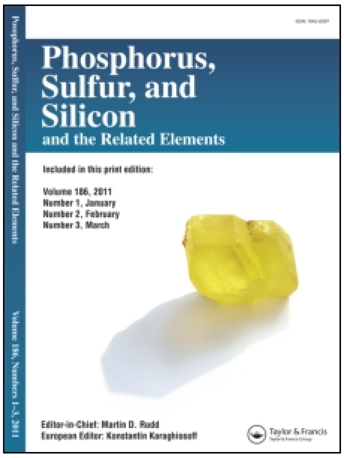

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Polyphosphorus Compounds: Recent Preparative and Structural Investigations

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POLYPHOSPHORUS COMPOUNDS: RECENT PREPARATIVE AND STRUCTURAL INVESTIGATIONS

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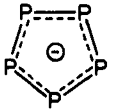
Abstract Several new types of alkalipolyphosphides (metalated phosphorus hydrides), three-membered phosphorus ring compounds, and polycyclic organophosphanes have been synthesized and structurally characterized by means of ^{31}P NMR spectroscopy.

POLYPHOSPHIDES WITH ISOLATED ANIONS

The reaction of P_2H_4 with n-BuLi or $LiPH_2$ afforded the polyphosphide Li_3P_7.[1] As has recently been found by ^{31}P NMR spectroscopic monitoring, several lithium hydrogenpolyphosphides, such as LiH_8P_7, LiH_4P_7, LiH_5P_8, $Li_2H_2P_{14}$, LiH_2P_7, Li_2HP_7, and a compound $Li_xH_yP_z$ not yet identified, are formed as intermediates. Most of these compounds could be obtained pure at low temperature.[2]

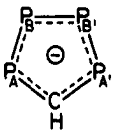
In the decomposition of Li_2HP_7[3,4] at room temperature as well as in the nucleophilic cleavage of white phosphorus with $LiPH_2$ or sodium the polyphosphides $M^I_2P_{16}$,[4,5] $M^I_3P_{21}$,[6] $M^I_4P_{26}$,[7] and $M^I_3P_{19}$[8] are formed. Their P_n^{m-} anions are conjuncto-phosphanes built up by P_9^- end groups and P_7^- or P_5^- middle groups.

The reaction of white phosphorus with sodium in boiling diglyme afforded small amounts of the compounds NaP_5, NaP_4CH, and NaP_3CH_2, whereas with lithium dihydrogenphosphide in tetrahydrofuran LiP_5 is formed beside other polyphosphides.[9] The pentaphosphacyclopentadienide anion, the tetraphosphacyclopentadienide ion, and the triphosphacyclobutenide ion are rings with unsubstituted P atoms of coordination number two that are stabilized by mesomerism.



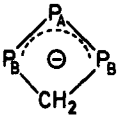
$[Na(diglyme)_x]^+$
$[Li(THF)_x]^+$

$\delta(^{31}P) = +470{,}2$ (sharp singlet)



$[Na(diglyme)_x]^+$

$\delta_A = +362{,}1, \delta_B = +355{,}1$
$J_{AB} = J_{A'B'} = -484{,}0$ Hz
$J_{BB'} = -505{,}4$ Hz
$J_{AA'} = -53{,}3$ Hz
$J_{AB'} = J_{A'B} = -3{,}6$ Hz

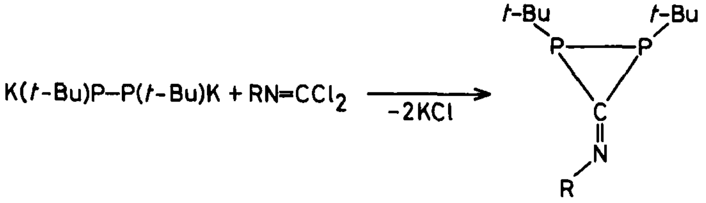


$[Na(diglyme)_x]^+$

$\delta_A = +272{,}0$
$\delta_B = +262{,}9$
$J_{AB} = -484{,}7$ Hz

THREE-MEMBERED PHOSPHORUS RING COMPOUNDS

In recent years numerous three-membered phosphorus heterocycles could be prepared.[3] Following the synthesis of diphosphiranes and methylenediphosphiranes[3] it has been found that diphosphiraneimines are also stable enough for existence and isolation. The decisive factor for their stabilization is an aryl substituent with one bulky group in o-position to the nitrogen beside tert-butyl groups on the phosphorus atoms.



