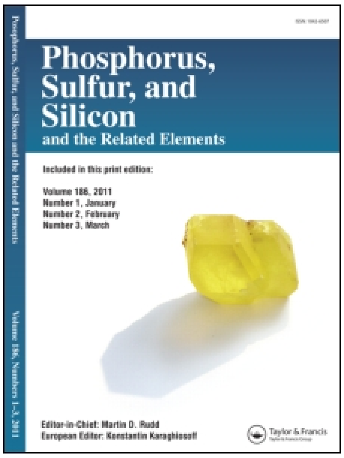

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Novel chain and ring polyphosphorus compounds

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To cite this Article Baudler, Marianne(1983) 'Novel chain and ring polyphosphorus compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 57 — 60

To link to this Article: DOI: 10.1080/03086648308075966

URL: http://dx.doi.org/10.1080/03086648308075966

Phosphorus and Sulfur, 1983, Vol. 18 pp. 57-60
0308-664X/83/1801-0057/$18.50/0

NOVEL CHAIN AND RING POLYPHOSPHORUS COMPOUNDS

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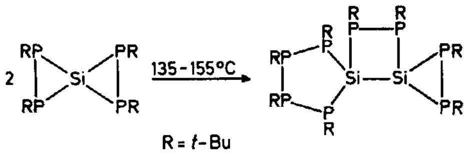
Abstract Compounds with a skeleton of phosphorus chains or rings have been rare until recently, as they are in general highly reactive. Nevertheless, considerable progress has been achieved in this field lately, especially regarding three-membered phosphorus ring compounds, metalated phosphorus hydrides and polycyclic organophosphanes.

THREE-MEMBERED PHOSPHORUS RING COMPOUNDS

In recent years, numerous triorganocyclotriphosphanes have become accessible as pure substances on various synthetic routes.[1] However, the reaction behaviour of these compounds has only scarcely been studied.

We have found that triorganocyclotriphosphanes, $(RP)_3$ (R = i-Pr, t-Bu), react with metal carbonyl-tetrahydrofuran complexes, $M(CO)_5THF$ (M = Cr, W), yielding the novel mononuclear and binuclear cyclotriphosphane-carbonylmetal complexes $(RP)_3M(CO)_5$ (R = i-Pr, t-Bu; M = Cr, W) and $(i\text{-}PrP)_3[Cr(CO)_5]_2$, respectively.[5] Their structures have been elucidated by ^{31}P-NMR spectroscopy and X-ray structure analysis. The P_3 ring functions as a 2- or a 4-electron donor, respectively, and it also behaves as a π-acceptor comparable to Ph_3P.[2]

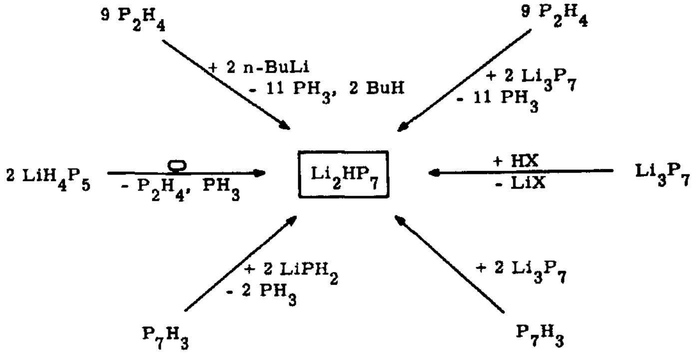
The first spirocyclic phosphorus three-membered ring compound $(t\text{-}BuP)_2Si(t\text{-}BuP)_2$ has been synthesized by cyclocondensation of K(t-Bu)P-P(t-Bu)K with silicon tetrachloride. The crystalline compound is formed as a mixture of two isomers, which can be isolated separately and which differ from each other in the relative arrangement of the trans-oriented tert-butyl groups at the two three-membered rings.[3] By heating $(t\text{-}BuP)_2Si(t\text{-}BuP)_2$ for one hour at about 140°C, a dimerization occurs yielding the new silaphosphane $(t\text{-}BuP)_8Si_2$. In this dispirocyclic compound a three-, a four- and a five-membered ring are linked by two adjacent silicon atoms.[4]



The synthesis of the spirocyclic compound (t-BuP)$_2$C(t-BuP)$_2$ has also been achieved. As an intermediate in the reaction of K(t-Bu)P-P(t-Bu)K with CCl$_4$, the diphosphirane (t-BuP)$_2$CCl$_2$ has been identified. Like (t-BuP)$_2$Si(t-BuP)$_2$ the carbon spirocycle is also formed as a mixture of two steric isomers, of which the more stable one could be isolated as colorless crystals.[5] According to the results of X-ray structure analysis, the endocyclic bond angles are 72° on carbon and 54° on phosphorus.

