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## Reactions of (Ph)tBuP-P(SiMe<sub>3</sub>)Li·3THF with [(PNP)TiCl<sub>2</sub>] and [<sup>Me</sup>NacNacTiCl<sub>2</sub>·THF]. Synthesis of first PNP titanium(IV) complex with phosphanylphosphinidene ligand [(PNP)Ti(Cl){η<sup>2</sup>-P-P(Ph)tBu}]

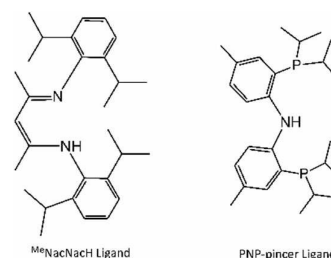
Aleksandra Ziółkowska,<sup>a</sup> Natalia Szykiewicz,<sup>a</sup> Aleksandra Wiśniewska,<sup>a</sup> Jerzy Pikies<sup>a</sup> and Łukasz Ponikiewski<sup>a</sup>

Lithium derivative of diphosphane (Ph)tBuP-P(SiMe<sub>3</sub>)Li (**1**) was isolated for the first time and investigated in reactions with β-diketiminato (<sup>Me</sup>Nacnac<sup>-</sup> = [Ar]NC(Me)CHC(Me)N[Ar]; Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and PNP-pincer (PNP = N[2-*i*Pr-4-methylphenyl]<sub>2</sub>) Ti(III) complexes. The β-diketiminato titanium(III) complex containing phosphanylphosphido ligand [<sup>Me</sup>NacNacTi(Cl){η<sup>2</sup>-P(SiMe<sub>3</sub>)-P(Ph)tBu}] (**2**) was prepared in reaction of [<sup>Me</sup>NacNacTiCl<sub>2</sub>·THF] with (Ph)tBuP-P(SiMe<sub>3</sub>)Li in toluene solution with good yield and purity. Respective titanium(IV) complex involving phosphanylphosphinidene ligand [<sup>Me</sup>NacNacTi(Cl){η<sup>2</sup>-P-P(Ph)tBu}] (**3**) was synthesized by oxidation of complex (**2**) with [iBu<sub>3</sub>PAGCl]<sub>4</sub>. Interestingly, an analogous PNP titanium(IV) complex [(PNP)Ti(Cl){η<sup>2</sup>-P-P(Ph)tBu}] (**4**) was obtained in the reaction of [(PNP)TiCl<sub>2</sub>] with (Ph)tBuP-P(SiMe<sub>3</sub>)Li in toluene solution and 1 : 1 molar ratio instead of the expected titanium(III) complex with phosphanylphosphido ligand. Solid-state structures of (Ph)tBuP-P(SiMe<sub>3</sub>)Li·3THF (**1**), [<sup>Me</sup>NacNacTi(Cl){η<sup>2</sup>-P(SiMe<sub>3</sub>)-P(Ph)tBu}] (**2**), [<sup>Me</sup>NacNacTi(Cl){η<sup>2</sup>-P-P(Ph)tBu}] (**3**) and [(PNP)Ti(Cl){η<sup>2</sup>-P-P(Ph)tBu}] (**4**) determined by single-crystal X-ray diffraction revealed that in all obtained complexes both, the phosphanylphosphinidene (Ph)tBuP-P and phosphanylphosphido (Ph)tBuP-P(SiMe<sub>3</sub>) ligands are bidently coordinated to the metal center.

### 1. Introduction

Titanium carbene and carbenoids complexes display rich and important chemistry.<sup>1, 2</sup> They exhibit Metallo-Wittig reactivity and are very good reagents in conversion of carbonyl compounds into alkenes.<sup>3, 4</sup> In many cases they are preferred because they are not basic, do not cause rearrangements of organic reagents and are only moderately sensitive to steric effect of organic reagent. Recently also nitrogen<sup>5, 6</sup> and phosphorus analogues gain increasing attention. Thermodynamic properties of the alkydine, nitrene and phosphinidene complexes of titanium(IV) cause that they are very promising reagents in Metallo-Wittig reactions and therefore, the further exploration of these classes of

complexes is important. The crucial point in the development of titanium chemistry, especially of phosphinidene complexes, was the introduction of β-diketiminato and PNP ancillary ligands<sup>7-9</sup> which render the resulting phosphinidene complexes sufficient stability.



**Scheme 1.** The scheme of β-diketiminato <sup>Me</sup>NacNacH and PNP ancillary ligands.

We have applied the above-mentioned ligands to our chemistry and very recently we have obtained Ti(III) complexes containing phosphanylphosphido (R<sub>2</sub>P-PSiMe<sub>3</sub>) units *via* metathesis reactions of R<sub>2</sub>P-P(SiMe<sub>3</sub>)Li with [<sup>Me</sup>NacNacTiCl<sub>2</sub>·THF] and [(PNP)TiCl<sub>2</sub>] (R = *t*Bu and *i*Pr). The oxidation of β-diketiminato titanium(III) complexes with phosphanylphosphido moiety lead to related Ti(IV) complexes with phosphanylphosphinidene (R<sub>2</sub>P-P) ligand.<sup>10</sup> Although the

<sup>a</sup> Gdansk University of Technology  
Faculty of Chemistry  
Department of Inorganic Chemistry  
Gabriela Narutowicza Str. 11/12  
80-233 Gdansk  
Poland

E-mail: lukasz.ponikiewski@pg.edu.pl

† Footnotes relating to the title and/or authors should appear here.

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PNP titanium(III) complexes with phosphanylphosphido moiety were proved to be very resist against oxidation, we were not able to obtain related Ti(IV) phosphanylphosphinidene complexes.<sup>11</sup>

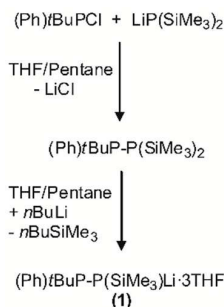
The special role in our synthesis play the lithiated diphosphanes as precursors of phosphanylphosphinidene R<sub>2</sub>P-P and phosphanylphosphido R<sub>2</sub>P-P(SiMe<sub>3</sub>) ligands (R is *t*Bu, *i*Pr, NEt<sub>2</sub>, NiPr<sub>2</sub>). Almost all phosphanylphosphido and phosphanylphosphinidene ligands in transition metals complexes involve exclusively sterically encumbered and electron donating aliphatic *t*Bu and *i*Pr groups. Nevertheless, bidently bonded phosphanylphosphinidene complexes with R = *i*Pr<sub>2</sub>N or Et<sub>2</sub>N are especially stable for Pt(0) center.<sup>12</sup> Interestingly, related complexes of early and medium transition metals are not stable and rearrange to phosphetanes.<sup>13, 14</sup> The complexes with Ph<sub>2</sub>P-P ligand of tungsten and niobium were only synthesized successfully in a different way by Cummins *et al.*<sup>15, 16</sup> Therefore, taking into account our previous results as well as the literature reports, we extended our studies on complexes with a new ligand which displays weaker electron-donating properties than *t*Bu<sub>2</sub>P-P or *i*Pr<sub>2</sub>P-P and only moderate steric hindrance.

Herein, we report on the synthesis, molecular structures and reactivity of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·3THF towards [(PNP)TiCl<sub>2</sub>] and [<sup>Me</sup>NacNacTiCl<sub>2</sub>·THF].

## 2. Result and discussion

### 2.1. Synthesis of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·*n*THF.

The synthesis, NMR-data and X-ray structures of lithium derivatives: *t*Bu<sub>2</sub>P-P(SiMe<sub>3</sub>)Li·*n*THF, *i*Pr<sub>2</sub>P-P(SiMe<sub>3</sub>)Li·*n*THF, Ph<sub>2</sub>P-P(SiMe<sub>3</sub>)Li·*n*THF and (*i*Pr<sub>2</sub>N)<sub>2</sub>P-P(SiMe<sub>3</sub>)Li·*n*THF are already known,<sup>17, 18</sup> whereas (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·*n*THF was described briefly and only <sup>31</sup>P-NMR data were published.<sup>19</sup> Thus, we conducted the reaction of (Ph)*t*BuP-P(SiMe<sub>3</sub>)<sub>2</sub> with *n*BuLi in THF at 0°C and obtained the yellow pale crystals of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·3THF (**1**) (Scheme 2).



