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Reactivity study of β-diketiminate titanium(III) complex with phosphanylphosphido ligand towards chlorophosphanes. A new method of synthesis of β-diketiminate titanium(IV) complexes with versatile phosphanylphosphinidenes

Aleksandra Ziółkowska,[a] Natalia Szynkiewicz,[a] Jerzy Pikies,[a] Łukasz Ponikiewski[*a]

Department of Inorganic Chemistry, Chemical Faculty, Gdansk University of Technology,
11/12 G. Narutowicza Str., 80-233 Gdansk, Poland.

ABSTRACT: The reactivity of β-diketiminate titanium(III) complex with phosphanylphosphido ligand $[^{Me}NacNacTi(Cl)\{\eta^2\text{-}P(SiMe_3)\text{-}P\mathit{t}Bu_2\}]$ (**1**) ($^{Me}NacNac^-$ = [Ar]NC(Me)CHC(Me)N[Ar]; Ar = 2,6-$\mathit{i}Pr_2Ph$) was investigated towards selected chlorophosphanes such as: $\mathit{t}Bu_2PCl$, $\mathit{i}Pr_2PCl$, Cy_2PCl, (Cy)*t*BuPCl, (Me)*t*BuPCl, (Ph)*t*BuPCl, Ph_2PCl, $(\mathit{i}Pr_2N)\mathit{t}BuPCl$ and $(Et_2N)_2PCl$. Reactions with $\mathit{t}Bu_2PCl$ and Ph_2PCl lead mainly to earlier described complex $[^{Me}NacNacTi(Cl)\{\eta^2\text{-}P\text{-}P\mathit{t}Bu_2\}]$ (**1a**), while the reactions with $\mathit{i}Pr_2PCl$, Cy_2PCl, (Cy)*t*BuPCl, (Me)*t*BuPCl, (Ph)*t*BuPCl lead to the mixtures of different β-diketiminate titanium(IV) complexes with phosphanylphosphinidene ligand: **1a** and $[^{Me}NacNacTi(Cl)\{\eta^2\text{-}P\text{-}P\mathit{i}Pr_2\}]$ (**1b**), **1a** and $[^{Me}NacNacTi(Cl)\{\eta^2\text{-}P\text{-}PCy_2\}]$ (**1c**), **1a** and $[^{Me}NacNacTi(Cl)\{\eta^2\text{-}P\text{-}P(Cy)\mathit{t}Bu\}]$ (**1d**), **1a** and $[^{Me}NacNacTi(Cl)\{\eta^2\text{-}P\text{-}P(Me)\mathit{t}Bu\}]$ (**1e**), **1a** and $[^{Me}NacNacTi(Cl)\{\eta^2\text{-}P\text{-}P(Ph)\mathit{t}Bu\}]$ (**1f**), 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 $(Et_2N)_2PCl$ the related titanium(IV) complex is not observe, but the phosphetane $\mathit{t}Bu_2P\text{-}P(\mu_2\text{-}PNEt_2)_2P\text{-}P\mathit{t}Bu_2$ (**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. [$Ru_3(CO)_9\{(P-P)P_3C_5tBu_5\}$] was obtained by Nixon and co-workers in the reaction of pentaphospha-ferrocene with [($Ru_3(CO)_{12}$)].[1] In the same year Scherer and co-workers presented a trinuclear tantalum complex [(Ta(1,3-$tBu_2C_5H_3)_3(P_4\{Fe_4(CO_4)\})(P_2)$)].[2] A few years later Fritz *et. al.* enriched the work on P-PR_2 chemistry with phosphinophosphinidene phosphoranes tBu$_2$P-P-PX(tBu)$_2$ (X = Me or Br) as transfer reagents of tBu$_2$P-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 π-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($SiMe_3$)Li.[6] It is worth to pointing out, that Cummins and Figueroa presented another approach to obtain complexes with R_2P-P ligands. They applied triply bonded phosphorus complexes of niobium and tungsten with terminally bonded P-ligand in reactions with R_2PCl and received related complexes with R_2P-P moieties.[7] Recently, the "reverse" metathesis of tBu$_2$P-PCl$_2$ with lithiated metal carbonyls was reported by Grubba *et. al.* as an alternative access to electrophilic phosphanyl-phosphinidene complexes. However, these complexes are highly reactive and only products of dimerization of monomeric species with tBu$_2$P-P moiety were isolated.[8] Very recently we have studied the synthesis and reactivity of phosphanylphosphido (RR'P-P($SiMe_3$)) 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 β-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 β-diketiminate titanium(III) complex with phosphanylphosphido ligand towards selected chlorophosphanes: $t\mathrm{Bu_2PCl}$, $i\mathrm{Pr_2PCl}$, $\mathrm{Cy_2PCl}$, (Cy)tBuPCl, (Me)tBuPCl, (Ph)tBuPCl, $\mathrm{Ph_2PCl}$, ($i\mathrm{Pr_2N}$)tBuPCl, $\mathrm{(Et_2N)_2PCl}$.

