 0.098(2) Å; **10c** by 0.024(1) Å], but C(2) is markedly displaced out of the plane [**7b** by −0.449(2) Å; **10c** by −0.331(2) Å] to meet the steric requirements of the five-membered ring. The *tert*-butyl groups are arranged nearly perpendicular to the benzene ring plane [**7b** C(9)-P(3)-C(3A)-C(7A) 95.93(11), C(9)-P(3)-C(3A)-C(4) 81.81(14); **10c** C(8)-P(3)-C(3A)-C(7A) 95.85(7), C(8)-P(3)-C(3A)-C(4) 84.57(9)]. The 2-trimethylsilyl groups of **7b** occupy a *gauche* [Si(2)-C(2)-P(3)-C(9) 55.52(9)] and the *anti* position [Si(1)-C(2)-P(3)-C(9) 174.43(6)] towards the *tert*-butyl group at phosphorus. In the 2-monosilylated **10c** the *anti* orientation of the $SiMe_3$ and CMe_3 groups is less pronounced [Si(2)-C(2)-P(3)-C(8) 151.83(4)]. The 2- and 1-trimethylsilyl groups are arranged almost perpendicular [Si(1)-N(1)-C(2)-Si(2) 90.68(8)] with the N−$SiMe_3$ group deviating somewhat more from the benzene ring plane [Si(1)-N(1)-C(7A)-C(7) 21.67(13)] than the N−Me group of **7b** [C(8)-N(1)-C(7A)-C(3A) 174.07(13)]. The N(1)-C(3A) and N(1)-C(2) bond lengths are similar in **7b** and **10c** and are consistent with sp^2-hybridization of nitrogen, which allows efficient conjugation with the benzene ring. These characteristics show that the new dialkylarylphosphine-type 3-*tert*-butyl-dihydro-1,3-benzazaphospholes with silyl-substituted (+I-effect) alkyl and *o*-amino-substituted (+M-effect) aryl group fulfil the criteria for sterically demanding or congested (two $SiMe_3$ groups adjacent to *t*BuP) and P-basic ligands.

Conclusions

N-Methyl-1,3-benzazaphospholes, accessible from *N*,*P*-diprimary *o*-phosphinoanilines by acid-catalysed condensation with excess paraformaldehyde, react with *t*BuLi in different modes, controlled by the polarity of the medium. In THF or diethyl ether, particularly in the presence of *t*BuOK to generate highly polar Lochmann-Schlosser bases, CH-lithiation with formation of 2-lithio-1-methyl-1,3-benzazaphospholes is enabled whereas a high content of hydrocarbons, supported by the presence of $ClSiMe_3$ for silylation of the resulting reactive Li-species, promotes *normal* (*n*-hexane) or *inverse* (toluene) addition and formation of silylated dihydrobenzazaphospholes. 1,2-Unsubstituted 1,3-benzazaphospholes undergo *N*-lithiation combined with *normal* addition in toluene and provide 1,2-bis(silyl)-dihydrobenzazaphospholes. The new P-*tert*-butyl-2,2′-bis(trimethylsilyl)-1,3-dihydrobenzazaphospholes

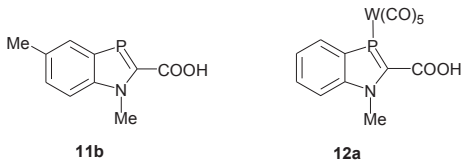


Chart 1. Compounds **11b** and **12a**.

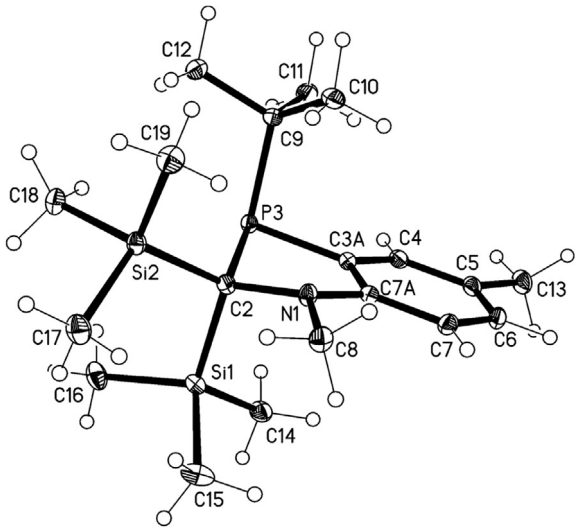


Fig. 1. Molecular structure of **7b** in the crystal (ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°): P(3)-C(3A) 1.8256(14), C(2)-P(3) 1.8922(14), P(3)-C(9) 1.9031(15), N(1)-C(7A) 1.3851(18), N(1)-C(2) 1.5006(18), N(1)-C(8) 1.4520(18), C(2)-Si(2) 1.9255(15), C(2)-Si(1) 1.9539(15), Si−CH_3 1.8674(17)-1.8808(16); C(7A)-N(1)-C(2) 112.33(11), C(7A)-N(1)-C(8) 119.19(12), N(1)-C(2)-P(3) 104.39(9), Si(2)-C(2)-Si(1) 109.87(7), C(3A)-P(3)-C(2) 88.18(6).

represent a novel heterocyclic type of sterically congested dialkylarylphosphine ligands with +I- and +M-substituents that increase the P-basicity. The synthetic accessibility, reported herein, paves the way for studies of their use as ligands in homogenous transition metal catalysed reactions.

