

Reactions of lithiated diphosphanes R₂P-P(SiMe₃)Li·*n*THF (R = tBu, iPr) with [(PNP)TiCl₂]. Two different coordination types of phosphanylphosphido ligand to the metal center

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abstract

[(PNP)TiCl₂] (PNP = N[2-PiPr₂-4-methylphenyl]₂) reacts with one equivalent of lithium derivative of diphosphane R₂P-P(SiMe₃)Li·*n*THF (R = tBu, iPr) in toluene and forms the first complex with g¹-coordination [(PNP)Ti(Cl){η¹-P(SiMe₃)-PtBu₂}] (1) and complex with η²-coordination [(PNP)Ti(Cl){η²-P(SiMe₃)-PiPr₂}] (2) of phosphanylphosphido ligands to the titanium center. The similar reaction with two equivalents of tBu₂P-P(SiMe₃)Li·*n*THF in toluene leads to solid 3 which contains 1 and excess of tBu₂P-P(SiMe₃)Li in the unit cell. In complex 2 disorder of the phosphanylphosphido ligand was observed. The disorder model shows that the phosphanylphosphido ligand coordinates to the metal center alternately as a bidentate and as a monodentate ligand.

Keywords: Coordination chemistry, Titanium complexes, Phosphido ligands, Phosphanylphosphido ligand, Organophosphorus chemistry

1. Introduction

The main focus of our group is the synthesis and reactivity studies of low valent polyphosphorus complexes especially with phosphanylphosphido (R₂P-PSiMe₃) and phosphanylphosphinidene (R₂P-P) ligands. There are some phosphanylphosphinidene complexes of Mo [1], Pt [2–6], W [7–9], Zr [10,11], Nb [12] and very recently Ti [13] already described. An important aspect, to be mentioned, is the isolation of a “bottle-able” free phosphanylphosphinidene by Bertrand and co-workers [14]. Unlike to phosphanylphosphinidene complexes, those ones which contain R₂P-PSiMe₃ moiety is a less known class of compounds and only few of them have been obtained so far (Hf [15], Zr [15,16], Ti [13] and Ru [17]). Previously, we have shown that the phosphanylphosphido complexes (R₂P-PSiMe₃) can be treated as intermediates in metathesis reactions of R₂P-P(SiMe₃)Li with transition metals complexes containing chlorido and appropriate auxiliary ligands and lead to related phosphanylphosphinidene complexes [10,13,15–20].

A crucial point of our studies is searching for appropriate ligands which are able to stabilize the target compounds. Recently, the well tunable β-diketiminato ancillary ligands [21–25] were used to stabilize Ti-phosphinidene complexes [26,27]. We have found, that ^{Me}Nacnac (^{Me}Nacnac[−] = [Ar]NC(Me)CHC(Me)N[Ar];

Ar = 2,6-*i*Pr₂C₆H₃) is the ligand which stabilizes Ti^{IV} phosphanylphosphinidenes very well. Moreover, there are only two β-diketiminato titanium complexes with phosphanylphosphido ligand described for the first time by our group [13].

Nevertheless, we are still interested in receiving more stable titanium complexes with R₂P-P(SiMe₃) and R₂P-P ligands. Therefore, we turned our attention towards the metathesis reactions of R₂P-P(SiMe₃)Li with titanium complexes containing (PNP) ligand (PNP = N[2-PiPr₂-4-methylphenyl]₂). In general, PNP – tridentate (pincer) ligands [28–35] are very well tunable, they also support low and high oxidation states of metals and adopt a variety of coordination modes [36,37].

In this article, we report on metathesis reactions of [(PNP)TiCl₂] with R₂P-P(SiMe₃)Li·*n*THF (R = tBu and *i*Pr), as well as the properties and single-crystal X-ray structures of [(PNP)Ti(Cl){η¹-P(SiMe₃)-PtBu₂}] (1) and [(PNP)Ti(Cl){η²-P(SiMe₃)-PiPr₂}] (2).

2. Results and discussion

2.1. Synthesis and X-ray crystal structures

Our starting complex was [(PNP)TiCl₂] reported by Mindiola and co-workers [29]. We have modified this synthetic protocol and it led to slightly better yield and to solid product of X-ray quality (see Experimental Section, X-ray structure see Supporting Information, Fig. S1).

