

# Metalated 1,3-azaphospholes: synthesis of lithium-1,3-benzazaphospholides and reactivity towards organoelement and organometal halides

Anushka Surana <sup>a</sup>, Shreeyukta Singh <sup>a</sup>, Raj Kumar Bansal <sup>b</sup>, Normen Peulecke <sup>a</sup>, Anke Spannenberg <sup>c</sup>, Joachim Heinicke <sup>a,\*</sup>

<sup>a</sup> Institut für Chemie und Biochemie, Ernst-Moritz-Arndt-Universität Greifswald, Soldmannstrasse 16, D-17487 Greifswald, Germany

<sup>b</sup> Department of Chemistry, University of Rajasthan, Jaipur 302 004, India

<sup>c</sup> Institut für Organische Katalyseforschung an der Universität Rostock e.V., Buchbinderstrasse 5-6, D-18055 Rostock, Germany

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## Abstract

Metalation of benzazaphospholes **1a–e** with *t*-BuLi provided the ambident anions **1a–e<sub>Li</sub>** in high selectivity. A crystal structure analysis of **1b<sub>Li</sub>**·3THF reveals monomers and coordination of lithium at nitrogen. The tungsten pentacarbonyl complexes also react preferably at nitrogen as shown by the reaction of **2a** and **2d** with *t*-BuLi. Addition at the P=C bond is a minor process in the case of **2a**. Compounds **1a, c<sub>Li</sub>** as well as **2d<sub>Li</sub>** react with alkyl halides at phosphorus to give the 3-alkyl-1,3-benzazaphospholes **3a** and **3d** or the respective W(CO)<sub>5</sub> complex **4d**. Even acetyl and pivaloyl chloride attack **1e<sub>Li</sub>** at phosphorus affording the *P*-acyl derivatives **5e** and **6e**. Silylation can occur at nitrogen or phosphorus to give **7** and/or **8** depending on steric and electronic effects exerted by the substituent in position 2. The different effect of 2-*t*-butyl groups on the steric hindrance at N and P is illustrated by the molecular geometry of **1d** determined by crystal structure analysis. Soft organometallic halides such as Me<sub>3</sub>SnCl, CpFe(CO)<sub>2</sub>I and CpW(CO)<sub>3</sub>Cl react with **1<sub>Li</sub>** preferably at phosphorus affording the stannyl or monomer organo-transition metal derivatives **9–11**. The products are characterized by multinuclear NMR data of all new compounds. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium benzazaphospholides; Metallophosphines; Low-coordinate phosphorus; Phosphorus heterocycles; Ambident anions

## 1. Introduction

The immense importance of cyclopentadienide anions for organometallic syntheses, transition metal complexes and their use in catalysis has inspired related research on metallation and complex chemistry of heterocyclic homologues containing one or more heteroatoms. Similarities of low coordinate phosphorus and carbon make phospholides [1–3] a preferred target, but pyrrolides [4–6] have also elicited considerable interest. Although the latter display a lower tendency for  $\pi$ -complexes, all three are known to occur in  $\sigma$ - and  $\eta^5$ - as well as other coordination modes. Five-membered heterocyclic anions containing both heteroele-

ments, phosphorus and nitrogen, have been studied to a much lesser extent [7–10], and to our knowledge only one transition metal complex,  $\eta^1(\text{N})\text{-Cp}^*\text{Fe}(\text{CO})_2\text{-1,2,4-diazaphospholide}$  [11], has been reported. Di- or triazaphospholide anions with one or two pyridine-like basic nitrogen atoms are substituted by electrophiles preferably at nitrogen, whereas monoazaphospholides behave as ambident nucleophiles [7–10]. It has been shown that methylation of *N*-lithiated 1,3-azaphospholides [12], 1,3-benzazaphospholides [13] as well as the homologous 1,3-benzazarsolides [14] occurs at phosphorus and arsenic, respectively, whilst silylation of 1,3-azaphospholides and 1,3-benzazarsolides and acylation of 1,3-benzazaphospholides and -arsolides were reported to take place at the ‘hard’ nitrogen atom. In view of the importance of the above mentioned anionic complexes we developed a convenient three-step synthesis of *1H*-1,3-benzazaphospholes [15] and studied the

\* Corresponding author. Tel.: +49-3834-864337; fax: +49-3834-864319.

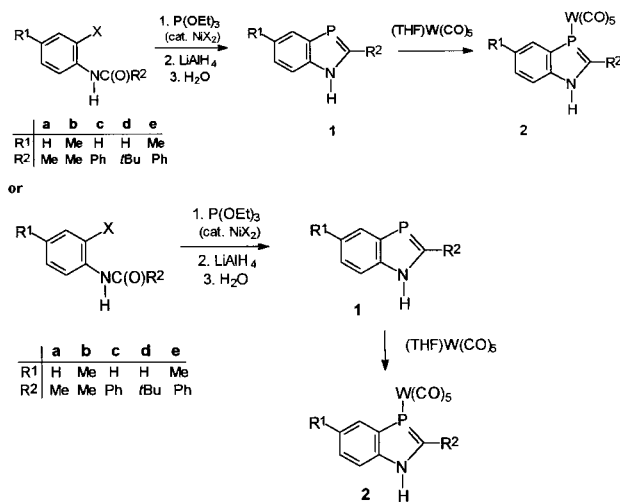
E-mail address: heinicke@mail.uni-greifswald.de (J. Heinicke).

reactivity of 1,3-benzazaphospholide anions towards various electrophiles including (organo)transition metal halides. We report here on a new metalation procedure, the metalation site and the dependence of *N*- or *P*-substitution on the nature of the electrophile and hitherto neglected substituent effects. To estimate the influence of the electron lone pair at phosphorus on the reactivity the study was extended to *1H*-1,3-benzazaphosphole)pentacarbonyl tungsten complexes without this feature.

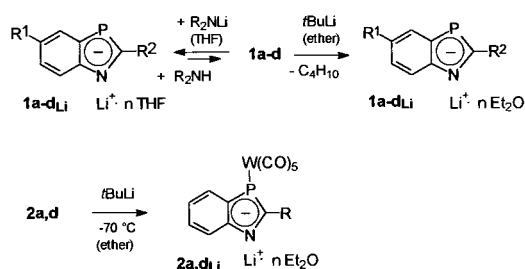
## 2. Results and discussion

### 2.1. Syntheses and structure of lithium 1,3-benzazaphospholides

The *1H*-1,3-benzazaphospholes were synthesized by nickel catalyzed phosphorylation of *o*-bromoanilides or *o*-chloroacetanilides and subsequent reduction of the resulting *o*-phosphonoanilides with excess  $\text{LiAlH}_4$  yielding **1a–e** [15] (Scheme 1). The carbonyl complexes **2** [15] were obtained from **1** by reaction with  $(\text{THF})\text{W}(\text{CO})_5$  in analogy to the synthesis of (2-phenyl-*1H*-1,3-benzazaphosphole)pentacarbonylchromium [13].



Scheme 1.



Scheme 2.

Lithiation of **1** can be accomplished by reaction with  $\text{LiNET}_2$  in ether or THF as proved earlier by trapping with methyl iodide [13] (Scheme 2). The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra allowed us to distinguish between **1** and **1<sub>Li</sub>** and thus it was shown that the acid–base equilibrium lies far to the right. However, in reactions with electrophiles except alkylations the dialkylamines can compete with **1<sub>Li</sub>** and must be removed. In order to replace amines completely from the coordination sphere of lithium, excess THF was added before removal of the solvent under vacuum. Although the resulting lithium 1,3-benzazaphospholides were apparently free of  $\text{Et}_2\text{NH}$  ( $^1\text{H}$ -NMR), the reactions with organometal chlorides or  $\text{Me}_3\text{SiCl}$  failed and led to high portions of seemingly unreacted **1**, and the *N*-acetylation of **1c** after lithiation with  $\text{Et}_2\text{NLi}$  [13] could not be reproduced. To avoid even catalytic amounts of amines, we studied the metalation with lithium organyls in diethyl ether at low temperature ( $-70\text{ }^\circ\text{C}$ ). *n*-Butyllithium reacts unselectively and furnishes ill-defined mixtures, but the more bulky and basic *t*-butyllithium was found to form selectively the 1,3-benzazaphospholides **1<sub>Li</sub>**. No or only trace amounts of side products were observed. The lithiation with *t*-butyllithium could also be transferred to the carbonyl complexes **2**. Lithiation of the NH-function is preferred to addition to the  $\text{P}=\text{C}$  bond in **2a**, and in the more bulky **2d** the addition is completely suppressed under mild conditions. Attack at the CO ligands was observed in neither case. The different behavior of *n*-BuLi and *t*-BuLi towards **1** and of *t*-BuLi towards **2a** and **2d** emphasizes the importance of steric hindrance for the selective metalation at nitrogen. In this context it should also be mentioned that the homologous *1H*-1,3-benzazarsole reacts with *t*-BuLi in a clear 1:2 fashion to give a heterocyclic  $-\text{AsBu}^-\text{CHLi}-\text{NLi}$ -species, even with an equimolar amount, although lithium-1,3-benzazarsolides generated with LDA are stable [14].

The lithium 1,3-benzazaphospholide etherates **1a–d<sub>Li</sub>**( $\text{Et}_2\text{O}$ )<sub>*n*</sub> are isolated from concentrated solution as pale yellow ( $\text{R}^2 = \text{Alk}$ ) to yellowish red ( $\text{R}^2 = \text{Ph}$ ), the carbonyl complexes **2a<sub>Li</sub>**( $\text{Et}_2\text{O}$ )<sub>*n*</sub> [16] and **2d<sub>eLi</sub>**( $\text{Et}_2\text{O}$ )<sub>*n*</sub> as orange powders. The compounds were characterized by multinuclear NMR studies. Proton NMR spectra (THF-*d*<sub>6</sub>) confirm *N*-metalation by lack of the NH singlet and allow to estimate the number of coordinated ether molecules which varies with the substituents and drying conditions between 0.1 and 2. The presence of excess crown ether (12-crown[4]) capturing  $\text{Li}^+$  has no significant influence on the NMR data ( $\Delta\delta = 0.03$  for H4 and H7, 0.11 for H5 and H6) indicating a rather ionic structure of **1<sub>Li</sub>** in solution. As compared to **1** the proton chemical shifts in **1<sub>Li</sub>** are upfield shifted, slightly for H4 and H7 ( $\Delta\delta \approx 0-0.2$ ) and markedly for H5 and H6 ( $\Delta\delta \approx 0.5$ ). The same shielding effects by metalation are observed in **2d<sub>Li</sub>**. The phosphorus chemical shifts of

Table 1  
Comparison of characteristic  $^{13}\text{C}$ -NMR data of  $\mathbf{1d}_{\text{Li}}$  and  $\mathbf{2d}_{\text{Li}}$

	C-2	C-3a	C-7a	C-7	C-4	C-5	C-6
$\Delta\delta$ ( $\mathbf{1d}_{\text{Li}}-\mathbf{1d}$ )	9.9	6.9	10	4.7	-1	-2	-4.3
$\Delta\delta$ ( $\mathbf{2d}_{\text{Li}}-\mathbf{2d}$ )	21.2	13.8	14.1	6.7	-0.4	-2.4	-3.3

