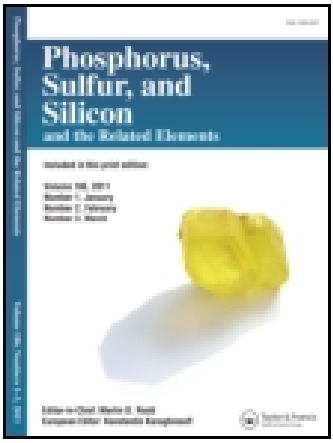

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Novel Benzo-and Pyrido-Anellated 1, 3-Azaphospholes

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Novel Benzo-and Pyrido-Anellated 1, 3-Azaphospholes

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We present the synthesis of OH-functional and bulky N-substituted benzazaphospholes, novel pyrido-azaphospholes, addition versus CH-metalation by tBuLi and reactions with electrophiles yielding a novel asymmetric P,N-heterocyclic ethylene-1,2-bis(phosphine) and phosphino-functional benzazaphospholes for hemilabile σ^3,σ^2–P,P′ coordination.

Keywords Ethylenebis(phosphine) ligands; heterophospholes; organolithium reagents; palladium catalysis; phosphaalkenes

Heterophospholes with planar 6π-electron systems are diagonal relatives of pyrrols, furans, or thiophenes. Like these, they are strongly stabilized by aromatic delocalization but provide at the double-bonded phosphorus atom (σ^2) a neutral coordination site[1] that differs strongly from the coordination behavior of carbanionic or carbene donor centers. Anellation by carbo- or heterocycles[2] provides steric protection and a tool to tune electronic properties at the σ^2-phosphorus donor site. For 1H-1,3-benzazaphospholes (BAPs),[3,4] P-C diagonalogues of indoles, we recently reported a novel convenient synthesis by nickel-catalyzed phosphonylation of 2-bromoanilides and subsequent reductive cyclization with $LiAlH_4$.[5,6] This method has now been applied to the synthesis of σ^2-P biaryl ligands (e.g., 2-(naphth-1-yl)-1,3-benzazaphosphol **1**) as well as, alkoxy- and hydroxy-functional BAPs **2** and **3** (Scheme 1) all characterized by X-ray crystal structure analysis. 2-Pyridyl 1H-1,3-benzazaphosphols could not be obtained in this way.

Attempts to extend the two-step procedure to pyrido-1,3-azaphospholes failed in both steps, the nickel-catalyzed P-C coupling and the reductive cyclization. These heterocycles were then

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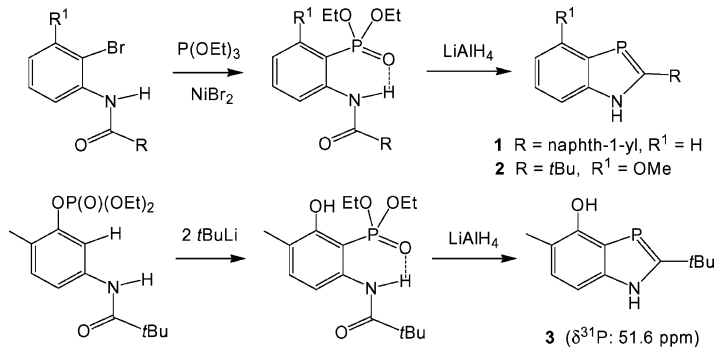
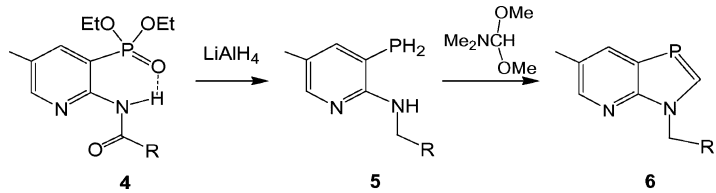


SCHEME 1

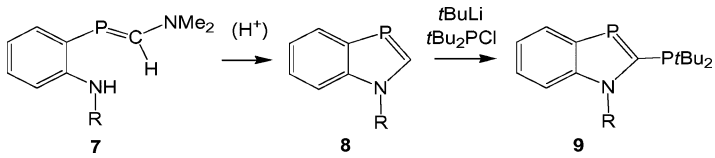
synthesized by $PdCl_2$-catalyzed C-P coupling of amino- or amido-bromopyridines with triethylphosphite (e.g. to **4**, reduction with $LiAlH_4$) to the respective aminophosphinopyridines **5** and condensation with $Me_2NCH(OMe)_2$, proceeding via phosphaalkenes to the azaphospholo[5,4-b]pyridines **6** (Scheme 2). Azaphospholo[4,5-b]pyridines, potential P,N alternative or hybrid ligands with pyridine-N and phosphorus on the same side, are analogously available from 3-amino-2-bromopyridines.