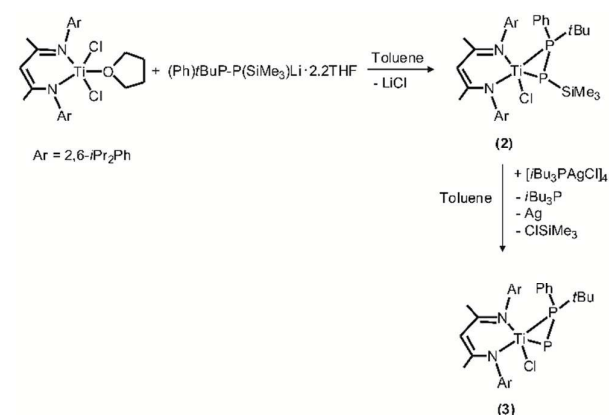
**Scheme 2.** The synthesis route of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·3THF.

The obtained crystals (**1**) were isolated and dried at 10<sup>-3</sup> mmHg at room temperature and yielded solid (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·2.2THF according to <sup>1</sup>H-NMR (Supporting Information, Figure S4). Two days later from the same mother liquor the symmetric diphosphane (Ph)*t*BuP-P*t*Bu(Ph), as the

side product, was isolated. This compound was already described by Brück and co-workers.<sup>20</sup> Additionally, stability of isolated compound (**1**) was tested in THF-*d*<sub>8</sub> solution. Therefore, the NMR tube was kept for two months at room temperature. After this time nothing has changed, only very slight increase of (Ph)*t*BuPH (s, -6.24 ppm) and (Ph)*t*BuPSiMe<sub>3</sub> (s, -26.5 ppm) signals were observed at <sup>31</sup>P-NMR spectrum.

### 2.2. Reactivity of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·2.2THF towards [<sup>Me</sup>NacNacTiCl<sub>2</sub>·THF].

(Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·2.2THF reacts in toluene solution in molar ratio 1 : 1 with [<sup>Me</sup>NacNacTiCl<sub>2</sub>·THF] yielding phosphanylphosphido titanium(III) complex [<sup>Me</sup>NacNacTi(Cl){η<sup>2</sup>-P(SiMe<sub>3</sub>)-P(Ph)*t*Bu}] (**2**) as green crystals (Scheme 3).



**Scheme 3.** The synthesis route of β-diketiminato titanium(III) complex with phosphanylphosphido ligand (**2**) and β-diketiminato titanium(IV) complex with phosphanylphosphinidene ligand (**3**).

To receive the related phosphanylphosphinidene complex of titanium(IV), (**2**) was oxidized with solution of [tBu<sub>3</sub>PAgCl]<sub>4</sub>. As a result, dark green crystals of [<sup>Me</sup>NacNacTi(Cl){η<sup>2</sup>-P-P(Ph)*t*Bu}] (**3**) were isolated in good yield (~70%) and purity. The X-ray structure of (**3**) clearly indicates two chirality centres in this molecule (P2 and Ti1, see Figure 5). The <sup>31</sup>P-NMR studies of (**3**) reveal only a presence of one set of resonances (d, 825.15 ppm and d, 109.60 ppm, J<sub>PP</sub> = 450.5 Hz). Thus, only two enantiomers are present in the solution. This assumption is supported by low-temperature <sup>31</sup>P-NMR investigation of (**3**). The spectrum at 248 K did not indicate a set of new signals and the shape of resonances remain unchanged. Additionally signals for second diastereomeric pair are not observed presumably due to a quick inversion of configuration at Ti1 atom.

### 2.3 Reactivity of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·2.2THF towards [(PNP)TiCl<sub>2</sub>].

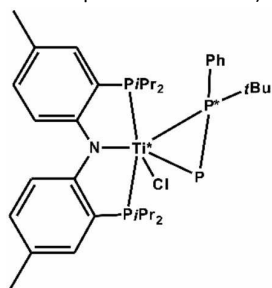
In the early reported reactions of *t*Bu<sub>2</sub>P-P(SiMe<sub>3</sub>)Li or *i*Pr<sub>2</sub>P-P(SiMe<sub>3</sub>)Li with [(PNP)TiCl<sub>2</sub>] in toluene solution in molar ratio 1 : 1 the titanium complexes with phosphanylphosphido P(SiMe<sub>3</sub>)-PR<sub>2</sub> (R = *t*Bu, *i*Pr) ligand were obtained. Additionally,

the oxidative elimination of  $-\text{SiMe}_3$  group was very difficult, hence the PNP-titanium(IV) complexes with P-*t*Bu<sub>2</sub> and P-*i*Pr<sub>2</sub> ligands were not formed.<sup>11</sup>

The reactivity of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·2.2THF (**1**) towards [(PNP)TiCl<sub>2</sub>] conducted in the same solvent and stoichiometry differs substantially from described above. This reaction yields directly titanium(IV) complex with phosphanylphosphinidene moiety [(PNP)Ti(Cl){η<sup>2</sup>-P-P(Ph)*t*Bu}] (**4**) isolated as red crystals (yield~40%). In our assumption, formation of the complex (**4**), may proceeds *via* the putative intermediate product [(PNP)Ti(Cl){η<sup>2</sup>-P(SiMe<sub>3</sub>)-P(Ph)*t*Bu}]. Unfortunately, all attempts to obtain crystals of mentioned intermediate compound was unsuccessful.

The elemental and X-ray analysis of (**4**) clearly point at the compound with the formula of [(PNP)Ti(Cl){η<sup>2</sup>-P-P(Ph)*t*Bu}]. The NMR spectra of dissolved (**4**) suggests, that unfortunately the crystalline product partially decomposes in C<sub>6</sub>D<sub>6</sub> or in THF-*d*<sub>6</sub> solutions. The signal of a free PNP<sup>H</sup> was detected in <sup>31</sup>P-NMR and the presence of N-H proton was observed in the <sup>1</sup>H-NMR spectrum (t, 8.3 ppm, *J*<sub>PH</sub> = 8.44 Hz) in both deuterated solvents. Complex (**4**) displays phosphinidene P signals in <sup>31</sup>P-NMR spectrum at very low field (d, 738.8 ppm, *J*<sub>pp</sub> = 457.8 Hz).

Complex (**4**) crystallizes as one of diastereomers racemic pair **4A** (for detailed NMR data see experimental section).



**Scheme 4.** The scheme of complex **4** (\* is the asymmetric center).

<sup>31</sup>P-NMR spectra of both, the reaction mixture and dissolved crystals of **4A** indicate the presence of two racemic pairs where the molar ratio is similar **4A** : **4B** ≈ 1 : 0.3. It does mean, that an equilibrium **4A** ⇌ **4B** is established in solution. The first stereogenic center is the phosphanyl P-atom, whereas the second one is probably the Ti-atom (See Scheme 4)

In order to explain the mechanism of the reaction (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·2.2THF with [(PNP)TiCl<sub>2</sub>] and the influence of replacing the R<sub>2</sub>P (R = *t*Bu, *i*Pr, Ph) onto RR'P (R = *t*Bu, R' = Ph) substituent in the lithium derivative of diphosphane in the reactions with [(PNP)TiCl<sub>2</sub>] VT-NMR studies and DFT calculations were performed. These results are described in 2.3 and 2.4 chapters.

### 2.3. VT-NMR Spectroscopic investigation

To understand the reaction pathway, we monitored the reaction of [(PNP)TiCl<sub>2</sub>] with (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li by VT <sup>31</sup>P-NMR. We mixed the reagents at 248 K and carried out <sup>31</sup>P{<sup>1</sup>H}-NMR measurements at three different range of temperature: a) 248 K, b) 273 K and c) 298 K. The last measurement (d) was repeated after an hour of keeping the NMR-tube at room temperature. All spectra are presented on Figure 1.

