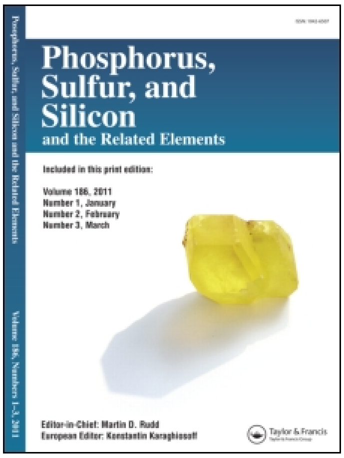

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REACTIVITY OF 1.2-DIPHOSPHINOBENZENE

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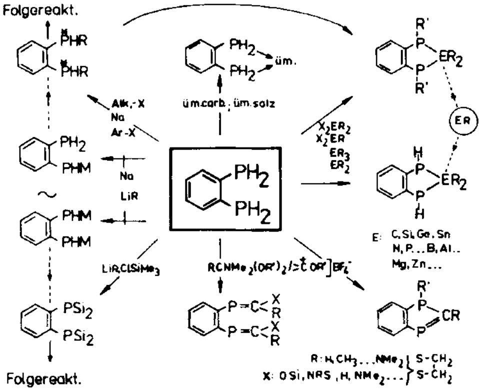
Abstract 1.2-Diphosphinobenzene as a versatile building block and a bifunctional prim. phosphine delivers with various reactants a large number of new P-organo compounds. The possibilities of formation of symm./antisymm. phosphines, benzocondensed P-E-P-heterocycles , 1.3-benzodiphospholes , 1.2-bis-alkylidenebenzenes , other systems with P=C-double bonds and their nmr-data are discussed.

1.2-Diphosphinobenzene(DPB) as a bifunctional,aromatic prim. phosphine is the starting material for a series of new types of phosphorus compounds (Scheme 1.) [1]. The chelating properties of DPB are obvious.With metal carbonyls partial or complete CO-exchange is observed, e.g. $M(DPB)_3$ M = Cr,Mo,W ; $(CO)_3FeDPB$. Reaction with transition metal salts results in formation of the corresponding chelate complexes. The mono- or bis-sodium compound of DPB with alkyl halides give the alkylated products. 1.2-Bis-alkylphosphinobenzenes (R = alk., ar.) are of interest as chelating P-ligands in catalyst systems for homogen. hytrations or may be used after metallation of the sec. phosphines to prepare benzocondensed P-E-P-heterocycles. By repeated metallation of

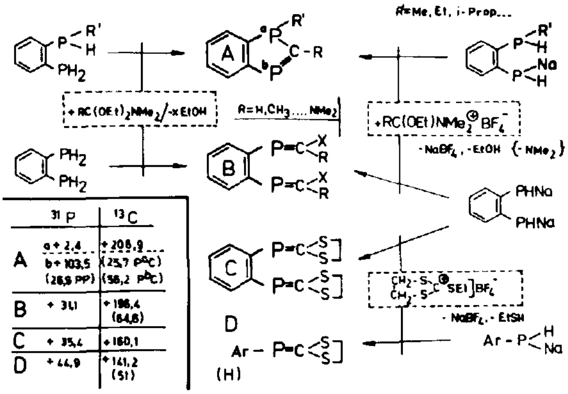
Scheme 1.



DPB with LiBu and reaction with chloro-TMS the di- and tetrasilylated phosphines are obtained, which can also be used for the preparation of P=C-double bond systems or of P-E-P-heterocycles, respectively.

Comparable with the reaction of prim. arom. phosphines with amid acetales[2] also DPB or o-$PH_2C_6H_4PHR$ gives compounds with dicoordinated phosphorus. Compounds of type A,B,C are available more easily by interaction of the sodium derivatives and O- or S-alkyl-carbeniumtetrafluoroborates (Scheme 2.). Besides of o-$C_6H_4(PHNa)_2$ also MPHAr and MPH_2 have been applied in the synthesis of D. P- and C-nmr-data of A,B,C and D are found to appear in the expected region. A side reaction, which we always observed, is the formation of P-alkyl-benzodiphospholes. This is in agreement with results of the interaction between MPHR and carbenium salts.

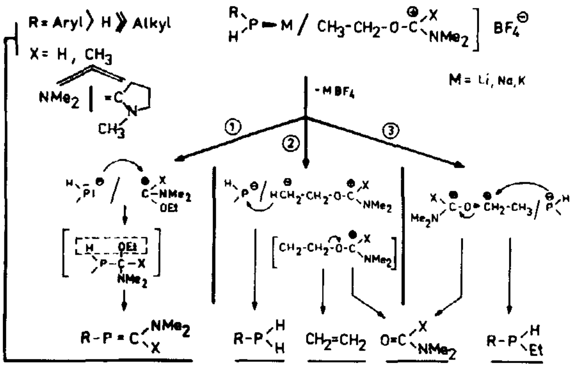
Scheme 2.