$\mathbf{1}_{\text{Li}}$  are observed in the region of  $\delta^{31}\text{P} = 56-71$ , that of  $\mathbf{2d}_{\text{Li}}$  at  $\delta = -43.5$ . The very similar values for the  $P$ -resonance of lithium 3,4-dimethylphospholide and its  $\text{W}(\text{CO})_5$  complex ( $\delta^{31}\text{P} = 55$  and  $-54.8$ ) [17] indicate a related nature of the phospho- $\pi$ -systems in benzazaphospholides and phospholides, despite anellation and the nitrogen atom in the former. The only slight upfield lithiation shifts in  $\mathbf{1}_{\text{Li}}$  as compared to those in  $\mathbf{1}$  ( $\Delta\delta$  up to 10) in comparison with the much larger difference between  $\mathbf{2d}_{\text{Li}}$  and  $\mathbf{2d}$  ( $\Delta\delta = 68$ ) may be attributed to repulsion of the increased  $\pi$ -electron density by the electron lone pair at phosphorus. Like the phosphorus chemical shifts, the  $P$ -C-coupling constants of  $\mathbf{1d}_{\text{Li}}$  and  $\mathbf{2d}_{\text{Li}}$  are strongly influenced by the different hybridization of phosphorus in the two types of benzazaphospholides. The most characteristic NMR data with respect to structure elucidation of  $\mathbf{1d}_{\text{Li}}$  and  $\mathbf{2d}_{\text{Li}}$  are the carbon resonances. As illustrated by the metalation shifts  $\Delta\delta$  of  $\mathbf{1d}_{\text{Li}}$  and  $\mathbf{2d}_{\text{Li}}$  (Table 1) 1,3-benzazaphospholides exhibit marked deshielding of the nuclei  $^{13}\text{C}$ -2 and  $^{13}\text{C}$ -7a in  $\alpha$ -position to nitrogen and slight deshielding of  $^{13}\text{C}$ -3a and  $^{13}\text{C}$ -7 in  $\beta$ -position to nitrogen. Their carbonyl complexes differ by equal effects on C-3a and C-7a and stronger deshielding for C-2. In both types, C-4 and more clearly C-5 and C-6 benefit from the  $\pi$ -polarization and appear at somewhat higher field (Table 1). These trends give evidence of delocalization of negative charge also into the anellated benzene ring and underline the influence of anellation on the properties and reactivity of the azaphospholide ring.

The coordination site of lithium cannot be deduced from the NMR data. Therefore, several attempts to grow single crystals of solvates with ether, THF, glyme, 12-crown[4], TMEDA or PMETA were made. For the X-ray crystal structure analysis suitable crystals containing two symmetry independent molecules of  $\mathbf{1b}_{\text{Li}}(\text{THF})_3$  could be obtained from a THF solution. The strong disorder of the coordinated solvent molecules does not allow a discussion of bond lengths and angles in detail. However, the X-ray crystal structure analysis of  $\mathbf{1b}_{\text{Li}}(\text{THF})_3$  confirmed the molecular composition, the monomeric nature, the metalation site and the preservation of the planar benzazaphosphole system without major changes of bond lengths and angles (Fig. 1).

The  $\sigma$ -coordination of the characterize triply THF-solvated lithium at nitrogen forms a clear contrast to the sandwich structures of the non-anellated lithi-

um(TMEDA) tetramethylphospholide [19] or the closer related  $\text{Li}(\text{Et}_2\text{O})_2^+$  and  $\text{Sm}(\text{THF})_2^+$  benzo[*b*]phospholides [20,21].  $\sigma$ -Coordination at the more electropositive phosphorus atom becomes dominant only when the aromaticity within the phospholide ring is weakened by double anellation as shown for the  $\text{Sm}(\text{THF})_2^+$  bis(dibenzophospholide) complex [21]. The higher electronegativity of nitrogen of course favors the  $N$ -coordination in  $\mathbf{1b}_{\text{Li}}(\text{THF})_3$ , but taking into account the strong  $\pi$ -donor activity of nitrogen within the five-membered aromatic ring it was not clear whether the lithium is bound in  $\sigma$ -N or  $\pi$ -mode. Thus, ab initio calculations of non-solvated monomer lithium 1,3-azaphospholides showed the minimum energy for the sandwich structure, ca. 11.6 kcal mol $^{-1}$  lower than for the  $N$ -lithiated isomer [22]. Similar results were obtained in calculations on monomer non-solvated lithium pyrrolides [23]. Consideration of non-solvated and solvated dimers lead here to lower energies for  $\sigma$ -/ $\pi$ -coordination which was later experimentally observed in sodium-tetramethylpyrrolide [24]. Anellation with two benzene rings, however, again caused preferred coordination at the heteroatom [23]. These findings suggest that the benzoanellation is the structure-determining element in  $\mathbf{1b}_{\text{Li}}(\text{THF})_3$  and that the energetic difference to  $\pi$ -coordination is low.

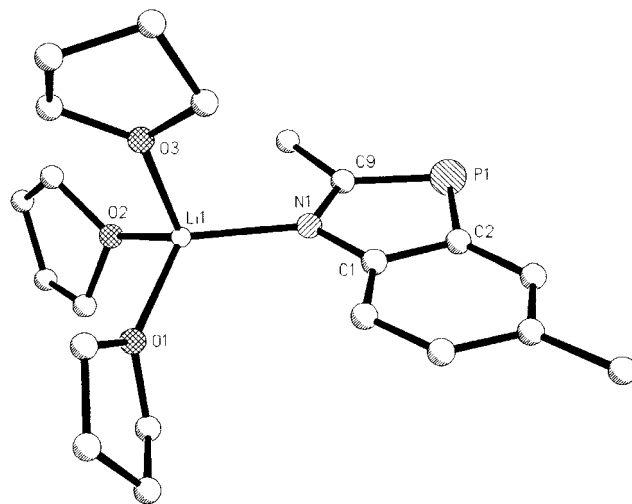
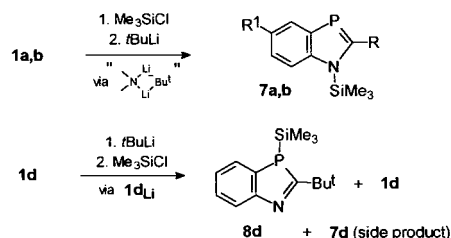


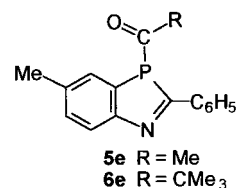
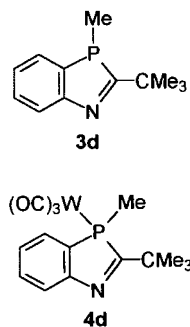
Fig. 1. Molecular structure of one of the two symmetry independent molecules of  $\mathbf{1b}_{\text{Li}}(\text{THF})_3$  (disorders and hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles ( $^\circ$ ): P1-C2, 1.778(5) [in the second molecule: 1.769(5)]; P1-C9, 1.741(5) [1.739(5)]; N1-C1, 1.387(5) [1.391(6)]; N1-C9, 1.353(5) [1.365(6)]; N1-C9-P1, 117.4(4) [117.2(4)].



Scheme 3.

## 2.2. Reactivity of 1,3-benzazaphospholides $1c_{\text{Li}}$ and 1,3-benzazaphospholide complexes $2c_{\text{Li}}$ towards electrophiles

Alkyl and acyl halides belong to the typical electrophiles used to characterize the reactivity of nucleophiles. Whilst di- or triazaphospholide anions are *N*-alkylated [7–10], 1,3-benzazaphospholides are alkylated at phosphorus as shown earlier by methylation of  $1c_{\text{Li}}$  with methyl iodide [13] and confirmed by the formation of **3d** from  $1d_{\text{Li}}$  and MeI. Since the *N*-alkylation of a pyrimidine-annelated 1,3-azaphosphole under superbasic conditions was recently claimed [25] we attempted the metalation of **1a** with NaH in DMF followed by alkylation of the yellow solution with *N*-pentylbromide. Even under these conditions the reaction occurred mainly at phosphorus. Besides the strong  $^{31}\text{P}$  signal for 3-pentyl-1,3-benzazaphosphole **3a** ( $\delta = 9.2$ ) impurities were detected at  $\delta = -11$ ,  $-52$  and  $-72$  which indicate accompanying addition reactions and a lower selectivity than in the metalation with *t*-BuLi. Therefore, no further efforts were made to afford metalation with NaH/DMF. Another possibility to favor *N*-metalation can be seen in the blockade of the phosphorus electron lone pair by complexation. But as indicated by formation of **4d** from  $2d_{\text{Li}}$  and MeI, the alkylation at phosphorus remains preferred even in  $\eta^1\text{-P}$  transition metal complexes of benzazaphospholides. This gives evidence that the electron lone pair at phosphorus is less important for the regioselectivity of alkylation reactions in benzazaphospholides than the  $\pi$ -charge distribution which remains high after complexation.



Attempts of acylations gave unexpected results. Whilst  $1c_{\text{Li}}$  obtained from **1c** and  $\text{LiNET}_2$  was reported to be acetylated at nitrogen [13] we observed acylation of  $1e_{\text{Li}}$  with acetyl and with pivaloyl chloride at phosphorus. The acetyl compound **5e** was not obtained in pure form due to easy decomposition to **1e** or hydrolysis by traces of moisture but was unambiguously characterized by typical NMR data in the crude product (molar content ca. 50%). The more stable *P*-pivaloyl derivative **6e** was isolated as pale yellow powder. It should be mentioned in this context that the homologous *N*-lithium 1,3-benzazarsolide displays a different selectivity and reacts with pivaloyl chloride to give the *N*-pivaloyl compound in low yield [14]. The latter, obtained in high yield and purity from *N*-trimethylsilyl-1,3-benzazarsolide and pivaloyl chloride, exhibits the  $^{13}\text{C}=\text{O}$  signal at  $\delta = 178.8$  and the  $^{13}\text{C}$  ring nuclei only slightly shifted relative to the starting material (maximum  $\Delta\delta$  is 3.5 and 2.4 for C-7 and C-5) [14]. The *P*-pivaloyl compound **6e**, however, displays a much stronger deshielded  $^{13}\text{C}=\text{O}$  signal with a large one-bond P–C coupling ( $\delta = 216.1$ ,  $^1J_{\text{PC}} = 64$  Hz) and for the ring carbon nuclei chemical shifts typically for 3*H*-1,3-benzazaphospholes. The *P*-acylation shows that the tendency for substitution at nitrogen is rather low even in the case of comparatively hard electrophiles. The stronger tendency for *N*-acylation in the related As compound may be due to the softer nature of As compared to P.

*N*-substitution of benzazaphospholides can be achieved with  $\text{Me}_3\text{SiCl}$ . In contrast to the clean *N*-silylation of 2-methyl-1,3-azaphospholide [12] or 1,3-benzazarsolide [14], it was found to be influenced by the reaction conditions and by the substituents in position 2. Addition of  $\text{Me}_3\text{SiCl}$  to  $1a_{\text{Li}}$  in ether at  $-70$  °C furnished a mixture of the *N*-silyl derivative **7a** and the hydrolysis product **1a**. Excess *t*-BuLi and  $\text{ClSiMe}_3$  (each 50%) increased the content of **7a** but provided small amounts of further substitution products with  $\delta(^{31}\text{P})$  in the range of 88–108 besides some **1a**. Clean *N*-silylation of 2-methyl-benzazaphospholes was achieved only by addition of *t*-BuLi to a solution of **1a** or **1b** in ether in the presence of  $\text{Me}_3\text{SiCl}$  (Scheme 3). An excess of *t*-BuLi and  $\text{Me}_3\text{SiCl}$  (equimolar amounts) improved the yield. The smooth course in the inverse procedure may be attributed to the slow substitution rate of  $\text{Me}_3\text{SiCl}$  by *t*-BuLi and silylation of lithium benzazaphospholides ‘in status nascendi’, e.g. more reactive mixed lithium clusters as intermediates containing  $\text{NLi}/t\text{-BuLi}$  units.