Reaction of the [(PNP)TiCl₂] with lithiated diphosphane – *t*Bu₂P–P(SiMe₃)Li·2.5THF in toluene solution yielded – [(PNP)Ti(Cl){η¹-P(SiMe₃)-PtBu₂}] (**1**) which is the first titanium^{III} phosphanylphosphido complex with η¹-coordination of R₂PP(SiMe₃) moiety to the metal center (Scheme 1).

The reaction shown in Scheme 1 was initiated at –30 °C and then the reaction mixture was stirred at room temperature for 2 h. X-ray diffraction quality crystals of **1** in form of orange plates were grown from pentane solution at +4 °C. Compound **1** proved to be very unstable and decomposed during further attempts of recrystallization. The molecular structure of **1** reveals a distorted bipyramidal trigonal geometry around the titanium metal center with P1 and P2 atoms from the PNP ligand in the axial positions and N1 atom from the PNP ligand, P3 atom from the phosphanylphosphido ligand and Cl1 atom in the equatorial positions (Fig. 1).

The short Ti1–P3 distance of 2.4529(7) Å is similar as in complex [MeNacnacTi(Cl){η²-P(SiMe₃)-PtBu₂}] (2.445(2) Å) with bidentate coordinated phosphanylphosphido ligand [13] and indicate rather double bond character. The Ti–P distances in [Cp₂Ti(PMe₃)Cl] Å and [(Cp₂Ti(μ₂-PMe₂))₂] are significantly longer (2.599(1) and 2.613(2) Å, respectively) [38,39]. The distance between P3–P4 2.1961(9) Å is typical for a short single P–P bond and is comparable to those found in similar zirconium and hafnium complexes with monodentate coordination of phosphanylphosphido ligand [15]. Geometry around the P3 atom is ideal planar (ΣP3 = 359.47°) (rms. deviations from the planarity = 0.0403). The geometry around P4 is pyramidal (ΣP4 = 321.35°).

The analogous reaction of [(PNP)TiCl₂] with *i*Pr₂P–P(SiMe₃)Li·1.3THF yields **2** (Scheme 2).

Single crystals of **2** were obtained from pentane solution at +4 °C and were determined by X-ray diffraction and solved as [(PNP)Ti(Cl){η²-P(SiMe₃)-PiPr₂}] (R factor 0.0901, P3–P4 distance 2.091(4) Å). The X-ray analysis of **2** reveals the highest difference peaks near the chloride and phosphorus atoms, therefore the model of disorder was applied. This structure solution indicates two types of the whole-molecule disorders caused by the phosphanylphosphido ligand which occupies two different sites in the crystal asymmetric unit. In this structure of **2** the phosphanylphosphido ligand coordinates at present to the metal center as a bidentate ligand (75 % occupancy) **2a** and as a monodentate ligand (25 % occupancy) **2b** (Fig. 2). The application of the disorder model results in the extension of distances between phosphorus atoms in the phosphanylphosphido unit. As a consequence this disorder model leads to complexes **2a** and **2b**. New solution is more reliable, which is also confirmed by the decrease of value of the R factor to 0.0648.

The coordination sphere around the titanium atom in **2a** is pseudooctahedral and consists of two phosphorus atoms from the phosphanylphosphido ligand, two phosphorus atoms, nitrogen

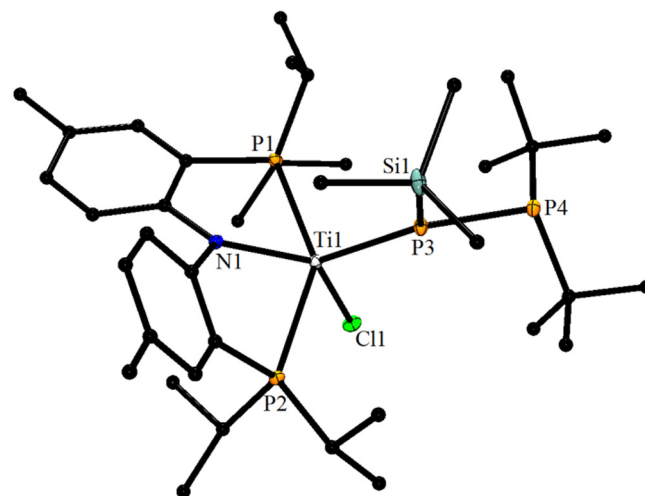
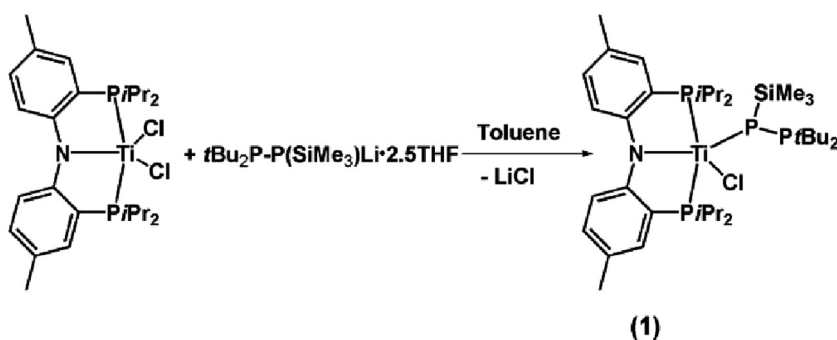