Experimental section

General

All operations with air sensitive compounds were carried out under dry nitrogen or argon using Schlenk techniques. Ethers,

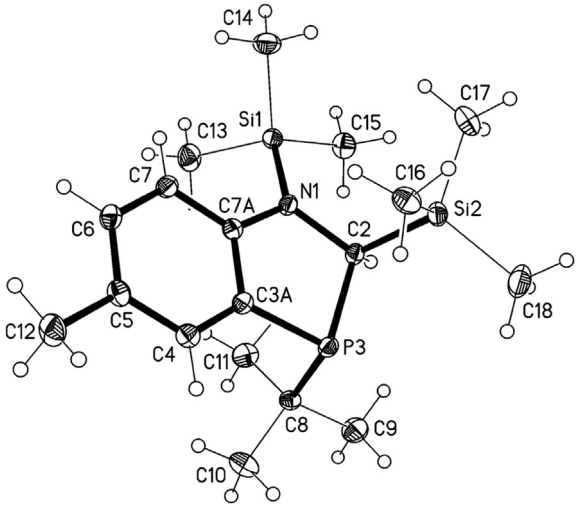


Fig. 2. Molecular structure of **10c** in the crystal (ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°): P(3)-C(3A) 1.8150(9), C(2)-P(3) 1.8756(9), P(3)-C(8) 1.8897(9), N(1)-C(7A) 1.4009(11), N(1)-C(2) 1.4980(12), N(1)-Si(1) 1.7548(8), C(2)-Si(2) 1.9042(10); Si(2)-CH_3 1.8629(11)-1.8710(11); C(7A)-N(1)-C(2) 111.08(7), C(7A)-N(1)-Si(1) 123.23(6), N(1)-C(2)-P(3) 108.23(6), C(3A)-P(3)-C(2) 88.83(4), Si(1)-N(1)-C(7A)-C(3A) −158.57(7), C(2)-N(1)-C(7A)-C(3A) 12.38(11), Si(2)-C(2)-P(3)-C(8) 151.83(4), Si(1)-N(1)-C(2)-Si(2) −90.68(8).

hexane and toluene were dried over sodium ketyl and freshly distilled before use. Commercially available starting materials were used as received unless indicated otherwise. The compounds **2a** [17] and **3c** [8a] were prepared as described in the literature. NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. Chemical shifts (δ) are given in ppm relative to Me_4Si and H_3PO_4 (85%), respectively. Coupling constants refer to J_{HH} in ^{1}H and J_{PC} in ^{13}C NMR data unless stated otherwise. Assignment numbers follow the nomenclature (cf. Scheme 1). HRMS measurements were performed in the Institut für Organische Chemie, Universität Göttingen, using a 7T Fourier transform ion cyclotron resonance mass spectrometer APEX IV (Bruker Daltonics) (ESI) and in the Department Chemie, Ludwig-Maximilians-Universität München using an MS700 (Jeol) (DEI).

*2-Amino-phenylphosphonic acid diethylester (**1a**)*

A mixture of 2-bromoaniline (0.50 g, 2.91 mmol), Et_3N (0.5 mL, 3.56 mmol), diethyl phosphite (0.50 mL, 3.90 mmol) and $Pd(PPh_3)_4$ (67 mg, 2 mol%) in toluene (15 mL) was heated at 100 °C for 14 h. Filtration, removal of the solvent in a vacuum and purification by column chromatography on silica gel using 4% ethyl acetate/hexane for elution furnished 0.50 g (75%) pale yellow oil. ^{1}H NMR ($CDCl_3$): δ = 1.32 (t, ^3J = 7.4 Hz, 6H, CH_3), 4.09 (m, 4H, OCH_2), 5.17 (vbr s, NH_2), 6.65 (br t, $^3J \approx$ 7.5, 7 Hz, 1H, H-5), 6.70 (ddd, ^3J = 8.4, $^4J_{PH}$ = 3.3, ^4J = 0.8 Hz, 1H, H-3), 7.26 (tt, ^3J = 8.3, 7.2, ^4J = 1.4 Hz, 1H, H-4), 7.44 (ddd, $^3J_{PH}$ = 14.3, ^3J = 7.5, ^4J = 1.6 Hz, 1H, H-6). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 21.2 ppm. The ^{1}H NMR data are in agreement with earlier reported 100 MHz ^{1}H NMR values [17].