In the case of **1c<sub>Li</sub>** this procedure is less selective and afforded a mixture. Besides the main product **7c** smaller amounts of **8c** and two unidentified PH compounds were formed. The selectivity for *N*-silylation is completely lost in reactions of the more bulky substituted 2-*t*-butyl moieties. The inverse procedure gave mainly **1d**, a smaller amount of **8d** and only traces of **7d**. The 'normal' reaction of **1d<sub>Li</sub>** with chlorotrimethylsilane yielded preferably **1d**, the *P*-substitution product **8d** and minor amounts of **7d**. Additionally, side products with  $\delta(^{31}\text{P}) = 8.1$  and  $-18.5$  and the typical carbon resonances of 3*H*-1,3-benzazaphospholes were observed.

The tendency for attack at phosphorus is enhanced in reactions of **1<sub>Li</sub>** with the softer organotin and especially with organo-transition metal halides. **1a<sub>Li</sub>** and  $\text{Me}_3\text{SnCl}$  gave a mixture which exhibits broad  $^{31}\text{P}$  resonances at  $\delta = 41.1$  and  $-39.6$ , respectively, the latter being consistent with *P*-stannylation. The preference for bonding at the heavier heteroatom is further increased in the 2-*t*-butyl benzazaphospholide **1d<sub>Li</sub>** which gave **9d** selectively (Scheme 4). As is evident from the NMR data [ $\delta(^{31}\text{P}) = -58.8$ ,  $^1J(\text{P}^{119}\text{Sn}) = 593.4$  Hz] the nature of this rather covalent *P*-metal derivative without facility for back donation differs strongly from that of the *N*-lithio species. The resemblance with *P*-trimethylstannylphospholes ( $\delta(^{31}\text{P}) = -46$  to  $-65$ ,  $^1J(\text{P}^{119}\text{Sn}) = 532\text{--}577$  Hz) [26] should be emphasized.  $\text{CpFe}(\text{CO})_2\text{I}$  reacts with **1<sub>Li</sub>** at low temperature ( $-70$  °C) in diethyl ether selectively to yield the easily soluble and air sensitive monomer transition metal phosphides. Representatives with 2-methyl-, 2-phenyl- and 2-*t*-butyl-substituents **10a,c,d** were obtained (Scheme 4). The products could not be isolated free of LiI-etherate due to the basicity at nitrogen and the high sensitivity of **10a,c,d** towards hydrolysis as well as the solubility of solvated LiI even in relatively unpolar solvents, but they were unequivocally characterized by  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{31}\text{P}$ -NMR as well as mass spectrometric data. By reaction with  $\text{CpFe}(\text{CO})_2\text{Cl}$  a nearly analytically pure sample of **10c** was obtained from the reaction of **1c<sub>Li</sub>** whilst lithium 2-methyl- and 2-*t*-butyl-1,3-benzazaphospholides gave mixtures. Although the mass spectra of **10c**

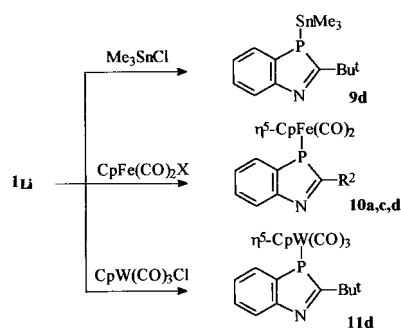
and **10d** reveal intensive  $(\text{M} - 2\text{CO})^+$  fragments (92 and 37%) the compounds were found thermally quite stable and did not convert to other complexes on heating in toluene (2 h, 80 °C). This resembles the thermal stability of cyclopentadienyldicarbonyl-tetraphenylphospholyiron [27] which do not form phosphoferrocenes although the latter are accessible by heating of 1-arylphospholes with  $[\text{CpFe}(\text{CO})_2]_2$  [1,2]. Irradiation of **10c** in THF with a medium pressure mercury lamp afforded mainly degradation to **1c** and only minor amounts of other phosphorus compounds ( $\delta(^{31}\text{P}) = -51.8$ ,  $-54.4$ ,  $-54.5$ ) which were not further analyzed.

The syntheses of the related tungsten complex **11d** from **1d<sub>Li</sub>** and  $\text{CpW}(\text{CO})_3\text{Cl}$  as well as of the mixed-valence ditungsten complex **12a**, accompanied by a small amount of **13a**, from **2a<sub>Li</sub>** and  $\text{CpW}(\text{CO})_3\text{Cl}$  are reported in detail in a separate paper [16].

Various attempts to form a benzazaphospholide complex by reaction of **1a<sub>Li</sub>** with  $\text{FeCl}_2$  in THF furnished an insoluble solid which gave only **1a** on repeated extraction with THF or methylene chloride. This corresponds with the negative results in attempts to prepare phosphindolyiron sandwich complexes from the isoelectronic lithium phosphindolides and  $\text{FeCl}_2$  [28]. Despite the existence of phosphindolide lithium and phosphindolide  $\text{Mn}(\text{CO})_3$  semisandwich complexes [19,28] this may be considered as a mark for a lower tendency of anellated than of non-anellated heterocyclopentadienides [1–6] to form  $\pi$ -complexes.

Attempts to synthesize sandwich or *N*-coordinated complexes of benzazaphospholides with electron-poor transition metal halides failed. **1a<sub>Li</sub>** and  $\text{ZrCl}_4$  (molar ratio 1:1) formed in THF a dark red product, but attempts to purify the solid obtained after evaporation of THF furnished a mixture of **1a** with small amounts (each ca. 20%) of two phosphorus compounds with chemical shifts in the region of *N*- and *P*-substituted 1,3-benzazaphospholes ( $\delta(^{31}\text{P}) = 93.4$ , 15.8). Substitution reactions of **1d<sub>Li</sub>** with  $\text{Cp}_2\text{ZrCl}_2$ ,  $\text{Cp}_2\text{ZrHCl}$ , or  $\text{Cp}_2\text{TiCl}_2$  failed; only **1d** was detected in the reaction mixtures. The pentacarbonyl tungsten complexes **2<sub>Li</sub>** seem to avoid substitution by hard electrophiles even more than the uncoordinated benzazaphospholides **1<sub>Li</sub>**. Thus, no trimethylsilyl derivatives could be obtained from **2a<sub>Li</sub>** with  $\text{Me}_3\text{SiCl}$ .

The *N*- and *P*-trimethylsilyl- as well as monomer organometallic benzazaphospholes are all highly air and extremely moisture sensitive. Nevertheless, they are thermally quite stable, and the silyl and stannyl derivatives can be distilled at low pressure without or with only slight decomposition. The high tendency to form NH-benzazaphospholes gives the silyl derivatives a high silylation potential, but attempts to use it for *N*-substitution have not yet been successful. Thus, treatment of **7a** in  $\text{Et}_2\text{O}$  with  $\text{CpFe}(\text{CO})_2\text{I}$  (3 h, 20 °C) did not lead



Scheme 4.

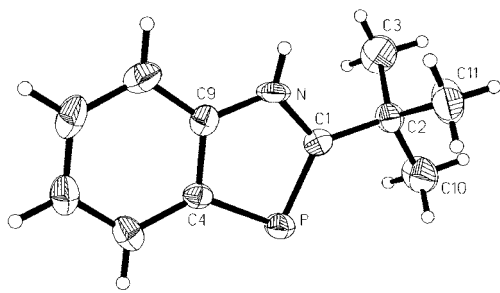


Fig. 2. Molecular structure of **1d** in the crystal (ORTEP plot). The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (°): P–C1, 1.712(4); P–C4, 1.793(3); N–C1, 1.374(4); N–C9, 1.380(4); C4–C9, 1.389(4); P–C1–C2, 128.8(3); N–C1–C2, 119.0(3); P–C1–N, 112.3(2); C1–P–C4, 90.1(2); P–C4–C9, 110.7(2); C1–N–C9, 115.1(3); N–C9–C4, 111.9(3). Deviations of C1, C4, C9, N, P from the best plane through these atoms: 0.0002, 0.0024, –0.0026, 0.0013, –0.0013 Å.

to **10a** but gave **1a** besides unreacted **7a**. The *N*- or *P*-substituted pentacarbonyltungsten complexes are also very sensitive to hydrolysis.

### 2.3. Structural and electronic influence on the selectivity

The ambident behavior of 1,3-benzazaphospholides can be understood in terms of the HSAB principle with substitution at nitrogen by hard and at phosphorus by soft electrophiles. As indicated by the different selectivity of the silylation of 2-methyl- or 2-phenyl- and 2-*t*-butyl-1,3-benzazaphospholides, steric factors have also to be considered. The steric impact may be attributed to the asymmetry of the planar five-membered P=C–N ring with respect to the sterically more open phosphorus as compared to nitrogen atom. This is well illustrated by the molecular structure of crystalline **1d** (Fig. 2), especially the larger angle P–C1–C2 as compared to N–C1–C2. Taking into account the van der Waals radii of methyl groups (2.0 Å) [29] at C3, C10 and C11 some steric interference with bulky *N*-substituents seems reasonable. Bond lengths and bond angles of the fused phosphazene system are not markedly influenced by the *t*-butyl group as seen from comparison with X-ray structural data of unsubstituted 1*H*-1,3-benzazaphosphole [P–C 1.695(9), 1.807(7); N–C 1.351(11), 1.371(9) Å; P–C1–N 115.7°] [18].

The particular properties of the 2-*t*-butyl benzazaphosphol(id)es are further influenced by the positive inductive effect of the *t*-butyl group. It increases somewhat the electron density at phosphorus, indicated by the upfield shift of  $\delta^{31}\text{P}$  of **1d** relative to the values of **1a–c** ( $\Delta\delta = 6–10$ ), and thus contributes to the preferred attack of  $\text{Me}_3\text{SiCl}$  and  $\text{Me}_3\text{SnCl}$  at phosphorus of **1d<sub>Li</sub>**. In this context it should be mentioned that **1d** adds water when treated with diluted aqueous  $\text{H}_2\text{SO}_4$  [15]

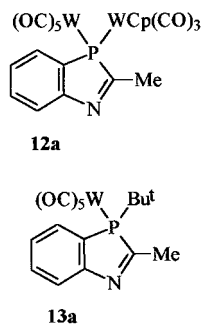
whereas **1a–c** are not attacked. The higher reactivity of the sterically rather hindered **1d** is similarly explained by the higher *P*-basicity which promotes the primary protonation step.