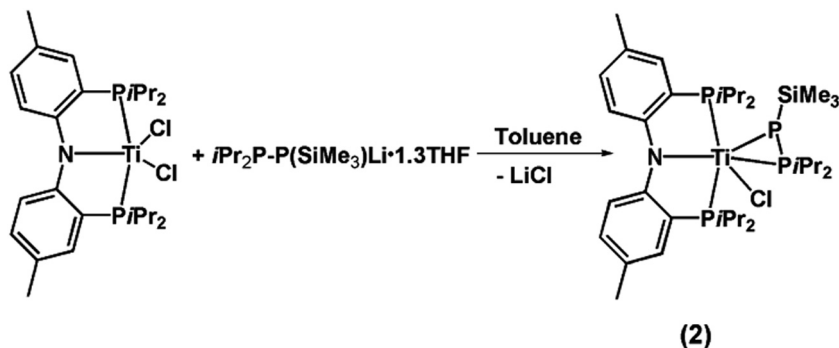
Fig. 1. Molecular structure of complex **1** (hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (°): Ti1–N1 2.0706(19), Ti1–Cl1 2.3303(7), Ti1–P1 2.5599(7), Ti1–P2 2.5888(7), Ti1–P3 2.4529(7), P3–P4 2.1961(9), P3–Si1 2.2347(9); P1–Ti1–P2 144.36(2), Ti1–P3–Si1 123.16(3), Ti1–P3–P4 138.03(3), P3–Ti1–Cl1 108.39(3), P1–Ti1–P3 103.41(2), P2–Ti1–P3 109.15(3), N1–Ti1–Cl1 131.51(5). Sum of the angles around the P atoms: ΣP3 = 359.47, ΣP4 = 321.35.

atom from the PNP ligand and chloride atom. **2b** reveals a distorted bipyramidal trigonal geometry around the titanium metal center with P1, P2 and P3 atoms in the equatorial positions and N1 and Cl1 atom in the axial positions.

For **2a** the distances between titanium and phosphorus atoms from the phosphanylphosphido ligand are Ti1–P3 2.380(3) Å and Ti1–P4 2.674(3) Å and are comparable to those observed in β-diketiminato complexes of titanium^{III} with the same geometry of phosphanylphosphido ligand [13]. The bond length Ti1–P3 in **2b** (2.517(15) Å) is slightly longer than in **1** (2.4529(7) Å) and is shorter than the Ph₂P–Ti in [Cp₂TiPPh₂(PMe₃)] (2.636(3) Å) [40], but is comparable to P–Ti in [(C₅Me₄–SiMe₂–PCy)Ti(NMe₂)₂] (2.504(1) Å) [41]. Surprisingly, the P3–P4 bond distance in **2a** is very short (2.091(4) Å). It is significantly shorter than corresponding bond in β-diketiminato titanium complex with bidentate coordination of phosphanylphosphido ligand in [MeNacnacTi(Cl){η²-P(SiMe₃)-PiPr₂}] (2.1169(9) Å) and shorter than in β-diketiminato titanium complexes with phosphanylphosphinidene ligand in [MeNacnacTi(Cl){η²-P–PiPr₂}] (2.1033(9) Å) [13]. The P3–P4 distance in **2b** (2.179(12) Å) is slightly shorter than those observed in hafnium and zirconium complexes with η¹ coordination of phosphanylphosphido ligand [Cp₂Zr(Cl){η¹-P(SiMe₃)-PiPr₂}] (2.187(2) Å) and [Cp₂Zr(Cl){η¹-P(SiMe₃)-PiPr₂}] (2.185(1) Å) [15]. The P3–P4 bond lengths resulting from crystal structure are however significantly shorter



Scheme 1. Reaction of [(PNP)TiCl₂] with *t*Bu₂P–P(SiMe₃)Li·2.5THF in toluene.



