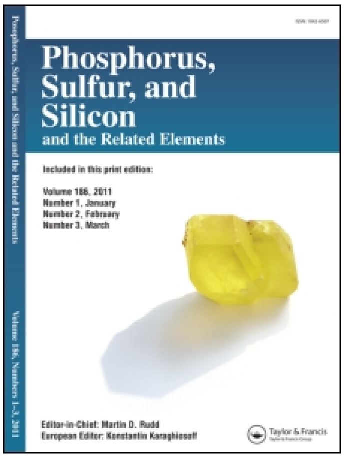

## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Neutral Hexacoordinate Phosphorus: Substituted Carbodiimide Phosphoranes and Other Chelated Substituted 2-Pyridine Derivatives

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# NEUTRAL HEXACOORDINATE PHOSPHORUS: SUBSTITUTED CARBODIIMIDE PHOSPHORANES AND OTHER CHELATED SUBSTITUTED 2-PYRIDINE DERIVATIVES

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Abstract A series of neutral hexacoordinate $\lambda^6$ phosphorus compounds of the general formula $X_{4-n}(CF_3)_n\overline{PN(R)C(Cl)N}(R)$ (n = 0, 1, 2, 3; R = cyclohexyl, isopropyl) has been prepared. The parent compounds are obtained by "insertion" of carbodiimide into the P-Cl bond of a $\lambda^5$-chlorophosphorane. Substituted pyridines also react readily with $\lambda^5$ chloro and fluoro phosphoranes to form 2-methylamino, thio and oxopyridine chelates of the form $X_4P(Epy)$ (E = O, NMe and S; X = F, Cl) in which the phosphorus achieves six coordination through acceptance of the pyridine nitrogen. Selected reactions and the fluxional behavior of the $\lambda^6$ systems are discussed.

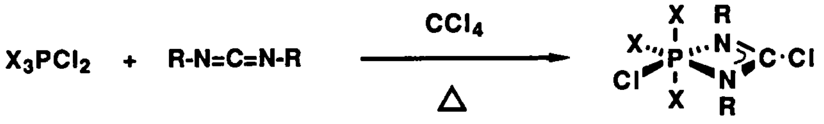
## INTRODUCTION

In recent years several classes of neutral hexacoordinate phosphorus(V) derivatives, in addition to the well known[1] $X_5P{\bullet}Base$ adducts, have been characterized. The six and five membered chelate rings formed by acetylacetone[2,3] and 8-hydroxyquinoline[4] have provided an extensive series of derivatives. Also of interest are the series of carbamate and thiocarbamate derivatives[5] in which nominally strained four membered rings are formed. We were interested to ascertain if additional four membered ring systems could be prepared and if such systems would show interesting reactivity

## RESULTS AND DISCUSSION

### 1) Carbodiimide Derivatives of Chloro and Trifluoromethyl Phosphoranes

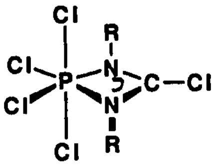
Refluxing chlorophosphoranes with carboiimides in $CCl_4$ (eq 1) for a few



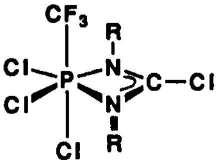
(1)

R = cyclohexyl or isopropyl X = Cl or $CF_3$

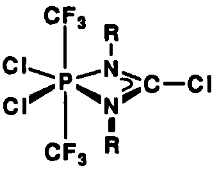
hours gave quantitative yields of hexacoordinate derivatives (**1-8**) *via* an apparent insertion reaction of the carbodiimide fragment into the P-Cl bond. An analogous tetrachlorophosphorus derivative with methyl substitution at nitrogen was obtained previously from a low yield reaction of $PCl_5$ and N,N'-dimethyl urea.[6]