*2-Amino-5-methyl-phenylphosphonic acid diethylester (**1b**)*

Compound **1b** was prepared in analogy to **1a** from 2-bromo-4-methylaniline (1.20 g, 6.45 mmol), Et_3N (1.1 mL, 7.89 mmol), diethyl phosphite (1.10 mL, 8.60 mmol) and $Pd(PPh_3)_4$ (149 mg, 2 mol %) in toluene (20 mL) as a pale yellow oil (1.19 g, 76% yield). ^{1}H NMR ($CDCl_3$): δ 1.30 (t, ^3J = 7.0 Hz, 6H, CH_3), 2.19 (s, 3H, 5-CH_3), 4.06 (m, 4H, OCH_2), 4.95 (br s, 2H, NH_2), 6.56 (dd, ^3J = 8.1, $^4J_{PH}$ = 6.9 Hz, 1H, H-3), 7.06 (dt, ^3J = 8.3, ^4J + $^5J_{PH}$ = 1.8 Hz, 1H, H-4), 7.23 (dd, $^3J_{PH}$ = 14.7, ^4J = 1.9 Hz, 1H, H-6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.16 (d, ^3J = 6.6 Hz, CH_3), 20.09 (s, 5-CH_3), 61.77 (d, ^2J = 4.0 Hz, OCH_2), 107.80 (d, ^1J = 183.1 Hz, C_q-1), 116.35 (d, ^3J = 13.3 Hz, C-3), 125.84 (d, ^3J = 13.3 Hz, C_q-5), 132.80 (d, ^2J = 6.6 Hz, C-6), 134.72 (d, ^4J = 2.7 Hz, C-4), 148.79 (d, ^2J = 8.0, C_q-2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 21.5. HRMS (ESI in MeOH+FA): $C_{11}H_{18}NO_3P$ (243.24), calcd. for $[M+H]^+$ 244.1097; found: 244.1099.

*2-Phosphino-4-methylaniline (**2b**)*

A solution of **1b** (0.50 g, 2.06 mmol) in diethyl ether (20 mL) was added dropwise at −10 °C to $LiAlH_4$ (0.24 g, 6.3 mmol) in diethyl ether (150 mL). After stirring for 3 d at room temperature water was added dropwise until the evolution of hydrogen ceased. The mixture was dried by Na_2SO_4 and filtered, and the residue was washed with ether. Removal of solvent in vacuum furnished 0.214 g (75%) pale yellow oil. ^{1}H NMR ($CDCl_3$): δ = 2.26 (s, 3H, 4-CH_3), 3.67 (d, $^1J_{PH}$ = 201.7 Hz, 2H, PH_2), 3.92 (br s, 2H, NH_2), 6.66 (dd, ^3J = 8.1, $^4J_{PH}$ = 2.1 Hz, 1H, H-6), 7.04 (ddt, ^3J = 8.1, ^4J = 1.5, $^5J \approx {}^5J_{PH}$ = 0.7 Hz, 1H, H-5), 7.30 (ddd, $^3J_{PH}$ = 11.4, ^4J = 1.5, ^5J = 0.6 Hz, 1H, H-3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.16 (s, 4-CH_3), 110.85 (d, ^1J = 9.3 Hz, C_q-2), 114.91 (br, C-6), 127.57 (d, ^3J = 10.6 Hz, C_q-4), 131.56 (s, C-5), 137.99 (d, ^2J = 29.2 Hz, C-3), 146.92 (d, ^2J = 2.7 Hz, C_q-1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −150.3. HRMS (ESI in MeOH, FA): $C_7H_{10}NP$ (139.13), calcd. for $[M+H]^+$ 140.0624; found: 140.0624. The NMR data are in good (^{31}P) and sufficient (^{1}H, 200 MHz) agreement, respectively, with data on **2b**, synthesized from *N*-methylamino benzenephosphonous acid diethyl ester [21]).

*1-Methyl-1H-1,3-benzazaphosphole (**3a**)*

A solution of **2a** [17] (160 mg, 1.28 mmol) in toluene (10 mL) was refluxed with paraformaldehyde (192 mg, 6.40 mmol, 5 equivalents) in the presence of *p*-toluenesulfonic acid hydrate (36 mg, 15 mol%) for 24 h. The mixture was diluted with diethyl ether (10 mL), extracted with cold aqueous NaOH (5%) followed by cold 10% aqueous H_2SO_4 to remove the catalyst and *N*-basic impurities, respectively, and dried with Na_2SO_4. Removal of the solvent under vacuum gave 114 mg (60%) colourless liquid. The NMR data are in good agreement with those of **3a** synthesized by condensation of *N*-methyl-2-phosphinoaniline with formiminomethylester hydrochloride [15b].