Scheme 2. Reaction of [(PNP)TiCl₂] with *i*Pr₂P-P(SiMe₃)Li·1.3THF in toluene.

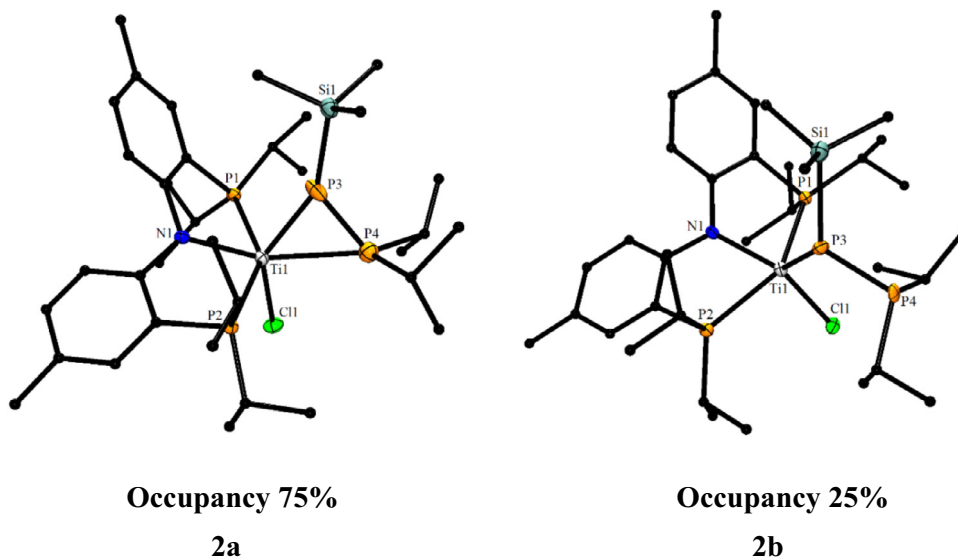


Fig. 2. Two different coordination types for the disorder model of complex **2** (hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (°) for η^2 -coordination (**2a**): Ti1-N1 2.023(15), Ti1-Cl1 2.410(6), Ti1-P1 2.598(9), Ti1-P2 2.610(11), Ti1-P3 2.380(7), Ti1-P4 2.685(7), P3-P4 2.091(4), P3-Si1 2.167(9); P1-Ti1-P2 149.1(4), P3-Ti1-P4 48.29(15), Ti1-P3-Si1 157.2(3), Ti1-P3-P4 73.50(19), P3-Ti1-Cl1 140.0(3), P4-Ti1-Cl1 95.1(2), P1-Ti1-P3 91.8(3), P2-Ti1-P3 105.6(3), P1-Ti1-P4 113.8(2), P2-Ti1-P4 96.8(3), N1-Ti1-Cl1 113.5(5). Sum of the angles around the P atoms: $\Sigma P3=359.23$, $\Sigma P4=329.5$; for η^1 -coordination (**2b**): Ti1-N1 2.16(4), Ti1-Cl1 2.153(14), Ti1-P1 2.82(2), Ti1-P2 2.63(3), Ti1-P3 2.517(15), P3-P4 2.179(12), P3-Si1 2.549(17); P1-Ti1-P2 144.2(7), P4-P3-Ti1 116.1(5), Ti1-P3-Si1 126.0(6), P3-Ti1-Cl1 107.0(6), P1-Ti1-P3 113.0(6), P2-Ti1-P3 90.9(7), N1-Ti1-Cl1 113.5(5). Sum of angles around the P atoms: $\Sigma P3 = 352.37$, $\Sigma P4 = 330.63$.

than distances obtained from DFT calculation (2.132 Å for **2a** and 2.222 Å for **2b** – See [Supporting Information, Figs. S6 and S7](#)).

