# Reactivity study of $\boldsymbol{\beta}$-diketiminate titanium(III) complex <br> with phosphanylphosphido <br> chlorophosphanes. A new method of synthesis of $\beta$ diketiminate titanium(IV) complexes with versatile phosphanylphosphinidenes 

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#### Abstract

The reactivity of $\beta$-diketiminate titanium(III) complex with phosphanylphosphido ligand $\quad\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) $\quad\left({ }^{\mathrm{Me}} \mathrm{NacNac}^{-}=\right.$ $\left.[\mathrm{Ar}] \mathrm{NC}(\mathrm{Me}) \mathrm{CHC}(\mathrm{Me}) \mathrm{N}[\mathrm{Ar}] ; \quad \mathrm{Ar}=2,6-i \mathrm{Pr}_{2} \mathrm{Ph}\right)$ was investigated towards selected chlorophosphanes such as: $t \mathrm{Bu}_{2} \mathrm{PCl}, i \mathrm{Pr}_{2} \mathrm{PCl}, \mathrm{Cy}_{2} \mathrm{PCl},(\mathrm{Cy}) t \mathrm{BuPCl},(\mathrm{Me}) t \mathrm{BuPCl},(\mathrm{Ph}) t \mathrm{BuPCl}$, $\mathrm{Ph}_{2} \mathrm{PCl},\left({ }_{\left(i r_{2}\right.} \mathrm{N}\right) t \mathrm{BuPCl}$ and $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$. Reactions with $t \mathrm{Bu}_{2} \mathrm{PCl}$ and $\mathrm{Ph}_{2} \mathrm{PCl}$ lead mainly to earlier described complex $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1a), while the reactions with $i \mathrm{Pr}_{2} \mathrm{PCl}, \mathrm{Cy}_{2} \mathrm{PCl},(\mathrm{Cy}) t \mathrm{BuPCl},(\mathrm{Me}) t \mathrm{BuPCl},(\mathrm{Ph}) t \mathrm{BuPCl}$ lead to the mixtures of different $\beta$ diketiminate titanium(IV) complexes with phosphanylphosphinidene ligand: 1a and $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}_{2} \mathrm{Pr}_{2}\right\}\right]$ (1b), 1a and $\left[{ }^{\mathrm{Me}} \mathrm{NaCNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{PCy}_{2}\right\}\right]$ (1c), 1a and $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}(\mathrm{Cy}) t \mathrm{Bu}\right\}\right]$ (1d), 1a and $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}(\mathrm{Me}) t \mathrm{Bu}\right\}\right]$ (1e), 1a and $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}(\mathrm{Ph}) t \mathrm{Bu}\right\}\right](\mathbf{1 f})$, respectively. The newly obtained compounds 1c and 1d were isolated and their identities unambiguously confirmed by X-ray diffraction, NMR spectroscopy and elemental analysis. In the reaction with $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$ the related titanium(IV) complex is not observe, but the phosphetane $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}\left(\mu_{2}-\mathrm{PNEt}_{2}\right)_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}$ (3) is formed.


KEYWORDS: Coordination chemistry; Titanium complexes; Phosphanylphosphido ligand; X-ray analysis; DFT calculations.

## 1. INTRODUCTION

The first report on phosphanylphosphinidene complexe appeared about three decades ago and was concerned on ruthenium cluster. $\left[\mathrm{Ru}_{3}(\mathrm{CO})_{9}\left\{(\mathrm{P}-\mathrm{P}) \mathrm{P}_{3} \mathrm{C}_{5} t \mathrm{Bu}_{5}\right\}\right]$ was obtained by Nixon and co-workers in the reaction of pentaphospha-ferrocene with $\left[\left(\mathrm{Ru}_{3}(\mathrm{CO})_{12}\right]\right.$.[1] In the same year Scherer and co-workers presented a trinuclear tantalum complex $[(\mathrm{Ta}(1,3-$ $\left.\left.t \mathrm{Bu}_{2} \mathrm{C}_{5} \mathrm{H}_{3}\right)_{3}\left(\mathrm{P}_{4}\left\{\mathrm{Fe}_{4}\left(\mathrm{CO}_{4}\right)\right\}\right)\left(\mathrm{P}_{2}\right)\right]$. [2] A few years later Fritz et. al. enriched the work on $\mathrm{P}-\mathrm{PR}_{2}$ chemistry with phosphinophosphinidene phosphoranes $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}-\mathrm{PX}(t \mathrm{Bu})_{2}(\mathrm{X}=\mathrm{Me}$ or Br$)$ as transfer reagents of $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}$ moiety,[3] which contributed to the first platinum complexes containing this phosphanylphosphinidene ligand.[4] In the meantime, the same researchers reported the reactions of molybdenum and cobalt complexes with strong $\pi$-acceptor spectators ligands (-CO) towards phosphinophosphinidene phosphoranes, which led to dimeric and bimetallic complexes respectively.[5] Further studies on this type of complexes were continued by Pikies and co-workers and were based on metathesis reaction of chlorido complexes with lithium salts of diphosphanes RR'P-P( $\left.\mathrm{SiMe}_{3}\right) \mathrm{Li}$.[6] It is worth to pointing out, that Cummins and Figueroa presented another approach to obtain complexes with $\mathrm{R}_{2} \mathrm{P}-\mathrm{P}$ ligands. They applied triply bonded phosphorus complexes of niobium and tungsten with terminally bonded P -ligand in reactions with $\mathrm{R}_{2} \mathrm{PCl}$ and received related complexes with $\mathrm{R}_{2} \mathrm{P}$ P moieties.[7] Recently, the "reverse" metathesis of $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{PCl}_{2}$ with lithiated metal carbonyls was reported by Grubba et. al. as an alternative access to electrophilic phosphanylphosphinidene complexes. However, these complexes are highly reactive and only products of dimerization of monomeric species with $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}$ moiety were isolated.[8] Very recently we have studied the synthesis and reactivity of phosphanylphosphido ( RR ' $\mathrm{P}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)$ ) and phosphanylphosphinidene (RR'P-P) titanium(III) complexes. Properties of these systems are mainly determined by the tendency of Ti-center to have the oxidation state of +IV which leads to a great diversity of auto-redox reactions including rearrangements of ancillary ligands.[6e, 9] It is confirmed that $\beta$-diketiminato ligand [10] and tridentate PNP ligand also called "hybrid-type" ligand display good ancillary properties. This feature of PNP system is associated with the presence of single hard nitrogen and double soft phosphorus atoms.[11] The number of reports on phosphinidene (P-R) Ti-complexes with mentioned supporting systems is limited to those reported by Mindiola and co-workers.[11-12] Reports focused on Ti-phosphido complexes concerned only the synthesis of bridge type compounds (with Cp type ancillary ligands).[13]

In this article, we describe the reactivity study of $\beta$-diketiminate titanium(III) complex with phosphanylphosphido ligand towards selected chlorophosphanes: $t \mathrm{Bu}_{2} \mathrm{PCl}, \operatorname{Pr}_{2} \mathrm{PCl}^{2}$, $\mathrm{Cy}_{2} \mathrm{PCl},(\mathrm{Cy}) t \mathrm{BuPCl},(\mathrm{Me}) t \mathrm{BuPCl},(\mathrm{Ph}) t \mathrm{BuPCl}, \mathrm{Ph}_{2} \mathrm{PCl},\left(i \mathrm{Pr}_{2} \mathrm{~N}\right) t \mathrm{BuPCl},\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$.

## 2. EXPERIMENTAL SECTION

THF was dried over Na /benzophenone and pentane was dried over Na /benzophenone/diglyme and then both solvents were distilled under argon. All synthetic reactions were conducted under argon atmosphere and were carried out using standard Schlenk technique. ${ }^{1} \mathrm{H},{ }^{31} \mathrm{P}$ and ${ }^{13} \mathrm{C}$ spectra in solution were recorded on Bruker AV300 MHz and Bruker AV400 MHz (external standard tetramethylsilane for ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C} ; 85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ for ${ }^{31} \mathrm{P}$ ). $\left[{ }^{\mathrm{Me}} \mathrm{NaCNacTi}(\mathrm{Cl})\left\{\eta^{2}\right.\right.$ -$\left.\left.\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P}_{\mathrm{H}} \mathrm{Bu}_{2}\right\}\right](\mathbf{1}),[6 \mathrm{e}](\mathrm{Cy}) t \mathrm{BuPCl}$, [14] ( $\left.i \mathrm{Pr}_{2} \mathrm{~N}\right) t \mathrm{BuPCl}[15]$ and $i \mathrm{Pr}_{2} \mathrm{P}-\mathrm{P}(\mathrm{Li})-\mathrm{PiPr}_{2}$ [16] were prepared according to procedures in literature. $\mathrm{Cy}_{2} \mathrm{PCl},(\mathrm{Me}) t \mathrm{BuPCl},(\mathrm{Ph}) t \mathrm{BuPCl}$, $t \mathrm{Bu}_{2} \mathrm{PCl}, i \mathrm{Pr}_{2} \mathrm{PCl}, \mathrm{Ph}_{2} \mathrm{PCl}$ and $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$ were commercially purchased.

General method for the synthesis of $\left[{ }^{\mathrm{Me}} \mathbf{N a c N a c T i}(\mathbf{C l})\left\{\eta^{2}-\mathbf{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{PtBu} \mathbf{H}_{2}\right\}\right]$ (1) with selected chlorophosphanes.

The complex $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) $(0.250 \mathrm{mg}, 0.318 \mathrm{mmol})$ was dissolved in 10 ml of THF and then dropwise added to the solution of chlorophosphane $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{PCl}$ (in 2 ml of THF). The green reaction mixture was heated for 48 h at $50^{\circ} \mathrm{C}$. After that time solvent was evaporated and slightly oily residue was obtained.