*1,5-Dimethyl-1H-1,3-benzazaphosphole (**3b**)*

Compound **3b** was synthesized by heating **2b** (248 mg, 1.78 mmol) with paraformaldehyde (214 mg, 7.13 mmol, 4 equivalents) and *p*-toluenesulfonic acid hydrate (51 mg, 15 mol%) in toluene (12 mL) for 24 h at reflux and workup as described for **3a** yielding 179 mg (62%) pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3H, 5-CH_3), 3.87 (d, $^4J_{PH}$ = 0.8 Hz, 3H, NCH_3), 7.16 (br d, ^3J = 8.4 Hz, 1H, H-6), 7.37 (br d, ^3J = 8.4 Hz, 1H, H-7), 7.80 (m, 1H, H-4), 8.32 (d, $^2J_{PH}$ = 37.8 Hz, 1H, H-2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.10 (s, 5-CH_3), 37.35 (d, ^3J = 2.7 Hz, NCH_3), 112.02 (s, CH-7), 126.49 (d, ^4J = 2.6 Hz, CH-6), 128.89 (d, ^2J = 21.3 Hz, CH-4), 129.38 (d, ^3J = 11.9 Hz, C_q-5), 141.29 (d, ^2J = 5.3 Hz, C_q-7a), 142.55 (d, ^1J = 39.8 Hz, C_q-3a), 161.94 (d, ^1J = 54.4 Hz, CH-2). ^{31}P NMR ($CDCl_3$): δ 69.8 (dd, $^2J_{PH}$ = 38.2, J = 3.0 Hz). HRMS (ESI in MeOH+FA): $C_9H_{10}NP$ (163.16), calcd. for $[M+H]^+$ 164.0624; found: 164.0624.

*Detection of 3-tert-butyl-1-methyl-2-trimethylsilyl-2,3-dihydro-1H-1,3- benzazaphosphole (6a), 3-tert-butyl-1-methyl-2-bis(trimethylsilyl)-2,3-dihydro-1H-1,3-benzazaphosphole (7a), and 2-tert-butyl-1-methyl-2,3-dihydro-1H-1,3-benzazaphosphole (**8a**)*

A pentane solution of *t*BuLi (0.38 mL 1.6 M, 0.61 mmol) was added to a solution of **3a** (59.7 mg, 0.40 mmol) and Me_3SiCl (0.08 mL, 0.64 mmol) in hexane/Et_2O (1:1) (10 mL) at −70 °C. The mixture was allowed to warm slowly to room temperature, stirred overnight, filtered, and the solid residue was washed with Et_2O. Removal of the solvent provided 107 mg of air-sensitive yellow oil, analysed by the NMR and HRMS data as a mixture of **6a**, **7a**, and **8a**, molar ratio 17:68:15% (by ^{1}H NMR integration), corresponding to yields of 16 mg (15%), 80 mg (57%) and 11 mg (13%).

6a − ^{1}H NMR (CD_3OD): δ = 0.03 (d, $^4J_{PH}$ = 0.8 Hz, 2-$SiMe_3$), 0.82 (d, $^3J_{PH}$ = 11.6 Hz, $PCMe_3$), 2.94 (s, 3H, NCH_3), 3.20 (d, $^2J_{PH}$ = 3 Hz, 2-CH_{trans}), 6.37 (br shoulders at d of **7a**, ^3J = 8.0 Hz, H-7), 6.60 (partly superimposed tdd, H-5), 7.14 (superimposed m, H-6), 7.22 (m, ^3J = 7.2, $^3J_{PH}$ = 4.8, ^4J = 1.4, ^5J = 0.6 Hz, H-4). ^{13}C{^{1}H} NMR (CD_3OD): δ = −2.13 (d, ^3J = 6.6 Hz, 2-$SiMe_3$), 26.26 (d, ^2J = 15.4 Hz, P*C*Me_3), 30.84 (d, ^1J = 25.0 Hz, P*C*Me_3), 37.89 (d, ^3J = 2.2 Hz, N−CH_3), 53.86 (d, ^1J = 39.9 Hz, PCN), 108.16 (s, C-7), 116.60 (d, ^3J = 7.3 Hz, C-5), 131.74 (s, C-6), 132.52 (d, ^2J = 21.9 Hz C-4), 156.63 (dbr s, C_q-7a); C_q3a-signal superimposed. ^{31}P{^{1}H} NMR (CD_3OD): δ = −7.0. HRMS (ESI in MeOH+FA): $C_{15}H_{26}NPSi$ (279.43), calcd. for $[M+H]^+$ 280.1645; found: 280.1646.

7a − ^{1}H NMR (CD_3OD): δ = −0.10 (d, ^4J = 0.8 Hz, 9H, 2-$SiMe_3$), 0.50 (br s, 9H, 2′-$SiMe_3$), 0.92 (d, $^3J_{PH}$ = 11.2 Hz, 9H, $PCMe_3$), 3.05 (s, 3H, NCH_3), 6.37 (br d, ^3J = 8.0 Hz, 1H, H-7), 6.61 (tdd, ^3J = 7.2, $^4J_{PH}$ = 2.0, ^4J = 0.8 Hz, 1H, H-5), 7.17 (m, 1H, H-6), 7.27 (ddd, $^3J \approx$ 7.4, $^3J_{PH}$ = 4.8, ^4J = 1.4, ^5J = 0.6 Hz, 1H, H-4). ^{13}C{^{1}H} NMR (CD_3OD): δ = 2.44 (d, ^3J = 7.3 Hz, 2-$SiMe_3$), 5.35 (br s, 2′-$SiMe_3$), 28.68 (d, ^2J = 14.7 Hz, P*C*Me_3), 34.95 (d, ^1J = 35.9 Hz, P*C*Me_3), 37.01 (d, ^3J = 1.5 Hz, NCH_3), 58.01 (d, ^1J = 56.5 Hz, PCN), 107.55 (s, C-7), 116.78 (d, ^3J = 8.1 Hz, C-5), 127.16 (d, ^1J = 4.4 Hz, C_q-3a), 130.94 (s, C-6), 132.11 (d, ^2J = 21.3 Hz C-4), 156.48 (d, ^2J = 2.2 Hz, C_q-7a). ^{31}P{^{1}H} NMR (CD_3OD): δ = 9.9. HRMS (ESI in MeOH+FA): $C_{18}H_{34}NPSi_2$ (351.61), calcd. for $[M+H]^+$ 352.2040; found: 352.2042.