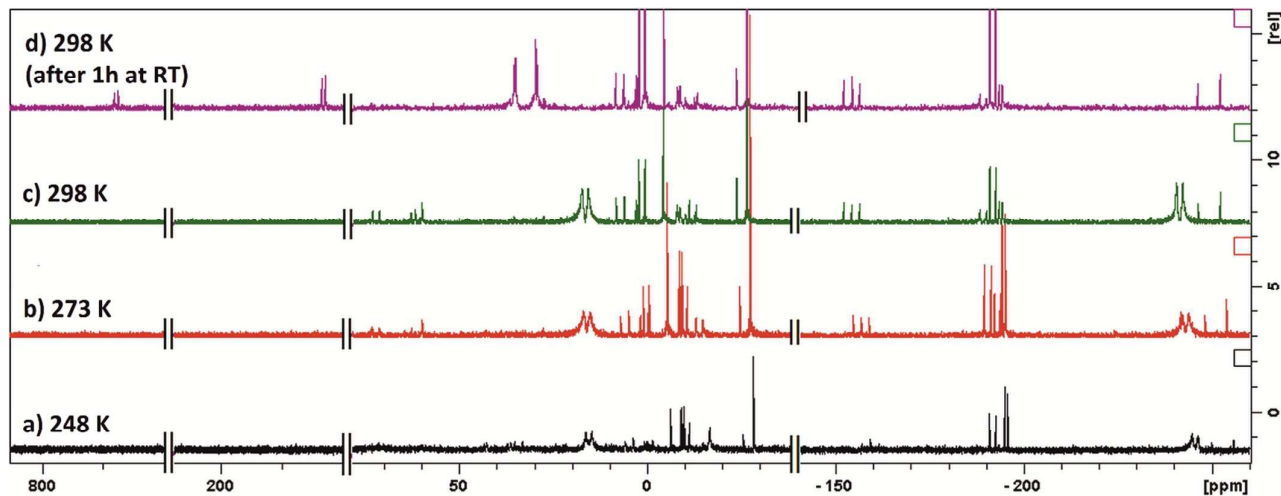
**a)** at this temperature we observe only protic contaminations of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li and formation of two diastereomers of (Ph)*t*BuP-P(SiMe<sub>3</sub>)H: d, -9.44 ppm, -195.44 ppm, (*J*<sub>pp</sub> = 118.53 Hz) and d, -10.36 ppm, -191.78 ppm, (*J*<sub>pp</sub> = 285.65 Hz). Additionally, we observe the formation of small amounts of (Ph)*t*BuPSiMe<sub>3</sub> (s, -28.23 ppm), (Ph)*t*BuPH (s, -6.20 ppm) and P(SiMe<sub>3</sub>)<sub>3</sub> (s, -255.87 ppm). At this temperature signals of [(PNP)Ti(Cl){η<sup>2</sup>-P-P(Ph)*t*Bu}] are not detected yet.

**b)** at this temperature a new signal (dd, -154.32 ppm, *J*<sub>pp</sub> = 326.97 Hz, *J*<sub>pp</sub> = 348.77 Hz) appears, which is coupled with two doublet of doublets in the range of 7.16 ppm (*J*<sub>pp</sub> = 14.53 Hz, *J*<sub>pp</sub> = 348.77 Hz) and 1.75 ppm (*J*<sub>pp</sub> = 14.53 Hz, *J*<sub>pp</sub> = 326.97 Hz). By applying the <sup>1</sup>H/<sup>31</sup>P-HMBC experiment we are able to observe, that the phosphorus atoms at 7.16 ppm and 1.75 ppm correlate with aromatic protons of the phenyl group (between 8.15 to 8.00 ppm) and with protons of the *tert*-butyl group (d, 1.67 ppm, *J*<sub>PH</sub> = 15.77 Hz). Additionally, the <sup>1</sup>H/<sup>31</sup>P-HMBC experiment shows that the phosphorus atom observed at -154.32 ppm correlates with the proton of  $-\text{SiMe}_3$  group (d, 0.269 ppm, *J*<sub>PH</sub> = 4.64 Hz) (See Supporting Information, Figure S15). These NMR results suggest, that in this reaction the triphosphorus unit with the formula (Ph)*t*BuP-P(SiMe<sub>3</sub>)-P(Ph)*t*Bu is created. The <sup>31</sup>P-NMR shifts found in literature indicate, that the signals of triphosphorus moiety (Ph)*t*BuP-P(SiMe<sub>3</sub>)-P(Ph)*t*Bu appeared in a form of two diastereomers (t, -136.37 ppm, d, 1.68 ppm, *J*<sub>pp</sub> = 374.7 Hz and t, -124.41 ppm, d, 4.71 ppm, *J*<sub>pp</sub> = 256 Hz).<sup>19</sup> The signals of triphosphorus moiety founded in our reaction mixture are differ from these reported by Fritz and co-workers and may suggest, that the triphosphorus moiety coordinate to the metal center. In order to find the phosphorus signals of PNP ligand we measured the <sup>31</sup>P-NMR for narrow field (between 100 and -50 ppm). This experiment allows to observe two doublets in the range of 39.69 ppm (*J*<sub>pp</sub> = 52.3 Hz) and 27.45 ppm (*J*<sub>pp</sub> = 52.3 Hz). These NMR results may suggest, that the titanium(II) complex with the formula of [(PNP)TiCl{(Ph)*t*BuP-P(SiMe<sub>3</sub>)-P(Ph)*t*Bu}] is created.

At 273 K in the range of 72.17 and -11.84 ppm (*J*<sub>pp</sub> = 297.9 Hz) an AX pattern of new and important complex is also observed. The <sup>1</sup>H/<sup>31</sup>P-HMBC experiment indicates that the P-atom observe in the range of 72.17 ppm correlates with protons of (Ph)*t*BuP group, while

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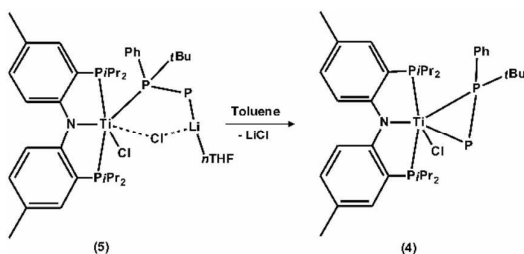


**Figure 1.** VT  $^{31}\text{P}$ -NMR spectra of reaction mixture of  $[(\text{PNP})\text{TiCl}_2]$  with  $(\text{Ph})\text{tBuP-P}(\text{SiMe}_3)\text{Li}$  in Toluene- $d_8$  solution in range of temperature from 248 K to 298 K.

the correlation of the second phosphorus atom (-11.84 ppm) with protons is not observed. Obtained results may suggest, that in the reaction mixture the phosphanylphosphinidenoid complex of the formula  $[(\text{PNP})\text{TiCl}_2\{\text{LiP-P}(\text{Ph})\text{tBu}\}]$  (**5**) is formed. Additionally, at 273 K weak signals of  $(\text{Ph})\text{tBuP-P}(\text{SiMe}_3)_2$  (0.255 and -193.00 ppm,  $J_{\text{PP}} = 257.04$  Hz) and  $\text{P}(\text{SiMe}_3)_3$  (-254.13 ppm) are detected.

c) at 298 K there are not any significantly changes, only the signals of  $(\text{Ph})\text{tBuP-P}(\text{SiMe}_3)_2$  become higher.

d) after 1 h at 298 K the resonances of  $(\text{Ph})\text{tBuP-P}(\text{SiMe}_3)\text{Li}$  and (**5**) disappeared and the doublets of  $(\text{Ph})\text{tBuP-P}(\text{SiMe}_3)_2$  enhanced and the resonances of (**4**) is appeared (for **4A**: 738.8 ppm, 116 ppm,  $^1J_{\text{PP}} = 457.8$  Hz). Thus, it seems very probably that (**5**) is converted to compound (**4**) after the elimination of LiCl (See Scheme 5).