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}H, ^{31}P and ^{13}C spectra in solution were recorded on Bruker AV300 MHz and Bruker AV400 MHz (external standard tetramethylsilane for ^{1}H, ^{13}C; 85% H_3PO_4 for ^{31}P). [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] (**1**),[6e] (Cy)tBuPCl, [14] (iPr$_2$N)tBuPCl [15] and iPr$_2$P-P(Li)-PiPr$_2$ [16] were prepared according to procedures in literature. Cy$_2$PCl, (Me)tBuPCl, (Ph)tBuPCl, tBu$_2$PCl, iPr$_2$PCl, Ph$_2$PCl and (Et$_2$N)$_2$PCl were commercially purchased.

General method for the synthesis of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] (1) with selected chlorophosphanes.

The complex [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] (**1**) (0.250 mg, 0.318 mmol) was dissolved in 10 ml of THF and then dropwise added to the solution of chlorophosphane R^{B}R^{C}PCl (in 2 ml of THF). The green reaction mixture was heated for 48 h at 50°C. After that time solvent was evaporated and slightly oily residue was obtained.

Reaction 1: [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] (1) with tBu$_2$PCl

R^{B} = tBu, R^{C} = tBu; 0.060 g, 0.318 mmol; the oily residue was dissolved in C_6D_6 and NMR spectroscopic investigated.

^{31}P{^{1}H}-NMR data of **1a** (298 K, C_6D_6): δ (d), 843.68 ppm (**P**-PtBu$_2$, J_{PP} = 450.5 Hz) and 143.52 ppm (P-**P**tBu$_2$, J_{PP} = 450.5 Hz);

Reaction 2: [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] (1) with iPr$_2$PCl

R^{B} = iPr, R^{C} = iPr; 0.048 g, 0.318 mmol of iPr$_2$PCl; the oily residue was dissolved in 5 ml of pentane and stored at +4°C. After 3 h dark-green crystals were appeared. The crystals were isolated and X-ray characterized as the complexes (**1a**) [^{Me}NacNacTi(Cl){η^2-P-PtBu$_2$}] (0.04 g, yield 38%). The remaining solution was concentrated and stored at +4°C again. After 24 h green crystals were appeared and characterized as (**1b**) [^{Me}NacNacTi(Cl){η^2-P-P*i*Pr$_2$}] (0.028 g, yield 27%).

^{31}P{^{1}H}-NMR data of **1a** (298 K, C_6D_6): δ (d), 844.32 ppm (**P**-P*t*Bu$_2$, J_{PP} = 450.5 Hz) and 143.65 ppm (P-**P***t*Bu$_2$, J_{PP} = 450.5 Hz);

^{31}P{^{1}H}-NMR data of **1b** (298 K, C_6D_6): δ 824.23 (**P**-P*i*Pr$_2$, J_{PP} = 443.2 Hz) and 118.37 ppm (P-**P***i*Pr$_2$, J_{PP} = 443.2 Hz);

Reaction 3: [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (1) with Cy$_2$PCl

R^B = Cy, R^C = Cy; 0.074 g, 0.318 mmol of Cy$_2$PCl; the oily residue was dissolved in 5 ml of pentane and stored at +4°C. After 1 h dark-green crystals were appeared and X-ray characterized as a new complex (**1c**) [^{Me}NacNacTi(Cl){η^2-P-PCy$_2$}] (0.055 g, yield 47%). The crystals of **1c** were isolated and the solution was concentrated to 2 mL of amount. After 12 h at +4 °C green crystals were appeared and were X-ray characterized as (**1a**) [^{Me}NacNacTi(Cl){η^2-P-P*t*Bu$_2$}] (0.022 g, yield 20%). Anal. Calcd for $C_{41}H_{63}ClN_2P_2Ti$ (**1c**): C, 67.51; H, 8.71; N, 3.84%. Found: C, 67.36; H, 8.75; N, 3.89%.