## Reaction 1: $\left[{ }^{\mathrm{Me}} \mathbf{N a c N a c T i}(\mathrm{Cl})\left\{\eta^{2}-\mathbf{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{Pt} \mathrm{Bu}_{2}\right\}\right](1)$ with $t \mathrm{Bu}_{2} \mathbf{P C l}$

$\mathrm{R}^{\mathrm{B}}=t \mathrm{Bu}, \mathrm{R}^{\mathrm{C}}=t \mathrm{Bu} ; 0.060 \mathrm{~g}, 0.318$ mmol; the oily residue was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}$ and NMR spectroscopic investigated.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of $\mathbf{1 a}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta(\mathrm{d}), 843.68 \mathrm{ppm}\left(\mathbf{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$ and $143.52 \mathrm{ppm}\left(\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$;

## Reaction 2: $\left[{ }^{\mathrm{Me}} \mathbf{N a C N a c T i}(\mathrm{Cl})\left\{\boldsymbol{\eta}^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{Pt} \mathrm{Bu}_{2}\right\}\right](1)$ with $i \mathrm{Pr}_{2} \mathbf{P C l}$

$\mathrm{R}^{\mathrm{B}}=i \mathrm{Pr}, \mathrm{R}^{\mathrm{C}}=i \mathrm{Pr} ; 0.048 \mathrm{~g}, 0.318 \mathrm{mmol}$ of $i \mathrm{Pr}_{2} \mathrm{PCl}$; the oily residue was dissolved in 5 ml of pentane and stored at $+4^{\circ} \mathrm{C}$. After 3 h dark-green crystals were appeared. The crystals were isolated and X-ray characterized as the complexes (1a) $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right](0.04$ g, yield $38 \%$ ). The remaining solution was concentrated and stored at $+4^{\circ} \mathrm{C}$ again. After 24 h
green crystals were appeared and characterized as (1b) $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{PiPr} r_{2}\right\}\right](0.028$ g, yield $27 \%$ ).
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of $\mathbf{1 a}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta(\mathrm{d}), 844.32 \mathrm{ppm}\left(\mathbf{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$ and $143.65 \mathrm{ppm}\left(\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$;
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$-NMR data of $\mathbf{1 b}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 824.23\left(\mathbf{P}-\mathrm{PiPr}_{2}, J_{\mathrm{PP}}=443.2 \mathrm{~Hz}\right)$ and 118.37 ppm $\left(\mathrm{P}-\mathrm{PiPr}_{2}, J_{\mathrm{PP}}=443.2 \mathrm{~Hz}\right)$;

## Reaction 3: $\left[{ }^{\mathrm{Me}} \mathrm{NaCNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{Pt} \mathrm{Bu}_{2}\right\}\right]$ (1) with $\mathrm{Cy}_{2} \mathbf{P C l}$

$\mathrm{R}^{\mathrm{B}}=\mathrm{Cy}, \mathrm{R}^{\mathrm{C}}=\mathrm{Cy} ; 0.074 \mathrm{~g}, 0.318 \mathrm{mmol}$ of $\mathrm{Cy}_{2} \mathrm{PCl}$; the oily residue was dissolved in 5 ml of pentane and stored at $+4^{\circ} \mathrm{C}$. After 1 h dark-green crystals were appeared and X-ray characterized as a new complex (1c) $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{PCy} \mathrm{y}_{2}\right\}\right](0.055 \mathrm{~g}$, yield $47 \%)$. The crystals of $\mathbf{1 c}$ were isolated and the solution was concentrated to 2 mL of amount. After 12 h at $+4{ }^{\circ} \mathrm{C}$ green crystals were appeared and were X-ray characterized as (1a) $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]\left(0.022 \mathrm{~g}\right.$, yield $20 \%$ ). Anal. Calcd for $\mathrm{C}_{41} \mathrm{H}_{63} \mathrm{ClN}_{2} \mathrm{P}_{2} \mathrm{Ti}(\mathbf{1 c})$ : C, 67.51; H, 8.71; N, 3.84\%. Found: C, 67.36; H, 8.75; N, 3.89\%.

NMR data of 1c: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (298 K, $\mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta$ 7.24-7.12 ( $6 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{3}$ ), 4.77 (s, 1 H , $\mathrm{NC}(\mathrm{Me}) \mathrm{CHC}(\mathrm{Me}) \mathrm{N}), 4.09$ (sept, $2 \mathrm{H}, J=6.8 \mathrm{~Hz}, \mathrm{CH}(\mathrm{Me})_{2}$ ), 3.17 (sept, 2H, $J=6.8 \mathrm{~Hz}$, $\mathrm{CH}(\mathrm{Me})_{2}$ ), 2.11 (broad m, 4H, Cy), 1.73 (broad m, 2H, Cy), 1.69 (broad m, 8H, Cy), 1.65 (d, $\left.6 \mathrm{H}, J=6.7 \mathrm{~Hz}, \mathrm{CH}(M e)_{2}\right), 1.57$ (broad m, $8 \mathrm{H}, \mathrm{Cy}$ ), $1.53\left(\mathrm{~d}, 6 \mathrm{H}, J=6.8 \mathrm{~Hz}, \mathrm{CH}(M e)_{2}\right), 1.49$ (s, $6 \mathrm{H}, \mathrm{NC}(M e) \mathrm{CHC}(M e) \mathrm{N}), 1.17\left(\mathrm{~d}, 6 \mathrm{H}, J=6.9 \mathrm{~Hz}, \mathrm{CH}(M e)_{2}\right), 1.12(\mathrm{~d}, 6 \mathrm{H}, J=6.8 \mathrm{~Hz}$, $\left.\mathrm{CH}(\mathrm{Me})_{2}\right) ;{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$-NMR (298 K, $\mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta 166.42$ (s, $\left.\mathrm{NC}(\mathrm{Me}) \mathrm{CHC}(\mathrm{Me}) \mathrm{N}\right), 142.92$ ( $\left.\mathrm{s}, \mathrm{Ar}-\mathrm{C}\right)$, 141.47 (Ar-C), 127.14 (Ar-C), 124.51 (Ar-C), 124.21 (Ar-C), $96.12 \quad$ (s, $\left.\mathrm{NC}\left(\mathrm{CH}_{3}\right) C \mathrm{HC}\left(\mathrm{CH}_{3}\right) \mathrm{N}\right), 40.06\left(\mathrm{~d}, J_{\mathrm{PC}}=7.2 \mathrm{~Hz}, \mathrm{Cy}\right), 31.81\left(\mathrm{~d}, J_{\mathrm{PC}}=1.2 \mathrm{~Hz}, \mathrm{Cy}\right), 29.00(\mathrm{~s}$, $\left.C H(\mathrm{Me})_{2}\right), 28.20\left(\mathrm{~s}, C \mathrm{H}(\mathrm{Me})_{2}\right), 27.73\left(\mathrm{dd}, J_{\mathrm{PC}}=11.9 \mathrm{~Hz}, J_{\mathrm{PC}}=13.0 \mathrm{~Hz}, \mathrm{Cy}\right), 26.16\left(\mathrm{dd}, J_{\mathrm{PC}}\right.$ $\left.=16.9 \mathrm{~Hz}, J_{\mathrm{PC}}=1.2 \mathrm{~Hz}, \mathrm{Cy}\right), 24.76\left(\mathrm{~s}, \mathrm{CH}(\mathrm{Me})_{2}\right), 24.42(\mathrm{~s}, \mathrm{NC}(\mathrm{Me}) \mathrm{CHC}(\mathrm{Me}) \mathrm{N}), 24.11(\mathrm{~s}$, $\left.\mathrm{CH}(M e)_{2}\right), 23.68\left(\mathrm{~s}, \mathrm{CH}(M e)_{2}\right), 23.09\left(\mathrm{~s}, \mathrm{CH}(M e)_{2}\right) ;{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 832.99$ $\left(\mathbf{P}-\mathrm{PCy}_{2}, J_{\mathrm{PP}}=442.8 \mathrm{~Hz}\right), 107.78\left(\mathrm{P}-\mathrm{PCy}_{2}, J_{\mathrm{PP}}=442.8 \mathrm{~Hz}\right) \mathrm{ppm}$.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of $\mathbf{1 a}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta(\mathrm{d}), 844.32\left(\mathbf{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$ and 143.65 ppm (P-PtBu $\left.{ }_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$.

## Reaction 4: $\left[{ }^{\mathrm{Me}} \mathbf{N a c N a c T i}(\mathrm{Cl})\left\{\boldsymbol{\eta}^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{Pt}\left(\mathrm{Bu}_{2}\right\}\right]\right.$ (1) with $(\mathrm{Cy}) t \mathrm{BuPCl}$

$\mathrm{R}^{\mathrm{B}}=\mathrm{Cy}, \mathrm{R}^{\mathrm{C}}=t \mathrm{Bu} ; 0.066 \mathrm{~g}, 0.318 \mathrm{mmol}$ of $(\mathrm{Cy}) t \mathrm{BuPCl}$; the oily residue was dissolved in 5 ml of pentane and stored at $+4{ }^{\circ} \mathrm{C}$. After 1 h dark-green crystals were appeared and X-ray
characterized as a new complex (1d) $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}(\mathrm{Cy}) t \mathrm{Bu}\right\}\right](0.065 \mathrm{~g}$, yield $58 \%$ ). The crystals of $\mathbf{1 d}$ were isolated and the solution was concentrated to 2 mL of volume. After 12 h at $+4^{\circ} \mathrm{C}$ green crystals were appeared and were X-ray characterized as (1a) $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right](0.015 \mathrm{~g}$, yield $14 \%)$. Anal. Calcd for $\mathrm{C}_{39} \mathrm{H}_{61} \mathrm{CIN}_{2} \mathrm{P}_{2} \mathrm{Ti}$ (1d): C, 66.60; H, 8.75; N, 3.99\%. Found: C, 66.78; H, 8.69; N, 3.91\%.