	^{31}P	^{13}C
A	a +2,4 b +103,5 (28,9 PP)	+208,9 (25,7 P^aC) (58,2 P^bC)
B	+34,1	+196,4 (64,8)
C	+35,4	+180,1
D	+44,9	+141,2 (51)

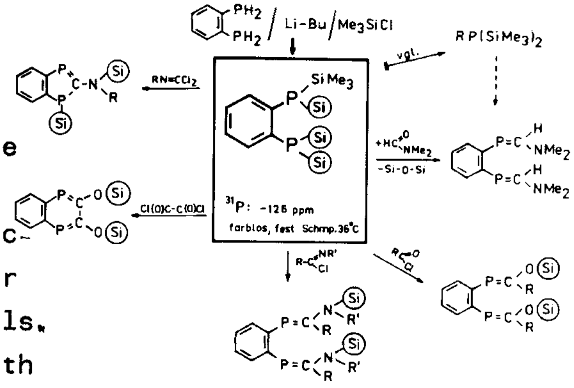
The reaction path is demonstr. in Scheme 3 and is mainly controlled by the basicity of the phosphide anion. MPHAr and also the 1,2-bis-sodiumphosphido-benzene, as well as $NaPH_2$ belong to the group which gives with carbenium salts mainly alkylidene phosphines[3].

Scheme 3.

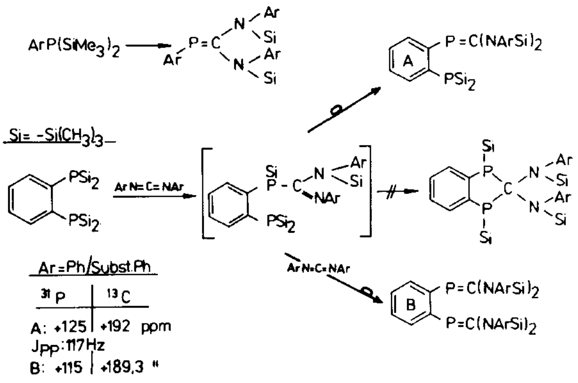


The persilylated DPB again is the starting material for the synthesis of further P=C-double bond systems (Scheme 4.). Generally one should expect this compound to give all those reactions known for $RP(SiMe_3)_2$, such as the interaction with acyl halides, DMF or CS_2 [4], the reaction with $(COCl)_2$ and other halides [5] or also the reaction with RC(NR)Cl or ArN=C=NAr [6,7]. But unfortunately the compounds or reactions do not follow these simple equations and numerous products could be detecdet by means of their P- nmr resonance signals. Best results we got with dimethylformamide, imidchlorides and diarylcarbodiimides. Comparable the Formation of phosphaguanidines the latter ones and persilylated DPB gives satisfying results. After reaction of the compounds in a 1:1 or 1:2 molar ratio leads to A or B . Reaction of the intermediate involving the neighbouring disilylphosphinogroup can be excludet. The 1.3-silylmigration is much faster than a cycloaddition leading to the 1.3-benzodiphospholene.

Scheme 4.

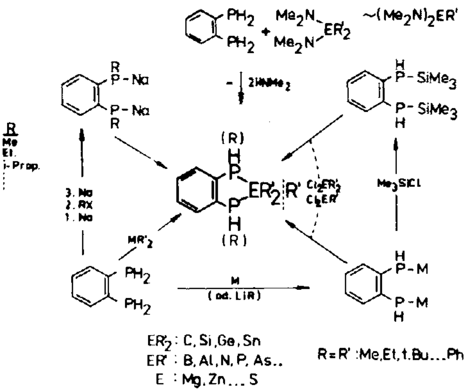


Scheme 5.



Aryl-alkyl-carbodiimides give the simple addition products,which are identical with the compounds formed by solvolysis of A and B. The versatility of DPB with respect to it's high P-H-acidity can be used as such or modified as the alkali metalphosphide or the silylphosphine. Their reactions with different organoelement derivatives is given in Scheme 6. Due to the high inversion barrier of the tervalent phosphorus all these P-E-P-heterocycles exist in form of two diastereomers. The calculated ΔG^{*}_{Tc} values for the diphospholenes are quite comparable with those of the diphospholanes [8]. The activation energy for the conversion of the cis- into the trans-form is less than 20 Kcal/mole.

Scheme 6.



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