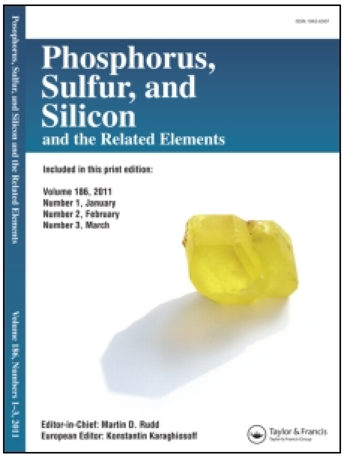

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NOVEL REACTIONS OF PENTACOORDINATE PHOSPHORUS SYSTEMS DERIVED FROM PYROCATECHOL

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Monocyclic chlorophosphoranes **1** and **2** have been used as models for investigations of nucleophilic displacement reactions at the pentacoordinate phosphorus atom. The chlorine ligands of **1** and **2** can be exchanged by nucleophiles under very mild conditions. The synthesis of the pentacoordinate phosphorus systems **4** and **5** via the reactions of **1** and **2** with a variety of nucleophiles is demonstrated. Special attention is paid to the reactions of chlorophosphoranes with such nucleophiles as organic phosphorus acids and thiocyanates.

INTRODUCTION

Our interest in nucleophilic substitution at the pentacoordinate phosphorus atom represents part of a more general concern with the chemistry of penta- and hexacoordinate phosphorus systems.

Nucleophilic displacement of pentacoordinate phosphorus compounds led to a variety of ligand-exchange reactions of considerable synthetic and mechanistic value.[1-5] Our previous work on mechanism of nucleophilic substitution at phosphoranes containing one or two catechol bidentate ligands proved that this process proceeds via addition-elimination mechanism with the formation of hexacoordinate intermediates.[6,7] It will now be demonstrated that the nucleophilic exchange of ligands in monocyclic chlorophosphoranes constitutes a very convenient route to novel phosphoranes. The synthesis of these phosphoranes has raised interesting questions about their structure and equilibria with tetra- and hexacoordinate phosphorus species. Furthermore these phosphoranes are showing promise as useful reagents in organic synthesis. The reactivity patterns of chlorophosphoranes **1** and **2** will be illustrated by discussing their reactions with organophosphorus acids and thiocyanates.

SYNTHESIS OF MONOCYCLIC PENTACOORDINATE PHOSPHORUS COMPOUNDS

In our search for convenient models for ligand exchange we turned our attention towards highly reactive and readily available chlorophosphoranes **1** and **2**. They could be prepared from corresponding P^{III} compounds by the action of elemental chlorine.[8,9]

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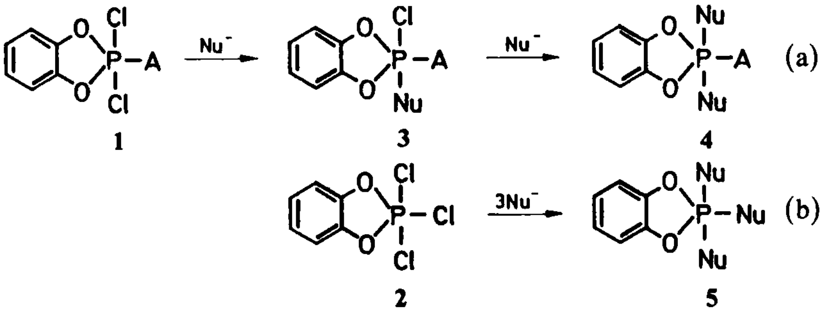


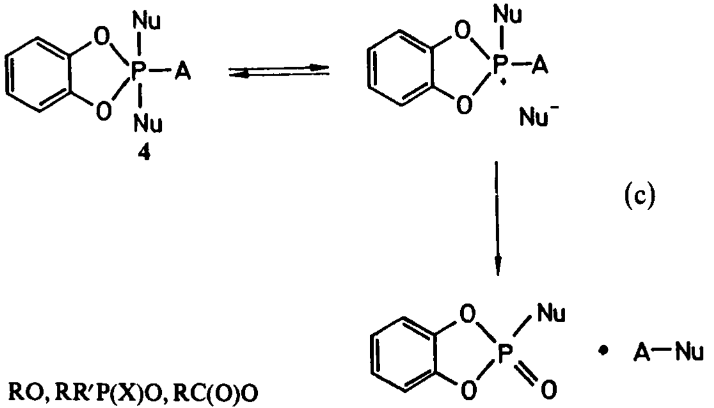
A = RO, R, RR′P(X)O
Nu = SCN, N_3, CN, RR′P(X)O
X = O, S, Se