8a – ^{1}H NMR (CD_3OD): δ = 0.94 (br s, $PCMe_3$), 3.12 (s, NCH_3), 3.71 (dd, ^3J = 8.8, $^2J_{PH}$ = 2.4 Hz, 2-$CH_{trans\ zu\ EP}$), 4.34 (ddt, $^1J_{PH}$ = 184.1, ^3J = 8.8, J = 1.4 Hz, PH), 6.48 (br d, ^3J = 8.0 Hz, H-7), 6.53 (tdd, ^3J = 7.2, ^4J = 2.0, $^4J_{PH}$ = 0.9 Hz, H-5), 6.95-7.50 (superimposed m, H-6, H-4). $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 27.38 (d, ^3J = 10.3 Hz, $PCMe_3$), 39.31 (d, ^2J = 19.9 Hz, 2-CMe_3), 41.77 (d, ^3J = 2.2 Hz, NCH_3), 73.35 (d, ^1J = 11.7 Hz, PCHN), 109.79 (s, C-7), 118.69 (d, ^3J = 7.3 Hz, C-5), 123.97 (d, ^1J = 11.0 Hz, C_q-3a), 131.13 (d, ^2J = 25.7 Hz, C-4), 131.25 (s, C-6; uncertain), 156.98 (s, C_q-7a). $^{31}P\{^1H\}$ NMR (CD_3OD): δ = –83.5 (d, $^1J_{PH}$ = 185.8 Hz). HRMS (ESI in MeOH + FA): $C_{12}H_{18}NP$ (207.25), calcd. for $[M+H]^+$ 208.1250; found: 208.1250.

*1,5-Dimethyl-2-trimethylsilyl-1H-1,3-benzazaphosphole (**5b**)*

A solution of *t*BuLi in pentane (0.56 mL, 0.90 mmol) was added slowly at –70 °C to a solution of **3b** (98 mg, 0.60 mmol) and *t*BuOK (80.8 mg, 0.72 mmol) in THF (10 mL). The mixture was allowed to warm slowly (within 5 h) to –30 °C, then cooled again to –70 °C. After Me_3SiCl (0.12 mL, 0.96 mmol) was added, the mixture was warmed to room temperature and stirred overnight. THF was removed in vacuum and diethyl ether added. Insoluble salts were separated by filtration (twice washed with ether), and the solvent was removed yielding 106 mg (75%) **5b** as pale yellow oil. ^{1}H NMR (CD_2Cl_2): δ 0.50 (d, $^4J_{PH}$ = 1.1 Hz, 9H, $SiMe_3$), 2.49 (s, 3H, 5-CH_3), 4.01 (d, $^4J_{PH}$ = 1.1 Hz, 3H, NCH_3), 7.26 (dt, ^3J = 8.7, $^4J \approx {}^5J_{PH} < 2$ Hz, 1H, H-6), 7.50 (br d, ^3J = 8.7 Hz, 1H, H-7), 7.86 (m, 1H, H-4). $^{13}C\{^1H\}$ and 135-DEPT NMR (CD_2Cl_2): δ 0.67 (d, ^3J = 7.9 Hz, $SiMe_3$), 21.35 (s, 5-CH_3), 37.67 (d, ^3J = 2.6 Hz, N–CH_3), 112.71 (s, C-7), 127.32 (d, ^4J = 2.6 Hz, C-6), 128.54 (d, ^2J = 19.9 Hz, C-4), 129.54 (d, ^3J = 11.9 Hz C_q-5), 144.12 (d, ^1J = 43.8 Hz, C_q-3a), 146.51 (d, ^2J = 4.0 Hz, C_q-7a), 180.22 (d, ^1J = 74.3 Hz, C_q-2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 114.6. HRMS (ESI in MeOH+FA): $C_{12}H_{19}NPSi$ (235.34), calcd. for $[M+H]^+$ 236.1019; found 236.1021.