### 2.4. Structure elucidation of substitution products

The structures of the *N*- or *P*-substituted benzazaphospholes and their pentacarbonyl tungsten complexes were elucidated by multinuclear NMR studies. Substitution at nitrogen preserves the electronic nature of 1*H*-1,3-benzazaphospholes [30] as seen by the similarity of the  $^{13}\text{C}$  resonances and P–C coupling constants of **7a,b** with those of **1a,b**. Only C2 and C7a were deshielded, slightly less than in the respective Li compounds, by the electron demand at nitrogen to bind the electropositive silyl group. This also reduces the  $\pi$ -donor strength of nitrogen and causes a marked downfield shift of the phosphorus resonance (**7**  $\Delta\delta = 22–26.5$ ) which thus is a sensible indicator of *N*-substituents with a polar covalent bond to nitrogen.

Substituents at phosphorus cause the opposite effect, strong upfield shifts of the  $^{31}\text{P}$  signals as compared to those of the parent benzazaphospholes, increasing qualitatively with the number of core electrons in the order  $\text{CH}_3$  (**3d**,  $\Delta\delta = -77$ ),  $\text{SiMe}_3$  (**8d**,  $\Delta\delta = -104$ ),  $\text{CpFe}(\text{CO})_2$  (**10a,c,d**,  $\Delta\delta = -107, -114, -119$ ),  $\text{SnMe}_3$  (**9d**,  $\Delta\delta = -124$ ),  $\text{CpW}(\text{CO})_3$  (**11d**,  $\Delta\delta = -167.5$ ). One-bond coupling satellites of **9d** [ $^1J(^{117/119}\text{Sn}^{31}\text{P}) = 568.7/592.8$  Hz], **11d** [ $^1J(^{183}\text{W}^{31}\text{P}) = 50.1$  Hz] and **12a** [ $^1J(^{183}\text{W}^{31}\text{P}) = 90.8$  ( $\text{W}^{\text{II}}$ ), 180.8 ( $\text{W}^{\text{0}}$ ) Hz] give additional evidence of *P*-substitution. The phosphorus chemical shifts and one-bond coupling constants are similar to those in 1- $\text{SnMe}_3$ - and  $\text{CpW}(\text{CO})_3$ -substituted phospholes [26,31]. The carbon chemical shifts of **8–12** coincide closer with those of **3d** and the few other known 3-organyl-3*H*-1,3-benzazaphospholes [32,33] than with **1**, **1<sub>Li</sub>** or *N*-substituted 1,3-benzazaphospholes. Typical for *P*-substituted 1,3-benzazaphospholes are smaller  $^1J(^{31}\text{P}-^{13}\text{C})$  coupling constants of C3a (13–18 Hz) as compared to those in **1** (41–43 Hz) and **1<sub>Li</sub>** (33–36.5 Hz) and, except in 3-alkylbenzazaphospholes, noticeable larger chemical shifts for C2, C5, C6, C7 and C7a than in **1** and **1<sub>Li</sub>**. This indicates a change of the nature of the  $\pi$ -system towards non-aromatic 3*H*-1,3-benzazaphospholes [34] and weakening of the aromaticity. The barrier for planarization of phosphorus does not seem to be sufficiently lowered in the rather covalent phosphorus transition metal bonds to allow extensive delocalization. Unfortunately, no single crystals could be obtained for closer structural characterization. A related  $\text{CpW}(\text{CO})_3$  phospholide complex studied by X-ray structure analysis was less pyramidal ( $\Sigma\text{CPC } 319.6^\circ$ ) [31] than 1-ben-

zylphosphole ( $\Sigma$ CPC 302.7°) [35] and classified from the structural standpoint as halfway between the pyramidal localized phospholes and planar delocalized phospholide ions. The nature of  $\eta^1$ -P transition metal 1,3-benzazaphospholides can be regarded as closely related.



### 3. Conclusions

*1H*-1,3-Benzazaphospholes **1** may be lithiated by *t*-BuLi at nitrogen without substantial addition to the P–C double bond. The resulting anions **1<sub>Li</sub>** are attacked by soft electrophiles like alkylhalides, Me<sub>3</sub>SnCl, CpFe(CO)<sub>2</sub>X (X = I, Cl) or CpW(CO)<sub>3</sub>Cl at phosphorus. Even reactions with acyl halides occur at phosphorus. *N*-substitution can be achieved with Me<sub>3</sub>SiCl but a clean regioselectivity and good yields need lithiation in the presence of the electrophile and lack of steric congestion in position **2**. *N*-silylation reduces the  $\pi$ -donor ability of nitrogen within the five-membered ring as indicated by the downfield shift of the <sup>31</sup>P resonance compared to **1**. This effect may also lower the aromatic stabilization and be responsible for the extreme hydrolytic sensitivity of *N*-silyl derivatives as well as the failure of attempts to prepare *N*-substituted benzazaphospholes with zirconium or titanium halides. The lithiation of benzazaphosphole–M(CO)<sub>5</sub> complexes leads preferably to the formally *N*-lithiated benzazaphospholide complexes which are attacked at phosphorus by MeI or CpW(CO)<sub>3</sub>Cl. This gives evidence that the substitution at phosphorus is not controlled by the electron lone pair, but by the  $\pi$ -charge density. *N*-substitution could not be achieved with **2<sub>Li</sub>** which suggests that in this case the destabilization would be even larger, or in turn, that the *N*-donor ability is more important in benzazaphosphole complexes than in uncomplexed benzazaphospholes. The comparison of the <sup>13</sup>C-NMR data shows that 3-transition metal substituted 1,3-benzazaphospholes are electronically closer related to non-aromatic *3H*-3-alkyl than to aromatic *1H*-1,3-benzazaphospholes. The decrease of aromaticity is probably due to the barrier for planarization of phosphorus which does not seem to be sufficiently lowered by the rather covalent character of the transition metal phosphorus bond.

## 4. Experimental

### 4.1. General considerations

All reactions were carried out under an atmosphere of dry Ar using Schlenk techniques. Ether, THF and hydrocarbons were dried with sodium/benzophenone ketyl, C<sub>6</sub>D<sub>6</sub> and THF-*d*<sub>8</sub> with sodium or with LiAlH<sub>4</sub>. All solvents were freshly distilled or recondensed before use. Glassware was heat-dried in vacuum immediately before use. The *1H*-1,3-benzazaphospholes **1a–e** and **2d** were synthesized as described in Ref. [15], CpFe(CO)<sub>2</sub>I and CpW(CO)<sub>3</sub>Cl were obtained by known procedures [36]. Other reagents were commercially available and used as purchased. NMR spectra were recorded on a multinuclear FT-NMR spectrometer Bruker Model ARX300 at 300.1 (<sup>1</sup>H), 75.5 (<sup>13</sup>C), and 121.5 (<sup>31</sup>P) MHz and are proton-decoupled unless stated otherwise. The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P chemical shifts are  $\delta$  values relative to Me<sub>4</sub>Si and H<sub>3</sub>PO<sub>4</sub> (85%), respectively. Assignment numbers of H and C atoms of the benzazaphosphole ring follow the position according to the nomenclature. *J* values quote to H–H (<sup>1</sup>H) or P–C (<sup>13</sup>C) couplings unless stated otherwise. The Et<sub>2</sub>O content given in the formula of etherate complexes is based on the integral ratio of Et<sub>2</sub>O and characteristic groups within the molecule. The chemical shift values of these Et<sub>2</sub>O molecules are not given. IR spectra were measured on a Perkin–Elmer Model system 2000 and mass spectra on a single-focusing mass spectrometer AMD40 (Intectra). Melting points (m.p.) were determined in sealed capillaries under Ar and are uncorrected. The highly air sensitive lithium and stannyl compounds were usually characterized by phosphorus analysis, other compounds by CHN analyses using an elemental analyzer LECO Model CHNS-932.

### 4.2. Lithiation

#### 4.2.1. Lithium-2-methyl-1,3-benzazaphospholide (**1a<sub>Li</sub>**)

(A) *With lithiumdiethylamide in THF*. A solution of lithium diethylamide, prepared from *n*-BuLi in hexane (1.15 ml, 1.9 mmol) and Et<sub>2</sub>NH (0.196 ml, 1.9 mmol) in Et<sub>2</sub>O (10 ml) at 0 °C, was added dropwise at –78 °C to 0.284 g (1.9 mmol) of **1a** dissolved in THF (20 ml). The solvent and Et<sub>2</sub>NH were removed from the yellow solution in vacuum to give **1a<sub>Li</sub>**·*n*THF as a yellow sticky solid. <sup>1</sup>H-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 2.64 (d, <sup>3</sup>J<sub>PH</sub> = 10.7 Hz, 3H, Me), 6.57 (t, <sup>3</sup>J ≈ 7 Hz, 1H, H-5), 6.72 (‘t’, <sup>3</sup>J = 7–8 Hz, 1H, H-6), 7.43 (d, <sup>3</sup>J = 8 Hz, 1H, H-7), 7.72 (d br, <sup>3</sup>J ≈ 7 Hz, 1H, H-4). <sup>13</sup>C-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 21.7 (d, <sup>2</sup>J = 33.9 Hz, Me), 116.0 (d, <sup>3</sup>J = 9.5 Hz, C-5), 118.3 (C-7), 118.9 (C-6), 127.3 (d, <sup>2</sup>J = 23.1 Hz, C-4), 149.7 (d, <sup>1</sup>J = 34.5 Hz, C-3a), 155.5 (C-7a), 184.2 (d, <sup>1</sup>J = 49.3 Hz, C-2). <sup>31</sup>P-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 65.8.

(B) *With t-BuLi in Et<sub>2</sub>O*. A solution of *t*-BuLi in pentane (7.9 ml, 10.37 mmol) was given to cold Et<sub>2</sub>O

(0 °C, 10 ml) and added dropwise at  $-78$  °C to **1a** (1.556 g, 10.37 mmol) dissolved in Et<sub>2</sub>O (20 ml). Volatiles were removed from the yellow solution in vacuum. The resulting powder was dried for 3 h at 30 °C/1.3 Torr to give 2.13 g (90%) of yellow–orange **1a<sub>Li</sub>·Et<sub>2</sub>O**. <sup>1</sup>H-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 2.60 (d, <sup>3</sup>*J*<sub>PH</sub> = 12.0 Hz, 3H, Me), 6.87 (‘t’dd, <sup>3</sup>*J* = 7.9, 7.1, <sup>4</sup>*J*<sub>PH</sub> = 2.0, <sup>4</sup>*J* = 0.8 Hz, 1H, H-5), 7.04 (‘t’, <sup>3</sup>*J* = 7–8 Hz, 1H, H-6), 7.36 (d, <sup>3</sup>*J* = 8.1, <sup>4</sup>*J* = 0.8 Hz, 1H, H-7), 7.71 (‘dd’, <sup>3</sup>*J* = 7.9, <sup>3</sup>*J*<sub>PH</sub> = 3.5 Hz, 1H, H-4). <sup>13</sup>C-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 20.3 (d, <sup>2</sup>*J* = 30.5 Hz, Me), 120.8 (d, <sup>3</sup>*J* = 10.5 Hz, C-5), 117.3 (C-7), 120.8 (C-6), 127.4 (d, <sup>2</sup>*J* = 23.1 Hz, C-4), 147.1 (d, <sup>1</sup>*J* = 36.4 Hz, C-3a), 151.6 (C-7a), 181.1 (d, <sup>1</sup>*J* = 50.9 Hz, C-2). <sup>31</sup>P-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 71.2. Anal. Found: P, 13.52. Calc. for C<sub>8</sub>H<sub>7</sub>LiNP·Et<sub>2</sub>O (229.19): P, 13.51%.