SCHEME 1

We have found that chlorines of dichlorophosphoranes **1** and trichlorophosphorane **2** undergo ligand exchange under very mild conditions with a variety of nucleophiles which leads to novel monocyclic pentacoordinate phosphorus compounds **4** and **5** according to Scheme 1. In some cases selective exchange of one chlorine atom in **1** which results in the formation of system **3** was possible.

Therefore the reactions (a) and (b) could be considered as a general synthetic approach towards monocyclic phosphoranes containing either different or the same substituents at phosphorus.[10,11]

Some of the phosphoranes **4** undergo thermal decomposition.



A = RO, RR′P(X)O, RC(O)O
Nu = Cl, Br, I, SCN, RR′P(X)O
X = O, S, Se

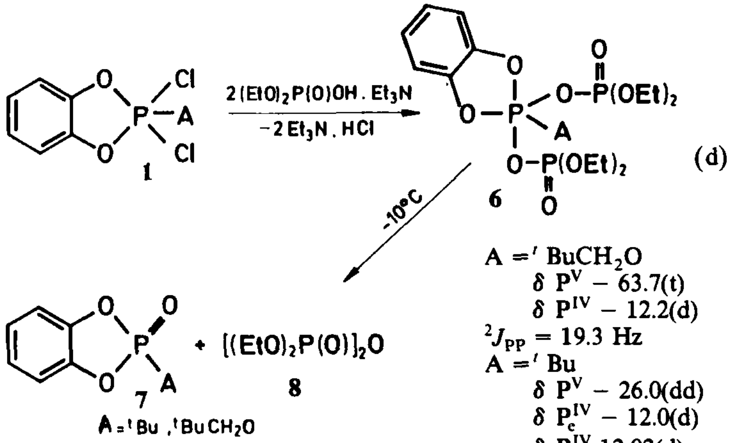
The reaction sequence involving the formation of **4** and their decomposition (c) constitutes an excellent method of the preparation of synthetically interesting A—Nu compounds.[10,12]

The reaction of **1** and **2** with nucleophiles such as organophosphorus acids and thiocyanates are of particular interest.

REACTIONS OF 1 AND 2 WITH ORGANOPHOSPHORUS ACIDS

The dichlorophosphoranes **1** react easily with diethylphosphoric, phosphorothioic and phosphoroselenoic acid. In all cases the course of the reactions can be monitored by F.T. ^{31}P NMR spectroscopy.[11]

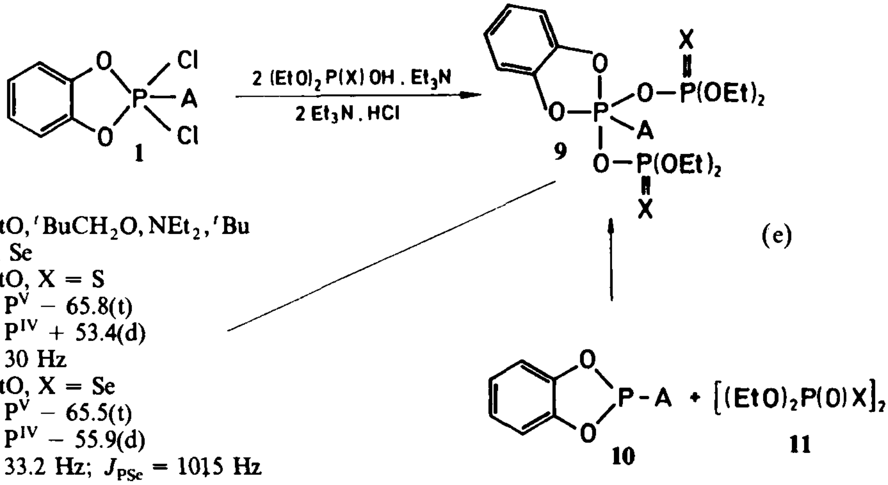
The reactions of **1** with diethyl phosphoric acid in the presence of triethylamine at −100°C results in the formation of thermally labile phosphoranes **6**. At about −10°C clean decomposition of **6** into the corresponding phosphates **7** and pyrophosphates **8** is observed.



