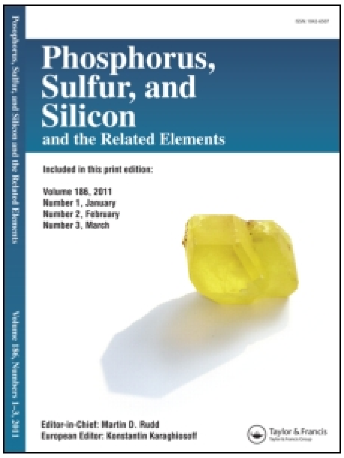

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

1,3-Benzodiphospholes - Synthesis and Reactivity

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To cite this Article Schmidt, H. , Issleib, K. and Leissring, E.(1990) '1,3-Benzodiphospholes - Synthesis and Reactivity', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 355 — 358

To link to this Article: DOI: 10.1080/10426509008038978

URL: http://dx.doi.org/10.1080/10426509008038978

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 355–358
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1.3-BENZODIPHOSPHOLES - SYNTHESIS AND REACTIVITY

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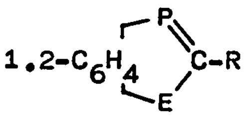
Abstract Methods of the preparation and the reaction behaviour of 1.3-benzodiphospholes as well as their nmr spectroscopic data are discussed

1.3-Benzo-element-phospholes,  (E: NR_2,O,S) are considered to be 10π-electron aromatic systems[1-3].

For 2-amino-1.3-benzodiphospholes (E: PR, R: NR_2) with probably non-planar tricoordinate phosphorus from nmr data aromatic stabilization is excluded[4].

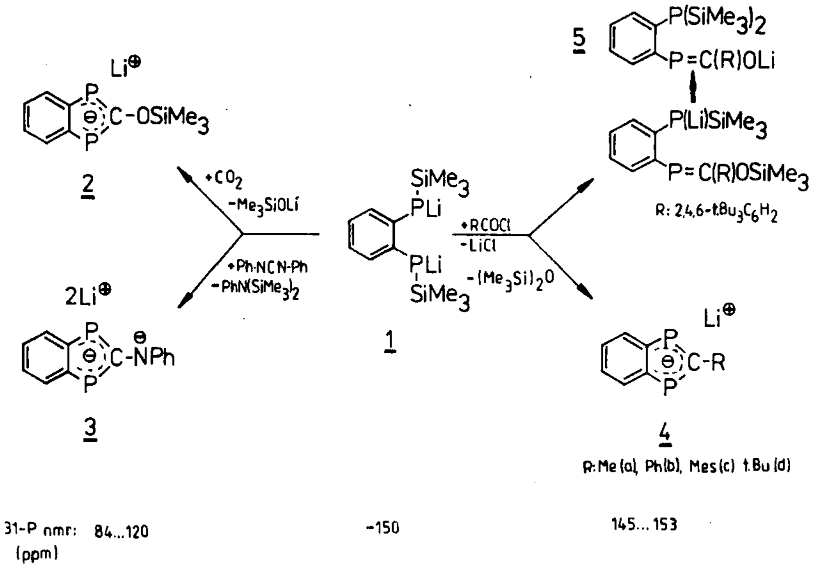
We wish to report the synthesis of 1.3-benzodiphospholyl anions, their reactions with electrophiles to form 2-organo-substituted 1.3-benzodiphospholes and the dicussion of the 31-P nmr spectroscopic data of both types of heterocycles.

Starting with the diphosphide **1** the insertion of heterocumulenes (CO_2[5] or Ph-NCN-Ph[6]) and electrophilic attack of carboxylic acid chlorides[7], respectively, yield in formation of 1.3-benzodiphospholyl anions **2**-**4** (Scheme 1).

One of the driving forces of these cyclization reactions is probably the installation of a conjugated 10π-electron aromatic system, as it is expected from MNDO calculations[8].

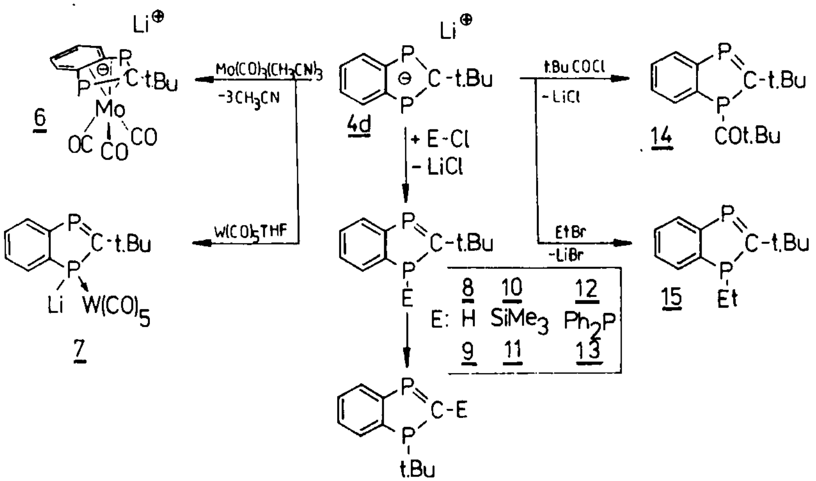
With the bulky 2.4.6-t.Bu_3-C_6H_2-COCl cyclization fails and after transsilylation the 1.3-oxaphosphaallylic anion **5** is formed.

