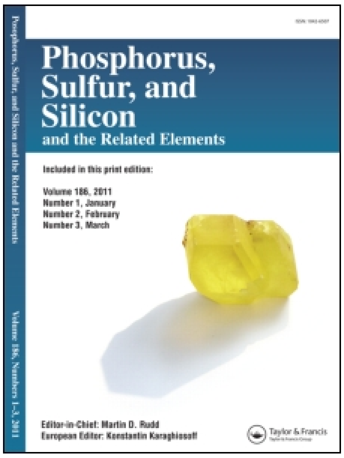

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LITHIUM-1,3-BENZAZAPHOSPHOLIDES: STRUCTURE AND REACTIVITY

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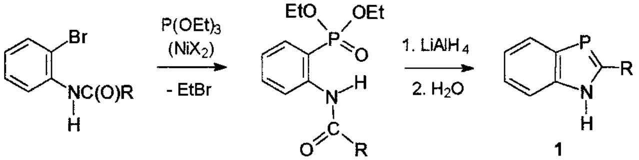
The formation, structure and electrophilic substitution reactions at phosphorus or nitrogen of N-*lithium-1,3-benzazaphospholides is reported.*

Keywords: Complexes; metalation; phosphorus heterocycles

Metalation and complexation of [^{1}H]-1,3-benzazaphospholes, being aza-analogues of benzophospholes or phospha-analogues of indoles, have been very sparingly investigated.[1,2] After the development of a new convenient synthetic access to [^{1}H]-1,3-benzazaphospholes (Eq. 1),[3,4] we studied the lithiation and subsequent substitution reactions.



(1)

Lithiation of [^{1}H]-1,3-benzazaphospholes with Et_2NLi without removing the amine limited the use of the resulting anions on P-alkylation.[1] Even if the amine was removed in vacuo, shifting the metalation equilibrium toward benzazaphospholides, N- or P-substitution

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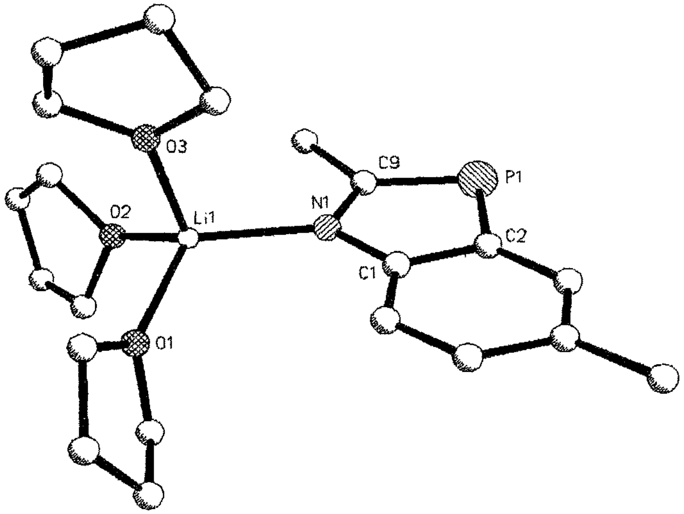
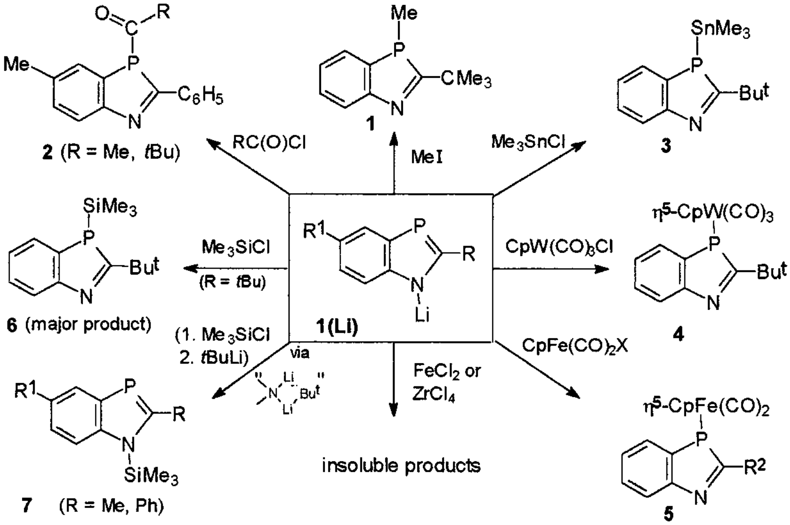


FIGURE 1 Crystal structure of **1(Li)**.

with *a*cyl halides or organometallic halides could not be achieved. Use of *t*-BuLi for the metalation solved this problem. **1(Li)** could be isolated in a pure state, in one case as single crystals, allowing a crystal structure analysis and detection of N-coordination (Figure 1). Nuclear magnetic resonance (NMR) shows only a slight upfield shift of the phosphorus resonance upon lithiation, and the ^{13}C nuclei of the five-membered ring are even deshielded ($\Delta\delta$ 7–10 ppm), but the remaining carbon nuclei of the benzene ring are clearly upfield shifted, indicating transfer of π-electron density from the five- to the six-membered ring.

Lithiation of a tungsten pentacarbonyl complex of **1**, investigated in a parallel study, showed a strong upfield shift of the phosphorus signal and thus much higher phosphido character (π back-donation).[5,6] The benzazaphospholides **1(Li)** behave as ambident anions and react with alkyl, acyl, and soft main group or transition organometallic halides at phosphorus, while silylation takes place at the nitrogen unless the substituent R hinders this attack (Eq. 2).