NMR data of **1c**: ^{1}H-NMR (298 K, C_6D_6): δ 7.24-7.12 (6H, C_6H_3), 4.77 (s, 1H, NC(Me)C*H*C(Me)N), 4.09 (sept, 2H, *J* = 6.8 Hz, C*H*(Me)$_2$), 3.17 (sept, 2H, *J* = 6.8 Hz, C*H*(Me)$_2$), 2.11 (broad m, 4H, Cy), 1.73 (broad m, 2H, Cy), 1.69 (broad m, 8H, Cy), 1.65 (d, 6H, *J* = 6.7 Hz, CH(*Me*)$_2$), 1.57 (broad m, 8H, Cy), 1.53 (d, 6H, *J* = 6.8 Hz, CH(*Me*)$_2$), 1.49 (s, 6H, NC(*Me*)CHC(*Me*)N), 1.17 (d, 6H, *J* = 6.9 Hz, CH(*Me*)$_2$), 1.12 (d, 6H, *J* = 6.8 Hz, CH(*Me*)$_2$); ^{13}C{^{1}H}-NMR (298 K, C_6D_6): δ 166.42 (s, N*C*(Me)CH*C*(Me)N), 142.92 (s, Ar-C), 141.47 (Ar-C), 127.14 (Ar-C), 124.51 (Ar-C), 124.21 (Ar-C), 96.12 (s, NC(CH$_3$)*C*HC(CH$_3$)N), 40.06 (d, J_{PC} = 7.2 Hz, Cy), 31.81 (d, J_{PC} = 1.2 Hz, Cy), 29.00 (s, *C*H(Me)$_2$), 28.20 (s, *C*H(Me)$_2$), 27.73 (dd, J_{PC} = 11.9 Hz, J_{PC} = 13.0 Hz, Cy), 26.16 (dd, J_{PC} = 16.9 Hz, J_{PC} = 1.2 Hz, Cy), 24.76 (s, CH(*Me*)$_2$), 24.42 (s, NC(Me)C*H*C(Me)N), 24.11 (s, CH(*Me*)$_2$), 23.68 (s, CH(*Me*)$_2$), 23.09 (s, CH(*Me*)$_2$); ^{31}P{^{1}H}-NMR (298 K, C_6D_6): δ 832.99 (**P**-PCy$_2$, J_{PP} = 442.8 Hz), 107.78 (P-**P**Cy$_2$, J_{PP} = 442.8 Hz) ppm.

^{31}P{^{1}H}-NMR data of **1a** (298 K, C_6D_6): δ (d), 844.32 (**P**-P*t*Bu$_2$, J_{PP} = 450.5 Hz) and 143.65 ppm (P-**P***t*Bu$_2$, J_{PP} = 450.5 Hz).

Reaction 4: [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (1) with (Cy)*t*BuPCl

R^B = Cy, R^C = *t*Bu; 0.066 g, 0.318 mmol of (Cy)*t*BuPCl; the oily residue was dissolved in 5 ml of pentane and stored at +4 °C. After 1 h dark-green crystals were appeared and X-ray characterized as a new complex (**1d**) $[^{Me}\mathrm{NacNacTi(Cl)}\{\eta^2\text{-P-P(Cy)}t\mathrm{Bu}\}]$ (0.065 g, yield 58%). The crystals of **1d** were isolated and the solution was concentrated to 2 mL of volume. After 12 h at +4°C green crystals were appeared and were X-ray characterized as (**1a**) $[^{Me}\mathrm{NacNacTi(Cl)}\{\eta^2\text{-P-P}t\mathrm{Bu}_2\}]$ (0.015 g, yield 14%). Anal. Calcd for $C_{39}H_{61}ClN_2P_2Ti$ (**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}H-NMR (298 K, C_6D_6): δ 7.17-6.88 (6H, C_6H_3), 4.63 (s, 1H, NC(Me)C*H*C(Me)N), 4.07 (sept., 1H, J_{HH} = 6.7 Hz, C*H*(Me)$_2$), 3.96 (sept, 1H, J_{HH} = 6.8 Hz, C*H*(Me)$_2$), 3.43 (sept., 1H, J_{HH} = 6.7 Hz, C*H*(CH_3)$_2$), 3.16 (m, C_6H_{11}), 2.54 (sept, 1H, J_{HH} = 6.7 Hz, C*H*(Me)$_2$), 1.66 (m, C_6H_{11}), 1.50 (d, 3H, J_{HH} = 6.8 Hz, CH(*Me*)$_2$), 1.46 (m, C_6H_{11}), 1.41 (s, 3H, NC(*Me*)CHC(*Me*)N), 1.31 (d, 3H, J_{HH} = 6.8 Hz, CH(*Me*)$_2$), 1.29 (d, 18H, J_{PH} = 14.79 Hz, PC(*Me*)$_3$), 1.24 (s, 3H, NC(*Me*)CHC(*Me*)N), 1.05 (m, C_6H_{11}), 0.99 (d, 3H, J_{HH} = 6.8 Hz, CH(*Me*)$_2$), 0.86 (d, 3H, J_{HH} = 6.6 Hz, CH(*Me*)$_2$) ppm; ^{13}C{^{1}H}-NMR (298 K, C_6D_6): δ 167.28 and 165.97 (*C*(CH_3)CH*C*(CH_3)), 143.46, 142.53, 141.68, 141.60, 126.99, 124.61, 124.28 (*C*$_6$H$_3$), 96.36 (γ-CH), 43.07 (d, J_{PC} = 3.7 Hz, Cy), 39.08 (d, J_{PC} = 3.67, Hz, P*C*(Me)$_3$,), 31.88 (s, Cy), 31.56 (s, PC(*Me*)$_3$), 29.18 (s, *C*H(Me)$_2$), 28.98 (s, *C*H(Me)$_2$), 28.55 (s, *C*H(Me)$_2$), 27.93 (dd, J_{CP} = 11.0 Hz, J_{CP} = 5.1 Hz, Cy), 27.74 (s, *C*H(Me)$_2$), 26.22 (dd, J_{CP} = 36.7 Hz, J_{CP} = 2.2 Hz), 24.94 (s, CH(*Me*)$_2$), 24.84 (s, NC(*Me*)CHC(*Me*)N), 24.76 (s, CH(*Me*)$_2$), 24.47 (s, NC(*Me*)CHC(*Me*)N), 24.13 (s, CH(*Me*)$_2$), 24.02 (s, CH(*Me*)$_2$) ppm; ^{31}P{^{1}H}-NMR (298 K, C_6D_6): δ 846.46 (**P**-P(Cy)*t*Bu, J_{PP} = 443.2 Hz), 117.92 (P-**P**(Cy)*t*Bu, J_{PP} = 443.2 Hz) ppm.

