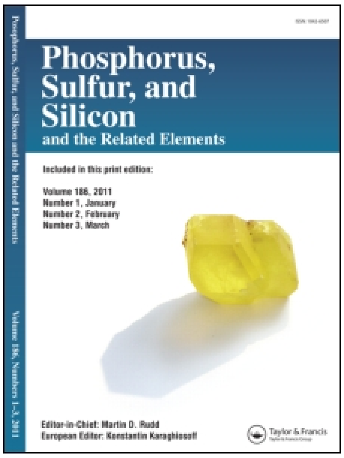

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Reactions of the Novel Diphosphine, *i*PrN = C[$CH_2P(N\textit{i}Pr_2)_2]_2$

Heike Hund[a]; Rolf-Dieter Hund[a]; Senay Has[a]; Gerd-Volker Röschenthaler[a]
[a] Institute of Inorganic and Physical Chemistry, University of Bremen, Bremen, Germany

To cite this Article Hund, Heike , Hund, Rolf-Dieter , Has, Senay and Röschenthaler, Gerd-Volker(1996) 'Synthesis and Reactions of the Novel Diphosphine, *i*PrN = C[$CH_2P(N\textit{i}Pr_2)_2]_2$', Phosphorus, Sulfur, and Silicon and the Related Elements, 111: 1, 193

To link to this Article: DOI: 10.1080/10426509608054822

URL: http://dx.doi.org/10.1080/10426509608054822

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 193
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND REACTIONS OF THE NOVEL DIPHOSPHINE, iPrN= C[CH$_2$P(NiPr$_2$)$_2$]$_2$

HEIKE HUND, ROLF-DIETER HUND, SENAY HAS and GERD-VOLKER RÖSCHENTHALER
Institute of Inorganic and Physical Chemistry, University of Bremen, Leobener Straße, 28334 Bremen, Germany

The aldimine nBuN=CHiPr 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 $\lambda^3\sigma^3$P-species, RPCl$_2$ or EtOPCl$_2$, form 1,2,3$\lambda^5\sigma^4$-diazaphospholenes[1]. The same diimine and (Et$_2$N)$_2$PCl is furnishing annellated azaphospholenes[1]. A 1,3,4$\lambda^5\sigma^4$-diazaphospholanium is formed from a $\lambda^3\sigma^2$-phosphenium and iPrN=CMe$_2$[2]. Phosphorus(III) amides P(NR$_2$)$_3$ (R= Me, Et) and O-trimethylsilylated diacetyldioxime give rise to yield the first monocyclic pentaazaphosphoranes .

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

During the course of the reaction probably iPrN=CMe$_2$ is formed which undergoes an imine-enamine tautomerism to give the phosphine (iPr$_2$N)$_2$PCH$_2$C(=NiPr)CH$_3$, precursor for diphosphine **1**. Surprisingly enough, ClP(NiPr$_2$)$_2$ and LDA in a 1:1 molar ratio react to form HP(NiPr$_2$)$_2$ and iPrN=CMe$_2$ and not the expected P(NiPr$_2$)$_3$ 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 iPrN=CMe$_2$, ClP(NiPr$_2$)$_2$ and LDA yield compound **1** or, if iPrN= CMe$_2$ and P(NiPr$_2$)$_3$ is reacting successively.

If ClP(NiPr$_2$)$_2$ and LDA is reacted in a 1:2 ratio besides compound **1**, HP(NiPr$_2$)$_2$ and (iPr$_2$N)$_2$PP(NiPr$_2$)$_2$ 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 CF$_3$C(O)CH=C(CF$_3$)O moiety on to the iPrN=C(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).