The reaction of [(PNP)TiCl₂] with the excess of *t*Bu₂P-P(SiMe₃)Li was carried out to lithiate P-Si bond and to obtain phosphanylphosphinidene complex under LiCl elimination. In reaction of [(PNP)TiCl₂] with 2 equiv of *t*Bu₂P-P(SiMe₃)Li·2.5THF in toluene, the red crystals of compound **3** with the formula of [(PNP)Ti(Cl){ η^1 -P(SiMe₃)-*t*Bu₂}]·[*t*Bu₂P-P(SiMe₃)Li·THF]₂ were obtained. It shows, that the excess of lithium diphosphane derivative does not lithiate the P-SiMe₃ moiety of **1** in toluene solution and the excess of *t*Bu₂P-P(SiMe₃)Li·THF cocrystallizes in the unit cell of the compound (See [Supporting Information, Fig. S3](#)).

Basing on those results, we decided to carry out the Hirshfeld populations analysis for complexes **1** and **2a** (The Hirshfeld population analysis graphics see [Supporting Information, Fig. S8](#)). We observed a high positive charge localized on the silicon atom of Me₃Si (0.335 for **1** and 0.346 for **2**) and the P atom connected to the -SiMe₃ is negatively charged (-0.110 for **1** and -0.114 for **2**). These features suggest the possibility of lithiation of the P-SiMe₃ bond and elimination the -SiMe₃ group as *t*Bu₂P-P(SiMe₃)₂. To prove this assumption, we have carried out the reaction of [(PNP)

TiCl₂] with 2 equivalents of *t*Bu₂P-P(SiMe₃)Li but in polar solvent – THF. ³¹P-NMR (reaction solution) contained large signals of *t*Bu₂P-P(SiMe₃)₂ 44.16, -201.13 (d, *J*_{P-P} = 399,64 Hz), and *t*Bu₂P-P(SiMe₃)H 19.42, -190.85 (d, *J*_{P-P} = 196.18 Hz), -197.27 (d, *J*_{P-H} = 188.92 Hz) (³¹P-NMR see [Supporting Information, Fig. S9](#)). The formation of *t*Bu₂P-P(SiMe₃)₂ may suggest, that the -SiMe₃ group was eliminated. The ³¹P-NMR spectrum did not contain any signals of titanium complexes, what can indicate, that in the solution may probably exist the paramagnetic PNP titanium^{III} complexes. We were trying to obtain the crystalline compounds from the reaction solution, but we did not success. We suppose that the presence of *t*Bu₂P-P(SiMe₃)₂ and *t*Bu₂P-P(SiMe₃)H in the reaction mixture increases the solubility of titanium^{III} complexes and hampers their isolation.

Taking into account our satisfying results with the oxidation of β -diketiminato titanium^{III} complexes we have tried to oxidize **1** with the use of [*i*Bu₃PAgCl]₄ or with I₂, but we did not succeed and we did not observe the silver mirror, nor any low field signals in ³¹P-NMR. This lack of reactivity is probably caused by the rigidity and steric hindrance of PNP ligand. The X-ray structure of **1** shows that Cl and SiMe₃ ligands are distant from each other and

intramolecular elimination of Me_3SiCl impose a rotation around the Ti-P3 bond. The elimination of only Me_3Si group via an oxidation (I_2 or $[\text{iBu}_3\text{PAgCl}]_4$) and formation of Ti^{IV} complex does not require the reorganization around Ti-P3 bond and should be feasible but it does not proceed. The difficulties in elimination of the Me_3Si group in $[(\text{PNP})\text{Cl}(\text{OAr})\text{Ta}=\text{NSiMe}_3]$ were also recently reported by Mindiola and co-workers [42].

2.2. DFT calculations

Starting geometries were taken from experimental X-ray data and optimized. After geometry optimization step, analytical frequencies were calculated [43], few low-intensity imaginary frequencies were found, corresponding to rotation of methyl groups, however calculated geometries should still be considered as local minima as long as rotation of methyl groups is not in the scope of this work.

For optimized structures Hirshfeld charges, bonding energies and molecular orbitals visualizations were also calculated. Natural Bonding Orbitals (NBO, version 6) [44] analysis was carried out to investigate bonding between phosphanylphosphido ligand and metal center. Coordinates and drawings of optimized geometries are available in SI.