#### 4.2.2. Lithium-2,5-dimethyl-1,3-benzazaphospholide (**1b<sub>Li</sub>**)

*t*-BuLi dissolved in pentane (0.87 ml, 1.62 mmol) and cold Et<sub>2</sub>O (0 °C, 10 ml) was added dropwise at  $-78$  °C to a solution of **1b** (0.266 g, 1.62 mmol) in Et<sub>2</sub>O (20 ml). The solvents were removed in vacuum (20 °C/1 Torr) to give 340 mg of a pale yellow powder, characterized by NMR data as **1b<sub>Li</sub>** containing 0.1–0.2 Et<sub>2</sub>O. <sup>1</sup>H-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 2.31 (s, 3H, 5-Me), 2.64 (d, <sup>3</sup>*J*<sub>PH</sub> = 11.4 Hz, 3H, Me), 6.64 (dd, <sup>3</sup>*J* = 8.2, <sup>5</sup>*J*<sub>PH</sub> = 1.4 Hz, 1H, H-6), 7.33 (d, <sup>3</sup>*J* = 8.2 Hz, 1H, H-7), 7.53 (br, 1H, H-4). <sup>13</sup>C-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 20.9 (d, <sup>2</sup>*J* = 32.7 Hz, Me-2), 21.7 (Me-5), 117.2 (C-7), 121.6 (C-6), 124.8 (d, <sup>3</sup>*J* = 11.3 Hz, C-5), 127.2 (d, <sup>2</sup>*J* = 21.6 Hz, C-4), 148.8 (d, <sup>1</sup>*J* = 36.2 Hz, C-3a), 151.8 (C-7a), 182.0 (d, <sup>1</sup>*J* = 52.5 Hz, C-2). <sup>31</sup>P-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 69.3.

#### 4.2.3. Lithium-2-phenyl-1,3-benzazaphospholide (**1c<sub>Li</sub>·Et<sub>2</sub>O**)

A solution of *t*-BuLi in pentane (1.5 ml, 1.95 mmol) and Et<sub>2</sub>O (10 ml) was added dropwise at  $-78$  °C to 0.412 g (1.95 mmol) of **1c** in Et<sub>2</sub>O (20 ml). Evaporation and drying of the orange brown solid powder for 2.5 h at 30 °C/1.3 Torr gave 0.52 g (92%) of yellowish-red **1c<sub>Li</sub>·Et<sub>2</sub>O** (Et<sub>2</sub>O content according to integral ratio in <sup>1</sup>H-NMR). It is readily soluble in THF but sparingly soluble in Et<sub>2</sub>O and toluene. <sup>1</sup>H-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 7.04 (‘t’*m*, <sup>3</sup>*J* = 7, <sup>4</sup>*J* = 1, <sup>4</sup>*J*<sub>PH</sub> = 2 Hz, 1H, H-5), 7.23 (‘t’*br*, <sup>3</sup>*J* = 7 Hz, <sup>4</sup>*J* and <sup>5</sup>*J*<sub>PH</sub> small, 1H, H-6), 7.28–7.42 (m, 3H, phenyl), 7.62 (dd, <sup>3</sup>*J* = 8.1, *J* = 1 Hz, 1H, H-7), 7.86 (dm, <sup>3</sup>*J* = 7.3 Hz, 2H, H-*o*), 7.93 (ddbr, <sup>3</sup>*J* = 8, <sup>3</sup>*J*<sub>PH</sub> = 3.7 Hz, 1H, H-4). <sup>13</sup>C-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 116.7 (d, <sup>3</sup>*J* = 11.3 Hz, C-5), 120.1 (C-7), 125.9 (C-6), 127.6–128.4 (Ph), 128.0 (d, <sup>2</sup>*J* = 22.6 Hz, C-4), 145.3 (d, <sup>2</sup>*J* = 24.8 Hz, C-*i*), 150.2 (d, <sup>1</sup>*J* = 32.9 Hz, C-3a), 156.7 (C-7a), 186.4 (d, <sup>1</sup>*J* = 50.5 Hz, C-2). <sup>31</sup>P-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 75.0. Anal. Found: P, 10.95. Calc. for C<sub>13</sub>H<sub>9</sub>LiNP·Et<sub>2</sub>O (291.26): P, 10.57%.

#### 4.2.4. Lithium-2-*t*-butyl-1,3-benzazaphospholide (**1d<sub>Li</sub>·Et<sub>2</sub>O**)

*t*-BuLi in pentane (4.7 ml, 6.2 mmol) and cold Et<sub>2</sub>O (0 °C, 10 ml) was added dropwise at  $-78$  °C to **1d** (1.192 g, 6.2 mmol) dissolved in Et<sub>2</sub>O (20 ml) affording a yellow solution. The solvent was removed in vacuo to give 0.56 g of the pale yellow powder **1d<sub>Li</sub>·Et<sub>2</sub>O**. <sup>1</sup>H-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 1.51 (d, <sup>4</sup>*J*<sub>PH</sub> = 1.0 Hz, 9H, CMe<sub>3</sub>), 6.61 (tdd, <sup>3</sup>*J* = 7.7, <sup>4</sup>*J*<sub>PH</sub> = 1.9, <sup>4</sup>*J* = 1 Hz, 1H, H-5), 6.78 (td, <sup>3</sup>*J* = 8.2, <sup>4</sup>*J* = 1.4 Hz, 1H, H-6), 7.46 (d, <sup>3</sup>*J* = 7.9 Hz, 1H, H-7), 7.78 (ddd, <sup>3</sup>*J* = 7.7, <sup>3</sup>*J*<sub>PH</sub> = 2.1, <sup>4</sup>*J* = 1.4 Hz, 1H, H-4). <sup>13</sup>C-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 33.0 (d, <sup>3</sup>*J* = 9.6 Hz, CMe<sub>3</sub>), 37.7 (d, <sup>2</sup>*J* = 19.9 Hz, CMe<sub>3</sub>), 116.5 (d, <sup>3</sup>*J* = 10.6 Hz, C-5), 118.0 (C-7), 119.7 (C-6), 127.4 (d, <sup>2</sup>*J* = 22.6 Hz, C-4), 147.0 (d, <sup>1</sup>*J* = 34.0 Hz, C-3a), 153.1 (C-7a), 199.5 (d, <sup>1</sup>*J* = 57.3 Hz, C-2). <sup>31</sup>P-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 56.6. Anal. Found: P, 10.86. Calc. for C<sub>11</sub>H<sub>13</sub>LiNP·Et<sub>2</sub>O (271.27): P, 11.42%.

#### 4.2.5. $\eta^1(P)$ -(Lithium-2-*t*-butyl-1,3-benzazaphospholide)-pentacarbonyl-tungsten (**2d<sub>Li</sub>**)

A solution of *t*-BuLi in pentane (0.15 ml, 0.275 mmol) was added at  $-70$  °C to a solution of **2d** [15b] (0.142 g, 0.275 mmol) in Et<sub>2</sub>O (10 ml). It was allowed to stir at  $-70$  °C for 30 min and then at 20 °C for 2 h. Evaporation of the solvent in vacuo afforded 0.204 g of an orange powder, identified by NMR as **2d<sub>Li</sub>·2Et<sub>2</sub>O**. <sup>1</sup>H-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 1.49 (s, 9H, CMe<sub>3</sub>), 6.79 (‘t’*d*, <sup>3</sup>*J*  $\approx$  7.1, 7.5 Hz, <sup>4</sup>*J*<sub>PH</sub>  $\approx$  1.4 Hz, 1H, H-5), 6.88 (‘t’, <sup>3</sup>*J*  $\approx$  7.0, 7.2 Hz, 1H, H-6), 7.59 (d, <sup>3</sup>*J* = 8.0 Hz, 1H, H-7), 7.75 (dd, <sup>3</sup>*J* = 7.4, <sup>3</sup>*J*<sub>PH</sub> = 1.4 Hz, 1H, H-4). <sup>13</sup>C-NMR (THF-*d*<sub>8</sub>):  $\delta$  = 32.4 (d, <sup>3</sup>*J* = 6.7 Hz, CMe<sub>3</sub>), 39.2 (d, <sup>2</sup>*J* = 22.3 Hz, CMe<sub>3</sub>), 118.95 (d, <sup>3</sup>*J* = 9.3 Hz, C-5), 121.05 (C-7), 122.5 (C-6), 126.5 (d, <sup>2</sup>*J* = 19.0 Hz, C-4), 150.3 (d, <sup>1</sup>*J* = 9.0 Hz, C-3a), 155.4 (d, <sup>2</sup>*J* = 12.3 Hz, C-7a), 203.1 (d, <sup>1</sup>*J* = 35.1 Hz, C-2), 200.6 (d sat, <sup>2</sup>*J* = 1.9, <sup>1</sup>*J*<sub>CW</sub> = 125.5 Hz, 4CO), 205.3 (d, <sup>2</sup>*J* = 17.3 Hz, 1CO). <sup>31</sup>P-NMR (THF-*d*<sub>8</sub>):  $\delta$  =  $-43.5$  (sat, <sup>1</sup>*J*<sub>PW</sub> = 141.5 Hz).

### 4.3. Substitution reactions

#### 4.3.1. 2-*t*-Butyl-3-methyl-1,3-benzazaphosphole (**3d**)

**2d** (521 mg (2.72 mmol)) was dissolved in Et<sub>2</sub>O (10 ml) and reacted with 2.09 ml of *t*-BuLi solution (1.3 M, 2.72 mmol) in pentane at  $-70$  °C. After 2 h at room temperature (r.t.) excess methyl iodide (0.2 ml, 3.21 mmol) in Et<sub>2</sub>O (10 ml) was added dropwise and stirred overnight. The solvent was removed and the product extracted with toluene. Distillation at 68 °C/3.7  $\times$  10<sup>-2</sup> Torr gave 302 mg (56%) of a colorless viscous liquid **3d**. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.13 (d, <sup>2</sup>*J*<sub>PH</sub> = 1.9 Hz, 3H, PMe), 1.35 (s, 9H, CMe<sub>3</sub>), 7.13 (‘t’*t*, <sup>3</sup>*J*  $\approx$  7.5 Hz, *J*<sub>PH</sub>  $\approx$  <sup>4</sup>*J*<sub>HH</sub> = 1–2 Hz, 1H, H-5 or H-6), 7.18 (‘t’*d*, <sup>3</sup>*J* = 7.6, *J* = 1.3 Hz, 1H, H-5 or H-6), 7.40 (ddd, <sup>3</sup>*J* = 7.3, <sup>3</sup>*J*<sub>PH</sub> = 2.7, <sup>4</sup>*J*<sub>HH</sub> = 1.0 Hz, 1H, H-4), 7.95 (d, <sup>3</sup>*J* = 7.8



Hz, 1H, H-7).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 11.5$  (d,  $^1J = 21.9$  Hz, PMe), 30.9 (d,  $^3J = 4.8$  Hz,  $\text{CMe}_3$ ), 40.6 (d,  $^2J = 18.5$ ,  $\text{CMe}_3$ ), 124.8 (C-7), 126.4 (d,  $^3J = 6.5$  Hz, C-5), 128.5 (d,  $^2J = 19.8$  Hz, C-4), 129.8 (C-6), 139.4 (d,  $^1J = 3.0$  Hz, C-3a), 158.8 (d,  $^2J = 10.3$  Hz, C-7a), 200.9 (d,  $^1J = 38.0$  Hz, C-2).  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -11.6$ . EIMS (70 eV);  $m/z$  (%): 206 (29), 205 (100) [ $\text{M}^+$ ], 204 (17), 190 (79) [ $\text{M} - 15^+$ ], 163 (17), 149 (26), 148 (92) [ $\text{M} - \text{Bu}^+$ ], 145 (24), 108 (12), 107 (44), 77 (12), 57 (20), 41 (14). Anal. Found: C, 69.67; H, 7.91; N, 6.90. Calc. for  $\text{C}_{12}\text{H}_{16}\text{NP}$  (205.24): C, 70.23; H, 7.86; N, 6.82%.