SCHEME 2

The latter route was also applied to the synthesis of novel bulky N-alkyl and N-aryl benzazaphospholes from N-secondary 2-phosphinoanilines and $Me_2NCH(OMe)_2$. The precursor anilines ($2\text{-}BrC_6H_4NHR$) were obtained by Pd-catalyzed amination of o-dibromobenzene (1-adamantyl, mesityl, 2,6-diisopropylphenyl) or reduction of 2-bromoanilides (neopentyl). The cyclization of the phosphaalkenes **7** is strongly hindered by bulky N-aryl groups but can be achieved by catalysis with a small amount of concentrated aqueous hydrochloric acid, which, surprisingly, did not add to the P = C bond but gave the stable BAPs **8**. Metallation of **8** by *t*BuLi is influenced by the steric bulk at nitrogen and strongly retarded for adamantyl and dip substituents. For N-neopentyl and mesityl groups, formation of 2-lithiobenzazaphosphols is preferred, as already described for N-methyl and

N-ethylbenzazaphosphole.[6,7] The 2-lithio-reagents were coupled with tBu$_2$PCl providing 2-di-*tert*-butylphosphino-BAPs **9** (Scheme 3),



SCHEME 3

a novel class of bulky and basic σ^3-P,σ^2-P′ ligands that are intended to stabilize late transition metal catalysts (after the reductive elimination step) by hemilabile coordination of the σ^2-P coordination site to the zero-valent metal. Related catalytic studies are in progress. The coordination strength at σ^2-P is weak for cationic transition metals; even (0.5) [Rh(COD)Cl]$_2$ was not added. However, as shown recently,[8,9] M^0(CO)$_5$ fragments (M = Cr, Mo, W) are bound firmly via strong back-bonding, indicated by the low downfield (Cr) or even upfield (Mo, W) coordination chemical shift of the ^{31}P NMR signals.

Despite the usual preference for CH-metalation of BAPs, tBuLi can also add at the P=C bond. Thus, conversion of 1-neopentylbenzazaphosphole to a novel heterocyclic 1,2-ethylenebis(phosphine) ligand **10** was observed. This can be explained by a normal/inverse

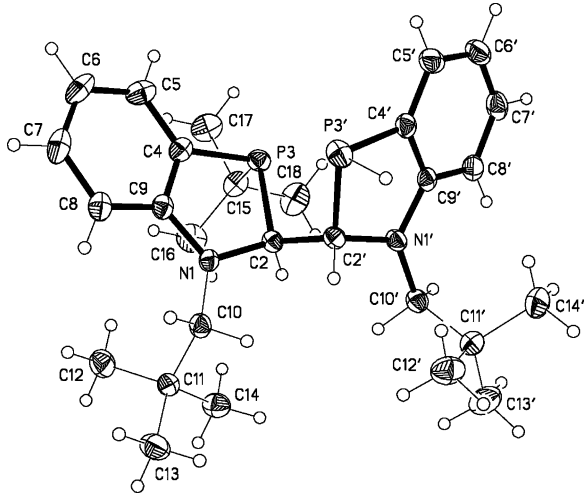


FIGURE 1 Molecular structure of a novel P,N-heterocyclic ethylene bis(phosphine) (*SSSS*-configuration).

two-step addition, first of a semiequivalent of *t*BuLi followed by the primary adduct. The observation of only two doublets in the $^{31}P\{^{1}H\}$ NMR spectra (D_8-THF, δ: –81.48 (d), 5.02 (d), $^{3}J_{PP} = 65.7$ Hz) gives evidence that the reaction proceeds with high diastereoselectivity. X-Ray crystal structure analysis revealed the isomers with *SSSS*- and *RRRR*-configuration (Figure 1).

For the electron-withdrawing pyrido-anellated azaphospholes the addition of *t*BuLi is the preferred reaction. This paves the way to synthesize 2-functionally substituted dihydro-pyrido-azaphospholes as P-asymmetric P, X hybrid ligands.

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