(d)

A = $^tBuCH_2O$
δ P^V – 63.7(t)
δ P^{IV} – 12.2(d)
$^2J_{PP}$ = 19.3 Hz
A = ^tBu
δ P^V – 26.0(dd)
δ P_e^{IV} – 12.0(d)
δ P_a^{IV} 12.02(d)
$^2J_{PP_e}$ = 45.2 Hz; $^2J_{PP_a}$ = 39.3 Hz
A = EtO, $^tBuCH_2O$, NEt_2, ^tBu

The same type of phosphoranes **9** have been obtained in the reactions of **1** with diethyl phosphorothioic or phosphoroselenoic acid. The structures of **9** have been supported by independent synthesis involving Arbuzov reaction between the corresponding tricoordinate phosphorus esters **10** and disulphides or diselenides **11**.[13]



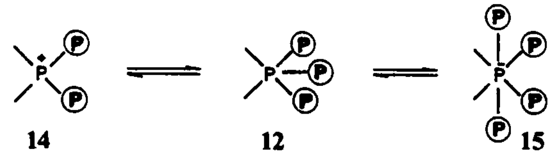
(e)

A = EtO, $^tBuCH_2O$, NEt_2, ^tBu
X = S, Se
A = EtO, X = S
δ P^V – 65.8(t)
δ P^{IV} + 53.4(d)
$^2J_{PP}$ = 30 Hz
A = EtO, X = Se
δ P^V – 65.5(t)
δ P^{IV} – 55.9(d)
$^2J_{PP}$ = 33.2 Hz; J_{PSe} = 1015 Hz

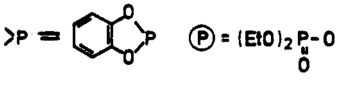
^{31}P NMR data clearly indicate the pentacoordinate nature of the compounds **6** with two phosphoryl ligands as well as the compounds **9** with two thiophosphoryl or selenophosphoryl ligands. These data do not give however an unambiguous answer concerning the positions of the ligands involved in TBP. In view of a lack of spectral differences between two phosphoryl ligands in **6** (A = EtO, ^{t}BuCH$_2$O, NEt$_2$) and in **9** (A = EtO, ^{t}BuCH$_2$O, NEt$_2$, ^{t}Bu) one could either assume that both are situated in the equatorial positions, or both might have chemical shifts which are indistinguishable under the experimental conditions. An alternative is that a fast, on the NMR time scale, ligand reorganization takes place. It is noteworthy that introduction of a ligand of low apicophilicity such as ^{t}Bu group to the phosphorane **6** results in the non-equivalency of phosphoryl ligands. It is most likely that this observation is due to slow reorganization of the ligands.

The reaction of trichlorophosphorane **2** with diethyl phosphoric acid at −70°C provides a route to the phosphorane **12** bearing three phosphoryl ligands.[11]

^{31}P NMR investigations of the above reaction at −100°C have shown the existence of equilibrium between neutral covalent phosphorane **12** and its ionic forms in CH$_2$Cl$_2$—CH$_3$CH$_2$Cl solution. This equilibrium depends strongly on temperature (see Figure 1). At −100°C it is shifted towards tetracoordinate **14** and hexacoordinate **15** phosphorus species, while at −70°C the only detectable species is the phosphorane **12**. ^{13}P NMR data concerning the structure of the discussed tetra-, penta- and hexacoordinate phosphorus compounds are unequivocal (see Figure 1).