For benzodiphospholyl anions a complete charge delocalization between both phosphorus atoms is demonstrated by 31-P resonances in the region of 145 to 153 ppm.



SCHEME 1

1,3-Benzodiphospholyl anions can act as mono- or pentahapto ligands (Scheme 2).



SCHEME 2

In the η^5-coordinate complex 6 the ligand shows the typical negative coordination shift ($\Delta\delta$ (4d/6): -126 ppm), known from side-on coordinate phosphaalkenes. The anionic phosphorus atom in 7 interacts as σ-donator with the P=C-moiety. Alcoholysis of anions like 4d fails. This unexpected result, also found in phosphindolyl anion chemistry[9], demonstrates a low basicity for both "phosphides". Hydrogen chloride protonates 4d but the obtained 2-t.Bu-1.3-benzodiphosphole 8 is stabilized by a [1,2]-substituent rearrangement to give the isomer 9. Similar dyotropic substituent migrations are observed after electrophilic attack of Me_3SiCl (10/11) or Ph_2PCl (12/13).

Reaction of 4d with alkyl or acyl halides results in stable 1.3-benzodiphospholes 14 and 15.

In consideration of the well known influence of the π-donor abilities of substituents at the P=C-moiety on the 31-P shifts of the σ^2-phosphorus it is expected that in benzodiphospholes like 14 and 15 the interaction between the σ^3-phosphorus lone pair and the C_6H_6-P=C-R substructure is weak and aromatic stabilization does not play a dominant role. Therefore it is not surprisingly, the chemistry of 1.3-benzodiphospholes is determined by non-aromatic behaviour. Electrophilic (HCl, MeOH) as well as nucleophilic addition (LiBu) yield in formation of 2.3-dihydrobenzodiphospholes 16-19 (Scheme 3).

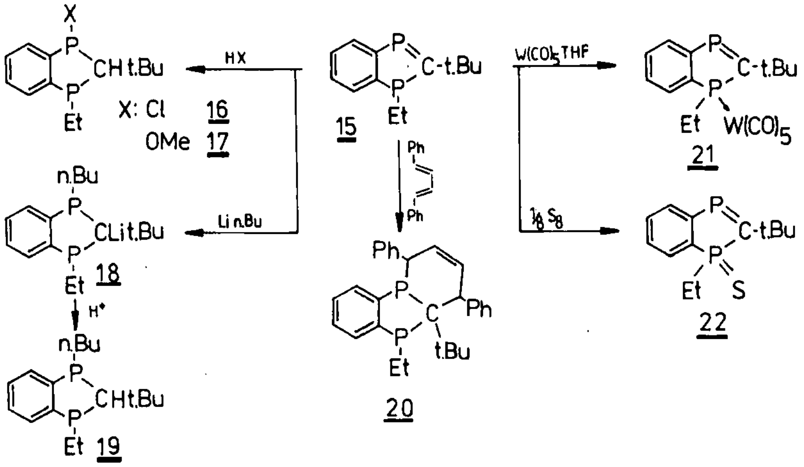
In spite of three chiral centres in these compounds, 16 exists in two diastereoisomers and 17-19 in one isomer, only.

Unlike 1.3-benzazaphospholes, with 1.3-dienes 15 undergoes Diels-Alder reaction to yield 20.

In case of a possible alternative interaction of two- and three-coordinate phosphorus against sulfur or $W(CO)_5$ the latter one acts as the nucleophilic centre (21, 22).

Summarized the reaction behaviour of 2-organo substituted 1.3-benzodiphospholes shows strong similarities to acyclic non-donor stabilized phosphaalkenes. The use of the σ^3-phosphorus lone pair for bonding (21, 22) influences the

31-P shift of the two-coordinate phosphorus insignificantly. This emphasizes the fact that the electronic interaction between this lone pair and the 8π-electron subunit, if it really exists, is weak. From MNDO calculations[8] instead of n/π interaction a σ/π stabilization between the PH-bond and the 8π-electrons is to assume.



SCHEME 3

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