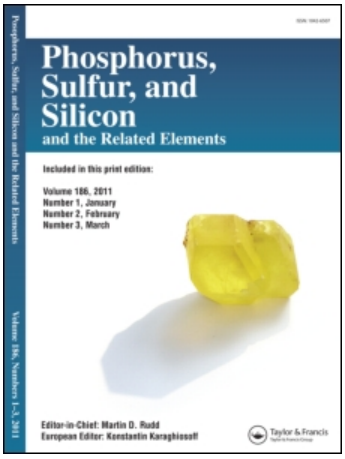

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OXIDATIVE-REARRANGEMENT REACTIONS OF σ^3, λ^3 DIALKYL(SILYLAMINO)PHOSPHINES WITH CHLOROPHOSPHINES; FORMATION OF A P–P BOND VIA A NEW ROAD TO PHOSPHINOPHOSPHORANIMINES

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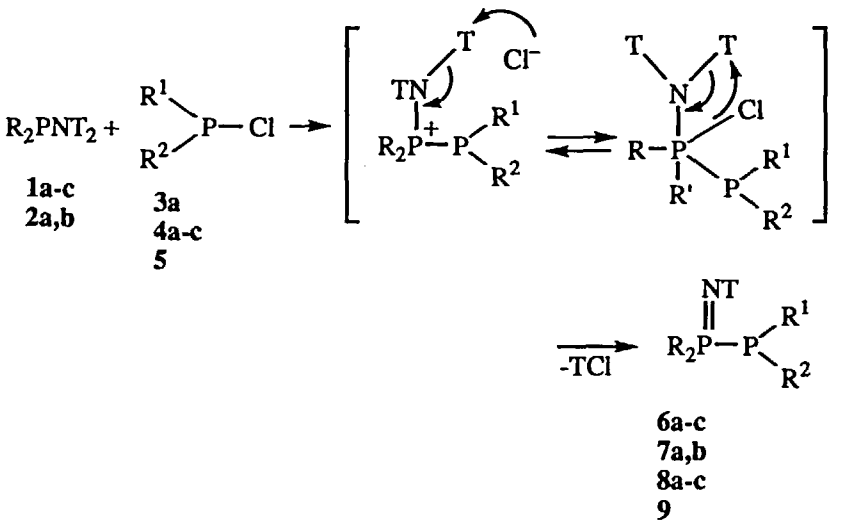
Abstract: Chlorophosphines react with trivalent (silylamino)phosphines *via* a direct oxidative addition process with elimination of trimethyl silyl chloride to produce phosphino-phosphoranimines with concomitant formation of a P-P bond. Oxidation of the phosphine center with sulfur and an exchange transformation of the phosphine are discussed.

INTRODUCTION

There are many bis-phosphorus compounds containing a P-P bond wherein both P-atoms are found in the same oxidation and coordination state. Methods of synthesis have been reviewed.[1] Bis-phosphorus compounds containing two phosphorus in different oxidation states (e. g. $P^{III}P^{V}$) are not so readily formed. The most inaccessible of this type of compounds are the phosphino-phosphoranimines ($\rangle P-\underset{|}{P}=N-$) which have been previously prepared by various means: reactions of $LiNT_2$ (T= $SiMe_3$) and chlorophosphines,[2] from the reactions of chlorophosphines with substituted amides abstracting HX with base,[3] as products in the reactions of amines with dicoordinate phosphines, T_2N-PET (E=CH, N)[4] and it has long been known that attempts to synthesise $N(PR_2)_3$ types of compounds lead in general to the isomeric form $R_2PP(R)_2=NPR_2$.[5] Our recent studies of the reactivity of (silylamino)phosphines (R_2PNT_2) with variety of organic compounds show that these reagents are good synthons for preparation of bifunctional compounds[6] yielding a variety of pentavalent phosphorus imines. The reaction route depends on the structure of the phosphine and on the nature of the halide.[7] We have recently found that when

the halogen is bound to an electron acceptor group such as $PhCH_2$, CH_2CN, CO, CH_2CO, etc. the reaction always proceeds with elimination of Me_3SiCl to form σ^4, λ^5 phosphoranimines.[6] We describe herein extension of this reaction to a selection of chlorophosphines which proceed directly to phosphino-phosphoranimines products.

Reactions of dialkyl **1a-c** and dialkoxy **2a,b** (silylamino)phosphines with chlorophosphines **3a**, **4a-d** and **5** were carried out by combining the reagents initially at 0°C in dichloromethane. The mixture was then allowed to warm to room temperature overnight yielding the iminophosphorano-phosphines **6-9** (Table).



