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SYNTHESIS AND REACTIONS OF THE NOVEL DIPHOSPHINE, $i\text{PrN}=\text{C}[\text{CH}_2\text{P}(\text{N}i\text{Pr}_2)_2]_2$

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The aldimine $n\text{BuN}=\text{CH}i\text{Pr}$ and phosphorus trichloride react to give phosphorus(III) amides in a 1:1 and 2:1 molar ratio. An imine-enamine tautomerism is proposed. In a [4+1] cycloaddition reaction diacetyl-(*N-n*-butyl)diimine and $\lambda^3\sigma^3\text{P}$ -species, RPCl_2 or EtOPCl_2 , form 1,2,3 $\lambda^5\sigma^4$ -diazaphospholenes¹. The same diimine and $(\text{Et}_2\text{N})_2\text{PCl}$ is furnishing annellated azaphospholenes¹. A 1,3,4 $\lambda^5\sigma^4$ -diazaphospholanium is formed from a $\lambda^3\sigma^2$ -phosphenium and $i\text{PrN}=\text{CMe}_2$ ². Phosphorus(III) amides $\text{P}(\text{NR}_2)_3$ ($\text{R}=\text{Me}$, Et) and *O*-trimethylsilylated diacetyldioxime give rise to yield the first monocyclic pentaazaphosphoranes.

O-trimethylsilylated diacetyldioxime and the phosphenium $(i\text{Pr}_2\text{N})_2\text{P}^+$ give a 1,3,2 $\lambda^5\sigma^4$ -diazaphospholenium ring system. For the phosphorus(III) triamide $\text{P}(\text{N}i\text{Pr}_2)_3$ which was prepared from $\text{ClP}(\text{N}i\text{Pr}_2)_2$ and $\text{HN}i\text{Pr}_2$ the reaction takes a completely different pathway, namely to furnish a bis(hydroxylamine) and diphosphine 1.

During the course of the reaction probably $i\text{PrN}=\text{CMe}_2$ is formed which undergoes an imine-enamine tautomerism to give the phosphine $(i\text{Pr}_2\text{N})_2\text{PCH}_2\text{C}(=\text{N}i\text{Pr})\text{CH}_3$, precursor for diphosphine 1. Surprisingly enough, $\text{ClP}(\text{N}i\text{Pr}_2)_2$ and LDA in a 1:1 molar ratio react to form $\text{HP}(\text{N}i\text{Pr}_2)_2$ and $i\text{PrN}=\text{CMe}_2$ and not the expected $\text{P}(\text{N}i\text{Pr}_2)_3$ which itself in the presence of catalytic amounts of LDA decomposes to furnish the same products. LDA acts as a hydride transfer agent. The ketimine $i\text{PrN}=\text{CMe}_2$, $\text{ClP}(\text{N}i\text{Pr}_2)_2$ and LDA yield compound 1 or, if $i\text{PrN}=\text{CMe}_2$ and $\text{P}(\text{N}i\text{Pr}_2)_3$ is reacting successively.

If $\text{ClP}(\text{N}i\text{Pr}_2)_2$ and LDA is reacted in a 1:2 ratio besides compound 1, $\text{HP}(\text{N}i\text{Pr}_2)_2$ and $(i\text{Pr}_2\text{N})_2\text{PP}(\text{N}i\text{Pr}_2)_2$ are obtained.

In diphosphine 1 P-C bonds are cleaved by bis(hexafluoropentadionato)palladium(II) to yield a phosphido-bridged complex 2. The second product originates from transfer of the $\text{CF}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{CF}_3)\text{O}$ moiety on to the $i\text{PrN}=\text{C}(\text{CH}_2)_2$ fragment.

1. A.M. KIBARDIN and A.N. PUDOVIK, *Zh. Obshch. Khim.* 63, 2430 (1993).
2. T.C. KIM, M.R. MAZIERES, R. WOLF and M. SANCHEZ, *Tetrahedron Lett.* 31, 4459 (1990).