NMR data of 1d: ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta$ 7.17-6.88 ( $6 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{3}$ ), $4.63(\mathrm{~s}, 1 \mathrm{H}$, $\mathrm{NC}(\mathrm{Me}) \mathrm{CHC}(\mathrm{Me}) \mathrm{N}), 4.07$ (sept., $\left.1 \mathrm{H}, J_{\mathrm{HH}}=6.7 \mathrm{~Hz}, \mathrm{CH}(\mathrm{Me})_{2}\right), 3.96$ (sept, $1 \mathrm{H}, J_{\mathrm{HH}}=6.8 \mathrm{~Hz}$, $\left.\mathrm{CH}(\mathrm{Me})_{2}\right), 3.43\left(\right.$ sept., $\left.1 \mathrm{H}, J_{\mathrm{HH}}=6.7 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 3.16\left(\mathrm{~m}, \mathrm{C}_{6} \mathrm{H}_{11}\right), 2.54\left(\mathrm{sept}, 1 \mathrm{H}, J_{\mathrm{HH}}=\right.$ $\left.6.7 \mathrm{~Hz}, \mathrm{CH}(\mathrm{Me})_{2}\right), 1.66\left(\mathrm{~m}, \mathrm{C}_{6} \mathrm{H}_{11}\right), 1.50\left(\mathrm{~d}, 3 \mathrm{H}, J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}(M e)_{2}\right), 1.46\left(\mathrm{~m}, \mathrm{C}_{6} \mathrm{H}_{11}\right)$, $1.41(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NC}(M e) \mathrm{CHC}(M e) \mathrm{N}), 1.31\left(\mathrm{~d}, 3 \mathrm{H}, J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}(M e)_{2}\right), 1.29\left(\mathrm{~d}, 18 \mathrm{H}, J_{\mathrm{PH}}=\right.$ $\left.14.79 \mathrm{~Hz}, \mathrm{PC}(M e)_{3}\right), 1.24(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NC}(M e) \mathrm{CHC}(M e) \mathrm{N}), 1.05\left(\mathrm{~m}, \mathrm{C}_{6} \mathrm{H}_{11}\right), 0.99\left(\mathrm{~d}, 3 \mathrm{H}, J_{\mathrm{HH}}=\right.$ $\left.6.8 \mathrm{~Hz}, \mathrm{CH}(M e)_{2}\right), 0.86\left(\mathrm{~d}, 3 \mathrm{H}, J_{\mathrm{HH}}=6.6 \mathrm{~Hz}, \mathrm{CH}(M e)_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ : $\delta 167.28$ and $165.97\left(C\left(\mathrm{CH}_{3}\right) \mathrm{CHC}\left(\mathrm{CH}_{3}\right)\right)$, 143.46, 142.53, 141.68, 141.60, 126.99, 124.61, $124.28\left(C_{6} \mathrm{H}_{3}\right), 96.36(\gamma-\mathrm{CH}), 43.07\left(\mathrm{~d}, J_{\mathrm{PC}}=3.7 \mathrm{~Hz}, \mathrm{Cy}\right), 39.08\left(\mathrm{~d}, J_{\mathrm{PC}}=3.67, \mathrm{~Hz}\right.$, $\mathrm{PC}(\mathrm{Me})_{3}$ ), $31.88(\mathrm{~s}, \mathrm{Cy}), 31.56\left(\mathrm{~s}, \mathrm{PC}(\mathrm{Me})_{3}\right)$, $29.18\left(\mathrm{~s}, \mathrm{CH}(\mathrm{Me})_{2}\right), 28.98\left(\mathrm{~s}, \mathrm{CH}(\mathrm{Me})_{2}\right), 28.55$ (s, $\left.C H(\mathrm{Me})_{2}\right), 27.93\left(\mathrm{dd}, J_{\mathrm{CP}}=11.0 \mathrm{~Hz}, J_{\mathrm{CP}}=5.1 \mathrm{~Hz}, \mathrm{Cy}\right), 27.74\left(\mathrm{~s}, C \mathrm{H}(\mathrm{Me})_{2}\right), 26.22\left(\mathrm{dd}, J_{\mathrm{CP}}\right.$ $\left.=36.7 \mathrm{~Hz}, J_{\mathrm{CP}}=2.2 \mathrm{~Hz}\right), 24.94\left(\mathrm{~s}, \mathrm{CH}(M e)_{2}\right), 24.84(\mathrm{~s}, \mathrm{NC}(M e) \mathrm{CHC}(M e) \mathrm{N}), 24.76(\mathrm{~s}$, $\left.\mathrm{CH}(\mathrm{Me})_{2}\right), 24.47(\mathrm{~s}, \mathrm{NC}(\mathrm{Me}) \mathrm{CHC}(\mathrm{Me}) \mathrm{N}), 24.13\left(\mathrm{~s}, \mathrm{CH}(M e)_{2}\right), 24.02$ (s, $\left.\mathrm{CH}(\mathrm{Me})_{2}\right) \mathrm{ppm}$; ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 846.46\left(\mathbf{P}-\mathrm{P}(\mathrm{Cy}) t \mathrm{Bu}, J_{\mathrm{PP}}=443.2 \mathrm{~Hz}\right), 117.92(\mathrm{P}-\mathbf{P}(\mathrm{Cy}) t \mathrm{Bu}$, $\left.J_{\mathrm{PP}}=443.2 \mathrm{~Hz}\right) \mathrm{ppm}$.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of 1a $\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta(\mathrm{d}), 844.32\left(\mathbf{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$ and 143.65 $\operatorname{ppm}\left(\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$.

## Reaction 5: $\left[{ }^{\mathrm{Me}} \mathbf{N a c N a c T i}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) with (Me) $t \mathrm{BuPCl}$

$\mathrm{R}^{\mathrm{B}}=\mathrm{Me}, \mathrm{R}^{\mathrm{C}}=t \mathrm{Bu} ; 0.044 \mathrm{~g}, 0.318 \mathrm{mmol}$ of $(\mathrm{Me}) t \mathrm{BuPCl}$; the oily residue was dissolved in 5 ml of pentane and stored at $+4^{\circ} \mathrm{C}$. After 3 h dark-green crystals were appeared and X-ray characterized as the complexes (1a) $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right](0.035 \mathrm{~g}$, yield $33 \%)$. Unfortunately, complex 1e was not obtained in the crystalline form. Therefore, after reaction the oily residue was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}$ and NMR spectroscopic investigated.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of 1a $\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta(\mathrm{d}), 844.32\left(\mathbf{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$ and 143.65 $\mathrm{ppm}\left(\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$-NMR data of $\mathbf{1 e}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta(\mathrm{d}), 830.06\left(\mathbf{P}-\mathrm{P}(\mathrm{Me}) t \mathrm{Bu}, J_{\mathrm{PP}}=457.8 \mathrm{~Hz}\right)$ and $91.82 \mathrm{ppm}\left(\mathrm{P}-\mathrm{P}(\mathrm{Me}) t \mathrm{Bu}, J_{\mathrm{PP}}=457.8 \mathrm{~Hz}\right)$.

## Reaction 6: [ $\left.{ }^{\mathrm{Me}} \mathbf{N a c N a c T i}(\mathrm{Cl})\left\{\boldsymbol{\eta}^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{Pt} \boldsymbol{B u} \mathbf{u}_{2}\right\}\right]$ (1) with $(\mathbf{P h}) t \mathrm{BuPCl}$

$\mathrm{R}^{\mathrm{B}}=\mathrm{Ph}, \mathrm{R}^{\mathrm{C}}=t \mathrm{Bu} ; 0.064 \mathrm{~g}, 0.318 \mathrm{mmol}$ of $(\mathrm{Ph}) t \mathrm{BuPCl}$; the oily residue was dissolved in 5 ml of pentane and stored at $+4^{\circ} \mathrm{C}$. After 2 h dark-green crystals were appeared and X-ray characterized as the complexes (1f) $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}(\mathrm{Ph}) t \mathrm{Bu}\right\}\right]$ ( 0.055 , yield $49 \%$ ), The crystals of $\mathbf{1 f}$ were isolated and the solution was stored at $+4^{\circ} \mathrm{C}$ again. 24 h later the green crystals were appeared which were characterized as (1a) $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right](0.02$ g, yield $19 \%$ ).
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of 1a ( $298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta(\mathrm{d}), 844.32\left(\mathbf{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$ and 143.65 $\operatorname{ppm}\left(\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of $\mathbf{1 f}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta(\mathrm{d}), 825.19\left(\mathbf{P}-\mathrm{P}(\mathrm{Ph}) t \mathrm{Bu}, J_{\mathrm{PP}}=443.2 \mathrm{~Hz}\right)$ and $109.63 \mathrm{ppm}\left(\mathrm{P}-\mathbf{P}(\mathrm{Ph}) t \mathrm{Bu}, J_{\mathrm{PP}}=443.2 \mathrm{~Hz}\right)$.

## Reaction 7: $\left[{ }^{\mathrm{Me}} \mathbf{N a C N a c T i}(\mathrm{Cl})\left\{\boldsymbol{\eta}^{2}-\mathbf{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{Pt} \mathrm{Bu}_{2}\right\}\right]$ (1) with $\mathbf{P h}_{2} \mathbf{P C l}$

$\mathrm{R}^{\mathrm{B}}=\mathrm{Ph}, \mathrm{R}^{\mathrm{C}}=\mathrm{Ph} ; 0.070 \mathrm{~g}, 0.318 \mathrm{mmol}$ of $\mathrm{Ph}_{2} \mathrm{PCl}$; the oily residue was dissolved in 5 ml of pentane and stored at $+4^{\circ} \mathrm{C}$. After 3 h dark-green crystals were appeared and X-ray characterized as the complexes (1a) $\left[{ }^{\mathrm{Me}} \mathrm{NaCNaCTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ ( $0,080 \mathrm{~g}$, yield $74 \%$ ). Unfortunately, complex $\mathbf{1 g}$ was not obtained in the crystalline form. Therefore, after reaction the oily residue was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}$ and NMR spectroscopic investigated.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of 1a (298 K, $\left.\mathrm{C}_{6} \mathrm{D}_{6}\right):(\mathrm{d}), 844.32\left(\mathbf{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$ and 143.65 $\mathrm{ppm}\left(\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of $\mathbf{1 g}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right):(\mathrm{d}), 780.29\left(\mathbf{P}-\mathrm{PPh}_{2}, J_{\mathrm{PP}}=472.3 \mathrm{~Hz}\right)$ and 88.05 ppm $\left(\mathrm{P}-\mathrm{PPh}_{2}, J_{\mathrm{PP}}=472.3 \mathrm{~Hz}\right)$.