6a-c
7a,b
8a-c
9

TABLE

Compound	R	R^1	R^2	$^1J_{PP}$ (Hz)
6a	Me	Ph	Ph	218
6b	Et	Ph	Ph	217
6c	^{n}Pr	Ph	Ph	217
7a	C_2H_5O	Ph	Ph	156
7b	^{i}PrO	Ph	Ph	146
8a	Me	Me	NT_2	270
8b	Me	Et	NT_2	268
8c	Me	^{i}Pr	NT_2	275
8d	Me	Ph	NT_2	307
9	Me	OEt	OEt	160

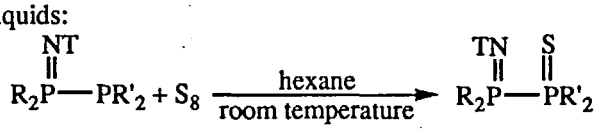
The phosphino-phosphoranimines **6**, **7** and **8** were isolated as air sensitive colorless liquids by vacuum distillation. The compounds, which are stable at ordinary

temperatures in an argon atmosphere, were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectra and elemental analysis. The phosphorus NMR spectra showed the characteristic two equal intensity doublets with P^{V} to high field and P^{III} to low field with a large one bond coupling (145-306 Hz) in each region. [2,4] In the ^{13}C NMR spectra of **6a-c, 7a-b** methyl and methylene C-atoms on P^{V} appeared as doublet of doublets in the ^{13}C NMR spectra due to both one bond coupling with P^{V} and two bond coupling with P^{III}. The same type of C-atoms bonded to P^{III} showed only a doublet structure due to the one bond coupling. Two bond coupling of the carbon on P^{III} to P^{V} was not observed.

The success of the reaction depends on the substituents on the chlorophosphine reagents. For example, chlorodiphenyl and chlorodiethoxyphosphines reacted smoothly with the full series of (silylamino)phosphines. However under the same conditions, dimethyl, diethyl and dipropyl chlorophosphines were without reaction even after several days at room temperature. Replacing one of the alkyl groups of the chlorophosphine with a bis-trimethylsilylamino group provided more reactive chlorophosphines and again phosphino-phosphoranimines were produced. We attribute these variances to the electrophilic character of the chlorophosphine center which is enhanced by the large -I substituents such as phenyl and bis(trimethylsilyl)amino. The first step of the reaction appears to be the nucleophilic addition of the chlorophosphine phosphorus with the formation of a phosphonium salt (or possibly a phosphorane intermediate). An oxidative elimination rearrangement follows in which Me_3SiCl is eliminated and the phosphoranimine center is developed.

The strength of the approach lies in the fact that there is little isomerization and/or rearrangement in the reactions. None of the products encountered herein exhibited isomerism or equilibria between different forms. A large variety of chlorophosphines can be used and the product is predictable. The generality of the route remains to be established.

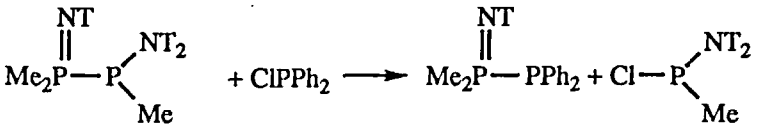
The phosphino-phosphoranimines can be further oxidized. Thus, treatment with sulfur in hexane at room temperature gave the phosphinesulfide-phosphoranimines as viscous light yellow liquids:



	R	R'
10a	Me	Ph
10b	Me	OEt
10c	EtO	Ph

The structures of **10a-c** were obtained by NMR studies and elemental analysis. The ^{31}P NMR spectra show doublets of doublets with smaller $^{1}J_{PP}$ values appropriate to coupling between two pentavalent phosphorus centers. The reaction of the phosphino-phosphoranimines with MeI or EtI resulted in cleavage of P-P bond to give a mixture of monophosphorus compounds. No products were isolated from this reaction mixture.

The phosphino-phosphoranimine **8a** reacts with diphenylchlorophosphine in CH_2Cl_2 again with cleavage of the P-P bond in the starting bis-phosphorus compound however a new P-P bond is formed. This is in contrast to the behaviour of differently substituted phosphino-phosphinimines which reacted with chlorophosphines to give R_2PPR_2 and $R_2PCl{=}NY$ products.[3]



8a **6a**

CONCLUSION

We show that (silylamino)phosphines react readily with chlorophosphines to provide a facile method of synthesis of phosphino-phosphoranimines. Development of this reaction will provide a route to a variety of potential bis-phosphorus ligands.

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