To confirm the above discussed disorder model we have calculated the total bonding energies for complexes **1** and **2** for monodentate and bidentate coordination types of phosphanylphosphido ligand. Small differences in bonding energies for **2** (1.40 kJ/mol) suggest that steric interactions are responsible for the type of coordination. When the phosphanyl group is rotated in such a way that its lone pair points towards metallic center it can create a weak bond with the metal center and therefore end up in a bidentate coordination. However net energy difference is so small that both types of **2** crystallized. Complex **1** indicates larger difference in bonding energy (11.47 kJ/mol) with bidentate coordinated ligand being lower in energy. However in this case the η^1 -coordination can be explained by larger steric effect of *t*Bu

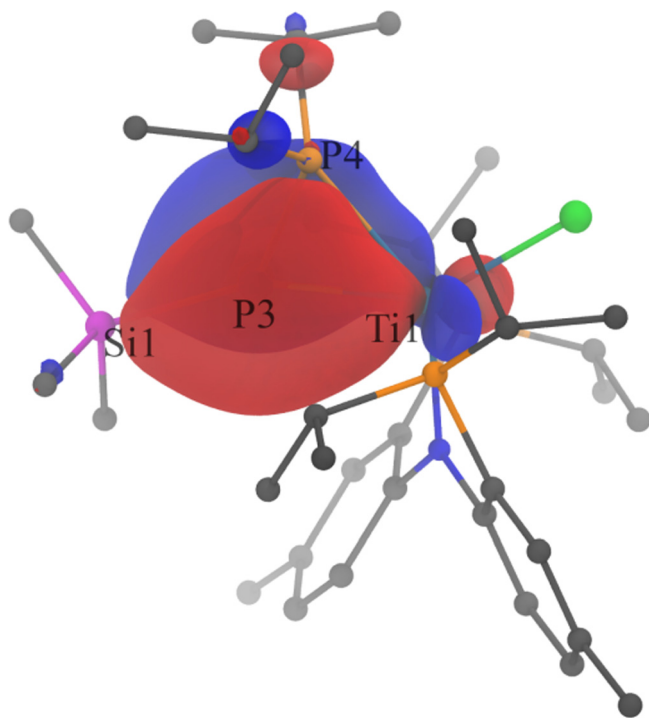


Fig. 3. Natural Localized Molecular Orbital created from π Natural Bonding Orbital between titanium metal center and phosphido phosphorus atom in complex **2**.

groups – making the geometry of bidentate coordination not accessible.

Natural Bonding Orbitals (NBO) analysis strongly suggests double bond character between Ti and phosphido P atoms in **1** and **2**. Natural Localized Molecular Orbital [45] created from Natural Bonding π Orbital between titanium metal center and phosphido phosphorus atom shows contribution of phosphanyl group in the said bond (Fig. 3).

This delocalization is also visible in the picture of HOMO-2 (second orbital lower in energy than highest occupied molecular orbital, where single occupied radical MO is considered the highest) (Fig. 4).

This is consistent with shortened bond length acquired from X-ray studies and implies structure shown in Scheme 3.

In **2** there is a visible delocalization of π electrons from the Ti-P bond to phosphanyl P atom which explains the relatively short P-P bond, visible in the X-ray structure (Scheme 3). For optimized

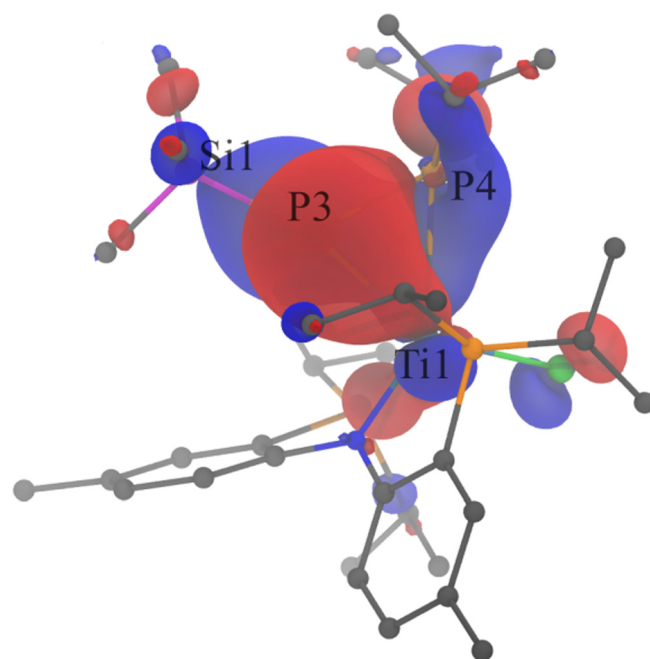
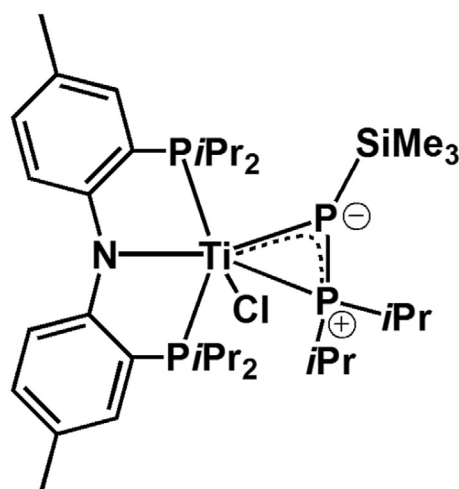