δ P^{IV+} − 25.3 (t)	δ P^{V} − 69.7 (q)	δ P^{VI} − 144.7 (qt)
δ P^{IV} − 16.0 (d)	δ P^{IV} − 13.5 (d)	δ P^{IV} − 14.5 (d)
$^2J_{PP}$ = 33.5 Hz	$^2J_{PP}$ = 21.2 Hz	$^2J_{PP}$ = 32 Hz



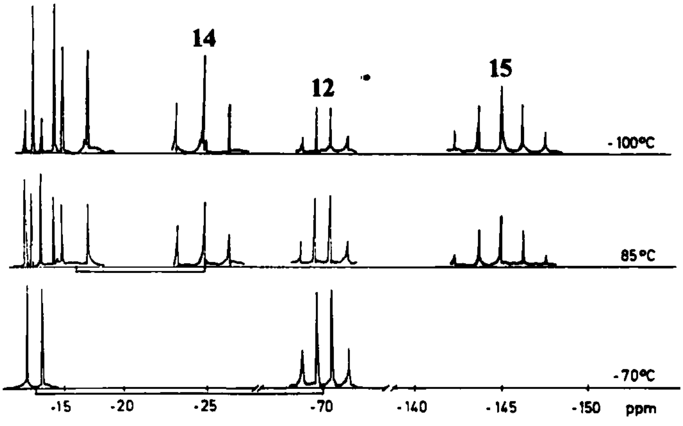
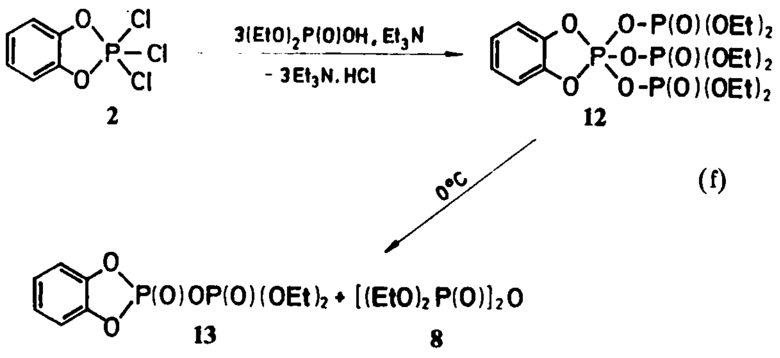


FIGURE 1 The proton-decoupled ^{31}P NMR spectrum of a mixture of **2** and diethyl phosphoric acid at different temperatures.

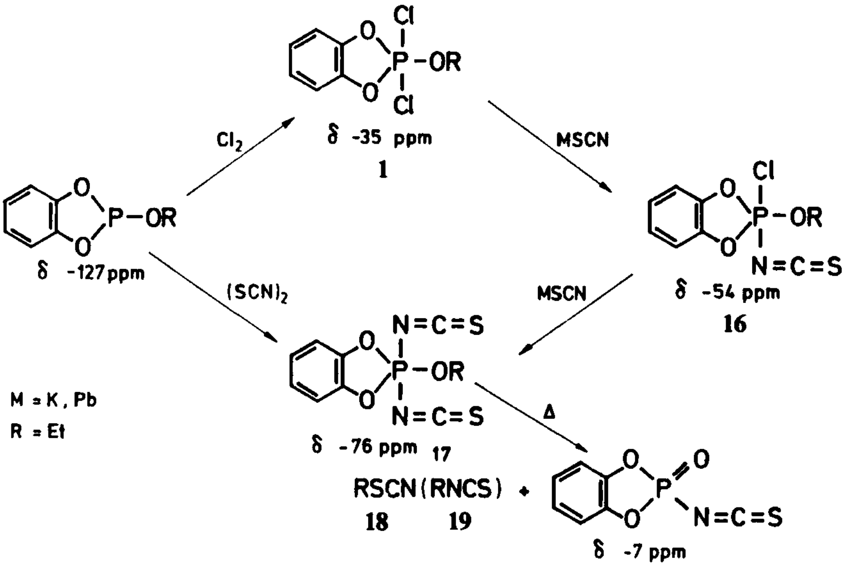


(f)

The phosphoranes **6**, **9** and **12** as well as hexacoordinate compound **15** constitute a new type of phosphorus oligomers containing one central P^V or P^{VI} atom and two, three or four adjacement P^{IV} atoms linged by the oxygen bridge.