Any attempts to isolate N-transition metal benzazaphospholides failed. Likewise, attempts to react **1(Li)** with Cp_2ZrCl_2 gave finally **1**. Small ^{31}P-NMR signals in the crude products in the range δ 120–130 ppm gave hints of primary N-substitution, but these products must be extremely sensitive to traces of moisture and perhaps deprotonate even the solvent. The monomer phosphido transition metal derivatives are also sensitive to moisture and air, but not to this extent. Their



(2)

structure follows from typical NMR data, in particular the ^{13}C chemical shifts and *J*(PC), allowing one to clearly distinguish ^{1}H and ^{3}H isomers. The ^{13}C-NMR of P-substituted organometallic derivatives are consistent rather with a localized than with a delocalized π-electron system, but in part the data lie in between those of the this types.[5]

N-Methyl-1,3-benzazaphosphole **8** is lithiated by *t*-BuLi at C2 as detected earlier by trapping with CO_2, Me_3SiCl, and Me_2S_2.[7] But as in **1(Li)**, the site of lithiation and that of attack by electrophiles must not be identicall. The electronegativity of carbon is slightly higher than of phosphorus, but the donor effect of nitrogen may cause an inverse polarity as found in the hydrolysis of isolated P=C–N species. Thus it was not clear if Li was bound to carbon or phosphorus. But recently we could get single crystals and demonstrate that Li is indeed bound to carbon (Figure 2). The P $\cdots$ Li (320, 344 pm) is only slightly shorter than the Van der Waals distance (by 45 and 20 pm) so that there are only weak interactions, if at all. The alkylation with MeI usually prefering attack at phosphorus did not work, but reaction with soft main group and transition organometallic reagents takes place at carbon (Eq. 3). The background is the very strong polarizability of the heteroatom π system and transfer of π-electron density from the five-membered to the six-membered ring, displayed by the carbenelike extreme deshielding of ^{13}C2 ($\Delta\delta$ 90) (J_{PC} doubled) and significant deshielding of ^{31}P ($\Delta\delta \approx 30$) and the other ^{13}C nuclei of the azaphosphole ring.

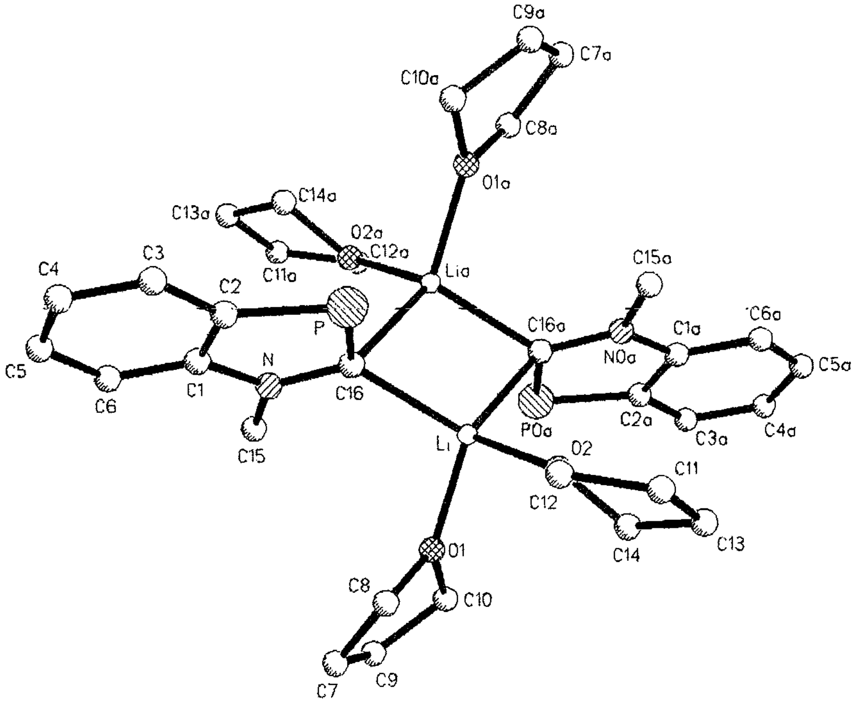
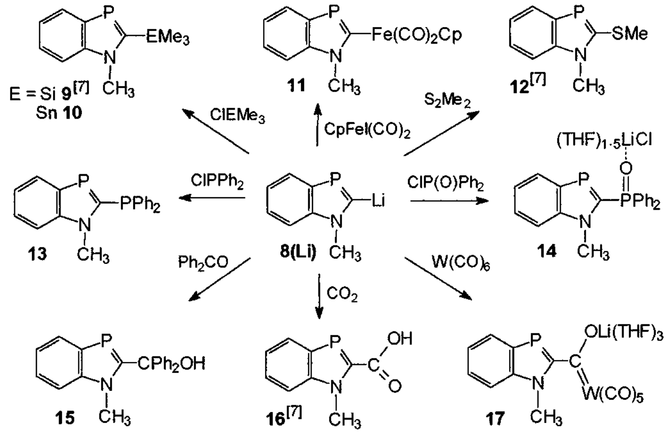


FIGURE 2 Crystal structure of **8(Li)(THF)$_2$**.

Nevertheless, the 2-lithio-benzazaphospholes are useful tools to synthesize functionally substituted benzazaphospholes (Eq. 3),[8] which might find use as ligands or even as hybride ligands with low-coordinate phosphorus and a classical Lewis base center.



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