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1,3,2,4-Oxaazaphosphatitanetidine. Structure and Properties

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The interaction of 1,3,2,4 -oxaazaphosphatitanetidines with chlorides of aluminium and zirconium, alcohols, piperidine and R₂NBr (R=SiMe₃) has been studied. The reaction routes have been determined with NMR spectra and X-ray structure analyses.

Keywords: four-membered heterocycle; iminophosphine; titanium

INTRODUCTION

Recently we have shown that on interection of iminophosphines with alcoxides and alcoxichlorides of titanium the reaction of 1,2-addition by P=N bond takes place as in the equation^[1,2].

d takes place as in the equation
$$(Me_3Si)_2NP$$
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The structure of these compounds is proved with results of X-ray study of the compound (Me₃Si)₂NP(OPr-i)N(SiMe₃)Ti(OPr-i)Cl₂^[3].

These compounds contain tri-coordinated phosphorus in oxidation state three so they are very active. Exept early studied reactions with some substances^[4] we have studied the interaction with AlCl₃, ZrCl₄, alcohols, pypiredine and R₂NBr (R=SiMe₃).

Properties Of 1,3,2,4-Oxaazaphosphatitanetidine

1,3,2,4-oxaazaphosphatitanetidines react readily with alcohols as in the equation

$$R_{2}N-P \xrightarrow{N} Ti(OR')_{3}+R"OH \xrightarrow{-Ti(OR')_{3}(OR")} R_{2}N-P \xrightarrow{NHR} H \xrightarrow{NR} P \xrightarrow{NR} OR'$$

$$R=SiMe_{3}R'=Et,i-Pr,R"=Me,Et,i-Pr,t-Bu$$

The reaction proceeds in two steps. The reaction rate depands on alcohol nature and dimineshes from methanol to tert, -butanol.

Piperidine reacts with these compounds according to the following reaction

$$R_{2}N-P \xrightarrow{N} TI(OEt)_{3}+HN \xrightarrow{TI(OEt)_{4}} R_{2}N-P-NHR \xrightarrow{P} R_{2}N-P=NR$$

$$R=SiMe_{3}$$

On attempts to distruct the four-membered cycle with aluminium or zirconium chlorides it was observed only exchange of alcoxygroups in titanium sphere coordination with chlorine atoms and the cycle preserved as in the equation

We have studied the reactions of some 1,3,2,4-Oxaazaphosphatitanetidines with R₂NBr (R=SiMe₃) (3).

On interaction of $(Me_3Si)_2NP(OPr-i)N(Me_3Si)Ti(OPr-i)_3$ with compound (3) the reaction proceeds in two steps. The first product with chemical shift 20 ppm converts during 3-4 days into another one with chemical shift -0.6 ppm which can be isolated in crystalline state.

NMR spectra results were insufficient to find out reactions nature. Therefore X-ray investigations were made. Obtained data gives such a sequence of processes

$$R_{2}N-P = \begin{cases} N & \text{Tr} \left(OPR-i\right)_{2} + R_{2}NBr - \frac{R_{4}N_{2}}{R_{2}} & R_{2}N \\ OPr-i & \text{Br} \end{cases} P = \begin{cases} N & \text{Tr} \left(OPr-i\right)_{3} \\ Pr-i & \text{Pr} \end{cases}$$

$$Me_{3}SIO = \begin{cases} N & \text{Tr} \left(OPr-i\right)_{2}Br \\ N & \text{Me} \end{cases}$$

$$Me_{3}SIO = \begin{cases} N & \text{Tr} \left(OPr-i\right)_{2}Br \\ N & \text{Me} \end{cases}$$

1,3-migration of SiMe₃-group takes place in this reaction.Molecular view of (4) is shown on the figure 1.This compound has a planar four-membered heterocycle.In this cycle inner distances P-N are shorter then outer ones. It can be explained with zwitterion nature of this cycle.

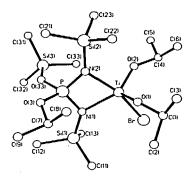


FIGURE 1: the structure of compound (4)

The compound (5) reacts with (3) in different manner as it is shown in the equations

$$R_{2}N-P \cap \begin{array}{c} R \\ N \\ O \\ Bu \end{array} (5) + R_{2}NBr - \begin{array}{c} R_{2}N \\ Br \end{array} P \cap \begin{array}{c} NR \\ OBu \\ \end{array} + nR_{4}N_{2} + \\ R=SiMe_{3} + 2n[*Ti(OBu)_{3}] + (1-2n)Ti(OBu)_{3}NR_{2}$$

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