#### 4.3.2. 2-Methyl-3-pentyl-1,3-benzazaphosphole (**3a**)

Compound **1a** (460 mg, 3.08 mmol) was dissolved in DMF (15 ml) and stirred at 20 °C with NaH (90 mg, 3.7 mmol) until the hydrogen evolution ceased (ca. 1 h). On addition of pentylbromide (0.46, 3.7 mmol) to the yellow solution the color turned immediately to pale yellow. After stirring overnight toluene was added and the solvent mixture removed in vacuo (twice repeated). The residue is impure oily **3a**,  $\delta^{31}\text{P}$  9.2, contaminated by smaller amounts of **1a** and side products with  $\delta^{31}\text{P}$  – 11, – 52, – 72.

#### 4.3.3. $\eta^1(\text{P})$ -(2-*t*-Butyl-3-methyl-1,3-benzazaphosphole)-pentacarbonyl-tungsten (**4d**)

**2d<sub>Li</sub>** was prepared from **2d** (198 mg, 0.384 mmol) and *t*-BuLi in pentane (0.20 ml, 0.384 mmol) as described above. The solid was dissolved in Et<sub>2</sub>O (10 ml). Methyl iodide (0.024 ml, 0.384 mmol) was added to this solution at – 70 °C. After stirring at r.t. for 2 h the precipitate was removed, and the solvent was evaporated in vacuo. The residual solid was dissolved in a small amount of THF. Addition of Et<sub>2</sub>O afforded an orange precipitate which was dried for 2 h at 20 °C yielding 190 mg of **4d** containing a small amount of LiI(Et<sub>2</sub>O)<sub>*n*</sub> (according to the  $^1\text{H}$  integral ratio 0.5Et<sub>2</sub>O per mol **4d**).  $^1\text{H-NMR}$  (THF-*d*<sub>8</sub>):  $\delta = 1.53$  (s, 9H,  $\text{CMe}_3$ ), 2.05 (d,  $^2J_{\text{PH}} = 8.1$  Hz, 3H, PMe), 7.43 ('t'dd,  $^3J = 7.4$ ,  $^4J_{\text{HH}} = 1.1$  Hz,  $^4J_{\text{PH}} = 3.6$  Hz, 1H, H-5), 7.53 ('t't',  $^3J = 7.6$ ,  $^4J_{\text{HH}} \approx ^5J_{\text{PH}} = 1.1$  Hz, 1H, H-6), 7.71, 7.73 (2d,  $^3J = 7.2$ , 7.3 Hz, 2H, H-7, H-4).  $^{13}\text{C-NMR}$  (THF-*d*<sub>8</sub>):  $\delta = 18.0$  (d,  $^1J = 21.7$  Hz, PMe), 30.5 (d,  $^3J = 2.1$  Hz,  $\text{CMe}_3$ ), 40.7 (d,  $^2J = 21.6$  Hz,  $\text{CMe}_3$ ), 124.9 (d,  $^3J = 3.0$  Hz, C-7), 128.3 (d,  $^3J = 8.9$  Hz, C-5), 128.6 (d,  $^2J = 14.9$  Hz, C-4), 132.4 (d,  $^4J = 1.2$  Hz, C-6), 136.1 (d,  $^1J = 53.4$  Hz, C-3a), 154.85 (d,  $^2J = 19.7$  Hz, C-7a), 192.2 (d,  $^1J = 5.8$  Hz, C-2), 197.1 (d sat,  $^2J = 6.5$  Hz,  $^1J_{\text{CW}} = 125.6$  Hz, 4 CO), 198.9 (d,  $^2J = 20.3$  Hz, 1CO).  $^{31}\text{P-NMR}$  (THF-*d*<sub>8</sub>):  $\delta = 3.4$  (sat,  $^1J_{\text{PW}} = 216.9$  Hz).

#### 4.3.4. 5-Methyl-2-phenyl-3-acetyl-1,3-benzazaphosphole (**5e**)

Acetyl chloride (0.1 ml, 1.4 mmol) was added at – 78 °C to the orange–red solution prepared from **1e** (226 mg, 1.0 mmol) and *t*-BuLi (0.77 ml, 1.3 M pentane solution, 1.0 mmol) in Et<sub>2</sub>O (10 ml) which immediately

turned to pale yellow. It was allowed to stir overnight and filtered. Removal of the solvent afforded a pale yellow solid. Extraction with  $\text{C}_6\text{D}_6$  (3 ml) gave a solution of 200 mg consisting of **5e** and **1e**,  $\delta^{31}\text{P}$  32.3 and 75.3, intensity ratio 1:1; crude yield of **5e** 37%. The solvent was evaporated and the residue extracted with hot toluene as well as with hot hexane, but **1e** enriched in the filtrate ( $^{31}\text{P}$  intensity ratio ca. 2:1) as well as in the residue ( $^{31}\text{P}$  intensity ratio ca. 4:1) which indicates partial decomposition of **5e**. (Addition of  $\text{CD}_3\text{OD}$  converts **5e** completely to **1e**.) **5e**.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 1.65$  (d,  $^3J_{\text{PH}} = 14.5$  Hz, 3H, MeCO), 2.13 (s, 3H, Me-5), 7.17–7.24 (ddd,  $^3J = 8.0$ ,  $J = 1.8$ , 0.6 Hz, 1H, H-6), 7.17–7.24 (m, Ph), 7.45 (m br, 1H, 4-H), 7.98 (d,  $^3J = 8.1$  Hz, 1H, H-7), 8.30 (dm, 2H, *o*-H).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 21.9$  (Me-5), 34.6 (d,  $^2J = 31$  Hz, CO Me), 124.8 (C-7), 130.7–130.9 (C-6, C-*p*, 2C-*m*), 130.9 (d,  $^2J = 18.8$  Hz, C-4, uncertain), 131.9 (d,  $^3J = 13.5$  Hz, 2C-*o*), 132.0 (C-5 superimposed), 137.1 (d,  $^2J = 22.3$  Hz, C-*i*), 137.7 (d,  $^1J = 8.1$  Hz, C-3a), 158.4 (d,  $^2J = 7.9$  Hz, C-7a), 175.6 (d,  $^1J = 31.6$  Hz, C-2), 210.2 (d,  $^1J = 49.7$  Hz, CO).  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 32.3$ .

#### 4.3.5. 5-Methyl-2-phenyl-3-pivaloyl-1,3-benzazaphosphole (**6e**)

**1e** (226 mg, 1.0 mmol) dissolved in Et<sub>2</sub>O (15 ml) was lithiated with *t*-BuLi (0.59 ml, 1.7 M pentane solution, 1.0 mmol) at – 78 °C. After 1 h at 20 °C the solution was cooled again to – 78 °C, and pivaloyl chloride (0.123 ml, 1.0 mmol) was added with stirring. After warming to r.t. (3 h) the orange–red color changes to pale yellow. The mixture was allowed to stir overnight and filtered. Removal of the solvent in vacuo ( $10^{-2}$  Torr) afforded a yellow oil which was extracted with warm hexane to give 100 mg of pale yellow powder of **6e** slightly contaminated by **1e**. On cooling the filtrate to – 78 °C, 130 mg of pure **6e**, m.p. 68–70 °C, was collected; total yield ca. 230 mg (66%).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 0.93$  (s, 9H,  $\text{CMe}_3$ ), 2.15 (s, 3H, Me-5), 7.02 (ddd,  $^3J = 8.0$ ,  $J = 1.8$ , 0.6 Hz, 1H, H-6), 7.17–7.24 (m, 3H, Ph), 7.58 (s m,  $^3J_{\text{PH}} \approx 2$ ,  $J \approx 1$  Hz, 1H, 4-H), 7.94 (d,  $^3J = 8.1$  Hz, 1H, H-7), 8.27 (dm, 2H, *o*-H).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 22.0$  (Me-5), 26.2 (d,  $^3J = 3.4$  Hz,  $\text{CMe}_3$ ), 52.2 (d,  $^2J = 28.3$  Hz,  $\text{CMe}_3$ ), 125.1 (C-7), 129.5 (2C, C-6, C-*p*), 130.4 (d,  $^4J = 7.9$  Hz, 2C-*m*), 130.9 (d,  $^2J = 19.9$  Hz, C-4), 131.7 (d,  $^3J = 18.4$  Hz, 2C-*o*), 132.8 (d,  $^3J = 3.4$  Hz, C-5), 137.0 (d,  $^1J = 7.1$  Hz, C-3a), 138.1 (d,  $^2J = 22.2$  Hz, C-*i*), 159.1 (d,  $^2J = 7.4$  Hz, C-7a), 179.7 (d,  $^1J = 29.6$  Hz, C-2), 216.1 (d,  $^1J = 64.0$  Hz, CO).  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 22.7$ . EIMS (70 eV, 170 °C);  $m/z$  (%): 311 (48) [ $\text{M}^+ + 2$ ], eventually by reductive decomposition during heating, 310 (71), 255 (13), 244 (28), 232 (64) [ $\text{M} - \text{Ph}^+$ ], 231 (87), 230 (64), 188 (20), 148 (23), 121 (68) [ $\text{MeC}_5\text{H}_3\text{P}^+$ ], 86 (77) [ $t\text{-BuCO}^+$ ], 77 (62), 57 (100) [ $t\text{-Bu}^+$ ]. Anal. Found: C, 73.61; H, 6.64; N 4.58. Calc. for  $\text{C}_{19}\text{H}_{20}\text{NOP}$  (309.35): C, 73.77; H, 6.52; N, 4.53%.