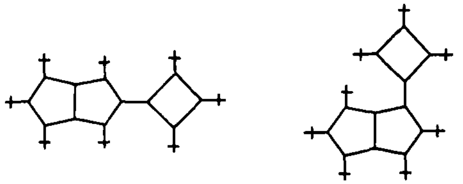
$R = 2{,}4\text{-}t\text{-}Bu_2C_6H_3$ $\delta(^{31}P) = -130{,}3, -172{,}1$ (26°C)
$^1J(PP) = -38{,}1$ Hz
$R = 2\text{-}t\text{-}BuC_6H_4$ $\delta(^{31}P) = -129{,}9, -170{,}8$ (25°C)
$^1J(PP) = -38{,}3$ Hz

Starting from functionalized cyclotriphosphanes of the type $(PR)_2PX$ ($X = SnMe_3$, Cl) the first 1,1'-bicyclotriphosphane $(t\text{-}BuP)_2P\text{-}P(t\text{-}BuP)_2$ has been synthesized.[10] Of the two possible configurational isomers, which differ from each other in the relative arrangement of the trans-oriented tert-butyl groups at the two three-membered rings, the sterically more favorable all-trans isomer (C_2 symmetry) is present as an enantiomeric pair. Thermolysis of this compound (128°C) leads not only to disproportionation, but also to isomerization resulting in 2,3,4,6-tetra-tert-butylbicyclo[3.1.0.]hexaphosphane that has already been described earlier.[11]

POLYCYCLIC ORGANOPHOSPHANES

The proved syntheses of polycyclic organophosphanes by dehalogenating $RPCl_2$ with magnesium in the presence of PCl_3 or of white phosphorus[3] produce the higher members of the series P_nR_{n-2} and P_nR_{n-4} with n > 10 only in very low yields. Therefore, a new approach involving the thermolytic dimerization of smaller bicyclic compounds has been developed. Thus, heating of the tert-butyl substituted bicyclo[3.1.0]hexaphosphane resulted in good yields of the dodecaphosphane $(t\text{-}Bu)_5P_8\text{-}P_4(t\text{-}Bu)_3$ which is formed as a mixture of two constitutional isomers.

$$2\ P_6(t\text{-}Bu)_4 \xrightarrow{\Delta} P_{12}(t\text{-}Bu)_8$$



As has been shown in our previous work,[3] the nonaphosphanes P_9R_3 have a P_9 skeleton analogous to the hydrocarbon deltacyclane and are formed as mixtures of two configurational isomers which differ in their spatial arrangements of the substituent on P^5. Recently we have found[12] that when crystallizing $P_9(t\text{-}Bu)_3$ exclusively the isomer of higher frequency precipitates, which on heating in solution is retransformed into the isomeric mixture. The dominating process therein is the change of configuration at P^5;

besides a quasi synchronous inversion occurs at P^8 and P^9 and possibly also at P^5,P^8,P^9 as is evident from the 2-D ^{31}P NMR exchange spectrum. The same inversion processes also take place in P_9Et_3 even though at a lower rate.

Polycyclic organophosphanes are generally susceptible to attack by atmospheric oxygen - especially in solution. As could be demonstrated by the preparation and structural characterization of the monoxides $P_6(t\text{-}Bu)_4O$ and $P_7(t\text{-}Bu)_5O$,[13] the oxygen reacts initially with exocyclic addition to the intact polycyclophosphane.

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