Fig. 4. HOMO-2 orbital in the complex **2**.



Scheme 3. The Lewis structure of **2**.

geometry of **2** the length of the P-P bond is 2.132 Å for bidentate and 2.222 Å for monodentate coordination of phosphanylphosphido ligand. The distances are significantly different from the obtained in the X-ray measurements, however it should be kept in mind, that for **2** the disorder model was constructed and the bond distance between two phosphorus atoms in the phosphanylphosphido ligand can be deviated and more reliable is the distance calculated by DFT methods.

3. Experimental section

3.1. General methods and materials

THF and toluene were dried over Na/benzophenone and distilled under argon. Pentane was dried over Na/benzophenone/diglyme and distilled under argon. All syntheses and manipulations were performed in flame-dried Schlenk-type glassware on a vacuum line. Solution ³¹P-NMR spectrum were recorded on Bruker Avance III HD 400 MHz spectrometer (external standard TMS for ¹H, ¹³C; 85% H₃PO₄ for ³¹P) at ambient temperature. Literature methods were used to prepare *t*Bu₂P-P(SiMe₃)Li-*n*THF [46] and *i*Pr₂P-P(SiMe₃)Li-*n*THF [47].

3.2. Synthesis

3.2.1. Preparation of [(PNP)TiCl₂] [29]

Basing on the procedure of the synthesis of [(PNP)TiCl₂] reported by Mindiola we were acted as follows: a toluene solution of [(PNP)Li] (4.000 g; 7.884 mmol) was added to toluene suspension of [TiCl₃(THF)₃] (2.920 g; 7.884 mmol) at -35 °C. After 1.5 h at room temperature the solvent was removed under vacuum, whereas the solid residue was extracted with small amounts of hot toluene. Resulting toluene solution was cooled to room temperature and red crystals were obtained (2.630 g; 61.90%).

3.2.2. Preparation of [(PNP)Ti(Cl){η¹-P(SiMe₃)-PtBu₂}] (**1**)

A solution of [(PNP)TiCl₂] (0.298 g; 0.544 mmol) in 10 ml of toluene was slowly added to a solution of *t*Bu₂P-P(SiMe₃)Li-2.5THF (0.250 g; 0.573 mmol) in 5 ml of toluene at -30 °C. After 3 h at room temperature solvent was evaporated and the solid product was dissolved in 20 ml of pentane. The red solution was filtrated and concentrated to a volume of 10 ml and left for crystallization at +4 °C. After 24 h, red crystals were isolated (0.302 g, yield 72.9%). *Anal. Calc.* for C₃₇H₆₇Cl₁N₁P₄Si₁Ti₁: C, 58.38; H, 8.87; N, 1.84. Found: C, 58.26; H, 8.96; N, 1.88%.

3.2.3. Preparation of [(PNP)Ti(Cl){η²-P(SiMe₃)-PiPr₂}] (**2**)

A solution of [(PNP)TiCl₂] (0.363 g; 0.660 mmol) in 12 ml of toluene was added dropwise to the solution of *i*Pr₂P-P(SiMe₃)Li-1.3THF (0.264 g; 0.690 mmol) in 5 ml of toluene cooled to -25 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3–4 h. The solvent was removed under vacuum and oily residue was dissolved in 20 ml of pentane. The resulting solution was filtered and concentrated under reduced pressure to the half of the volume. Red crystals were obtained after night of crystallization at +4 °C (0.344 g, yield 71.10%). *Anal. Calc.* for C₃₅H₆₃Cl₁N₁P₄Si₁Ti₁: C, 57.34; H, 8.66; N, 1.91. Found: C, 57.17; H, 8.69; N, 1.90%.