^{31}P{^{1}H}-NMR data of **1a** (298 K, C_6D_6): δ (d), 844.32 (**P**-P*t*Bu$_2$, J_{PP} = 450.5 Hz) and 143.65 ppm (P-**P***t*Bu$_2$, J_{PP} = 450.5 Hz).

Reaction 5: $[^{Me}\mathrm{NacNacTi(Cl)}\{\eta^2\text{-P(SiMe}_3\text{)-P}t\mathrm{Bu}_2\}]$ (1) with (Me)*t*BuPCl

R^B = Me, R^C = *t*Bu; 0.044 g, 0.318 mmol of (Me)*t*BuPCl; the oily residue was dissolved in 5 ml of pentane and stored at +4°C. After 3 h dark-green crystals were appeared and X-ray characterized as the complexes (**1a**) $[^{Me}\mathrm{NacNacTi(Cl)}\{\eta^2\text{-P-P}t\mathrm{Bu}_2\}]$ (0.035 g, yield 33%). Unfortunately, complex **1e** was not obtained in the crystalline form. Therefore, after reaction the oily residue was dissolved in C_6D_6 and NMR spectroscopic investigated.

^{31}P{^{1}H}-NMR data of **1a** (298 K, C_6D_6): δ (d), 844.32 (**P**-P*t*Bu$_2$, J_{PP} = 450.5 Hz) and 143.65 ppm (P-**P***t*Bu$_2$, J_{PP} = 450.5 Hz).

^{31}P{^{1}H}-NMR data of **1e** (298 K, C_6D_6): δ (d), 830.06 (**P**-P(Me)*t*Bu, J_{PP} = 457.8 Hz) and 91.82 ppm (P-P(Me)*t*Bu, J_{PP} = 457.8 Hz).

Reaction 6: [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (1) with (Ph)*t*BuPCl

R^B = Ph, R^C = *t*Bu; 0.064 g, 0.318 mmol of (Ph)*t*BuPCl; the oily residue was dissolved in 5 ml of pentane and stored at +4°C. After 2 h dark-green crystals were appeared and X-ray characterized as the complexes (**1f**) [^{Me}NacNacTi(Cl){η^2-P-P(Ph)*t*Bu}] (0.055, yield 49%), The crystals of **1f** were isolated and the solution was stored at +4°C again. 24 h later the green crystals were appeared which were characterized as (**1a**) [^{Me}NacNacTi(Cl){η^2-P-P*t*Bu$_2$}] (0.02 g, yield 19%).

^{31}P{^{1}H}-NMR data of **1a** (298 K, C_6D_6): δ (d), 844.32 (**P**-P*t*Bu$_2$, J_{PP} = 450.5 Hz) and 143.65 ppm (P-**P***t*Bu$_2$, J_{PP} = 450.5 Hz).

^{31}P{^{1}H}-NMR data of **1f** (298 K, C_6D_6): δ (d), 825.19 (**P**-P(Ph)*t*Bu, J_{PP} = 443.2 Hz) and 109.63 ppm (P-**P**(Ph)*t*Bu, J_{PP} = 443.2 Hz).