## Reaction $\left[{ }^{\mathrm{Me}} \mathbf{N a C N a c T i}(\mathrm{Cl})\left\{\boldsymbol{\eta}^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{Pt} \mathrm{Bu}_{2}\right\}\right]$ (1) with $\left(\mathrm{iPr}_{2} \mathbf{N}\right) t \mathrm{BuPCl}$

$\mathrm{R}^{\mathrm{B}}=\left(i \mathrm{Pr}_{2}\right) \mathrm{N}, \mathrm{R}^{\mathrm{C}}=t \mathrm{Bu} ; 0.071 \mathrm{~g}, 0.318 \mathrm{mmol}$ of $\left(i \mathrm{Pr}_{2} \mathrm{~N}\right) t \mathrm{BuPCl}$; in the reaction the products in crystalline form were not obtained, therefore the oily residue was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}$ and NMR spectroscopic investigated.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of $\mathbf{1 a}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right):(\mathrm{d}), 844.32\left(\mathbf{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$ and 143.65 $\operatorname{ppm}\left(\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, J_{\mathrm{PP}}=450.5 \mathrm{~Hz}\right)$.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$-NMR data of other compounds ( $298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): 82.04 (small signal of $\left(i \mathrm{Pr}_{2} \mathrm{~N}\right) t \mathrm{BuP}$ $\left.\mathrm{P}\left(i \mathrm{Pr}_{2} \mathrm{~N}\right) t \mathrm{Bu}\right), 144.62 \mathrm{ppm}$ (unreacted $\left.\left(\mathrm{iPr}_{2} \mathrm{~N}\right) t \mathrm{BuPCl}\right)$.

## Reaction $\left[{ }^{\mathrm{Me}} \mathbf{N a c N a c T i}(\mathbf{C l})\left\{\eta^{2}-\mathbf{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{Pt} \mathrm{Bu}_{2}\right\}\right]$ with $\left(\mathrm{Et}_{2} \mathbf{N}\right)_{2} \mathbf{P C l}$

$\mathrm{R}^{\mathrm{B}}=\mathrm{Et}_{2} \mathrm{~N}, \mathrm{R}^{\mathrm{C}}=\mathrm{Et}_{2} \mathrm{~N} ; 0.067 \mathrm{~g}, 0.318 \mathrm{mmol}$ of $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$; after the reaction in the crystalline form the complexes of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\mathrm{NEt}_{2}\right\}\right]_{2}$ (2) and $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTiCl}_{2}(\mathrm{THF})\right]$ were obtained. The crystals of both complexes were isolated and the reaction solution was evaporated. The oily residue was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}$ and NMR spectroscopic investigated.

The NMR data of phosphetane (3) (see Scheme 4): ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 3.28$ (broad m, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), 1.45 (d, $t \mathrm{Bu}$ groups, $36 \mathrm{H}, J=11,24 \mathrm{~Hz}$ ), ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spin system $\mathrm{AA}^{\prime} \mathrm{M}_{2} \mathrm{XX}$ ': $\delta 58.62\left(\mathrm{~m}, t \mathrm{Bu}_{2} \mathrm{P}_{(1)}\right), 20.36\left(\mathrm{~m}, \mathrm{P}_{(2)} \mathrm{NEt}_{2}\right),-24.89\left(\mathrm{~m}, \mathrm{P}_{(3)}-\right.$ unsubstituted $)$ ppm. ${ }^{1} J_{\mathrm{P}(1) \mathrm{P}(3)}=-245.5 \mathrm{~Hz},{ }^{1} J_{\mathrm{P}(3) \mathrm{P}(2)}=-208.7 \mathrm{~Hz},{ }^{2} J_{\mathrm{P}(3) \mathrm{P}\left(3^{\prime}\right)}=172.4 \mathrm{~Hz},{ }^{2} J_{\mathrm{P}(1) \mathrm{P}(2)}=13.8 \mathrm{~Hz}$, ${ }^{4} J_{\mathrm{P}(1) \mathrm{P}\left(1^{\prime}\right)}=0.6 \mathrm{~Hz},{ }^{3} J_{\mathrm{P}(3) \mathrm{P}\left(1^{\prime}\right)}=0.4 \mathrm{~Hz}$.

## Synthesis of $\left(t \mathbf{B u}_{2} \mathbf{P}\right)\left(\boldsymbol{i P r} \mathbf{r}_{2} \mathbf{P}\right)_{2} \mathbf{P}$

To a solution of $\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{2} \mathrm{PLi} \cdot 2 \mathrm{THF}(0.100 \mathrm{~g} ; 0.240 \mathrm{mmol})$ in 4 ml of THF cooled to $0^{\circ} \mathrm{C}$ a chlorophosphane $t \mathrm{Bu}_{2} \mathrm{PCl}(0.043 \mathrm{ml} ; 0.240 \mathrm{mmol})$ was added. The reaction solution was stirred about 3 h at room temperature and then the solvent was removed under vacuum. The solid residue was treated with 1 ml of $\mathrm{C}_{6} \mathrm{D}_{6}$. The solution was decanted from the precipitated LiCl and analyzed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\},{ }^{31} \mathrm{P}$ and ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectroscopy. The NMR results reveal that in the reaction two compounds are formed: $\left(t \mathrm{Bu}_{2} \mathrm{P}\right)\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{2} \mathrm{P}$ and $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}(\mathrm{H})-\mathrm{PiPr}_{2}$.

NMR data of $\left(t \mathrm{Bu}_{2} \mathrm{P}\right)\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{2} \mathrm{P}:{ }^{1} \mathrm{H}-\mathrm{NMR}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 2.35$ (sept, $J_{\mathrm{PH}}=7.1 \mathrm{~Hz}, i \mathrm{Pr}_{2} \mathrm{P}$, $4 \mathrm{H}), 1.42\left(\mathrm{~d}, J_{\mathrm{PH}}=12.2 \mathrm{~Hz}, t \mathrm{Bu}_{2} \mathrm{P}, 18 \mathrm{H}\right), 1.34,1.29,1.26,1.24\left(\mathrm{~d}, J_{\mathrm{PH}}=7.1 \mathrm{~Hz}, i \mathrm{Pr}_{2} \mathrm{P}, 24 \mathrm{H}\right)$; ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 42.89\left(\mathrm{~d}, J_{\mathrm{PP}}=459.2 \mathrm{~Hz},\left(t \mathrm{Bu}_{2} \mathbf{P}\right)\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{2} \mathrm{P}\right), 9.77\left(\mathrm{~d}, J_{\mathrm{PP}}=\right.$ $\left.397.2 \mathrm{~Hz},\left(t \mathrm{Bu}_{2} \mathrm{P}\right)\left(i \mathrm{Pr}_{2} \mathbf{P}\right)_{2} \mathrm{P}\right),-102.44\left(\mathrm{~m},\left(t \mathrm{Bu}_{2} \mathrm{P}\right)\left(\mathrm{Pr}_{2} \mathrm{P}\right)_{2} \mathbf{P}\right) \mathrm{ppm}$.

NMR data of $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}(\mathrm{H})-i \mathrm{Pr}_{2}:{ }^{1} \mathrm{H}-\mathrm{NMR}\left(298 \mathrm{~K}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 3.02\left(\mathrm{~d}, J_{\mathrm{PH}}=188.9 \mathrm{~Hz}, t \mathrm{Bu}_{2} \mathrm{P}-\right.$ $\left.\mathrm{P}(\mathrm{H})-\mathrm{PiPr}_{2}, 1 \mathrm{H}\right), 1.96$ (sept., $\left.J_{\mathrm{PH}}=6.72 \mathrm{~Hz}, \mathrm{PiPr}_{2}, 4 \mathrm{H}\right), 1.05\left(\mathrm{~d}, J_{\mathrm{PH}}=11.9 \mathrm{~Hz}, t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}(\mathrm{H})-\right.$ $\left.\mathrm{PiPr}_{2}, 18 \mathrm{H}\right), 0.52,0.47,0.42,037\left(\mathrm{~d}, J_{\mathrm{PH}}=6.72 \mathrm{~Hz}, \mathrm{PiPr}_{2}, 12 \mathrm{H}\right) ;{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}(298 \mathrm{~K}$, $\left.\mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 23.32\left(\mathrm{dd}, J_{\mathrm{PP}}=109.8 \mathrm{~Hz}, J_{\mathrm{PP}}=206.9 \mathrm{~Hz} t \mathrm{Bu}_{2} \mathbf{P}-\mathrm{P}(\mathrm{H})-\mathrm{PiPr}_{2}\right),-0.19\left(\mathrm{dd}, J_{\mathrm{PP}}=109.8\right.$ $\left.\mathrm{Hz}, J_{\mathrm{PP}}=213.2 \mathrm{~Hz} t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}(\mathrm{H})-\mathrm{PiPr} \mathrm{P}_{2}\right),-137.18\left(\mathrm{dd}, J_{\mathrm{PP}}=206.9 \mathrm{~Hz}, J_{\mathrm{PP}}=213.2 \mathrm{~Hz} t \mathrm{Bu}_{2} \mathrm{P}-\right.$ $\left.\mathbf{P}(\mathrm{H})-\mathrm{PiPr}_{2}\right) \mathrm{ppm}$.

Table 1. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$-NMR data of byproducts observed in reaction 1-7.

| Reaction | Byproducts | $\delta_{\mathrm{P} 1}[\mathrm{ppm}]$ | $\delta_{\mathrm{P} 2}[\mathrm{ppm}]$ | $\delta_{\mathrm{P} 3}[\mathrm{ppm}]$ | $J_{\mathrm{PP}}[\mathrm{Hz}]$ |
| :--- | :--- | :--- | :--- | :--- | :--- |