**Scheme 5.** The probable conversion of the complex (**5**) to final complex (**4**).

Based only on VT-NMR spectroscopic results, it is very difficult to propose exact mechanism of the above reaction.  $[(\text{PNP})\text{Ti}(\text{Cl})\{\eta^2\text{-P-P}(\text{Ph})\text{tBu}\}\text{Me}]$  (**4**) contains the titanium(IV) atom, what indicates that the isolated complex (**4**) is product of the oxidation process.

We may only suspect that a part of intermediates and products may contain also the titanium(III) atoms and for this reason are not visible in NMR spectrum. It seems very possible, that the formation of PNP titanium(II) complex with the triphosphorus moiety is connected with the creation of phosphanylphosphinidenoid complex (**5**). Additionally, the increase of  $(\text{Ph})\text{tBuP-SiMe}_3$  signals may suggest, that all reactions and transformation have radical character. All attempts of isolation the other intermediates products were unsuccessful.

#### 2.4. DFT calculations

According to experimental data, there is a dramatic difference between reactivity of  $[\text{Me}_5\text{NacNacTi}(\text{Cl})\{\eta^2\text{-P}(\text{SiMe}_3)\text{P}(\text{Ph})\text{tBu}\}]$  and  $[(\text{PNP})\text{Ti}(\text{Cl})\{\eta^2\text{-P}(\text{SiMe}_3)\text{P}(\text{Ph})\text{tBu}\}]$ . In the latter case, the  $(\text{Ph})\text{tBuP-SiMe}_3$  anion coordinated to the metal center easily eliminates the silyl group even in absence of strong oxidants. On the contrary, in our previous works concerning analogous Ti(III) complexes of  $\text{R}_2\text{P-P-SiMe}_3$  ( $\text{R} = i\text{Pr}$  or  $t\text{Bu}$ )<sup>10, 11</sup> the replacement of NacNac with PNP resulted in an opposite effect. The respective PNP-Ti(IV) complexes were not obtained and  $\text{SiMe}_3$  could not be removed. Therefore, to investigate these different reactivity patterns of Ti(III) complexes towards desilylation, DFT calculations have been performed. Using Fukui functions and their condensed counterparts, we confirmed that reactivity of Ti(III) compounds may be modified depending on the presence of two particular groups: supporting ligand ( $^{\text{Me}}\text{NacNac}$  or PNP) and respective  $\text{RR}'\text{P-PSiMe}_3$  ligand ( $\text{R} = \text{Ph}$ ,  $t\text{Bu}$  and  $\text{R}' = \text{Ph}$ ,  $t\text{Bu}$ ). Data presented in Table 1, show a general trend of decreasing

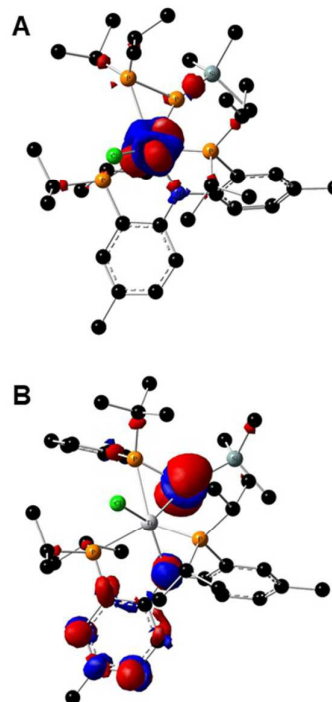
electrophilicity of Ti(III) atom in PNP complexes compared to <sup>Me</sup>NacNac ones.

**Table 1.** Values of condensed nucleophilic  $f^-$  and electrophilic  $f^+$  Fukui functions and the  $\Delta f$  dual descriptor calculated based on Hirshfield population analysis (HPA) for complexes.

Compound	Ti(III)		
	$f^+$	$f^-$	$\Delta f$
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-PtBu <sub>2</sub> }]	0.197	0.131	0.066
[(PNP)Ti(Cl){ $\eta^1$ -P(SiMe <sub>3</sub> )-PtBu <sub>2</sub> }]	0.169	0.105	0.064
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P <i>i</i> Pr <sub>2</sub> }]	0.189	0.134	0.055
[(PNP)Ti(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P <i>i</i> Pr <sub>2</sub> }]	0.170	0.113	0.057
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P(Ph)tBu}]	0.180	0.132	0.056
[(PNP)Ti(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P(Ph)tBu}]	0.014	-0.013	0.027
P-SiMe <sub>3</sub>			
Compound	$f^+$	$f^-$	$\Delta f$
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-PtBu <sub>2</sub> }]	0.043	0.077	-0.034
[(PNP)Ti(Cl){ $\eta^1$ -P(SiMe <sub>3</sub> )-PtBu <sub>2</sub> }]	0.048	0.083	-0.035
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P <i>i</i> Pr <sub>2</sub> }]	0.046	0.092	-0.046
[(PNP)Ti(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P <i>i</i> Pr <sub>2</sub> }]	0.069	0.072	-0.003
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P(Ph)tBu}]	0.044	0.079	-0.035
[(PNP)Ti(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P(Ph)tBu}]	0.212	-0.076	0.288
PRR'			
Compound	$f^+$	$f^-$	$\Delta f$
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-PtBu <sub>2</sub> }]	0.023	0.031	-0.009
[(PNP)Ti(Cl){ $\eta^1$ -P(SiMe <sub>3</sub> )-PtBu <sub>2</sub> }]	0.040	0.038	0.002
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P <i>i</i> Pr <sub>2</sub> }]	0.027	0.032	-0.005
[(PNP)Ti(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P <i>i</i> Pr <sub>2</sub> }]	0.018	0.023	-0.005
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P(Ph)tBu}]	0.022	0.030	-0.007
[(PNP)Ti(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P(Ph)tBu}]	0.033	0.039	-0.006
Si			
Compound	$f^+$	$f^-$	$\Delta f$
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-PtBu <sub>2</sub> }]	0.027	0.025	0.002
[(PNP)Ti(Cl){ $\eta^1$ -P(SiMe <sub>3</sub> )-PtBu <sub>2</sub> }]	0.020	0.014	0.006
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P <i>i</i> Pr <sub>2</sub> }]	0.027	0.020	0.007
[(PNP)Ti(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P <i>i</i> Pr <sub>2</sub> }]	0.030	0.019	0.010
[ <sup>Me</sup> NacNacTi(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P(Ph)tBu}]	0.027	0.028	-0.001
[(PNP)Ti(Cl){ $\eta^2$ -P(SiMe <sub>3</sub> )-P(Ph)tBu}]	0.018	0.012	0.006

Even though both ligands have conjugated bond systems with heteroatoms, the distribution of electron density within the complex suggests that the PNP moiety is more polarizable. As follows from HPA (Supporting Information, Figure S25, S30), the electron density in PNP complexes is shifted towards the most electronegative atoms in the molecule (Cl, N). On the contrary, the <sup>Me</sup>NacNac group has a less polarizable charge distribution, with the

negative charge localized mainly at high electronegative nitrogen atoms. Therefore, in the case of the <sup>Me</sup>NacNac systems, we may assume that the electron density from RR'P-PSiMe<sub>3</sub> ligands is shifted towards the titanium atom and NacNac ring, facilitating the elimination of SiMe<sub>3</sub> irrespective of P-PRR' units. In contrast, in PNP systems substituents attached to RR'P-PSiMe<sub>3</sub> ligand significantly change the reactivity of the whole molecule. As a result, there is a notable contrast between analogous complexes that only differ in the type of substituents attached to P-PR<sub>2</sub> moiety.



**Figure 2.** Visualization of electrophilic Fukui functions  $f^+$  for [(PNP)Ti(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)P*i*Pr<sub>2</sub>}] (A) and [(PNP)Ti(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)P(Ph)tBu}] (B). Red area corresponds to positive value of  $f^+$  ( $f^+ > 0$ ) and blue one with negative value ( $f^+ < 0$ ) of electrophilic Fukui function, showing fragments favorable for nucleophilic attack.