*3-tert-Butyl-1,5-dimethyl-2,2-bis(trimethylsilyl)-2,3-dihydro-1H-1,3-benzazaphosphole (**7b**)*

A solution of *t*BuLi in pentane (0.49 mL 1.6 M, 0.78 mmol) was added to a solution of **3b** (85 mg, 0.52 mmol) and Me_3SiCl (0.11 mL, 0.88 or 0.83 mmol) in THF (10 mL) at –70 °C. The mixture was allowed to warm slowly to room temperature and stirred overnight. The precipitate was separated and washed with diethyl ether. Removal of the solvent in vacuum provided 146 mg yellow oil, consisting of compounds **7b** and **5b**, molar ratio 67:33% (by ^{1}H NMR integration of $SiMe_3$ signals), corresponding to 111 mg (58%) and 35 mg (29%) yield. Overlayering a concentrated ethereal solution of the mixture with hexane provided colourless crystals of **7b**. Selected bond lengths and angles are shown in Fig. 1, for crystal data see Table 1. **7b** – ^{1}H NMR (CD_2Cl_2): δ = –0.10 (d, ^4J = 1.1 Hz, 9H, 2-$SiMe_3$), 0.48 (br s, 9H, 2′-$SiMe_3$), 0.92 (d, $^3J_{PH}$ = 11.3 Hz, 9H, $PCMe_3$), 2.26 (s, 3H, 5-CH_3), 3.01 (s, 3H, NCH_3), 6.25 (br d, ^3J = 8.3 Hz, 1H, H-7), 7.0 (ddt, $^3J \approx 8$, ^4J = 1.8, $^5J \approx {}^5J_{PH} \approx 1$ Hz, 1H, H-6), 7.13 (ddd, $^3J_{PH}$ = 4.8, ^4J = 1.8, ^5J = 0.9 Hz, 1H, H-4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 2.17 (d, ^3J = 6.6 Hz, 2-$SiMe_3$), 4.98 (br s, 2′-$SiMe_3$), 20.68 (s, 5-CH_3), 28.21 (d, ^2J = 14.6 Hz, $PCMe_3$), 34.13 (d, ^1J = 37.1 Hz, $PCMe_3$), 36.61 (s, N–CH_3), 57.15 (d, ^1J = 57.1 Hz, PCN), 106.21 (s, C-7), 124.62 (d, ^3J = 8.0 Hz, C_q-5), 126.71 (d, ^1J = 5.3 Hz, C_q-3a), 130.30 (s, C-6), 131.85 (d, ^2J = 21.2 Hz, C-4), 153.58 (d, ^2J = 2.6 Hz, C_q-7a). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 10.9. HRMS (ESI in MeOH+FA): $C_{19}H_{36}NPSi_2$ (365.64), calcd. for $[M+H]^+$ 366.2197; found: 366.2199. The NMR data of the side product **5b** are in good accordance with those given above.

*2-tert-Butyl-1,5-dimethyl-3-trimethylsilyl-2,3-dihydro-1H-1,3-benzazaphosphole (**9b**)*

A solution of *t*BuLi in pentane (0.52 mL 1.6 M, 0.83 mmol) was added to a solution of **3b** (90 mg, 0.55 mmol) and Me_3SiCl (0.11 mL, 0.87 mmol) in toluene (10 mL) at –70 °C. The mixture was allowed to warm slowly to room temperature and stirred overnight. The precipitate was separated and washed with diethyl ether. Removal of the solvent in vacuum provided 123 mg **9b** as an air-sensitive pale yellow oil that was slightly contaminated by the isomeric **6b** (yields by NMR ratio ca. 70:5%). ^{1}H NMR (C_6D_6): δ = –0.01 (d, $^3J_{PH}$ = 4.5 Hz, 9H, $SiMe_3$), 1.02 (s, 9H, 2-CMe_3), 2.16 (s, 3H, 5-CH_3), 2.77 (s, 3H, NCH_3), 3.38 (d, $^2J_{PH}$ = 2.6, Hz, 1H, PCHN), 6.25 (br d, ^3J = 8.1 Hz, 1H, H-7), 6.91 (ddd, ^3J = 8.1 ^4J = 1.8, $^5J_{PH}$ = 0.9 Hz, 1H, H-7), 7.07 (ddd, $^3J_{PH}$ = 5.8, ^4J = 1.8, ^5J = 0.9 Hz, 1H, H-4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = –2.69 (d, ^2J = 11.9 Hz, $SiMe_3$), 21.11 (s, 5-CH_3), 27.08 (d, ^3J = 10.6 Hz, 2-CMe_3), 39.31 (d, ^2J = 19.9 Hz, 2-CMe_3), 42.08 (d, ^3J = 2.7 Hz, NCH_3), 75.2 (d, ^1J = 19.9 Hz, PCHN), 108.25 (s, C-7), 123.32 (d, ^3J = 11.9 Hz, C_q-5), 126.90 (d, ^1J = 6.6 Hz, C_q-3a), 129.43 (s, C-6), 129.64 (d, ^2J = 21.2 Hz, C-4), 154.46 (s, C_q-7a). $^{31}P\{^1H\}$-NMR (C_6D_6): δ = –91.2; –5.6 (**6b**, ≤5 mol%). HRMS (ESI in MeOH+FA): $C_{16}H_{28}NPSi$ (293.46), calcd. for $[M+H]^+$ 294.1801; found: 294.1804.