Reaction 7: [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (1) with Ph$_2$PCl

R^B = Ph, R^C = Ph; 0.070 g, 0.318 mmol of Ph$_2$PCl; the oily residue was dissolved in 5 ml of pentane and stored at +4°C. After 3 h dark-green crystals were appeared and X-ray characterized as the complexes (**1a**) [^{Me}NacNacTi(Cl){η^2-P-P*t*Bu$_2$}] (0,080 g, yield 74%). Unfortunately, complex **1g** was not obtained in the crystalline form. Therefore, after reaction the oily residue was dissolved in C_6D_6 and NMR spectroscopic investigated.

^{31}P{^{1}H}-NMR data of **1a** (298 K, C_6D_6): (d), 844.32 (**P**-P*t*Bu$_2$, J_{PP} = 450.5 Hz) and 143.65 ppm (P-**P***t*Bu$_2$, J_{PP} = 450.5 Hz).

^{31}P{^{1}H}-NMR data of **1g** (298 K, C_6D_6): (d), 780.29 (**P**-PPh$_2$, J_{PP} = 472.3 Hz) and 88.05 ppm (P-**P**Ph$_2$, J_{PP} = 472.3 Hz).

Reaction [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (1) with (*i*Pr$_2$N)*t*BuPCl

R^B = (*i*Pr$_2$)N, R^C = *t*Bu; 0.071 g, 0.318 mmol of (*i*Pr$_2$N)*t*BuPCl; in the reaction the products in crystalline form were not obtained, therefore the oily residue was dissolved in C_6D_6 and NMR spectroscopic investigated.

^{31}P{^{1}H}-NMR data of **1a** (298 K, C_6D_6): (d), 844.32 (**P**-P*t*Bu$_2$, J_{PP} = 450.5 Hz) and 143.65 ppm (P-**P***t*Bu$_2$, J_{PP} = 450.5 Hz).

^{31}P{^{1}H}-NMR data of other compounds (298 K, C_6D_6): 82.04 (small signal of (*i*Pr$_2$N)*t*BuP-P(*i*Pr$_2$N)*t*Bu), 144.62 ppm (unreacted (*i*Pr$_2$N)*t*BuPCl).

Reaction [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] with (Et$_2$N)$_2$PCl

R^B = Et$_2$N, R^C = Et$_2$N; 0.067 g, 0.318 mmol of (Et$_2$N)$_2$PCl; after the reaction in the crystalline form the complexes of [^{Me}NacNacTi(Cl){NEt$_2$}]$_2$ (**2**) and [^{Me}NacNacTiCl$_2$(THF)] were obtained. The crystals of both complexes were isolated and the reaction solution was evaporated. The oily residue was dissolved in C_6D_6 and NMR spectroscopic investigated.

The NMR data of phosphetane **(3)** (see Scheme 4): ^{1}H-NMR (298 K, C_6D_6): δ 3.28 (broad m, 4 H, *CH$_2$*CH$_3$), 1.45 (d, *t*Bu groups, 36H, *J* = 11,24 Hz), ^{31}P{^{1}H}-NMR (298 K, C_6D_6) spin system AA'M$_2$XX': δ 58.62 (m, *t*Bu$_2$P$_{(1)}$), 20.36 (m, P$_{(2)}$NEt$_2$), -24.89 (m, P$_{(3)}$ – unsubstituted) ppm. $^1J_{P(1)P(3)}$ = -245.5 Hz, $^1J_{P(3)P(2)}$ = -208.7 Hz, $^2J_{P(3)P(3')}$ = 172.4 Hz, $^2J_{P(1)P(2)}$ = 13.8 Hz, $^4J_{P(1)P(1')}$ = 0.6 Hz, $^3J_{P(3)P(1')}$ = 0.4 Hz.

Synthesis of (*t*Bu$_2$P)(*i*Pr$_2$P)$_2$P

To a solution of (*i*Pr$_2$P)$_2$PLi·2THF (0.100 g; 0.240 mmol) in 4 ml of THF cooled to 0°C a chlorophosphane *t*Bu$_2$PCl (0.043 ml; 0.240 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 C_6D_6. The solution was decanted from the precipitated LiCl and analyzed by ^{31}P{^{1}H}, ^{31}P and ^{1}H-NMR spectroscopy. The NMR results reveal that in the reaction two compounds are formed: (*t*Bu$_2$P)(*i*Pr$_2$P)$_2$P and *t*Bu$_2$P-P(H)-P*i*Pr$_2$.