Comparing the electrophilic Fukui functions for [(PNP)Ti(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)P*i*Pr<sub>2</sub>}] and [(PNP)Ti(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)P(Ph)tBu}] as shown (Figure 2 A and B), one may notice that in the case of [(PNP)Ti(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)P*i*Pr<sub>2</sub>}] (as well as [(PNP)Ti(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)PtBu<sub>2</sub>}] presented in Supporting Information, Figure S34) the titanium atom is the most electrophilic region of the molecule (positive values of  $f^+$  are located on Ti(III) atom), contrary to complex with the (Ph)tBuP-PSiMe<sub>3</sub> moiety. In the latter case, P-SiMe<sub>3</sub> is the region of the molecule that is most favorable for nucleophilic attack. It corresponds to values of values of  $f_{Ti}^+$  and  $f_{P-SiMe_3}^+$  for [(PNP)Ti(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)P*i*Pr<sub>2</sub>}] ( $f_{Ti}^+ = 0.170$ ,  $f_{P-SiMe_3}^+ = 0.069$ ) and [(PNP)Ti(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)P(Ph)tBu}] ( $f_{Ti}^+ = 0.014$  and  $f_{P-SiMe_3}^+ = 0.212$ ), respectively. Moreover, atomic charges show that in [(PNP)Ti(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)P*i*Pr<sub>2</sub>}] the electron density shifts from PNP to Ti, Cl and *i*Pr<sub>2</sub>P-PSiMe<sub>3</sub>. On the contrary, the presence of two polarizable ligands coordinated to Ti(III) center in [(PNP)Ti(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)P(Ph)tBu}] causes the electrons to be strongly withdrawn from P-SiMe<sub>3</sub> towards the most electronegative atoms in a molecule:

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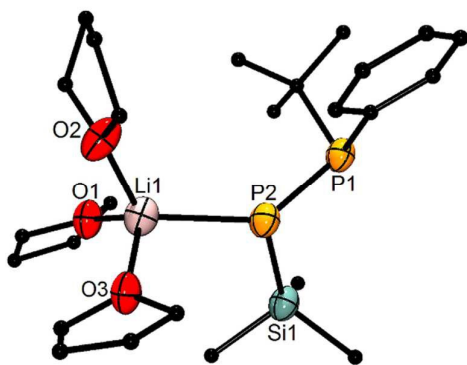
## Journal Name

Cl, N and PNP phosphorus atoms. Therefore, to investigate how electronic properties change as the alkyl group is replaced by a phenyl ring, we calculated Fukui and condensed Fukui functions of three selected RR'P-P(SiMe<sub>3</sub>)Li systems (for computational data and detailed description of obtained results see SI). Computational data revealed that, in each case the PSiMe<sub>3</sub> phosphorus atom is unambiguously the most favorable position for electrophilic attack. However, a tendency to increase of nucleophilicity of the PSiMe<sub>3</sub> moiety with simultaneous decrease of electron density at RR'P may be observed when Ph groups are replaced with *t*Bu. As a consequence, the electron density shifts towards the PPh<sub>2</sub> or (Ph)*t*BuP moiety, simultaneously pulling electrons from SiMe<sub>3</sub> to PSiMe<sub>3</sub> atom. In the case of *t*Bu<sub>2</sub>P-PSiMe<sub>3</sub>, negative charge is rather contained, focused within the area of PSiMe<sub>3</sub> unit while, unlike other anions, the SiMe<sub>3</sub> is more electron-rich (the visualization of isosurfaces of the dual descriptor for Ph<sub>2</sub>P-PSiMe<sub>3</sub> (A), (Ph)*t*BuP-PSiMe<sub>3</sub> (B), and *t*Bu<sub>2</sub>P-PSiMe<sub>3</sub> (C), see supporting information Figure S16).

By applying the presented theoretical considerations to the behavior of anions in PNP complexes, we may assume that both *t*Bu<sub>2</sub>P-PSiMe<sub>3</sub> and *i*Pr<sub>2</sub>P-PSiMe<sub>3</sub> groups are less polarizable than PNP. Hence, electrons from *t*Bu<sub>2</sub>P-PSiMe<sub>3</sub> and *i*Pr<sub>2</sub>P-PSiMe<sub>3</sub> are not strongly withdrawn from these moieties, but rather donated, resulting in stronger binding and less favorable removal of the silyl group from PSiMe<sub>3</sub>. As the electron density may be delocalized over the phenyl group, the reactivity of PNP complex involving (Ph)*t*BuP-PSiMe<sub>3</sub> ligand changes significantly: the nucleophilicity of the PSiMe<sub>3</sub> atom dramatically decreases after complexation to Ti(III) and it becomes electrophilic center of a molecule.

## 2.5. X-ray studies

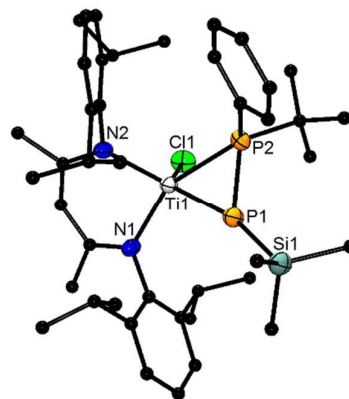
X-ray suitable crystals of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·3THF (**1**) were grown in THF/pentane solution. Complex (**1**) crystallizes in monoclinic space group (Cc).



**Figure 3.** The molecular structure of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·3THF (**1**) (elipsoids 50%, H atoms were omitted for clarity). Important bond lengths (Å), bond angles (deg.): P1-P2 2.146(3), P2-Si1 2.193(4), P2-Li1 2.518(17); P1-P2-Si1 101.10(14), P1-P2-Li1 138.6(4), Si1-P2-Li1 110.0(4). Sum of the angles around the P atoms:  $\Sigma P1 = 308.5(2)$ ,  $\Sigma P2 = 349.7(5)$ .

In (**1**) Li1 atom adopts distorted tetrahedral environment with three THF molecules and P2 atom. The phosphorus atom P1 presents a pyramidal geometry ( $\Sigma P = 308.5(2)^\circ$ ), whereas the geometry around P2 is almost planar ( $\Sigma P = 349.7(5)^\circ$ ). The Li1-P2 distance of 2.518(17) Å is slightly shorter than these observed in another lithium covalent derivatives *t*Bu<sub>2</sub>P-P(SiMe<sub>3</sub>)Li·3THF (2.555(9) Å) and *i*Pr<sub>2</sub>P-P(SiMe<sub>3</sub>)Li·3THF (2.535(8) Å and 2.536(7) Å). More significant difference is observed for P1-P2 distance (2.146(3) Å) which is much shorter than these in *t*Bu<sub>2</sub>P-P(SiMe<sub>3</sub>)Li·3THF (2.178(2) Å) and *i*Pr<sub>2</sub>P-P(SiMe<sub>3</sub>)Li·3THF (2.171(7) Å and 2.178(7) Å).<sup>17, 18</sup>

The good quality crystals of (**2**) were grown from pentane solution. The complex (**2**) crystallizes in monoclinic space group *P*<sub>2</sub><sub>1</sub>/*n* with four molecules in the unit cell. (**2**) reveals a five-coordinated titanium complex in a distorted square pyramidal environment at the metal center, where the chloride ion occupies an axial position.

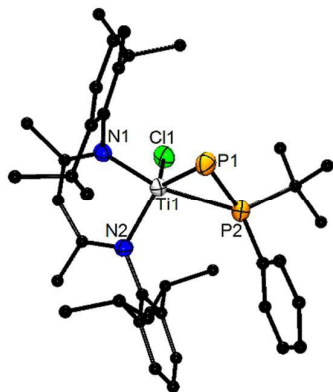


**Figure 4.** The molecular structure of [<sup>Me</sup>NacNacTi(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)-P(Ph)*t*Bu}] (**2**) (elipsoids 50%, the H atoms omitted for clarity). Important bond lengths (Å), bond angles (deg): P1-P2 2.1150(15), P1-Ti1 2.4481(12), P2-Ti1 2.5950(12), Ti1-Cl1 2.2969(13), Ti-N1 2.073(3), Ti-N2 2.074(3), P1-Si1 2.2564(15); Ti1-P1-P2 68.87(4), Ti1-P2-P1 61.64(4), P1-Ti1-P2 49.49(4), P1-Ti1-Cl1 123.21(5), P2-Ti1-Cl1 100.73(4), N1-Ti1-N2 89.22(12), N1-Ti1-Cl1 103.35(10), N2-Ti1-Cl1 103.40(10), P2-P1-Si1 122.57(6), Si1-P1-Ti1 165.10(6). Sum of the angles around the P atoms:  $\Sigma P1 = 356.54(3)$ ,  $\Sigma P2 = 331.83(9)$ .