*3-tert-Butyl-5-methyl-1,2-bis(trimethylsilyl)-2,3-dihydro-1H-1,3-benzazaphosphole (**10c**)*

A pentane solution of *t*BuLi (0.43 mL 1.6 M, 0.68 mmol) was added to a solution of **3c** (67 mg, 0.45 mmol) and excess Me_3SiCl (0.09 mL, 0.72 mmol) in toluene (10 mL) at –70 °C. The mixture was allowed to warm slowly to room temperature and stirring continued overnight. Insoluble solids were filtered off and washed with Et_2O. Removal of the solvent gave 112 mg (71%) pale yellow oil, which crystallized from *n*-hexane. Selected bond lengths and angles of **10c** are shown in Fig. 2, for crystal data see Table 1. ^{1}H NMR ($CDCl_3$): δ = –0.01 (d, ^4J = 1.1 Hz, 9H, 2-$SiMe_3$), 0.32 (s, 9H, 1-$SiMe_3$), 0.91 (d, $^3J_{PH}$ = 12.1 Hz, 9H, CMe_3), 2.26 (s, 3H, 5-CH_3), 3.54 (d, $^2J_{PH}$ = 4.9 Hz, 1H, PCH), 6.64 (br d, ^3J = 7.9 Hz, 1H, H-7), 6.94 (dd, ^3J = 7.9, ^4J = 2 Hz, 1H, H-6), 6.94 (dd, $^3J_{PH}$ = 5.5, ^4J = 2 Hz, 1H, H-4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = –2.37 (d, ^3J = 6.6 Hz, 2-$SiMe_3$), 0.71 (s, 1-$SiMe_3$), 20.56 (s, 5-CH_3), 26.32 (d, ^2J = 14.6 Hz, CMe_3), 31.05

Table 1
Crystal data and structure refinement for **7b** and **10c**.

Compound	**7b**	**10c**
Empirical formula	$C_{19}H_{36}NPSi_2$	$C_{18}H_{34}NPSi_2$
Formula weight	365.64	351.61
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 13.0201(4) Å	a = 11.4350(2) Å
	b = 9.6441(4) Å	b = 8.9663(2) Å
	c = 18.1251(6) Å	c = 21.1862(5) Å
	β = 101.452(3)°	β = 100.654(3)°
Volume	2230.61(14) Å^3	2134.79(8) Å^3
Z	4	4
Density (calculated)	1.089 Mg/m^3	1.094 Mg/m^3
Absorption coefficient	0.23 mm^{-1}	0.24 mm^{-1}
F(000)	800	768
Crystal size	0.40 × 0.30 × 0.08 mm^3	0.40 × 0.35 × 0.35 mm^3
ϑ range for data collection	2.29–28.28°	2.41–30.88°
Index ranges	$-17 \le h \le 17$,	$-16 \le h \le 15$,
	$-12 \le k \le 12$,	$-12 \le k \le 12$,
	$-24 \le l \le 24$	$-30 \le l \le 30$
Reflections collected	47141	93591
Independent reflections	5466 [R(int) = 0.044]	6465 [R(int) = 0.028]
Completeness	98.9% to ϑ = 28.28°	99.7% to ϑ = 30.00°
Data/parameters	5466/219	6465/209
Goodness-of-fit on F^2	1.045	1.034
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0367,	$R1$ = 0.0292,
	$wR2$ = 0.0895	$wR2$ = 0.0789
R indices (all data)	$R1$ = 0.0503,	$R1$ = 0.0335,
	$wR2$ = 0.0975	$wR2$ = 0.0822
Largest diff. peak and hole	0.43 and –0.23 e·Å^{-3}	0.46 and –0.34 e·Å^{-3}

(d, ^1J = 25.2 Hz, CMe_3), 48.99 (d, ^1J = 39.8 Hz, PCN), 111.57 (s, ^3J = 2.2 Hz, C-7), 126.16 (d, ^3J = 8.0 Hz, C_q-5), 127.07 (d, ^1J = 8.0 Hz, C_q-3a), 130.22 (s, C-6), 132.44 (d, ^2J = 22.6 Hz, C-4), 153.36 (d, ^2J = 2.7 Hz, C_q-7a). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −6.3 ppm. HRMS (DEI^+): $C_{18}H_{34}NPSi_2$ (351.61), calcd. for $[M]^+$ 351.1967; found: 351.1972.