REACTIONS OF 1 WITH THIOCYANATES

Isothiocyanatophosphoranes **17** have been synthesized under very mild conditions (−70°C) by stepwise ligand substitution of the corresponding dichlorophosphoranes **1** using a suitable thiocyanate.[10] Lead thiocyanate is superior to the potassium or trimethylsilyl thiocyanates due to its higher reactivity. Formation of the chloroisothiocyanatophosphoranes **16** as intermediates was detected by ^{31}P NMR spectroscopy. We have shown also the possibility of preparation of **17** by addition of thiocyanogen $(SCN)_2$ to tricoordinate phosphorus compounds **10**. Alkoxy-isothiocyanatophosphoranes **17** decompose in excellent yield into the corresponding alkyl thiocyanates **18** and alkyl isothiocyanates **19**, thus providing a new and



SCHEME 2

attractive method for the synthesis of **18** and **19** including optically active ones.[10,14] The application of the method is illustrated by Scheme 2. Formation of chiral **18** and **19** is accompanied by the inversion of configuration at carbon atom. This process is also highly stereoselective.

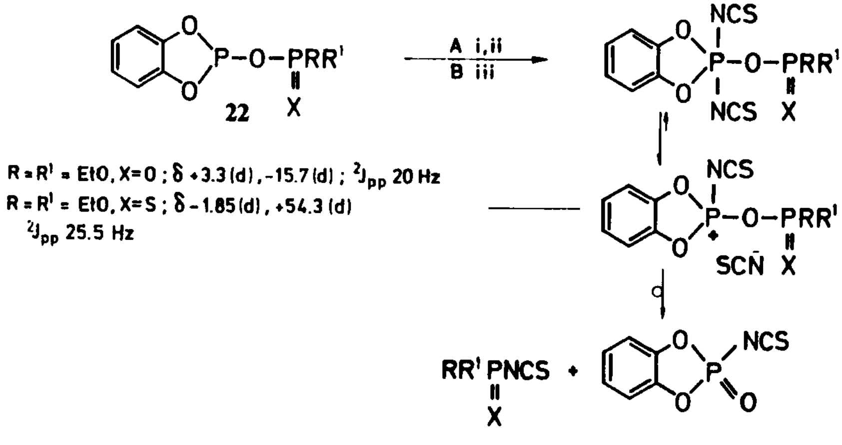
Recently we have found two alternative synthetic approaches A and B leading to acyl, phosphoryl, thiophosphoryl and selenophosphoryl isothiocyanates.[10,15] The mixed anhydrides **22** which are the starting materials in both cases are readily available by condensation of chloridite **20** with the corresponding sodium salt of acids **21**.[16,17]

$X = O, S, Se$
$R = R' = EtO,\ n\text{-}PrO, {}^{t}BuCH_2O$
$R = EtO,\ R' = Et;\ R = {}^{t}Bu,\ R' = Ph;\ R = {}^{t}Bu,\ R' = MeO$

One of the approaches involves oxidative addition of elemental chlorine to mixed anhydrides **22** followed by exchange of chlorine ligands employing lead thiocyanate. The other involves oxidative addition of thiocyanogen to the anhydrides **22**.

It is interesting to note that the intermediates of these two reactions being detected by ^{31}P NMR spectroscopy are of phosphonium structure. However the equilibrium of phosphonium species with appropriate phosphoranes is very likely.

The methods discussed above have been satisfactorily applied for the synthesis of optically active compounds of high enantiomeric purity (95–100%). The following optically active systems: RR′P(S)Cl, RR′P(S)Br, RR′P(S)NCS and



$R = R' = EtO, X = O;\ \delta\ +3.3\ (d), -15.7\ (d);\ {}^2J_{PP}\ 20\ Hz$
$R = R' = EtO, X = S;\ \delta\ -1.85\ (d), +54.3\ (d)$
${}^2J_{PP}\ 25.5\ Hz$

i. $Cl_2, CH_2Cl_2, -60°C$; ii. $Pb(SCN)_2, -50°C$; iii. $(SCN)_2, CH_2Cl_2, -50°C$

SCHEME 3

RR'P(S)NHC(S)NRR' using mixed anhydrides have been obtained. It should be emphasized that the reactions A and B provide an unique approach to the latter types of compounds.

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