#### 4.3.6. 2-Methyl-1-trimethylsilyl-1,3-benzazaphosphole (7a)

Excess  $\text{Me}_3\text{SiCl}$  (0.40 ml, 3.15 mmol) was added at  $-78^\circ\text{C}$  to a solution of **1a** (0.394 g, 2.63 mmol) in  $\text{Et}_2\text{O}$  (5 ml). After stirring for 15 min, a solution of  $t\text{-BuLi}$  (1.50 ml, 2.63 mmol) in  $\text{Et}_2\text{O}$  was added. The pale yellow mixture formed was stirred for 2 h at r.t. and then filtered. The solvent was removed under reduced pressure and the yellow oily residue, nearly pure **7a**, was distilled in high vacuum at  $50\text{--}60^\circ\text{C}/7 \times 10^{-6}$  Torr to give 0.532 g (91%) of a colorless oil which is extremely sensitive to hydrolysis.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 0.25$  (d sat,  $^2J_{\text{SiH}} = 6.7$  Hz, 9H,  $\text{SiMe}_3$ ), 2.58 (d,  $^3J_{\text{PH}} = 14.9$  Hz, 3H, Me), 7.11 (t' dd,  $^3J = 7.7$ , 7.0,  $^4J = 1.9$ , 1.0 Hz, 1H, H-5), 7.22 (t' dd,  $^3J = 8.5$ , 7.0,  $^4J = 1.4$ ,  $^5J_{\text{PH}} = 1.0$  Hz, 1H, H-6), 7.64 (ddd  $^3J = 8.5$ ,  $^4J = 1.8$ , 1.0 Hz, 1H, H-7), 8.10 (dddd,  $^3J = 7.7$ ,  $^4J = 1.5$ ,  $^5J = 0.6$ ,  $^3J_{\text{PH}} = 4.5$  Hz, 1H, H-4).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.28$  (sat,  $^1J_{\text{SiC}} = 58$  Hz,  $\text{SiMe}_3$ ), 21.9 (d,  $^2J = 30.8$  Hz, Me), 117.0 (C-7), 121.2 (d,  $^3J = 10.8$  Hz, C-5), 124.4 (d,  $^4J = 2.1$  Hz, C-6), 129.5 (d,  $^2J = 21.6$  Hz, C-4), 144.7 (d,  $^1J = 35.2$  Hz, C-3a), 149.8 (d,  $^2J = 4.9$  Hz, C-7a), 182.4 (d,  $^1J = 46.9$  Hz, C-2).  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 95.1$ . Anal. Found: C, 59.37; H, 7.35; N, 6.47. Calc. for  $\text{C}_{11}\text{H}_{16}\text{NPSi}$  (221.31): C, 59.70; H, 7.29; N, 6.33%.

#### 4.3.7. 2,5-Dimethyl-1-trimethylsilyl-1,3-benzazaphosphole (7b)

Excess  $\text{Me}_3\text{SiCl}$  (0.78 ml, 6.15 mmol) was added at  $-78^\circ\text{C}$  to a solution of **1b** (0.846 g, 5.18 mmol) in  $\text{Et}_2\text{O}$  (5 ml), followed by  $t\text{-BuLi}$  in pentane (3.10 ml, 5.27 mmol). After stirring for 2 h at r.t. the precipitate was removed. Evaporation of the solvent left 0.976 g of an orange syrupy mass which was sublimed in high vacuum at  $85\text{--}95^\circ\text{C}/1.2 \times 10^{-5}$  Torr, yielding 0.54 g (44%) of **7b** which is extremely sensitive to hydrolysis.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 0.21$  (s, sat,  $^2J_{\text{SiH}} = 6.7$  Hz, 9H,  $\text{SiMe}_3$ ), 2.29 (s, 3H, Me-5), 2.55 (d,  $^3J_{\text{PH}} = 14.8$  Hz, 3H, Me-2), 7.05 (dd,  $^3J = 8.8$ , 7.0,  $^4J = 1.1$  Hz, 1H, H-6), 7.55 (d br,  $^3J = 8.8$  Hz, 1H, H-7), 7.86 (dm,  $^3J_{\text{PH}} = 4.7$  Hz, 1H, H-4).  $^{13}\text{C-NMR}$ , CH-COSY ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.24$  ( $\text{SiMe}_3$ ), 21.7 (Me-5), 21.9 (d,  $^2J = 31.2$  Hz, Me-2), 116.6 (C-7), 126.0 (d,  $^4J = 2.2$  Hz, C-6), 129.4 (d,  $^2J = 21.7$  Hz, C-4), 130.1 (d,  $^3J = 11.0$  Hz, C-5), 145.1 (d,  $^1J = 35.3$  Hz, C-3a), 148.1 (d,  $^2J = 4.8$  Hz, C-7a), 182.2 (d,  $^1J = 46.9$  Hz, C-2).  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 94.5$ . EIMS (70 eV);  $m/z$  (%): 235 (100) [ $\text{M}^+$ ]. Anal. Found: C, 61.83; H, 7.81; N, 6.25. Calc. for  $\text{C}_{12}\text{H}_{18}\text{NPSi}$  (235.34): C, 61.24; H, 7.71; N, 5.95%.

#### 4.3.8. 2-Phenyl-1-trimethylsilyl-1H-1,3-benzazaphosphole (7c) and 2-phenyl-3-trimethylsilyl-3H-1,3-benzazaphosphole (8c)

$t\text{-BuLi}$  (0.27 ml, 0.47 mmol) was added dropwise to a solution of **1c** (100 mg, 0.47 mmol) and  $\text{Me}_3\text{SiCl}$  (0.07 ml, 0.56 mmol) in  $\text{Et}_2\text{O}$  ( $-70^\circ\text{C}$ ). After **1d** the mix-

ture was filtered and the solvent removed in vacuo. The crude product, analyzed by NMR, consisted mainly of **7c** ( $\delta^{31}\text{P}$  100.5) and lower contents of phosphines with  $\delta^{31}\text{P} - 52.7$ ,  $-81.3$  and  $-153.5$  (intensity ratio 50:27:6:17%). Compounds **7c** and **8c** were identified by characteristic  $^{13}\text{C-NMR}$  data. **7c**.  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 2.8$  (s,  $\text{SiMe}_3$ ), 118.0 (C-7), 121.5 (d,  $^3J = 11.3$  Hz, C-5), 124.8 (d,  $^4J = 2.8$  Hz, C-6), 140.0 (d,  $^2J_{\text{PC}} = 20.4$  Hz, C-*i*), 145.7 (d,  $^1J_{\text{PC}} = 38.1$  Hz, C-3a), 150.3 (d,  $^2J_{\text{PC}} = 5.8$  Hz, C-7a), 186.2 (d,  $^1J_{\text{PC}} = 47.6$  Hz, C2). **8c**.  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -0.3$  (d,  $^2J_{\text{PC}} = 10.6$  Hz,  $\text{SiMe}_3$ ), 123.0 (C-7), 128.1 (C-6), 136.5 (d,  $^1J_{\text{PC}} = 16.1$  Hz, C-3a), 159.0 (C-7a), 175.7 (d,  $^1J_{\text{PC}} = 50.9$  Hz, C2).

#### 4.3.9. 2-*t*-Butyl-1-trimethylsilyl-1H-1,3-benzazaphosphole (7d) and 2-*t*-butyl-3-trimethylsilyl-3H-1,3-benzazaphosphole (8d)

$\text{1d}_1 \cdot \text{Et}_2\text{O}$  (350 mg, 1.29 mmol) was reacted with  $\text{Me}_3\text{SiCl}$  (0.28 ml, 2.20 mmol) at  $-70^\circ\text{C}$  in  $\text{Et}_2\text{O}$ . After addition, stirring was continued overnight. Filtration and removal of the solvent in vacuo left a yellow oil consisting mainly of **1d** ( $\delta^{31}\text{P}$  68.1), **8d** ( $\delta^{31}\text{P} - 38.7$ ) (molar ratio ca. 3:1), small amounts of **7d** ( $\delta^{31}\text{P}$  91.6) and side products with  $\delta^{31}\text{P}$  8.0 and  $-18$ . **8d** and **7d** were enriched by distillation at  $45\text{--}50^\circ\text{C}/6 \times 10^{-6}$  Torr but could not be separated. Crystallization attempts led to hydrolysis of the silyl compounds. **8d**.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -0.05$  (d,  $^3J_{\text{PH}} = 4.2$  Hz,  $\text{SiMe}_3$ ), 1.43 ( $\text{CMe}_3$ ), 7.0–8.1 ( $\text{C}_6\text{H}_4$ ).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 0.10$  (d,  $^2J_{\text{PC}} = 10.5$  Hz,  $\text{SiMe}_3$ ), 31.6 (d,  $^3J_{\text{PC}} = 5.2$  Hz,  $\text{CMe}_3$ ), 34.7 (d,  $^2J_{\text{PC}} = 13.2$  Hz,  $\text{CMe}_3$ ), 124.6 (C-7), 125.4 (d,  $^3J_{\text{PC}} = 7.0$  Hz, C-5), 128.2 (C-6), 128.7 (d,  $^2J_{\text{PC}} = 18.3$  Hz, C-4), 136.9 (d,  $^1J_{\text{PC}} = 5.7$  Hz, C3a), 160.4 (d,  $^2J_{\text{PC}} = 7.3$  Hz, C7a), 200.3 (d,  $^1J = 55.1$  Hz, C-2). **7d**.  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 6.5$  (s,  $\text{SiMe}_3$ ), 29.3 (d,  $^3J = 4.7$  Hz,  $\text{CMe}_3$ ), 40.1 (d,  $^2J_{\text{PC}} = 19.3$  Hz,  $\text{CMe}_3$ ), 118.5 (C-7), 121.0 (d,  $^3J = 10$  Hz, C-5), 123.8 (d,  $^4J = 2$  Hz, C-6), 129.8 (d,  $^2J = 17$  Hz, C-4), ca. 143.5 (d, superimposed, C-3a), 150.4 (br, C-7a), 198.1 (d,  $^1J_{\text{PC}} = 47.9$  Hz, C2).

#### 4.3.10. 2-*t*-Butyl-3-trimethylstannyl-1,3-benzazaphosphole (9d)

Compound **1d** (1.046 g (5.47 mmol)) was dissolved in  $\text{Et}_2\text{O}$  and lithiated with 5.47 mmol of  $t\text{-BuLi}$  solution at  $-70^\circ\text{C}$ . Then a solution of 1.089 g (5.47 mmol)  $\text{Me}_3\text{SnCl}$  in  $\text{Et}_2\text{O}$  was added at  $-78^\circ\text{C}$ . The mixture was stirred for 20 h and filtered. The solvent was removed in vacuo, and the residue was sublimed at  $88\text{--}98^\circ\text{C}/0.5 \times 10^{-4}$  Torr yielding 0.848 g (44%) of colorless **9d**, m.p.  $65\text{--}68^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -0.06$  (d sat,  $^3J_{\text{PH}} = 2.2$ ,  $^2J_{\text{SnH}} = 53.6$ , 51.3 Hz, 9H,  $\text{SnMe}_3$ ), 1.44 (d,  $^4J_{\text{PH}} = 0.7$  Hz, 9H,  $\text{CMe}_3$ ), 7.06 (t' dd,  $^3J \approx 7.4$ ,  $^4J_{\text{PH}} = 2.8$ ,  $^4J = 1.1$  Hz, 1H, H-5), 7.23 (t' d,  $^3J = 7\text{--}8$ ,  $^4J = 1.3$  Hz, 1H, H-6), 7.65 (m,  $^3J = 7.5$ ,  $^3J_{\text{PH}} = 2.4$ ,  $^4J = 1.3$ ,  $^5J = 0.6$  Hz, 1H, H-4), 8.15 (dm,

$^3J = 8.0$ ,  $^4J$  and  $^5J = 1.1$ – $0.6$  Hz, 1H, H-7).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -6.4$  (d,  $^2J = 5.4$  Hz,  $\text{SnMe}_3$ ), 31.7 (d,  $^3J = 5.3$  Hz,  $\text{CMe}_3$ ), 40.1 (d,  $^2J = 18.9$  Hz,  $\text{CMe}_3$ ), 124.8 (C-7), 125.0 (d,  $^3J = 7.1$  Hz, C-5), 127.8 (C-6), 127.8 (d,  $^2J = 19.0$  Hz, C-4), 139.2 (d,  $^1J = 13.1$  Hz, C-3a), 160.3 (d,  $^2J = 5.3$  Hz, C-7a), 200.2 (d,  $^1J = 52.8$  Hz, C-2).  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -58.8$  ( $^1J_{\text{P}117/119\text{Sn}} = 567.8$ , 593.4 Hz). Anal. Found: P, 8.56. Calc. for  $\text{C}_{14}\text{H}_{22}\text{NPSn}$  (354.02): P, 8.75%.