METALATED PHOSPHORUS HYDRIDES

The reaction of P_2H_4 with n-BuLi or $LiPH_2$ yields the polyphosphide Li_3P_7 as the final product.[1] Before this compound precipitates, a red-orange oil appears which consists essentially of Li_2HP_7. Other intermediates of the reaction are the highly reactive monolithiated phosphanes LiH_3P_2, LiH_4P_3, and LiH_4P_5, which could be identified and structurally characterized by ^{31}P-NMR spectroscopy. For instance, LiH_4P_5 is the monolithium salt of cyclopentaphosphane, P_5H_5. Dilithium hydrogen heptaphosphide is also formed in various reactions and



can be isolated in the pure state. Like dihydrobullvalene, the P_7H^{2-} ion is capable of a degenerate Cope rearrangement between two valence tautomers.[1]

At room temperature Li_2HP_7 decomposes with the formation of dilithium hexadecaphosphide, which has been characterized by its ^{31}P-NMR spectrum.[1] This polyphosphide is also obtained by the reaction of white phosphorus with $LiPH_2$ (1.92:1) in boiling tetrahydrofuran.[6]

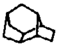
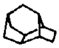
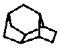
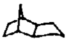
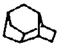
Li_3P_7 reacts with methylbromide (1:2) to give $LiMe_2P_7$, which can be converted by acetylacetone into dimethyl-heptaphosphane(3), P_7Me_2H. With Cl(t-Bu)P-P(t-Bu)Cl a cyclocondensation takes place yielding $Li(t\text{-}Bu)_2P_9$, which subsequently gives $P_9(t\text{-}Bu)_2H$.

POLYCYCLIC ORGANOPHOSPHANES

The structures of organo-substituted polyphosphorus compounds with condensed ring systems constitute the decisive key to understanding the complex structures of the polycyclic hydrides P_nH_{n-2m} ($n \geqq 4$, $m = 1-7$), which because of their low solubilities and poor crystallizability have not yet proved amenable to NMR or X-ray investigation. The breakthrough in the production of polycyclic organophosphanes on a preparative scale came with the discovery of directed and generally applicable synthetic methods.[1,7]

A series of novel organophosphanes with 9 or more than 9 P atoms has been synthesized and structurally characterized either by ^{31}P-NMR spectroscopy or by X-ray structure analysis. Of particular interest are the triorgano-nonaphosphanes, P_9R_3, because of their marked thermal stability and tendency towards formation. According to the spectroscopic findings, these compounds possess a P_9-skeleton analogous to that of the hydrocarbon deltacyclane.[8] Our results to date[7,9] are summarized in Table I. Of particular interest are the findings in the series P_9R_5, where besides the phosphorus skeleton with a structure analogous to noradamantane,[1] an additional constitutional isomer of lower relative frequency could be detected, whose structure is analogous to the hydrocarbon brexane. The compounds $P_{10}R_6$ so far prepared do not possess a skeleton analogous to adamantane but exhibit a P_{10}-framework, which is built up by a norbornane unit and a five-membered ring linked by a common zero bridge. The polycyclic organophosphanes of the formula $P_{10}R_4$, $P_{11}R_5$, $P_{12}R_4$, and $P_{13}R_5$ show very similar properties because of their extremely close structural relationships. All the compounds are formally derived from a central P_8- and P_9-group, respectively, by one or two additional two-atom bridges, giving new five-membered rings and therewith structures of relatively high thermodynamic stability.

TABLE I New polycyclic organophosphanes

P_nR_m / R	P_9R_5 a	P_9R_5 b	$P_{10}R_6$	$P_{10}R_4$	$P_{11}R_5$	$P_{12}R_4$	$P_{13}R_5$
Me							
Et							
i-Pr							
t-Bu							

a: Isomer mit noradamantan-analogem Gerüst
b: Isomer mit brexan-analogem Gerüst

Acknowledgement This work was supported by the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Fonds der Chemischen Industrie.

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