NMR data of (*t*Bu$_2$P)(*i*Pr$_2$P)$_2$P: ^{1}H-NMR (298 K, C_6D_6): δ 2.35 (sept, J_{PH} = 7.1 Hz, *i*Pr$_2$P, 4H), 1.42 (d, J_{PH} = 12.2 Hz, *t*Bu$_2$P, 18H), 1.34, 1.29, 1.26, 1.24 (d, J_{PH} = 7.1 Hz, *i*Pr$_2$P, 24H); ^{31}P{^{1}H}-NMR (298 K, C_6D_6): δ 42.89 (d, J_{PP} = 459.2 Hz, (*t*Bu$_2$**P**)(*i*Pr$_2$P)$_2$P), 9.77 (d, J_{PP} = 397.2 Hz, (*t*Bu$_2$P)(*i*Pr$_2$**P**)$_2$P), -102.44 (m, (*t*Bu$_2$P)(*i*Pr$_2$P)$_2$**P**) ppm.

NMR data of *t*Bu$_2$P-P(H)-*i*Pr$_2$: ^{1}H-NMR (298 K, C_6D_6): δ 3.02 (d, J_{PH} = 188.9 Hz, *t*Bu$_2$P-P(H)-P*i*Pr$_2$, 1H), 1.96 (sept., J_{PH} = 6.72 Hz, P*i*Pr$_2$, 4H), 1.05 (d, J_{PH} = 11.9 Hz, *t*Bu$_2$P-P(H)-P*i*Pr$_2$, 18H), 0.52, 0.47, 0.42, 037 (d, J_{PH} = 6.72 Hz, P*i*Pr$_2$, 12H); ^{31}P{^{1}H}-NMR (298 K, C_6D_6): δ 23.32 (dd, J_{PP} = 109.8 Hz, J_{PP} = 206.9 Hz *t*Bu$_2$**P**-P(H)-P*i*Pr$_2$), -0.19 (dd, J_{PP} = 109.8 Hz, J_{PP} = 213.2 Hz *t*Bu$_2$P-P(H)-**P***i*Pr$_2$), -137.18 (dd, J_{PP} = 206.9 Hz, J_{PP} = 213.2 Hz *t*Bu$_2$P-**P**(H)-P*i*Pr$_2$) ppm.

Table 1. ^{31}P{^{1}H}-NMR data of byproducts observed in reaction 1-7.

Reaction	Byproducts	δ_{P1} [ppm]	δ_{P2} [ppm]	δ_{P3} [ppm]	J_{PP} [Hz]

Reaction 1	$t\mathrm{Bu_2P_{(1)}H}$	(s) 19.49			
	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(1)}}t\mathrm{Bu_2}$	(s) 39.66			
Reaction 2	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(1)}}t\mathrm{Bu_2}$	(s) 39.79			
	$t\mathrm{Bu_2P_{(1)}H}$	(s) 19.56			
	$i\mathrm{Pr_2P_{(1)}}$-$\mathrm{P_{(1)}}i\mathrm{Pr_2}$	(s) -12.11			
	$(i\mathrm{Pr_2P_{(1)}})_3\mathrm{P_{(2)}}$	(d) 3.51	(m) -113.94		357.9
	$(t\mathrm{Bu_2P_{(1)}})(i\mathrm{Pr_2P_{(2)}})_2\mathrm{P_{(3)}}$	(d) 43.06	(d) 9.96	(m) -102.27	459.6 397.1
	$i\mathrm{Pr_2P_{(1)}}$-$\mathrm{P_{(2)}(H)}$-$\mathrm{P_{(1)}}i\mathrm{Pr_2}$	(d) -3.42	(t) -139.99		203.4
	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(3)}(H)}$-$\mathrm{P_{(2)}}i\mathrm{Pr_2}$	(dd) 23.52	(dd) 0.02	(dd) -137.09	108.9 210.5 217.2
Reaction 3	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(1)}}t\mathrm{Bu_2}$	(s) 39.61			
	$t\mathrm{Bu_2P_{(1)}H}$	(s) 19.59			
Reaction 4	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(1)}}t\mathrm{Bu_2}$	(s) 39.82			
	$t\mathrm{Bu_2P_{(1)}H}$	(s) 19.56			
	$(t\mathrm{Bu_2P_{(1)}})((\mathrm{Cy})t\mathrm{BuP_{(2)}})_2\mathrm{P_{(3)}}$*	(d) 57.23	(d) 32.06	(m) -99.86	486.8 508.6
Reaction 5	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(1)}}t\mathrm{Bu_2}$	(s) 39.86			
	$t\mathrm{Bu_2P_{(1)}H}$	(s) 19.61			
	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(2)}(SiMe_3)H}$	(d) 19.24	(d) -190.65		196.2
	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(2)}(SiMe_3)_2}$	(d) 44.45	(d) -200.83		400.0
	$(\mathrm{Me})t\mathrm{BuP_{(1)}}$-$\mathrm{P_{(1)}(Me)}t\mathrm{Bu}$	(s) -31.04			
	$((\mathrm{Me})t\mathrm{BuP_{(1)}})_3\mathrm{P_{(2)}}$*	(d) 38.94	(m) -105.84		460.9
	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(2)}(H)}$-$\mathrm{P_{(1)}}t\mathrm{Bu_2}$	(d) 26.47	(t) -136.79		228.2
	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(3)}(H)}$-$\mathrm{P_{(2)}(Me)}t\mathrm{Bu}$	(dd) 23.33	(dd) -16.96	(dd) -115.90	130.7 188.6 247.0
Reaction 6	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(1)}}t\mathrm{Bu_2}$	(s) 39.44			
	$t\mathrm{Bu_2P_{(1)}H}$	(s) 19.75			
	$(\mathrm{Ph})t\mathrm{BuP_{(1)}}$-$\mathrm{P_{(1)}(Ph)}t\mathrm{Bu}$	(s) -4.69			
	$((\mathrm{Ph})t\mathrm{BuP_{(1)}})_3\mathrm{P_{(2)}}$*	(d) 45.69	(m) -100.86		482.3
	$t\mathrm{Bu_2P}$-$\mathrm{P(SiMe_3)_2}$	(d) 44.03	(d) -201.44		400.0
	$t\mathrm{Bu_2P}$-$\mathrm{P(SiMe_3)H}$	(d) 18.59	(d) -191.21		196.1
Reaction 7	$t\mathrm{Bu_2P_{(1)}H}$	(s) 19.78			
	$\mathrm{Ph_2P}$-$\mathrm{PPh_2}$	(s) -15.11			
	$t\mathrm{Bu_2P_{(1)}}$-$\mathrm{P_{(2)}Ph_2}$	(d) 32.85	(d) -26.29		247.0