| Reaction 1 | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)} \mathrm{H}$ | (s) 19.49 |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(1)} t \mathrm{Bu}_{2}$ | (s) 39.66 |  |  |  |
| Reaction 2 | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(1)} t \mathrm{Bu}_{2}$ | (s) 19.56 |  |  |  |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)} \mathrm{H}$ |  |  |  |  |
|  | $i \mathrm{Pr}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(1)} i \mathrm{Pr}_{2}$ | (s) -12.11 |  |  |  |
|  | $\left(i \mathrm{Pr}_{2} \mathrm{P}_{(1)}\right)_{3} \mathrm{P}_{(2)}$ | (d) 3.51 | (m) -113.94 |  | 357.9 |
|  | $\left(t \mathrm{Bu}_{2} \mathrm{P}_{(1)}\right)\left(i \mathrm{Pr}_{2} \mathrm{P}_{(2)}\right)_{2} \mathrm{P}_{(3)}$ | (d) 43.06 | (d) 9.96 | (m) - | 459.6 |
|  |  |  |  | 102.27 | 397.1 |
|  | $i \mathrm{Pr}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(2)}(\mathrm{H})-\mathrm{P}_{(1)} \mathrm{Pr}_{2}$ | (d) -3.42 | (t) -139.99 |  | 203.4 |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(3)}(\mathrm{H})-\mathrm{P}_{(2)} i \mathrm{Pr}_{2}$ | (dd) 23.52 | (dd) 0.02 | (dd) - | 108.9 |
|  |  |  |  | 137.09 | 210.5 |
|  |  |  |  |  | 217.2 |
| Reaction 3 | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(1)} t \mathrm{Bu}_{2}$ | (s) 39.61 |  |  |  |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)} \mathrm{H}$ | (s) 19.59 |  |  |  |
| Reaction 4 | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(1)} t \mathrm{Bu}_{2}$ | (s) 39.82 |  |  |  |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)} \mathrm{H}$ | (s) 19.56 |  |  |  |
|  | $\left(t \mathrm{Bu}_{2} \mathrm{P}_{(1)}\right)\left((\mathrm{Cy}) t \mathrm{BuP}_{(2)}\right)_{2} \mathrm{P}_{(3)}{ }^{*}$ | (d) 57.23 | (d) 32.06 | (m) -99.86 | 486.8 |
|  |  |  |  |  | 508.6 |
| Reaction 5 | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(1)} t \mathrm{Bu}_{2}$ | (s) 39.86 |  |  |  |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)} \mathrm{H}$ | (s) 19.61 |  |  |  |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(2)}\left(\mathrm{SiMe}_{3}\right) \mathrm{H}$ | (d) 19.24 | (d) -190.65 |  | 196.2 |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(2)}\left(\mathrm{SiMe}_{3}\right)_{2}$ | (d) 44.45 | (d) -200.83 |  | 400.0 |
|  | $(\mathrm{Me}) t \mathrm{Bu} \mathrm{P}_{(1)}-\mathrm{P}_{(1)}(\mathrm{Me}) t \mathrm{Bu}$ | (s) -31.04 |  |  |  |
|  | $\left((\mathrm{Me}) t \mathrm{BuP}_{(1)}\right)_{3} \mathrm{P}_{(2)} *$ | (d) 38.94 | (m) -105.84 |  | 460.9 |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(2)}(\mathrm{H})-\mathrm{P}_{(1)} t \mathrm{Bu}_{2}$ | (d) 26.47 | (t) -136.79 |  | 228.2 |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(3)}(\mathrm{H})-\mathrm{P}_{(2)}(\mathrm{Me}) t \mathrm{Bu}$ | (dd) 23.33 | (dd) -16.96 |  | 130.7 |
|  |  |  |  | $115.90$ | 188.6 |
|  |  |  |  |  | 247.0 |
| Reaction 6 | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(1)} t \mathrm{Bu}_{2}$ | (s) 39.44 |  |  |  |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)} \mathrm{H}$ | (s) 19.75 |  |  |  |
|  | $(\mathrm{Ph}) t \mathrm{Bu} \mathrm{P}_{(1)}-\mathrm{P}_{(1)}(\mathrm{Ph}) t \mathrm{Bu}$ | (s) -4.69 |  |  |  |
|  | $\left((\mathrm{Ph}) t \mathrm{BuP} \mathrm{P}_{(1)}\right)_{3} \mathrm{P}_{(2)} *$ | (d) 45.69 | (m) -100.86 |  | 482.3 |
|  | $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)_{2}$ | (d) 44.03 | (d) -201.44 |  | 400.0 |
|  | $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right) \mathrm{H}$ | (d) 18.59 | (d) -191.21 |  | 196.1 |
| Reaction 7 | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)} \mathrm{H}$ | (s) 19.78 |  |  |  |
|  | $\mathrm{Ph}_{2} \mathrm{P}-\mathrm{PPh}_{2}$ | (s) -15.11 |  |  |  |
|  | $t \mathrm{Bu}_{2} \mathrm{P}_{(1)}-\mathrm{P}_{(2)} \mathrm{Ph}_{2}$ | (d) 32.85 | (d) -26.29 |  | 247.0 |

* the compounds were characterized by analogy to shifts for compounds $\left(t \mathrm{Bu}_{2} \mathrm{P}\right)\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{2} \mathrm{P}$ and $\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{3} \mathrm{P}$.


## 3. RESULTS AND DISCUSSION

### 3.1. Reactions of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) with chlorophosphanes.

The earlier performed DFT studies (condensed Fukui functions) of model compound $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) suggested amphiphilic character of $\mathrm{P}-\mathrm{SiMe}_{3}\left(f^{+}\right.$ 0.043 and $f^{-} 0.077$ ).[6f] In our latest work we presented the reactivity of $\beta$-diketiminate titanium(III) complexes with phosphanylphosphido ligands towards nucleophilic reagents: $\mathrm{Ph}_{2} \mathrm{PLi},\left(\mathrm{Me}_{3} \mathrm{Si}_{2} \mathrm{NLL}^{2}, t \mathrm{Bu}_{2} \mathrm{NLi}, t \mathrm{BuOLi}\right.$ that reacted via two different reactivity patterns. The first is the elimination of $-\mathrm{SiMe}_{3}$ group and lithiation of the phosphorus atom in the $\mathrm{P}\left(\mathrm{SiMe}_{3}\right)$ $\mathrm{P} t \mathrm{Bu}_{2}$ and the second is the substitution reaction of the chloride atom and oxidation of $\mathrm{Ti}(\mathrm{III})$.[9] Hence, we decided to examine the reactivity of $\left[{ }^{\mathrm{Me}} \mathrm{NaCNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)\right.\right.$ $\left.\mathrm{P} t \mathrm{Bu}_{2}\right\}$ ] (1) towards chlorophosphanes. We used selected reagents with different electronic
and steric properties such as: $t \mathrm{Bu}_{2} \mathrm{PCl} \quad i \mathrm{Pr}_{2} \mathrm{PCl}, \mathrm{Cy}_{2} \mathrm{PCl}, \quad(\mathrm{Cy}) t \mathrm{BuPCl}, \quad(\mathrm{Me}) t \mathrm{BuPCl}$, $(\mathrm{Ph}) t \mathrm{BuPCl}, \mathrm{Ph}_{2} \mathrm{PCl},\left(\mathrm{Pr}_{2} \mathrm{~N}\right) t \mathrm{BuPCl},\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$ in our investigations.

Taking into account that our starting complex $\left[{ }^{\mathrm{Me}} \mathrm{NaCNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) spontaneously (albeit slowly) rearranges in polar solvents,[6e] the first reactions were conducted in non-polar solvents: toluene or pentane (the same conditions such as in reactions conducted in THF solution $-48 \mathrm{~h}, 50^{\circ} \mathrm{C}$ - described below). Unfortunately, in all cases, we only isolated starting material (complex 1). Additionally, in ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$-NMR spectra of reaction mixtures, we observed only the signals of unreacted chlorophosphanes (example ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum after reaction with $(\mathrm{Ph}) t \mathrm{BuPCl}$ see Figure S 72 ). Therefore, we continued our studies by applying THF as solvent. To minimize the spontaneous rearrangement of starting titanium complex, we added the solution of 1 to chlorophosphanes. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$-NMR spectra of reaction mixtures indicate, that in the reactions of $\mathbf{1}$ with $i \mathrm{Pr}_{2} \mathrm{PCl}, \mathrm{Cy}_{2} \mathrm{PCl},(\mathrm{Cy}) t \mathrm{BuPCl}$, $(\mathrm{Me}) t \mathrm{BuPCl},(\mathrm{Ph}) t \mathrm{BuPCl}, \mathrm{Ph}_{2} \mathrm{PCl}$ two different $\beta$-diketiminate titanium(IV) complexes with phosphanylphosphinidene ligand are formed in each case (Scheme 1).


Scheme 1. Reaction of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{Pt} \mathrm{Bu}_{2}\right\}\right]$ (1) with selected chlorophosphanes.
Especially, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$-NMR investigation of the reaction mixture in the low field region $(850 \div 780 \mathrm{ppm})$ clearly confirmed that in reaction of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) with $i \mathrm{Pr}_{2} \mathrm{PCl}$ two complexes $\mathbf{1 a}$ and $\mathbf{1 b}$ are formed. Analogously in the reactions of $\mathbf{1}$ with $\mathrm{Cy}_{2} \mathrm{PCl},(\mathrm{Cy}) t \mathrm{BuPCl},(\mathrm{Me}) t \mathrm{BuPCl},(\mathrm{Ph}) t \mathrm{BuPCl}, \mathrm{Ph}_{2} \mathrm{PCl}$ two complexes are formed 1a-1c, 1a$\mathbf{1 d}, \mathbf{1 a - 1 e}, \mathbf{1 a - 1 f}$ and $\mathbf{1 a - 1 g}$ respectively. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ data of the $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}\right.\right.$ -$\left.\left.\mathrm{P}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}\right\}\right](\mathbf{1} \mathbf{x})$ complexes are presented in Table 2.