*1,5-Dimethyl-1H-1,3-benzazaphosphole-2-carboxylic acid (**11b**)*

A solution of *t*BuLi in pentane (0.6 mL, 0.96 mmol) was added slowly at −70 °C to a solution of **6** (104 mg, 0.64 mmol) and *t*BuOK (85.3 mg, 0.76 mmol) in THF (20 mL). The mixture was allowed to warm slowly (within 5 h) to −30 °C, then cooled again to −70 °C. A slow stream of gaseous carbon dioxide was passed through for 40 min which turned the orange-red colour, formed during the lithiation, to yellow. The mixture was allowed to warm slowly to room temperature and stirring continued overnight to complete the conversion. Then excess Me_3SiCl (0.13 mL, 1.02 mmol) was added at −70 °C to trap the lithium. After 2–3 h at room temperature the precipitate was filtered off, twice washed with ether and the solvent removed in vacuum. The residual yellow solid was treated with methanol (10 mL) yielding 96 mg (72%) of **7**, mp. 210–215 °C (dec.). The compound is only slightly soluble in methanol or diethyl ether but readily soluble in THF. Single crystals were obtained by slow concentration of the d_8-THF solution. ^1H NMR (d_8-THF): δ 2.42 (s, 3H, 5-CH_3), 4.22 (d, $^4J_{PH}$ = 1.5 Hz, 3H, NCH_3), 7.28 (br d, ^3J = 8.7 Hz, 1H, H-6), 7.59 (br d, ^3J = 8.7 Hz, 1H, H-7), 7.81 (m, 1H, H-4), 11.66 (s vbr, 1H, OH). $^{13}C\{^1H\}$ NMR (d_8-THF): δ 21.30 (s, 5-CH_3), 34.77 (d, ^3J = 4.0 Hz, N–CH_3), 114.30 (s, C-7), 129.62 (d, ^4J = 3.2 Hz, C-6), 129.63 (d, ^2J = 20.4 Hz, C-4), 130.67 (d, ^3J = 13.3 Hz, C_q-5), 143.49 (d, ^1J = 37.1 Hz, C_q-3a), 145.46 (d, ^2J = 8.0 Hz, C_q-7a), 162.38 (d, ^1J = 51.7 Hz, C-2), 166.48 (d, ^2J = 21.2 Hz, COOH). $^{31}P\{^1H\}$ NMR (d_8-THF): δ 115.0. HRMS (DEI^+): $C_{10}H_{11}NO_2P$ (207.17), calcd. for $[M]^+$ 207.0449; found: 207.0463.

*Pentacarbonyl-η1P-(1-methyl-1H-1,3-benzazaphosphole-2-carboxylic acid)tungsten(0) (**12a**)*

A solution of $W(THF)(CO)_5$ was prepared by irradiation of $W(CO)_6$ (81 mg, 0.23 mmol), dissolved in THF (85 mL), by using a medium pressure mercury UV-immersion lamp (2.5 h, 20 °C). Then **11a** (40.6 mg, 0.21 mmol) was added. After stirring for 24 h the solvent was removed and the residue extracted with diethyl ether. Removal of the solvent gave 74 mg (68%) pale brown solid. ^1H NMR (d_8-THF): δ = 4.32 (d, $^4J_{PH}$ = 3.4 Hz, 3H, NCH_3), 7.34 (tdd, ^3J = 8.1, 6.9, ^4J = 0.9, $^5J_{PH}$ = 2.1 Hz, 1H, H-5), 7.61 (ddt, ^3J = 8.7, 6.9, ^4J = 1.5, $^5J_{PH}$ = 2 Hz, 1H, H-6), 7.89 (br d, ^3J = 8.7 Hz, 1H, H-7), 8.02 (tt, $^3J \approx {}^3J_{PH} \approx$ 8.1, $^4J \approx {}^5J \approx$ 0.9 Hz, 1H, H-4). $^{13}C\{^1H\}$ NMR (d_8-THF): δ = 35.38 (s, N–CH_3), 115.63 (d, ^3J = 4.0 Hz, C-7), 122.53 (d, ^3J = 15.9 Hz, C-5), 128.36 (d, ^4J = 11.9 Hz, C-6), 129.41 (d, ^2J = 5.3 Hz, C-4), 137.89 (d, ^1J = 25.3 Hz, C_q-3a), 146.37 (d, ^2J = 2.7 Hz, C_q-7a), 154.21 (d, ^1J = 27.9 Hz, COOH), 163.45 (d, ^2J = 17.2 Hz, COOH), 195.29 (d, sat, ^2J = 10.7, $^1J_{CW}$ = 126.0 Hz, 4 *cis*-CO), 200.15 (d, ^2J = 33.2 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR (d_8-THF): δ = 84.64 (satellites, $^1J_{PW}$ = 260.8 Hz). IR (KBr): ν_{CO} = 2078 (wm), 1928 (vs) cm^{-1}. MS (EI, 70 eV, 90 °C): *m/z* (%) = 517 (0.3) $[M^+]$, 461 (0.5), 377 (1.2), 349 (0.6), 306 (0.8), 193 (4.8). HRMS (ESI in MeOH): $C_{14}H_9NO_7PW$ (518.04), calcd. for $[M(^{184}W)+H]^+$ 517.9621; found: 517.9623 and correct isotopic pattern.

*Crystal structure analysis of **7b** and **10c***

Crystals of **7b** and **10c** were mounted on glass fibers in inert oil, and data (Table 1) were recorded at 100 K on an Oxford Diffraction Xcalibur E diffractometer using MoK_α-radiation. Absorption corrections were based on multi-scans. The structures were refined by full-matrix least-squares on F^2 [22]. Hydrogen atoms were included using a riding model or rigid methyl groups.

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Appendix A. Supplementary material

CCDC 971420, 971421 contains 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.

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