The P1-P2 distance (2.1150(15) Å) in (**2**) is comparable to these observed in early synthesized by our research group complexes: [<sup>Me</sup>NacNacTi(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)-PtBu<sub>2</sub>}] (2.125(2) Å) and [<sup>Me</sup>NacNacTi(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)-P*i*Pr<sub>2</sub>}] (2.1169(9) Å). The Ti1-P1 distance (2.4481(12) Å) is comparable to the data for [<sup>Me</sup>NacNacTi(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)-PtBu<sub>2</sub>}] (2.445(2) Å) and for [<sup>Me</sup>NacNacTi(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)-P*i*Pr<sub>2</sub>}] (2.4768(10) Å).<sup>10</sup> The Ti1-P2 distance of 2.5950(12) Å is significantly shorter than in [<sup>Me</sup>NacNacTi(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)-PtBu<sub>2</sub>}] (2.6759(18) Å), but is near to the related distance in [<sup>Me</sup>NacNacTi(Cl){ $\eta^2$ -P(SiMe<sub>3</sub>)-P*i*Pr<sub>2</sub>}] (2.5648(9) Å). The geometry around P1 ( $\Sigma P1 = 356.54(3)^\circ$ ) is almost planar, whereas around P2 more pyramidal ( $\Sigma P2 = 331.83(9)^\circ$ ). The NCCCN unsaturated backbone of <sup>Me</sup>NacNac ligand is almost planar with 0.063(3) Å deviation from planarity and titanium atom is out of the NCCCN plane by 0.894(2) Å.

The value of bond lengths of the N-C and C-C in the backbone of the  $\beta$ -diketiminato skeleton are between single and double bond lengths (delocalization of the double bond).

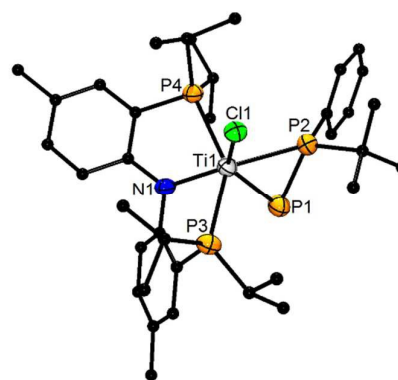
Crystals of **(3)** were grown from pentane solution. Compound crystallizes in monoclinic space group  $P2_1/c$  with four molecules in the unit cell and the titanium atom adopt the square pyramidal geometry (Figure 5).



**Figure 5.** The molecular structure of  $[\text{MeNacNaTi}(\text{Cl})\{\eta^2\text{-P-P}(\text{Ph})\text{tBu}\}]$  (**3**) (ellipsoids 50%, the H atoms omitted for clarity). Important bond lengths (Å), bond angles (deg.): P1-P2 2.1037(8), P1-Ti1 2.3237(7), P2-Ti1 2.5128(7), Ti1-Cl1 2.2910(6), Ti1-N1 2.0283(18), Ti1-N2 2.0468(18); Ti1-P1-P2 68.95(2), Ti1-P2-P1 59.66(2), P1-Ti1-P2 51.39(2), P1-Ti1-Cl1 123.59(3), P2-Ti1-Cl1 104.27(2), N1-Ti1-N2 93.88(7), N1-Ti1-Cl1 103.20(5), N2-Ti1-Cl1 109.36(5),  $\Sigma\text{P2} = 326.3(6)$ .

The very short P1-P2 distance of 2.1037(8) Å is comparable to the values found in already described  $[\text{MeNacNaTi}(\text{Cl})\{\eta^2\text{-P-PR}_2\}]$ , (R = *t*Bu, *i*Pr)<sup>10</sup>. The Ti1-P1 distance (2.3237(7) Å) lies in the range between single and double Ti-P bond, whereas Ti1-P2 distance (2.5128(7) Å) is typical for single Ti-P bond. These values are similar to Ti-P distances reported previously for  $[\text{MeNacNaTi}(\text{Cl})\{\eta^2\text{-P}(\text{SiMe}_3)\text{-PR}_2\}]$ . The phosphorus atom P2 presents a rather pyramidal geometry ( $\Sigma\text{P2} = 326.3(6)^\circ$ ). Similar as in **(2)**, unsaturated NCCCN ligand in **(3)** is almost planar with 0.056(8) Å deviation from planarity but the Ti1 atom is strongly deviated from the plane of N,N-ligand framework by 1.034(3) Å.

The good quality crystals of  $[(\text{PNP})\text{Ti}(\text{Cl})\{\eta^2\text{-P-P}(\text{Ph})\text{tBu}\}]$  (**4**) were obtained from pentane. It crystallizes in the monoclinic space group  $P2_1/c$  with four molecules in the unit cell. The structure of **(4)** (Figure 6) displays a monomeric species in a distorted octahedral geometry.



**Figure 6.** The molecular structure of  $[(\text{PNP})\text{Ti}(\text{Cl})\{\eta^2\text{-P-P}(\text{Ph})\text{tBu}\}]$  (**4**) (ellipsoid 50%, the H atoms omitted for clarity). Important bond lengths (Å), bond angles (deg.): P1-P2 2.1284(17), P2-Ti1 2.5353(15), P1-Ti1 2.3533(15), P4-Ti1 2.6418(14), P3-Ti1 2.6138(14), Ti1-Cl1 2.4344(13), Ti1-N1 2.061(4); P1-P2-Ti1 59.86(5), P1-Ti1-P2 51.45(4), P2-P1-Ti1 68.69(5), P3-Ti1-P4 145.54(5), P1-Ti1-P3 88.16(5), P2-Ti1-P3 122.43(5), P1-Ti1-P4 116.47(5), P2-Ti1-P4 92.02(4), Cl1-Ti1-N1 121.62(11),  $\Sigma\text{P2} = 326.16(6)$ .

The crystallographic structure shows that the Ti1-P1 distance (2.3533(15) Å) is shorter than a typical single bond between tertiary phosphine and titanium atom, *i.e.* Ti-P distance of 2.564(2) Å in  $[\text{Cp}_2\text{Ti}(\text{PMe}_3)\{\eta^2\text{-P}\equiv\text{CtBu}\}]$ ,<sup>21</sup> whereas the double bond distance is *e.g.* 2.2066(4) Å in  $[(\text{PNP})\text{Ti}=\text{PTrip}(\text{CH}_2\text{tBu})]$  (Trip = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>).<sup>9</sup> The distance between Ti1 and phosphanyl phosphorus P2 atom is 2.5353(15) Å and is typical for a single bond. Both Ti-P (phosphinide phosphorus) and Ti-P (phosphanyl phosphorus) bond distances are comparable to related values in  $[\text{MeNacNaTi}(\text{Cl})\{\eta^2\text{-P-PtBu}_2\}]$ . The Ti-N distance 2.061(4) Å is short and comparable with distances in complexes  $[(\text{PNP})\text{TiCl}(\text{N}(\text{SiMe}_3)_2)]$  2.057(2) Å<sup>22</sup> and  $[(\text{PNP})\text{Ti}=\text{CHPh}(\text{CH}_2\text{SiMe}_3)]$  2.061(6) Å.<sup>23</sup> The molecular structure of **(4)** reveals slightly longer P-P bond (P1-P2 2.1284(17) Å), but it still remains in the range of a double P-P bond in a bidentate coordination. The sum of angles around the P2 atom is 326.16(6)° and presents the same geometry such as the P2 atom in complex **(3)**.