Table 2. The chemical shifts $[\mathrm{ppm}]$ and coupling constants [ Hz$]$ of phosphorus atoms in ${ }^{31} \mathrm{P}\{\mathrm{H}\}-\mathrm{NMR}$ in obtained complexes.

|  | $\mathbf{P ( 1 )}[\mathbf{p p m}]$ | $\mathbf{P}(\mathbf{2})[\mathbf{p p m}]$ | $\boldsymbol{J}_{\mathbf{P}(\mathbf{1}) \mathbf{P}(\mathbf{2})}[\mathbf{H z}]$ |
| :--- | :---: | :---: | :---: |
| $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}(1)-\mathrm{P}(2) t \mathrm{Bu}_{2}\right\}\right](\mathbf{1 a )}[6 \mathrm{e}]$ | 843.68 | 143.52 | 450.5 |
| $\left[{ }^{\mathrm{Me}} \mathrm{NaCNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}(1)-\mathrm{P}(2) i \mathrm{Pr}_{2}\right\}\right](\mathbf{1 b})[6 \mathrm{e}]$ | 824.23 | 118.37 | 443.2 |
| $\left[{ }^{\mathrm{Me}} \mathrm{NaCNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}(1)-\mathrm{P}(2) \mathrm{Cy}_{2}\right\}\right](\mathbf{1 c})$ | 832.99 | 107.78 | 442.8 |
| $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}(1)-\mathrm{P}(2)(\mathrm{Cy}) t \mathrm{Bu}\right\}\right](\mathbf{1 d})$ | 846.46 | 117.92 | 443.2 |


| $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}(1)-\mathrm{P}(2)(\mathrm{Me}) t \mathrm{Bu}\right\}\right] \quad(\mathbf{1 e})$ | 830.06 | 91.82 | 457.8 |
| :--- | :---: | :---: | :---: |
| $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}(1)-\mathrm{P}(2)(\mathrm{Ph}) t \mathrm{Bu}\right\}\right](\mathbf{1 f})[6 \mathrm{f}]$ | 825.19 | 109.63 | 443.2 |
| $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}(1)-\mathrm{P}(2) \mathrm{Ph}_{2}\right\}\right](\mathbf{1 g})$ | 780.29 | 88.05 | 472.3 |

The solubility differences of obtained complexes, allowed separating complexes from reaction mixtures. For the described reactions the complexes $\mathbf{1 a}, \mathbf{1 b}, \mathbf{1 c}, \mathbf{1 d}$ and $\mathbf{1 f}$ were separately isolated in the crystalline form. Unfortunately, we were not able to obtain 1e and $\mathbf{1 g}$ in crystalline form. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$-NMR examinations of reaction solutions also reveal the formation of different compounds mainly with newly formed $\mathrm{P}-\mathrm{P}$ and $\mathrm{P}-\mathrm{H}$ bonds in each reaction. In reaction 1 , two compounds were found as main byproducts: $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}$ [17] and $t \mathrm{Bu}_{2} \mathrm{PH}$ [18]. Most of the resulting byproducts were observed in the reaction of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) with $i \mathrm{Pr}_{2} \mathrm{PCl}$. In this reaction, in addition with two complexes $\mathbf{1 a}$ and $\mathbf{1 b}$ following compounds are also formed: $i \operatorname{Pr}_{2} \mathrm{P}-\mathrm{PiPr}_{2},[17]\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{3} \mathrm{P}$, $\left(t \mathrm{Bu}_{2} \mathrm{P}\right)\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{2} \mathrm{P}, \quad i \mathrm{Pr}_{2} \mathrm{P}-\mathrm{PH}-\mathrm{P} i \mathrm{Pr}_{2}$ [4a] and $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{PH}-\mathrm{Pi}_{2} \mathrm{Pr}_{2}$. The tetraphosphorus compound $\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{3} \mathrm{P}$ was earlier synthesized and characterized by Scheer and co-workers in the reaction of $i \mathrm{Pr}_{2} \mathrm{P}-\mathrm{P}(\mathrm{Li})-\mathrm{P}_{\mathrm{P}} \mathrm{Pr}_{2}$ with $i \mathrm{Pr}_{2} \mathrm{PCl},[2]$ while the $\left(t \mathrm{Bu}_{2} \mathrm{P}\right)\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{2} \mathrm{P}$ is observed for the first time. To confirm that, we additionally performed reaction of $i \mathrm{Pr}_{2} \mathrm{P}-\mathrm{P}(\mathrm{Li})-{\mathrm{P} i \mathrm{Pr}_{2} \text { with } t \mathrm{Bu} \mathbf{L}_{2} \mathrm{PCl} \text { and as }}^{2}$ a result we received the desired compound $\left(t \mathrm{Bu}_{2} \mathrm{P}\right)\left(i \mathrm{Pr}_{2} \mathrm{P}\right)_{2} \mathrm{P}$ (doublets at 43.06 ppm and 9.96 ppm and multiplet at $-102.27 \mathrm{ppm}, J_{\mathrm{PP}}=397.1 \mathrm{~Hz}$ and $J_{\mathrm{PP}}=459.6 \mathrm{~Hz}$, for all NMR spectra of the reaction see SI, Figure S63-S71). In reactions 3 and 4 as byproducts symmetrical diphosphane $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}$ was found along with $t \mathrm{Bu}_{2} \mathrm{PH}$. Additionally in reaction 4 the weak signals of $\left(t \mathrm{Bu}_{2} \mathrm{P}\right)((\mathrm{Cy}) t \mathrm{BuP})_{2} \mathrm{P}$ were observed (doublets at 57.23 ppm and 32.06 ppm and multiplet at $-99.86 \mathrm{ppm}, J_{\mathrm{PP}}=486.8 \mathrm{~Hz}$ and $J_{\mathrm{PP}}=508.6 \mathrm{~Hz}$, see SI, Figure S25-S26). In reaction 5 were found symmetrical diphosphanes $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}$, (Me) $t \mathrm{BuP}-\mathrm{P}(\mathrm{Me}) t \mathrm{Bu}[19]$ and also $t \mathrm{Bu}_{2} \mathrm{PH},((\mathrm{Me}) t \mathrm{BuP})_{3} \mathrm{P}, t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{PH}-\mathrm{P} t \mathrm{Bu}_{2}$ [20] and $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{PH}-\mathrm{P}(\mathrm{Me}) t \mathrm{Bu}$ as byproducts. In reaction 6, except symmetrical diphosphanes $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}$, $(\mathrm{Ph}) t \mathrm{BuP}-\mathrm{P}(\mathrm{Ph}) t \mathrm{Bu}[21]$ and other byproducts were also found including $t \mathrm{Bu}_{2} \mathrm{PH},((\mathrm{Ph}) t \mathrm{BuP})_{3} \mathrm{P}$ and $(\mathrm{Ph}) t \mathrm{BuP}-\mathrm{PH}-\mathrm{P} t \mathrm{Bu}_{2}$. In reaction 7 we observed as byproducts only $t \mathrm{Bu}_{2} \mathrm{PH}, \mathrm{Ph}_{2} \mathrm{P}-\mathrm{PPh}_{2}$ [22] and $\mathrm{Ph}_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}$ [23]. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$-NMR data of all byproducts are listed in the experimental section in Table 1. Very generally the reactions of 1 with $R^{B} R^{C} \mathrm{PCl}$ can be considered as a reduction of $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{PCl}$ by T (III) compounds leading to the formation of new P-P bonds. Taking into account, the byproducts $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}, \mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}$ and $t \mathrm{Bu} u_{2} \mathrm{PH}$ it seems very probable, that the main process is a reduction of $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{{ }^{C}} \mathrm{PCl}$ which proceeds according to a radical mechanism, thereby $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}$. or $t \mathrm{Bu} u_{2} \mathrm{P}$. radicals are released. Thus the first step should lead to a nearly symmetric intermediate with a ligand of formula $\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}$ (the optimization of
the example of $\beta$-diketiminate titanium(III) complex with triphopshorus ligand (see SI, Figure S73).

At the beginning, we have considered the nucleophilic substitution of $\mathrm{P}-\mathrm{SiMe}_{3}$ phosphorus of $\mathbf{1}$ into the P -atom of $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{PCl}$ yielding [ ${ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{1,2-\eta-t \mathrm{Bu} \mathbf{x}_{2} \mathrm{P}-\mathrm{P}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}\right\}$ ] or $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})-\left\{1,2-\eta-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ and $\mathrm{Me}_{3} \mathrm{SiCl}$. Unfortunately, the $\left(i \mathrm{Pr}_{2} \mathrm{~N}\right) t \mathrm{BuPCl}$ does not react with 1 and does not confirm this assumption. In order to better understand the electronic properties of chlorophosphanes we calculated Fukui $f^{+}, f^{\circ}$ and $\Delta f$ for these compounds. The obtained results reveal that the chlorophosphanes $\mathrm{Ph}_{2} \mathrm{PCl}, t \mathrm{Bu}_{2} \mathrm{PCl}$, $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl},(\mathrm{Ph}) t \mathrm{BuPCl},(\mathrm{Me}) t \mathrm{BuPCl}, i \mathrm{Pr}_{2} \mathrm{PCl}$ indicate the weak nucleophilic character $(\Delta f<$ $0)$. The $\mathrm{Cy}_{2} \mathrm{PCl}$ and $(\mathrm{Cy}) t \mathrm{BuPCl}$ display stronger nucleophilic properties, while the $\left(i \operatorname{Pr}_{2} \mathrm{~N}\right) t \mathrm{BuPCl}$ as the only one shows the electrophilic ones. The values of $f^{+}, f^{+}$and $\Delta f$ are depicted in Table 3.

Table 3. Values of condensed nucleophilic $f$ and electrophilic $f^{+}$functions and $\Delta f$ dual descriptor calculated based on Hirshfield population analysis (HPA).

| Chlorophosphane | $\boldsymbol{f}^{+}$ | $\boldsymbol{f}$ | $\boldsymbol{\Delta} \boldsymbol{f}$ |
| :--- | :---: | :---: | :---: |
| $t \mathrm{Bu}_{2} \mathrm{PCl}$ | 0.242 | 0.317 | -0.075 |
| $i \mathrm{Pr}_{2} \mathrm{PCl}$ | 0.264 | 0.332 | -0.069 |
| $\mathrm{Cy}{ }_{2} \mathrm{PCl}$ | 0.032 | 0.320 | -0.288 |
| $(\mathrm{Cy}) t \mathrm{BuPCl}$ | 0.041 | 0,317 | $-0,276$ |
| $(\mathrm{Me}) t \mathrm{BuPCl}$ | 0.302 | 0.338 | -0.035 |
| $(\mathrm{Ph}) t \mathrm{BuPCl}$ | 0.160 | 0.246 | -0.086 |
| $\mathrm{Ph}_{2} \mathrm{PCl}$ | 0.192 | 0.212 | -0.020 |
| $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$ | 0.048 | 0.101 | -0.054 |
| $\left(i \mathrm{Pr}_{2} \mathrm{~N}\right) t \mathrm{BuPCl}$ | 0.205 | 0.125 | 0.080 |

The obtained DFT results indicate a different initial stage of this reaction. It is very likely that the reaction starts with a nucleophilic attack of $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{PCl}$ on the $\mathrm{Ti}(\mathrm{III})$ center and after removal of $\mathrm{Me}_{3} \mathrm{SiCl}$ leads to the same triphosphorus intermediate. Furthermore, this route is consistent with the lack of reactivity of $\left(i \mathrm{Pr}_{2} \mathrm{~N}\right) t \mathrm{BuPCl}$.


Scheme 2. The probable mechanism leading to the formation of titanium(III) complexes with triphosphorus ligand.