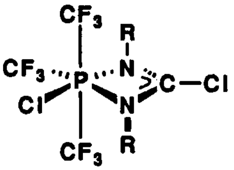
**1, 2**



**3, 4**



**5, 6**



**7, 8**

**R = cyclohexyl or isopropyl**

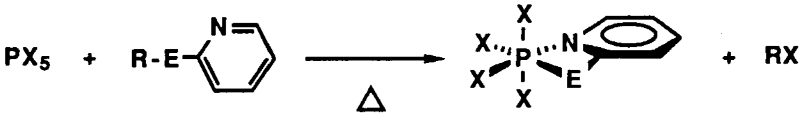
These carbodiimide derivatives (**1-8**) are air stable, moisture sensitive, colorless solids with sharp melting points varying from 70 to 165°C. They are characterized by very high field $^{31}P$ NMR chemical shifts: **1** [-204.7], **2** [-205.2], **3** [-181.7], **4** [-181.8], **5** [-155.8], **6** [-155.7], **7** [-154.9] and **8** [-155.3] ppm. Surprisingly, $CH_3(CF_3)_3PCl$ did not react with the carbodiimides although this tetraalkyl phosphorane is known to react readily in situations where metathetical removal of the halogen can be effected.[3,5] Possible reasons for the failure of the reaction is that the pathway may in fact require a dichlorinated starting material or that $(CF_3)_3CH_3PCl$ is too sterically hindered to react with this reagent.

The stereochemistry of the series **1-8** was readily deduced from $^{19}F$ and $^{31}P$ NMR spectra which showed coupling constant and chemical shift patterns consistent with the structures indicated. This data suggests that $CF_3$ groups preferentially occupy axial rather than radial positions, as illustrated. The NMR spectra also clearly indicate that there is only one isomer formed in each case (in contrast isomeric mixtures were found previously in the carbamate and acetylacetone derivatives containing one $CF_3$ on the $\lambda^6$ phosphorus).[3,5] The NMR spectra show no temperature variations and all expected couplings are resolved, including informative couplings to the single proton on isopropyl substituents of diisopropylcarbodiimide, which strongly suggests that the molecules are not fluxional. The crystal structure of the cyclohexyl derivative **5** shows the molecular structure depicted: the two $CF_3$ groups are perpendicular to the plane of the molecule containing the $PN_2C$ ring and three chlorine atoms. PN bond lengths are essentially equal (1.84 Å), as are the N-C bond lengths (1.31 Å) showing that the nitrogens are equivalently bound to the phosphorus and that formulation of the $N_2C$ substituent as a delocalized bidentate mono-anion is appropriate. (An earlier, much less reliable structure, had suggested that the ring might display dissimilar P-N binding.[6a]) The NPN angle is 70° emphasizing the small bite of the ligand

Although compounds containing extensive chlorine substitution are moisture sensitive (leading to phosphoryl derivatives in which one P-N bond is broken) these $\lambda^6$ compounds are relatively inert and the system has not shown an extensive substitutional chemistry.

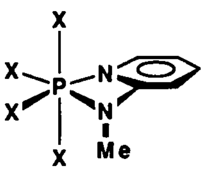
*2) Pyridine Based Four Membered Chelate Complexes*

Phosphorus pentachloride or pentafluoride reacts readily with α-substituted pyridines or their silylated derivatives to form the $\lambda^6$ derivatives **9-13** in good yield (eq 2).



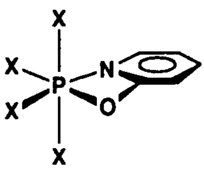
(2)

R = H, X = Cl; R = Me$_3$Si, X = F, Cl E = NMe, O, S

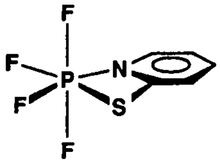


**9, 10**

X = Cl or F



**11, 12**



**13**

The $^{19}F$, $^{31}P$ and $^{1}H$ NMR spectra of these compounds are also consistent with a hexacoordinate phosphorus centre, particularly the characteristic high field $^{31}P$ NMR chemical shift: **9** [-195.7], **10**

[-132.3], **11** [-184.5], **12** [-131] and **13** [-136.4] ppm. In the tetrafluoro compound, axial, radial and radial' (2:1:1) fluorine signals were readily distinguishable in the normal temperature $^{19}F$ spectra of the sulphur (**13**) derivative and at -50°C in the NMe (**10**) derivative. In the case of the oxygen derivative, **12**, only a pentet of rather broad lines was observed to the lowest accessible temperature. The simplest process responsible for equilibrating the fluorine environments is likely to be a simple dissociation of the coordinated pyridine N atom to open the chelate ring and produce an intermediate of lower coordination number. It is, however, notable that the $^{31}P$ NMR shift does not change significantly with temperature indicating that species of lower coordination number are not present in significant concentration. The barrier to the scrambling process follows the order S>NMe>O.

## ACKNOWLEDGEMENT

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