## Conclusions

Reaction of  $[(\text{PNP})\text{TiCl}_2]$  with  $(\text{Ph})\text{tBuP-P}(\text{SiMe}_3)\text{Li}\cdot 2.2\text{THF}$  in toluene solution in 1 : 1 molar ratio leads to first titanium(IV) complex with phosphanylphosphinidene ligand  $[(\text{PNP})\text{Ti}(\text{Cl})\{\eta^2\text{-P-P}(\text{Ph})\text{tBu}\}]$  (**4**). The result of this reaction is unexpected, because reactions of  $[(\text{PNP})\text{TiCl}_2]$  with  $\text{tBu}_2\text{P-P}(\text{SiMe}_3)\text{Li}\cdot n\text{THF}$  and  $i\text{Pr}_2\text{P-P}(\text{SiMe}_3)\text{Li}\cdot n\text{THF}$  yielded stable titanium(III) complexes with phosphanylphosphido ligands. In order to clarify different properties of  $(\text{Ph})\text{tBuP-P}(\text{SiMe}_3)\text{Li}\cdot 2.2\text{THF}$  and different reaction pathway the VT-NMR spectroscopic investigation and DFT calculations were performed. Theoretical calculations revealed that stability of the P-SiMe<sub>3</sub> bond depends on the combination of two important aspects: the presence of the particular stabilizing ligand (PNP or MeNacNac) and the character of the R,R' groups on phosphanyl phosphorus atom. Obtained results indicate that the phenyl group on the phosphanyl phosphorus atom decreases the



electron density on the phosphido phosphorus atom in the (Ph)*t*BuP-PSiMe<sub>3</sub> anion and consequently facilitates the elimination of the SiMe<sub>3</sub> from the phosphanylphosphido ligand.

The reaction of [MeNacNacTiCl<sub>2</sub>·THF] with (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·2.2THF in toluene solution and in molar ratio 1 : 1 leads to formation of β-diketimate titanium(III) complex with phosphanylphosphido ligand (**2**). In the reaction with [iBu<sub>3</sub>PAGCl]<sub>4</sub> (**2**) was oxidized to β-diketimate titanium(IV) complex with phosphanylphosphinidene ligand (**3**).

## Experimental section

Toluene and THF were dried over Na/benzophenone, pentane and petroleum ether were dried over Na/benzophenone/diglym and distilled under argon. All reactions were performed under argon atmosphere using Schlenk techniques. <sup>31</sup>P, <sup>13</sup>C, and <sup>1</sup>H spectra in solution were recorded on Bruker AV300 MHz and Bruker AV400 MHz (external standard tetramethylsilane for <sup>1</sup>H, <sup>13</sup>C; 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P). Literature methods were used to prepare P(SiMe<sub>3</sub>)<sub>2</sub>Li·*n*THF,<sup>24</sup> (Ph)*t*BuPX (X = Br, Cl),<sup>25</sup> [MeNacNacTiCl<sub>2</sub>·THF],<sup>26</sup> [(PNP)TiCl<sub>2</sub>]<sup>9</sup> and [iBu<sub>3</sub>PAGCl]<sub>4</sub>.<sup>27</sup>

### Synthesis of (Ph)*t*BuP-P(SiMe<sub>3</sub>)<sub>2</sub>

To a solution of P(SiMe<sub>3</sub>)<sub>2</sub>Li·1.73THF (12.686 g; 41.102 mmol) in 150 ml of THF cooled to 0°C (Ph)*t*BuP-Cl (8.246 g; 41.102 mmol) in 50 ml of THF was added. After 24 h at room temperature the solvent was removed under vacuum. Formed yellow oil was dissolved in 100 ml of petroleum ether. Precipitate of LiCl was filtered off and solvent was removed. The oily residue was purified by fractional distillation under reduced pressure to yield the main product with boiling point of 85–90°C/10<sup>-3</sup> mmHg. Yield 67.50%, 9.503 g.

<sup>1</sup>H-NMR (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 7.79–7.01 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 1.30 (d, 18H, *t*Bu, *J*<sub>PCH</sub> = 13.083 Hz), 0.21 (d, 18H, SiMe<sub>3</sub>, *J*<sub>PSiCH</sub> = 5.257 Hz) ppm; <sup>13</sup>C{<sup>1</sup>H} (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 137.99 (C<sub>6</sub>H<sub>5</sub>), 135.64 (*o*-C<sub>6</sub>H<sub>5</sub>), 128.68 (*p*-C<sub>6</sub>H<sub>5</sub>), 127.70 (*m*-C<sub>6</sub>H<sub>5</sub>), 30.61 (*C-t*Bu), 29.11 (*C-t*Bu), 7.96 (SiMe<sub>3</sub>) ppm; <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 1.35 (d, *P-P*(Ph)*t*Bu, *J*<sub>PP</sub> = 260.09 Hz), -191.80 (d, *P-P*(Ph)*t*Bu, *J*<sub>PP</sub> = 260.09 Hz) ppm.

### Synthesis of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·2.2THF (**1**)

To the solution of (Ph)*t*BuP-P(SiMe<sub>3</sub>)<sub>2</sub> (4.346 g; 12.706 mmol) in 300 ml of THF cooled to 0°C and *n*BuLi (5.081 ml, 12.706 mmol, 2.5 M) was added dropwise. The mixture reaction was kept at 0°C for next 3 h and next warmed mixture was stirred for 24h. Solvent was removed under vacuum and residue was dissolved in 30 ml of pentane and small amount of THF was added. After 24 hours at -30°C light yellow crystals were obtained. Yield of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·2.2THF was 71.24%, 3.933 g.

<sup>1</sup>H-NMR (298 K, THF-*d*<sub>8</sub>): δ = 7.66–6.95 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 3.53 (m, 8.8H, OCH<sub>2</sub>CH<sub>3</sub> – 2.2 molecules of THF), 1.69 (m, 8.8H, OCH<sub>2</sub>CH<sub>3</sub> – 2.2 molecules of THF), 0.87 (d, 9H, *t*Bu, *J*<sub>PCH</sub> = 11.13

Hz), 0.21 (d, 9 H, SiMe<sub>3</sub>, *J*<sub>PSiCH</sub> = 4.52 Hz), 0.00 (dd, 9H, SiMe<sub>3</sub>, *J*<sub>PSiCH</sub> = 3.30 Hz, *J*<sub>PSiCH</sub> = 0.98 Hz,) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, [D<sub>8</sub>]thf): δ = 146.95 (C<sub>6</sub>H<sub>5</sub>), 135.25 (*o*-C<sub>6</sub>H<sub>5</sub>), 127.91 (*p*-C<sub>6</sub>H<sub>5</sub>), 125.49 (*m*-C<sub>6</sub>H<sub>5</sub>), 66.68 (OCH<sub>2</sub>CH<sub>3</sub>), 28.42 (*C-t*Bu), 24.56 (OCH<sub>2</sub>CH<sub>3</sub>), 13.10 (*C-t*Bu), 5.05 (SiMe<sub>3</sub>) ppm; <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, [D<sub>8</sub>]thf): δ = 16.32 (d, *P-P*(Ph)*t*Bu, *J*<sub>PP</sub> = 258.23 Hz), -241.82 (d, *P-P*(Ph)*t*Bu, *J*<sub>PP</sub> = 258.23 Hz) ppm.

In order to increase the efficiency, the mother liquor after separation of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·3THF (**1**) was concentrated about half of volume and left at -30°C. Unfortunately, two days later colourless crystals of the symmetric diphosphane (Ph)*t*BuP-P*t*Bu(Ph) were obtained.

### Synthesis of [MeNacNacTi(Cl){η<sup>2</sup>-P(SiMe<sub>3</sub>)-P(Ph)*t*Bu}] (**2**)

[MeNacNacTiCl<sub>2</sub>·THF] was dissolved in 10 ml of toluene solution (0.315 g; 0.517 mmol) and cooled to -20°C. Next the solution of (Ph)*t*BuP-P(SiMe<sub>3</sub>)Li·2.2THF (0.224 g; 0.517 mmol) in 5 ml of toluene was added. After 1.5 h at room temperature the volatiles were evaporated and the residue was treated with 20 ml of pentane. The mixture was filtered and concentrated to 15 ml of volume. About 5 hours later at +4°C the green crystals were obtained. Yield 61.84%, 0.245 g.