The titanium oxidation state in the complexes with triphosphorus ligand $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{t \mathrm{Bu} \mathbf{L}_{2} \mathrm{P}-\mathrm{P}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}\right\}\right]$ is +III and tendency to reach oxidation number +IV causes destabilization of the triphosphorus unit and generates radicals: $t \mathrm{Bu}_{2} \mathrm{P} \cdot$ or $/$ and $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}$. Comparison of amounts of $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, \mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}, \mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, \mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{PH}$, and $t \mathrm{Bu} u_{2} \mathrm{PH}$ in reaction solutions may assume, that in reaction $3\left(1+\mathrm{Cy}_{2} \mathrm{PCl}\right)$ and in reaction $4(1+$ $(\mathrm{Cy}) t \mathrm{BuPCl}) t \mathrm{Bu}_{2} \mathrm{P} \cdot$ radicals are released and in reaction $7\left(\mathbf{1}+\mathrm{Ph}_{2} \mathrm{PCl}\right)$ almost entirely $\mathrm{Ph}_{2} \mathrm{P}$. radicals are released. In reactions $2,4,5$, and 6 we observed releasing $t \mathrm{Bu}_{2} \mathrm{P}$. and $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}$. Furthermore, we additional observed sequences leading to the formation of compounds with new P-P bonds in these reactions as well, however with the involvement of phosphido P -atom. We also observed the formation of $\left(t \mathrm{Bu}_{2} \mathrm{P}\right)\left(\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}\right)_{2} \mathrm{P}$ and/or $\left(\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}\right)_{3} \mathrm{P}, \mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}-\mathrm{PH}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}$, $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{PH}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}$ and $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{PH}-\mathrm{P} t \mathrm{Bu}_{2}$

Experimental data indicate that the substituents on the P -atoms in chlorophosphanes determine their reactivity towards $\mathbf{1}$. The inductive and mesomeric effects of the substituents influence on the molar ratio of final products. In order to define whether these differences arise from the energy effects accompanying both reactions, we have determined the free energy values of the corresponding reactions (A and B) by applying DFT calculations. Based on the $\Delta \mathrm{G}$ values we also determined the values of the equilibrium constants $\mathrm{K}_{\mathrm{A}}$ and $\mathrm{K}_{\mathrm{B}}$ and then the molar ratio between the reaction products $\mathbf{1 a}$ and new titanium complexes with $R^{B} R^{C} P$-P ligand (Scheme 3 and Table 4).


Scheme 3. Possible reactions of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) with selected chlorophosphanes.
We found that there is a good agreement between the computational results and the experimental data (by comparison of molar ratio between 1a : 1x $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\right.\right.$ $\left.\left.\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}\right\}\right]$ ). Hence, the differences in the composition of reaction products may be explained on the grounds of thermodynamics.

Table 4. Calculated and experimental data of the reactions of complex $\left[{ }^{\mathrm{Me}} \mathrm{NaCNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu} u_{2}\right\}\right]$ (1) with selected chlorophosphanes: $\Delta G_{A}, \Delta G_{B}$ - values of calculated free energies of reactions $A$ and $B ; K_{A}, K_{B}$ - values of calculated equilibrium constants of reactions A and $\mathrm{B}, \mathrm{X}_{\mathrm{CALC}}$ - calculated molar ration of complexes obtained after A route and obtained after B route, $\mathrm{X}_{\mathrm{EXP}}$ - experimental molar ration of complexes obtained after A route and obtained after B route.

|  | $\mathbf{R R ' P C l}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

DFT calculations indicate smaller values of product according to the A reaction. Especially, this is clearly visible in the slow reactions with $\mathrm{Cy}_{2} \mathrm{PCl}$ and $(\mathrm{Cy}) t \mathrm{BuPCl}$. These results may indicate that in these cases the spontaneous decomposition of $\mathbf{1}$ is significant. The $\mathrm{P}-\mathrm{P}$ bond cleavage according to the radical mechanism may depend on two main factors:
electronic properties of organic substituents on the phosphanyl phosphorus atom and consequently from their steric hindrance. Our results show that the stability of the generated $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}$. radicals is an important factor. The particular example is reaction $7\left(1+\mathrm{Ph}_{2} \mathrm{PCl}\right)$ in which 1a is formed almost solely and only a small amount of $\left[{ }^{\mathrm{Me}} \mathrm{NaCNacTi}(\mathrm{Cl})\left\{\eta^{2} \mathrm{P}-\mathrm{PPh}_{2}\right\}\right]$ $(\mathbf{1 g})$ is created. Additionally in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ spectrum, a large signal of $\mathrm{Ph}_{2} \mathrm{P}-\mathrm{PPh}_{2}$ is visible whereas the signal of $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}$ is at the noise level. Analogous observation of stability of phosphanyl radicals was described by Grubba and co-workers. He suggests, that the stability of phosphanyl radicals strongly depends on the size of the P -substituent and decreases such that: $\mathrm{Ph}_{2} \mathrm{P} \cdot>(\mathrm{Ph}) t \mathrm{BuP} \cdot>\left(i \mathrm{Pr}_{2} \mathrm{~N}\right)_{2} \mathrm{P} \cdot>t \mathrm{Bu}_{2} \mathrm{P} \cdot$. Furthermore, the $\mathrm{Ph}_{2} \mathrm{P} \cdot$ radical exhibits the highest degree of spin density delocalization due to the presence of aromatic rings.[24] The significant factors which influence the molar ratio $\mathbf{1 a}: \mathbf{1 x}(x \neq a)$ are the nucleophilic properties of related chlorophosphanes. For the most nucleophilic species $\mathrm{Cy}_{2} \mathrm{PCl}$ and $(\mathrm{Cy}) t \mathrm{BuPCl}$ we observe products which indicate the liberating of $t \mathrm{Bu}_{2} \mathrm{P} \cdot$ radicals as $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}$ and $t \mathrm{Bu}_{2} \mathrm{PH}$. The small amount of $\mathbf{1 a}$ in reaction solutions should be attributed to a spontaneous rearrangement of $\mathbf{1}$ leading to $\mathbf{1 a}$.

We also conducted the reaction of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) with $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$ in THF solution in molar ratio $1: 1\left(\Delta f\right.$ calculated for $\left.\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}-0.054\right)$. 1 reacts with $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$ yielding two different crystalline products. Both compounds were X -ray characterized as $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTiCl}_{2}(\mathrm{THF})\right]$ (green crystals in form of blocks) and $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\mathrm{NEt}_{2}\right\}\right]_{2}$ (2) (green crystals in form of plates). The $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTiCl}_{2}\right.$ (THF)] was earlier reported by Mindiola and co-workers.[25] After isolation of both obtained crystalline products, the remained solution was ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ investigated. Surprisingly, the NMR results revealed a formation of additional several compounds: $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{3} \mathrm{P},\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{P}$ $\mathrm{P}\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2}, \quad t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right) \mathrm{H}$, and a compound 3 with $\mathrm{AA}^{\prime} \mathrm{M}_{2} \mathrm{XX}$ ' spin pattern, but unfortunately, we have not been able to isolate it so far.


Scheme 4. Structure of phosphetane (3).
To confirm the formula of $\mathbf{3}$, we conducted a simulation of its ${ }^{31} \mathrm{P}$ spectra (See SI, Figure S60-S62). The established ${ }^{31} \mathrm{P}-\mathrm{NMR}$ data (See SI, Figure S53-S59) closely resemble these
found earlier in a series for phosphetanes of formula $\mathrm{A}-\mathrm{P}\left(\mu_{2}-\mathrm{PNR}_{2}\right)_{2} \mathrm{P}-\mathrm{B}$ where $\mathrm{R}=\mathrm{Et}$ or $i \mathrm{Pr}$; $\mathrm{A}, \mathrm{B}=\mathrm{PR}_{2}$ or/and $\mathrm{SiMe}_{3}$ which are formed in reactions of $\left[\mathrm{Cp}_{2} \mathrm{HfCl}_{2}\right]$ or $\left[\mathrm{CpZrCl}_{3}\right]$ with $\left(\mathrm{R}_{2} \mathrm{~N}\right)_{2} \mathrm{P}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right) \mathrm{Li}$ or via thermal rearrangement of $\left[\mathrm{Cp}_{2} \mathrm{Hff}(\mathrm{Cl})\left(\eta^{1}-\left(\mathrm{Me}_{3} \mathrm{Si}\right) \mathrm{P}-\mathrm{P}\left(\mathrm{NEt}_{2}\right)_{2}\right]\right.$ [26] or in reaction of $\left(i \mathrm{Pr}_{2}\right)_{2} \mathrm{P}-\mathrm{P}\left(\mathrm{Me}_{3} \mathrm{Si}\right) \mathrm{Li}$ with $\left[{ }^{\mathrm{Me}} \mathrm{NacNacFeCl}_{2} \mathrm{Li}\right]$. [27] Such phosphetanes are not formed in reactions of $\left(\mathrm{R}_{2} \mathrm{~N}\right)_{2} \mathrm{P}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right) \mathrm{Li}$ with $\left[\mathrm{L}_{2} \mathrm{PtCl}_{2}\right]$ ( $\mathrm{L}=$ tertiary phosphanes) but $\left[\mathrm{L}_{2} \mathrm{Pt}\left\{\eta^{2}-\mathrm{P}=\mathrm{P}\left(\mathrm{NR}_{2}\right)_{2}\right\}\right]$ can be isolated.[6a] In all processes leading to phosphetanes, compounds with $\mathrm{TM}-\mathrm{NR}_{2}$ (TM - transition metals) moieties were isolated. Thus $\mathrm{TM}-\mathrm{NR}_{2}$ bonds are formed rather for early ( $\mathrm{Ti}, \mathrm{Zr}, \mathrm{Hf}$ ) or medium ( Fe ) TM than for late ( Pt ) ones. Scheme 5 shows the probable stoichiometry of reaction 1 with $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$ leading to 3 .



Scheme 5. The reaction of $\left[{ }^{\mathrm{Me}} \mathrm{NaCNaCTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{Pt} \mathrm{Bu}_{2}\right\}\right]$ (1) with $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$.