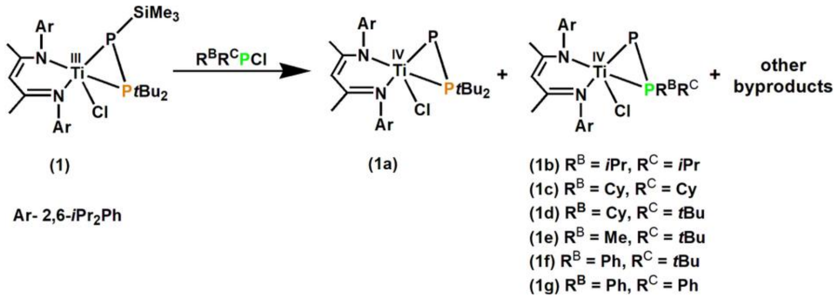
* the compounds were characterized by analogy to shifts for compounds $(t\mathrm{Bu_2P})(i\mathrm{Pr_2P})_2\mathrm{P}$ and $(i\mathrm{Pr_2P})_3\mathrm{P}$.

3. RESULTS AND DISCUSSION

3.1. Reactions of $[^{\mathrm{Me}}\mathrm{NacNacTi(Cl)}\{\eta^2\text{-}\mathrm{P(SiMe_3)}\text{-}\mathrm{P}t\mathrm{Bu_2}\}]$ (1) with chlorophosphanes.

The earlier performed DFT studies (condensed Fukui functions) of model compound $[^{\mathrm{Me}}\mathrm{NacNacTi(Cl)}\{\eta^2\text{-}\mathrm{P(SiMe_3)}\text{-}\mathrm{P}t\mathrm{Bu_2}\}]$ (**1**) suggested amphiphilic character of P-SiMe$_3$ (f^+ 0.043 and f^- 0.077).[6f] In our latest work we presented the reactivity of β-diketiminate titanium(III) complexes with phosphanylphosphido ligands towards nucleophilic reagents: $\mathrm{Ph_2PLi}$, $\mathrm{(Me_3Si)_2NLi}$, $t\mathrm{Bu_2NLi}$, $t\mathrm{BuOLi}$ that reacted *via* two different reactivity patterns. The first is the elimination of –SiMe$_3$ group and lithiation of the phosphorus atom in the $\mathrm{P(SiMe_3)}$-$\mathrm{P}t\mathrm{Bu_2}$ and the second is the substitution reaction of the chloride atom and oxidation of Ti(III).[9] Hence, we decided to examine the reactivity of $[^{\mathrm{Me}}\mathrm{NacNacTi(Cl)}\{\eta^2\text{-}\mathrm{P(SiMe_3)}\text{-}\mathrm{P}t\mathrm{Bu_2}\}]$ (**1**) towards chlorophosphanes. We used selected reagents with different electronic and steric properties such as: tBu$_2$PCl iPr$_2$PCl, Cy$_2$PCl, (Cy)tBuPCl, (Me)tBuPCl, (Ph)tBuPCl, Ph$_2$PCl, (iPr$_2$N)tBuPCl, (Et$_2$N)$_2$PCl in our investigations.