Anal. Calcd for C<sub>42</sub>H<sub>64</sub>ClN<sub>2</sub>P<sub>2</sub>SiTi: C, 65.23; H, 8.73; N, 4.58%. Found: C, 64.08; H, 8.22; N, 3.74%.

### Synthesis of [MeNacNacTi(Cl){η<sup>2</sup>-P-P(Ph)*t*Bu}] (**3**)

[MeNacNacTi(Cl){η<sup>2</sup>-P(SiMe<sub>3</sub>)-P(Ph)*t*Bu}] (0.200 g; 0.260 mmol) was dissolved in 8 ml of toluene and a solution of [iBu<sub>3</sub>PAGCl]<sub>4</sub> (0.09 g; 0.065 mmol) in toluene was added. Colour of the solution changed from green to green-brown and silver mirror appeared on Schlenk flask. After 3 h solvent was removed under vacuum and formed residue was treated of 15 ml of pentane. The resulting reaction mixture was filtered, concentrated to 7 mL of volume and left at +4°C. After 16 hours dark-green crystals were collected. Yield 69.45%, 0.126 g.

Anal. Calcd for C<sub>41</sub>H<sub>57</sub>ClN<sub>2</sub>P<sub>2</sub>Ti: C, 66.90; H, 8.35; N, 4.00%. Found: C, 65.82; H, 8.22; N, 3.74%.

<sup>1</sup>H-NMR (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 7.59–6.96 (6H C<sub>6</sub>H<sub>3</sub> and 5H C<sub>6</sub>H<sub>5</sub>), 4.83 (s, 1H, γ-CH), 3.06 (sept., 4H, *J* = 6.96 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.61 (s, 6H, C(CH<sub>3</sub>)CHC(CH<sub>3</sub>)), 1.12 (d, 12H, *J* = 6.96 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.03 (d, 12H, *J* = 6.96 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.96 (d, 9H, *J* = 12.59 Hz, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 160.97 (C(CH<sub>3</sub>)CHC(CH<sub>3</sub>)), 142.12 (C<sub>6</sub>H<sub>5</sub>), 140.69 (C<sub>6</sub>H<sub>3</sub>), 135.39 (*o*-C<sub>6</sub>H<sub>3</sub>), 135.24 (*o*-C<sub>6</sub>H<sub>5</sub>), 127.92 (*m*-C<sub>6</sub>H<sub>5</sub>), 127.66 (*p*-C<sub>6</sub>H<sub>5</sub>), 125.05 (*m*-C<sub>6</sub>H<sub>3</sub>), 122.75 (*p*-C<sub>6</sub>H<sub>3</sub>), 93.53 (γ-CH), 29.67 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.08 (C(CH<sub>3</sub>)<sub>3</sub>), 22.48 (CH(CH<sub>3</sub>)<sub>2</sub>), 19.92 (C(CH<sub>3</sub>)CHC(CH<sub>3</sub>)), 13.44 (C(CH<sub>3</sub>)<sub>3</sub>) ppm; <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 825.15 (*P-P*(Ph)*t*Bu, *J*<sub>PP</sub> = 450.5 Hz), 109.60 (*P-P*(Ph)*t*Bu, *J*<sub>PP</sub> = 450.5 Hz) ppm.

### Synthesis of [(PNP)Ti(Cl){η<sup>2</sup>-P-P(Ph)*t*Bu}] (**4**)

To a solution of [(PNP)TiCl<sub>2</sub>] (0.350 g; 0.639 mmol) in 10 ml of toluene a solution of (Ph)tBuP-P(SiMe<sub>3</sub>)Li·2.2THF (0.278 g; 0.639 mmol) in 5 ml of toluene at -25°C was added. The reaction mixture was warmed to room temperature and maintained for 1 h under these conditions. Subsequently, the volatiles were removed under vacuum. Red, crude residue was dissolved in 25 ml of pentane, filtered and concentrated to 10 ml of volume. The storage solution at +4°C for 16 hours yielded the red crystal.

Yield 51.94%, 0.235 g.

Anal. Calcd for C<sub>36</sub>H<sub>54</sub>ClNP<sub>4</sub>Ti: C, 61.07; H, 7.69; N, 1.98%. Found: C, 60.90; H, 7.74; N, 2.04%.

Major diastereomer: <sup>1</sup>H-NMR (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 7.704 – 6.89 (5H form the (Ph)tBuPP moiety and 6 H form the PNP ligand), 2.613 (m, 2H, PCH(CH<sub>3</sub>)<sub>2</sub>), 2.20 (m, 2H, PCH(CH<sub>3</sub>)<sub>2</sub>), 2.16 (s, 3H, Ar-CH<sub>3</sub>), 1.64 (d, J = 15.41 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.55 (dd, 3H, J = 14.81 Hz, J = 7.04 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (dd, 3H, J = 15.16 Hz, J = 6.97 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.11 (dd, 3H, J = 15.16 Hz, J = 6.97 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 0.96 (dd, 3H, J = 11.74 Hz, J = 6.97, PCH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 147.03 (d, J = 20.54 Hz, Ar-CH), 135.54 (d, J = 15.22 Hz, Ar-C<sub>ipso</sub>), 132.34 (s, Ar-CH), 130.26 (s, Ar-CH), 129.516 (s, Ar-C<sub>ipso</sub>), 128.56 (s, Ar-C<sub>ipso</sub>), 128.11 (dd, J = 13.64, J = 0.60 Hz, Ar-C<sub>ipso</sub>), 127.88 (d, J = 24 Hz, Ar-CH), 122.96 (s, Ar-C<sub>ipso</sub>), 116.88 (t, J = 1.76, Ar-CH), 34.07 (s, PC(CH<sub>3</sub>)<sub>3</sub>), 29.44 (d, J = 13.20 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 23.14 (d, J = 11.60 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 22.36 (s, PC(CH<sub>3</sub>)<sub>2</sub>), 20.54 (s, Ar-CH<sub>3</sub>), 20.13 (d, J = 13.62 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 20.04 (d, J = 8.89 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 18.89 (d, J = 9.83 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 738.8 (broad d, J<sub>pp</sub> = 457.8 Hz, J<sub>pp</sub> = 11.4 Hz, P-P(Ph)tBu), 116.0 (broad dt J<sub>pp</sub> = 457.8 Hz, J<sub>pp</sub> = 13.6 Hz, P-P(Ph)tBu), 35.3 (broad d, J<sub>pp</sub> = 42.6, PNP), 29.8 (dd, J<sub>pp</sub> = 42.6, 13.6 Hz, PNP).

Minor diastereomer in the <sup>1</sup>H-NMR spectrum was observed near the strongest signals: <sup>1</sup>H-NMR (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 2.21 (s, 3H, Ar-CH<sub>3</sub>), 1.66 (d, J = 15.47 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.50 (dd, 3H, J = 14.28 Hz, J = 7.18 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.42 (dd, 3H, J = 15.36 Hz, J = 6.97 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.04 (dd, 3H, J = 15.11 Hz, J = 7.04 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 0.94 (dd, 3H, J = 15.34 Hz, J = 6.88, PCH(CH<sub>3</sub>)<sub>2</sub>). In the <sup>13</sup>C-NMR spectrum the signals of major diastereomer were weak, the signals of minor distereoisomer were invisible. <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, C<sub>6</sub>D<sub>6</sub>): δ = 764.68 (broad d, J<sub>pp</sub> = 457.8 Hz, P-P(Ph)tBu), 115.99 (broad d, J<sub>pp</sub> = 457.8 Hz, P-P(Ph)tBu), 36.43 (broad d, J<sub>pp</sub> = 40.4, 15.44 Hz, PNP), 30.29 (dd, J<sub>pp</sub> = 40.4, 11.58 Hz, PNP).

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We present the reactivity of  $[(\text{PNP})\text{TiCl}_2]$  and  $[\text{MeNacNacTiCl}_2 \cdot \text{THF}]$  towards the lithium derivative of diphosphane  $(\text{Ph})\text{tBuP-P}(\text{SiMe}_3)\text{Li} \cdot n\text{THF}$ .

