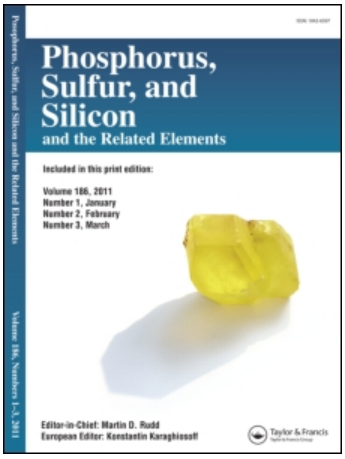

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1,3,2,4-Oxaazaphosphatitanetidine. Structure and Properties

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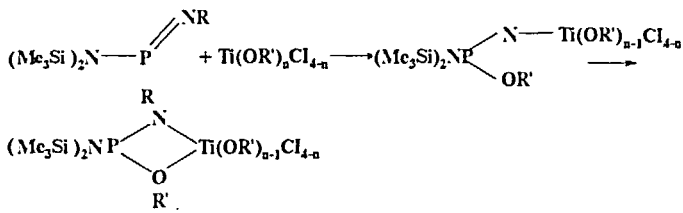
The interaction of 1,3,2,4 -oxaazaphosphatitanetidines with chlorides of aluminium and zirconium, alcohols, piperidine and R_2NBr (R=$SiMe_3$) has been studied. The reaction routes have been determined with NMR spectra and X-ray structure analyses.

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].



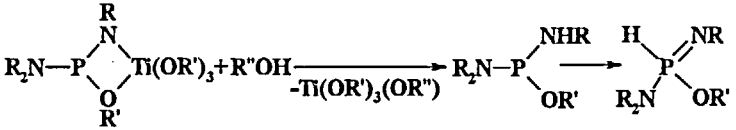
(1)R= $SiMe_3$, n= 4: R' =Et, i-Pr, Bu; n= 3-1: R' = Et, i-Pr.
(2)R = CMe_3, n = 4: R' = i-Pr; n = 3-1: R' = Et, i-Pr.

The structure of these compounds is proved with results of X-ray study of the compound $(Me_3Si)_2NP(OPr\text{-}i)N(SiMe_3)Ti(OPr\text{-}i)Cl_2$[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 $AlCl_3$, $ZrCl_4$, alcohols, pypiredine and R_2NBr (R=$SiMe_3$).

Properties Of 1,3,2,4-Oxaazaphosphatitanetidine

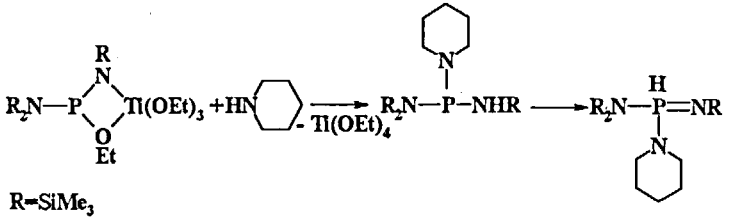
1,3,2,4-oxaazaphosphatitanetidines react readily with alcohols as in the equation



R=$SiMe_3$,R'=Et,i-Pr,R"=Me,Et,i-Pr,t-Bu

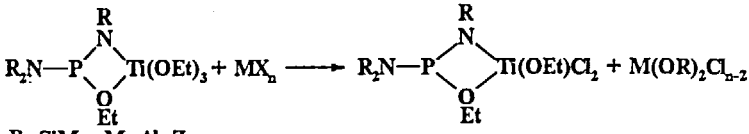
The reaction proceeds in two steps.The reaction rate depands on alcohol nature and dimineshes from methanol to tert.-butanol.

Piperidine reacts with these compounds according to the following reaction



R=$SiMe_3$

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

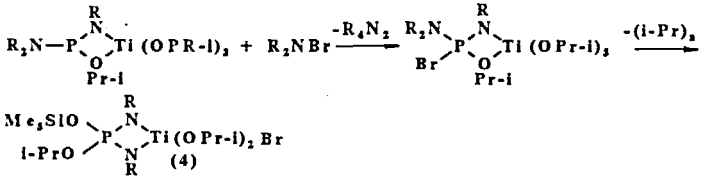


R=$SiMe_3$,M=Al, Zr

We have studied the reactions of some 1,3,2,4-Oxaazaphosphatitanetidines with R_2NBr (R=$SiMe_3$) (3).

On interaction of $(Me_3Si)_2NP(OPr\text{-}i)N(Me_3Si)Ti(OPr\text{-}i)_3$ 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



1,3-migration of $SiMe_3$-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.

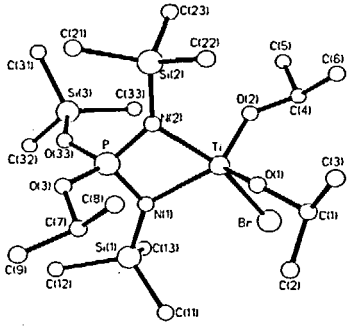
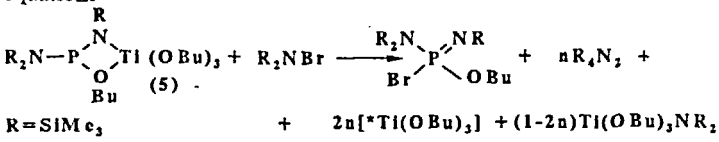


FIGURE 1: the structure of compound (4)

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



$R = SiMe_3$ + $2n[^*Ti(OBu)_3]$ + $(1-2n)Ti(OBu)_3NR_2$

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