#### 4.3.11. 3-( $\eta^5$ -Cyclopentadienyl-irondicarbonyl)-2-methyl-1,3-benzazaphosphole (**10a**)

**1a** (500 mg, 3.34 mmol) dissolved in  $\text{Et}_2\text{O}$  (20 ml) was lithiated with *t*-BuLi in pentane (1.92 ml, 3.34 mmol) at  $-78$  °C. The solvent was removed in vacuo and the residue redissolved in  $\text{Et}_2\text{O}$ . At  $-70$  °C a solution of  $\text{CpFe}(\text{CO})_2\text{I}$  (1.014 g, 3.34 mmol) in  $\text{Et}_2\text{O}$  (15 ml) was added. After stirring for 5 h the red-brown mixture was filtered. The solvent was removed in vacuo (2 h, 0.01 Torr), and the residue was extracted with toluene to give 438 mg (26%) of **10a** as red powder containing a small amount of  $\text{Et}_2\text{O}$  bound to LiI.  $^1\text{H-NMR}$  (THF- $d_8$ ):  $\delta = 2.55$  (d,  $^3J = 9.1$  Hz, 3H, Me), 5.04 (s, 5H, Cp), 7.01 (‘t’,  $^3J = 7.4$ , 7.2 Hz,  $^4J = 2$  Hz, 1H, H-5), 7.20 (t,  $^3J = 7.7$ , 7.2 Hz, 1H, H-6), 7.64 (d,  $^3J = 7.4$  Hz, 1H, H-4), 7.76 (d,  $^3J = 7.9$  Hz, 1H, H-7).  $^{13}\text{C-NMR}$  (THF- $d_8$ ):  $\delta = 22.0$  (d,  $^2J = 28.0$  Hz, Me), 87.0 (s, Cp), 123.1 (d,  $^3J = 6.4$  Hz, C-5), 124.3 (C-7), 126.4 (C-6), 128.1 (d,  $^2J = 20.2$  Hz, C-4), 150.3 (d,  $^1J = 18.8$  Hz, C-3a), 158.4 (d,  $^2J = 8.0$  Hz, C-7a), 202.3 (d,  $^1J = 47.6$  Hz, C-2), 214.1 (d,  $^2J = 4.8$  Hz, CO).  $^{31}\text{P-NMR}$  (THF- $d_8$ ):  $\delta = -35.6$ .

#### 4.3.12. 3-( $\eta^5$ -Cyclopentadienyliron dicarbonyl)-2-phenyl-1,3-benzazaphosphole (**10c**)

(A) A solution of *t*-BuLi in hexane (0.30 ml, 0.52 mmol) and  $\text{Et}_2\text{O}$  (10 ml, 0 °C) was added to **1c** (110 mg, 0.52 mmol), dissolved in  $\text{Et}_2\text{O}$  (20 ml,  $-78$  °C), and allowed to warm to 20 °C. Then it was cooled again to  $-70$  °C and a solution of  $\text{CpFe}(\text{CO})_2\text{I}$  (0.158 g, 0.52 mmol) in  $\text{Et}_2\text{O}$  (5 ml) was added. The resulting red-brown mixture was stirred for 2 h and then filtered. The solvent was removed from the filtrate in vacuum, and the residue was extracted with toluene to give **10c** as a red powder, containing a small amount of  $\text{Et}_2\text{O}$  bound to LiI.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.53$  (s, 5H, Cp), 7.06 and 7.08 (m superimposed, *p*-H, 5-H), 7.19 (‘t’, 2H, H-*m*), 7.32 (‘t’,  $^3J = 7.1$  Hz, 1H, H-6), 7.78 (d,  $^3J = 7.5$  Hz, 1H, H-4), 8.00 (d,  $^3J = 7.6$  Hz, 2H, H-*o*), 8.81 (d,  $^3J = 7.9$  Hz, 1H, H-7).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 86.0$  (s, Cp), 124.4 (d,  $^3J = 7.1$  Hz, C-5), 127.1 (C-7), 127.8 (C-6), 128.2 (partially superimposed, C-4), 128.6 and 129.8 (2C-*o* and 2C-*m*), 130.6 (C-*p*), 139.6 (d,  $^2J = 22.1$  Hz, C-*i*), 151.4 (d,  $^1J = 19.7$  Hz, C-3a), 158.0 (d,  $^2J = 3.7$  Hz, C-7a), 207.5 (d,  $^1J = 46.1$  Hz, C-2), 213.6 (d,  $^2J = 8.1$  Hz, CO).  $^{31}\text{P-NMR}$ :  $\delta = -38.9$  ( $\text{C}_6\text{D}_6$ ),  $-43.5$  (THF-

$d_8$ ). EIMS (70 eV, 140 °C);  $m/e$  (%): 387 (8) [ $\text{M}^+$ ], 332 (21), 331 (92) [ $\text{M} - 2\text{CO}^+$ ], 330 (12), 329 (10), 212 (16), 211 (100) [ $\text{M} - \text{CpFe}(\text{CO})_2^+$ ], 183 (20), 107 (39), 57 (43), 56 (71).

(B)  $\text{CpFe}(\text{CO})_2\text{Cl}$  (536 mg, 2.53 mmol) was added to a solution prepared from **1c** (535 mg, 2.53 mmol) in  $\text{Et}_2\text{O}$  and *t*-BuLi in pentane (1.49 ml, 2.53 mmol). Work-up as above gave 470 mg (48%) of red-brown **10c** contaminated by a small amount of  $\text{CpFe}(\text{CO})_2\text{Cl}$ .  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.58$  (s, 5H, Cp), 7.03–7.18 (m, 2H, H-5, H-*p*), 7.19 (‘t’,  $^3J = 7$ –8 Hz, 2H, H-*m*), 7.30 (‘t’,  $^3J = 8.0$ , 7.1,  $^4J = 1.3$  Hz, 1H, H-6), 7.90 (d br,  $^3J = 7.5$  Hz, 1H, H-4), 8.15 (d br,  $^3J = 7.6$  Hz, 2H, H-*o*), 8.36 (d,  $^3J = 8.0$  Hz, 1H, H-7).  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -44.1$ . Anal. Found: P, 7.2. Calc. for  $\text{C}_{20}\text{H}_{14}\text{FeNO}_2\text{P}$  (387.16): P, 8.00%.

#### 4.3.13. 2-*t*-Butyl-3-( $\eta^5$ -cyclopentadienyliron dicarbonyl)-1,3-benzazaphosphole (**10d**)

A solution of  $\text{CpFe}(\text{CO})_2\text{I}$  (0.320 g, 1.055 mmol) in  $\text{Et}_2\text{O}$  (green) was added at  $-78$  °C to the equimolar amount of **1d**<sub>Li</sub> dissolved in  $\text{Et}_2\text{O}$  (20 ml). The resulting red-brown mixture was allowed to stir for 1 day and then filtered. The solvent was removed in vacuo to give a red powder, characterized by NMR as **10d** containing 1.5 $\text{Et}_2\text{O}$ , bound via LiI. Dissolution in THF and addition of hexane furnished 240 mg (61%) of a brown precipitate of **10d** containing small amounts of  $\text{Et}_2\text{O}$  (LiI).  $^1\text{H-NMR}$  (THF- $d_8$ ):  $\delta = 1.31$  (s, 9H,  $\text{CMe}_3$ ), 4.45 (s, 5H, Cp), 6.94 (‘t’,  $^3J = 7.3$ , 7.4 Hz,  $^4J_{\text{PH}} = 2.6$  Hz, 1H, H-5), 7.10 (‘t’,  $^3J = 7.5$ , 7.6 Hz, 1H, H-6), 7.61 (d,  $^3J = 7.6$  Hz, 1H, H-4), 7.66 (d,  $^3J = 7.9$  Hz, 1H, H-7).  $^{13}\text{C-NMR}$  (THF- $d_8$ ):  $\delta = 31.6$  (d,  $^3J = 5.0$  Hz,  $\text{CMe}_3$ ), 40.3 (d,  $^2J = 19.7$  Hz,  $\text{CMe}_3$ ), 87.2 (s, Cp), 123.3 (d,  $^3J = 5.9$  Hz, C-5), 124.6 (C-7), 125.95 (C-6), 127.5 (d,  $^2J = 20.2$  Hz, C-4), 151.5 (d,  $^1J = 18.0$  Hz, C-3a), 156.0 (d,  $^2J = 7.0$  Hz, C-7a), 215.8 (d,  $^1J = 63.5$  Hz, C-2), 214.8 (d,  $^2J = 9.5$  Hz, CO).  $^{31}\text{P-NMR}$ :  $\delta = -54.0$  (THF- $d_8$ ),  $-52.2$  ( $\text{C}_6\text{D}_6$ ). EIMS (70 eV, 140 °C);  $m/e$  (%): 367 (20) [ $\text{M}^+$ ], 339 (4), 311 (37) [ $\text{M} - 2\text{CO}^+$ ], 191 (55) [ $\text{M} - \text{FeC}_3\text{H}_4^+$ ], 176 (98), 136 (40), 135 (47), 121 (100), 107 (35), 56 (44).  $\text{C}_{18}\text{H}_{18}\text{FeNO}_2\text{P}$  (367.17).

#### 4.3.14. Crystal structure determination

X-ray data of the compounds **1b**<sub>Li</sub>(THF)<sub>3</sub> and **1d** were collected on a STOE-IPDS diffractometer using graphite monochromated Mo- $K_\alpha$  radiation. *Crystal data for 1b*<sub>Li</sub>(THF)<sub>3</sub>: crystal dimensions  $0.4 \times 0.3 \times 0.2$ , orange prisms, space group  $P2_1/n$ , monoclinic,  $a = 11.512(2)$ ,  $b = 23.741(5)$ ,  $c = 16.565(3)$  Å,  $\beta = 92.13(3)$ ,  $V = 4524(1)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.132$  g cm<sup>-3</sup>, 10 826 reflections measured, 5797 were independent of symmetry and 2580 were observed ( $I > 2\sigma(I)$ ),  $R_1 = 0.067$ ,  $wR_2$  (all data) = 0.186, 479 parameters. *Crystal data for 1d*: crystal dimensions  $0.5 \times 0.3 \times 0.2$ , colorless prisms, space group  $Fdd2$ , orthorhombic,  $a = 23.670(5)$ ,  $b =$

29.490(6),  $c = 6.185(1)$  Å,  $V = 4317(1)$  Å<sup>3</sup>,  $Z = 16$ ,  $\rho_{\text{calcd}} = 1.177$  g cm<sup>-3</sup>, 5670 reflections measured, 1635 were independent of symmetry and 1033 were observed ( $I > 2\sigma(I)$ ),  $R_1 = 0.035$ ,  $wR_2$  (all data) = 0.049, 122 parameters.

**Solution and refinement.** The structures were solved by direct methods (SHELXS-86) [37] and refined by full-matrix least-squares techniques against  $F^2$  (SHELXL-93) [38]. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 162623 and 162622 for **1b<sub>Li</sub>(THF)<sub>3</sub>** and **1d**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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