3.2.4. Preparation of [(PNP)Ti(Cl){η¹-P(SiMe₃)-PtBu₂}]·[*t*Bu₂P-P(SiMe₃)Li-THF]₂ (**3**)

[(PNP)TiCl₂] (0.214 g; 0.390 mmol) was dissolved in 15 ml of toluene and added to the solution of *t*Bu₂P-P(SiMe₃)Li-2.5THF (0.440 g; 1.000 mmol) in 10 ml of toluene at -30 °C. Reaction mixture was allowed to warm to room temperature and stirred for 3 h.

The dark-red solution turned red-orange. The solvent was then removed under reduced pressure and the solid residue was extracted with 25 ml of pentane and filtered. The filtrate was concentrated under reduced pressure to 10–12 ml and left at +4 °C. After two days red crystals were received from pentane solution (0.281 g, yield 66.10%). *Anal. Calc.* for C₅₂H₁₀₂Cl₁Li₁N₁O₁P₆Si₂Ti₁: C, 57.32; H, 9.44; N, 1.29. Found: C, 57.38; H, 9.48; N, 1.32%.

3.3. X-ray crystallography

Diffraction data were collected on a diffractometer equipped with a PILATUS100K using Cu Kα radiation with graphite monochromatization (λ = 1.54178 Å) for [(PNP)TiCl₂] and using Mo Kα radiation with graphite monochromatization (λ = 0.71073 Å) for **1**, **2** and **3**. Good quality single-crystal specimens of [(PNP)TiCl₂], **1** and **2** were selected for the X-ray diffraction experiments at 150 K and of **3** at 100 K. The structures were solved by direct methods and refined against F² using the SHELXS-97 and SHELXL-97 programs [48] run under WINGX [49]. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were usually refined using the isotropic model with U_{iso}(H) values fixed to be 1.5 times U_{eq} of C atoms for -CH₃ or 1.2 times U_{eq} for -CH, -CH₂ groups and aromatic H.

3.4. DFT calculations

All calculations were performed using the Amsterdam Density Functional (ADF) software (version 2016.101) [50–52]. They were carried out with the General Gradient Approximation (GGA) functional BLYP [53] (Becke for the exchange part and Lee, Young and Parr [54–56] for the correlation part) with Grimme's -D3 dispersion correction and Becke-Johnson's [57] damping functions. Basis sets used were all electron, triple-ζ valence with two polarization function (TZ2P) [58] for all calculation except frequencies and large frozen-core approximation, double-ζ valence with no polarization functions (DZ) basis set for frequencies calculations. Basis set included scalar zeroth-order regular approximation (scalar ZORA) model [59,60] for relativistic effects. Functional and basis set were chosen because of our experience with using these settings for calculating complexes with R₂PP ligands [13]. Calculations were performed for unrestricted open-shell doublet state.

4. Conclusion

Reactions of [(PNP)TiCl₂] with R₂P-P(SiMe₃)Li-*n*THF (R = *t*Bu, *i*Pr) in molar ratio 1:1 in toluene have yielded related titanium^{III} complexes with different coordination mode of phosphanylphosphido ligand: [(PNP)Ti(Cl){η¹-P(SiMe₃)-PtBu₂}] (**1**) with η¹-coordination and [(PNP)Ti(Cl){η²-P(SiMe₃)-iPr₂}] (**2**) with η²-coordination of mentioned ligand. Additionally for **2** a model of disorder was applied to show two types of coordination (monodentate and bidentate) of *i*Pr₂P-P(SiMe₃) moiety to the metal center. The reaction of [(PNP)TiCl₂] with excess (1:2) of *t*Bu₂P-P(SiMe₃)Li-2.5THF in toluene has led to complex **3** [(PNP)Ti(Cl){η¹-P(SiMe₃)-PtBu₂}]·[*t*Bu₂P-P(SiMe₃)Li-THF]₂ which contain excess lithium derivative of diphosphane cocrystallized in the unit cell. The choice of PNP pincer ligand for better stabilization of the titanium^{III} complexes was not successful and to our surprise, the complexes **1** and **2** were less stable and more sensitive towards further attempts of recrystallization than β-diketiminato titanium complexes.

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Appendix A. Supplementary data

CCDC 1538574–1538577 contains the supplementary crystallographic data for **1**, **2**, **3** and **PNPTiCl₂**. 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. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2017.08.007>.

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