### 3.2. X-ray studies

X-ray suitable crystals of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{PCy}_{2}\right\}\right]$ (1c) grow from a saturated pentane solution and crystallize in monoclinic space group $P 2_{1} / n$ with four molecules in the unit cell. The metal center of (1c) adopts a pseudo-trigonal-bipyramidal geometry with one nitrogen atom of $\beta$-diketiminate ligand, phosphinidene phosphorus atom and chloride atoms in the equatorial position. The axial position is occupied by one nitrogen atom of $\beta$ diketiminate ligand and phosphanyl phosphorus atom of the $\mathrm{Cy}_{2} \mathrm{P}-\mathrm{P}$ ligand.


Figure 1. Molecular structure of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{PCy}_{2}\right\}\right]$ (1c), (hydrogen atoms omitted for clarity). Important bond lengths ( $\AA$ ), bond angles (deg): N1-Ti1 2.031(10), N2-Ti1 1.984(9), P1-P2 2.114(5), P1-Ti1 2.322(4), P2-Ti1 2.512(4), Cl1-Ti1 2.313(3); P1-P2-Ti1 59.52(14), N1-Ti1-N2 93.9(4), P1-Ti1-P2 51.70. The sum of the angles around the P atoms: $\Sigma \mathrm{P} 2=328.3(5)$

The values of Ti-P bond lengths (Ti1-P1 2.322(4) $\AA$ and Ti1-P2 2.512(4) $\AA$ ) indicate that the coordination of phosphanylphosphinidene ligand to the metal center is near $\eta^{2}$ (P2-P1-Ti1 $\left.=68.78(16)^{\circ}\right)$. The same distances and coordination were also observed in early described $\beta$ diketiminate titanium(IV) complexes with phosphanylphosphinidene ligand $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-{\left.\left.\mathrm{P} t \mathrm{Bu}_{2}\right\}\right] \quad \text { (1a) }} \quad(\mathrm{Ti1}-\mathrm{P} 1 \quad 2.334(3) \quad \AA\right.\right.$, $\quad \mathrm{Ti1}-\mathrm{P} 2 \quad 2.523(3) \quad \AA),[6 e]$ $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}_{\mathrm{P}}^{\mathrm{Pr}}{ }_{2}\right\}\right]$ (1b) (Ti1-P1 2.3237(7) $\AA, \mathrm{Ti1}-\mathrm{P} 2$ 2.4933(7) $\left.\AA\right)[6 \mathrm{e}]$ and $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}(\mathrm{Ph}) t \mathrm{Bu}\right\}\right]$ (1f) (Ti1-P1 2.3237(7) $\AA$, Ti1-P2 2.5128(7) $\left.\AA\right)$.[6f] The P1-P2 distance ( $\mathrm{P} 1-\mathrm{P} 22.114(5) \AA$ ) is typical for $\mathrm{P}=\mathrm{P}$ double bond in side-on geometry and is comparable to the complex with the same pseudo-trigonal-bypyramidal geometry on the metal center $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1a) (2.112(4) $\AA$ ). The NCCCN unsaturated backbone of the $\beta$-diketiminate ligand is almost planar, with $0.0391(2) \AA$; the titanium atom is out of plane of the diamine ligand framework by 0.944 (3) $\AA$. The value of bond lengths of the $\mathrm{N}-\mathrm{C}$ and C - C in the backbone of the $\beta$-diketiminate ligand are between single and double bond lengths and the results suggest the delocalization of the double bond of the ligand.

X-ray suitable crystals of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}(\mathrm{Cy}) t \mathrm{Bu}\right\}\right]$ (1d) grow from a saturated pentane solution. 1d crystallizes in monoclinic space group $P 2_{1} / c$ with four molecules in the unit cell. The titanium atom adopts a pseudo square pyramidal geometry, where the chloride ion occupies an axial position.


Figure 2. Molecular structure of $\left[{ }^{\mathrm{Me}} \mathrm{NaCNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}(\mathrm{Cy}) t \mathrm{Bu}\right\}\right]$ (1d), (hydrogen atoms omitted for clarity). Important bond lengths ( $\AA$ ), bond angles (deg): N1-Ti1 2.046(3), N2-Til 2.034(3), P1-P2 2.1039(19), P1-Ti1 2.3153(15), P2-Ti1 2.5079(16), Cl1-Ti1 2.3059(13); P1-P2-Ti1 59.50(5), N1-Ti1-N2 93.30(14), P1-Ti1-P2 51.54(5). The sum of the angles around the P atoms: $\Sigma \mathrm{P} 2=330.2(3)$.

1d complex is isostructural with earlier described complex 1c. The P-P distance in $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P}(\mathrm{Cy}) t \mathrm{Bu}\right\}\right](\mathbf{1 d})(2.1039(19) \AA)$ is typical for double bond between two phosphorus atoms. The distance is slightly shorter to these observed in 1c, but is comparable to the distances observed in phosphanylphosphinidene titanium(IV) complexes with distorted square pyramidal environment on the titanium center: [ ${ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\right.$ $\mathrm{Pi}_{\mathrm{Pr}}^{2}$ \}] (1b) (2.1038(8) $\AA$ ).

Complex 2 crystallizes in the monoclinic space group $P 2_{1} / n$ with a four molecules in the unit cell. In the molecule the titanium atom adopts the disorder tetrahedral geometry ( $\tau_{4}=$ $0.88, \tau_{4}{ }^{\prime}=0.86$ ) [28] (Figure 3).


Figure 3. Molecular structure of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\mathrm{NEt}_{2}\right\}\right]_{2}$ (2), (hydrogen atoms omitted for clarity). Important bond lengths $(\AA)$, bond angles (deg): N1-Ti1 2.101(4), N2-Ti1 2.099(4), N3-Ti1 2.009(4), Cl1-Ti1 2.4648(17); N1-Ti1-N2 87.51(15), Cl1-Ti1-N3 97.6(4). The sum of the angles around the N atoms: $\Sigma \mathrm{N} 3=358.2(2)$.

In the obtained structure the diethylamino ligand from the $\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl}$ is observed. The Ti1-N3 distance is $2.009(4) \AA$ and is significantly longer to these observed in $\left[\mathrm{Ti}\left(\mathrm{NEt}_{2}\right)_{3} \mathrm{Cl}\right]$ (1.864(4) $\AA, 1.860(4) \AA$ and $1.860(4) \AA$ respectively).[29] Additionally, the sum of angles around the nitrogen atom is $358.2(2)^{\circ}$, which may suggests multiple bonds between titanium and nitrogen atoms. The NCCCN unsaturated backbone of the ligand is almost planar with $0.0323(2) \AA$ deviation from the planarity and the titanium atom is out of plane of the diamine ligand framework by $0.847(3) \AA$. The bond lengths $\mathrm{C}-\mathrm{N}$ and $\mathrm{C}-\mathrm{C}$ in the backbone skeleton suggest similar as in 1c and 1d structure the delocalization of double bond lengths. The $\mathrm{T}-\mathrm{Ti}$ distance is $3.841(4) \AA$, which is definitely too long for there to be significant metal-metal bonding interaction.

## 4. Conclusions

Reactions of $\beta$-diketiminate Ti(III) complex with phosphanylphosphido ligand $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) towards chlorophosphanes $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{PCl}$ were studied. These reactions can be seen as oxidation of $\mathbf{1}$ to $\mathrm{Ti}(\mathrm{IV})$ complexes with phosphanylphosphinidene ligand $\quad\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right] \quad$ (1a) or/and $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}^{-}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}\right\}\right]$ (1x). Reduction byproducts possess new $\mathrm{P}-\mathrm{P}$ bond mainly $t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{P} t \mathrm{Bu}_{2}, \quad t \mathrm{Bu}_{2} \mathrm{P}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}, \quad \mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}-\mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}$ or $\mathrm{P}-\mathrm{H}$ bond, in great majority $t \mathrm{Bu}_{2} \mathrm{PH}$. This composition of byproducts supports a radical mechanism of discussed
redox process. The nucleophilic properties (not electrophilic) of phosphorus atoms in $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{PCl}$ are essential for the results of studied reactions. The molar ratio 1a : 1x depends on the substituents $R^{B}$ and $R^{C}$ and is driven by the nucleophilic properties of $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{PCl}$ in the first stage of reaction sequences - the nucleophilic addition of chlorophosphane to $\mathrm{Ti}(\mathrm{III})$ center and by the stability of liberated radicals $t \mathrm{Bu}_{2} \mathrm{P}$. vs $\mathrm{R}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}} \mathrm{P}$. The weak nucleophile $\mathrm{Ph}_{2} \mathrm{PCl}$ reacts with $\mathbf{1}$ yielding $\mathbf{1 a}$ almost solely and relatively stable $\mathrm{Ph}_{2} \mathrm{P}$. radicals are liberated in the oxidation stage of reaction. Quite different outcomes are observed in the case of strong nucleophiles: $\mathrm{Cy}_{2} \mathrm{PCl}$ and $(\mathrm{Cy}) t \mathrm{BuPCl}$. The reactions are slow (steric hindrance) and $t \mathrm{Bu}_{2} \mathrm{P}$. radicals are released along with $\left[{ }^{\mathrm{Me}} \mathrm{NaCNaCTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}_{-} \mathrm{PR}^{\mathrm{B}} \mathrm{R}^{\mathrm{C}}\right\}\right] \quad$ (1x) formation. $\left(i \mathrm{Pr}_{2} \mathrm{~N}\right) t \mathrm{BuPCl}$ does not react with $\mathbf{1}$ because of its very low nucleophilicity. In the reaction of $\left[{ }^{\mathrm{Me}} \mathrm{NacNacTi}(\mathrm{Cl})\left\{\eta^{2}-\mathrm{P}\left(\mathrm{SiMe}_{3}\right)-\mathrm{P} t \mathrm{Bu}_{2}\right\}\right]$ (1) with $\quad\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PCl} \quad$ a formation of phosphetane $\mathbf{3}$ was observed.

## APPENDIX A. Supporting information

CCDC 1898633-1898635 contains the supplementary crystallographic data for 1c, 1d, $\mathbf{2}$. These data can be obtained free of charge via http///www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

## ACKNOWLEDGMENT

Ł. P thanks the Dean of Chemical Faculty for financial support (DS 033154). The authors thank TASK Computational Center for the access to computational resources. The authors thank KNMF (Karlsruhe Nano Micro Facility) KIT Karlsruhe for X-ray single crystal measurements. Ł. P. thanks Prof Dieter Fenske and O. Fuhr for help and friendly atmosphere in Karlsruhe.

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