Taking into account that our starting complex [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] (**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 h, 50°C – described below). Unfortunately, in all cases, we only isolated starting material (complex **1**). Additionally, in ^{31}P{^{1}H}-NMR spectra of reaction mixtures, we observed only the signals of unreacted chlorophosphanes (example ^{31}P{^{1}H}-NMR spectrum after reaction with (Ph)tBuPCl see Figure S72). 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}P{^{1}H}-NMR spectra of reaction mixtures indicate, that in the reactions of **1** with iPr$_2$PCl, Cy$_2$PCl, (Cy)tBuPCl, (Me)tBuPCl, (Ph)tBuPCl, Ph$_2$PCl two different β-diketiminate titanium(IV) complexes with phosphanylphosphinidene ligand are formed in each case (Scheme 1).



Scheme 1. Reaction of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] (**1**) with selected chlorophosphanes.

Especially, the ^{31}P{^{1}H}-NMR investigation of the reaction mixture in the low field region (850 ÷ 780 ppm) clearly confirmed that in reaction of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] **(1)** with iPr$_2$PCl two complexes **1a** and **1b** are formed. Analogously in the reactions of **1** with Cy$_2$PCl, (Cy)tBuPCl, (Me)tBuPCl, (Ph)tBuPCl, Ph$_2$PCl two complexes are formed **1a-1c**, **1a-1d**, **1a-1e**, **1a-1f** and **1a-1g** respectively. The ^{31}P{^{1}H}-NMR data of the [^{Me}NacNacTi(Cl){η^2-P-PR^{B}R^C}] (**1x**) complexes are presented in Table 2.

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

	P(1) [ppm]	**P(2) [ppm]**	**$J_{P(1)P(2)}$ [Hz]**
[^{Me}NacNacTi(Cl){η^2-P(1)-P(2)tBu$_2$}] (**1a**) [6e]	843.68	143.52	450.5
[^{Me}NacNacTi(Cl){η^2-P(1)-P(2)iPr$_2$}] (**1b**) [6e]	824.23	118.37	443.2
[^{Me}NacNacTi(Cl){η^2-P(1)-P(2)Cy$_2$}] (**1c**)	832.99	107.78	442.8
[^{Me}NacNacTi(Cl){η^2-P(1)-P(2)(Cy)tBu}] (**1d**)	846.46	117.92	443.2

[^{Me}NacNacTi(Cl){η^2-P(1)-P(2)(Me)*t*Bu}] (**1e**)	830.06	91.82	457.8
[^{Me}NacNacTi(Cl){η^2-P(1)-P(2)(Ph)*t*Bu}] (**1f**) [6f]	825.19	109.63	443.2
[^{Me}NacNacTi(Cl){η^2-P(1)-P(2)Ph$_2$}] (**1g**)	780.29	88.05	472.3

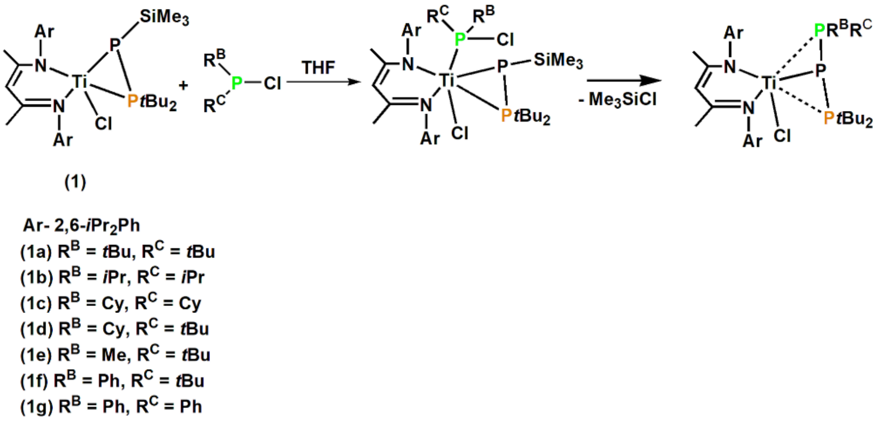
The solubility differences of obtained complexes, allowed separating complexes from reaction mixtures. For the described reactions the complexes **1a, 1b, 1c**, **1d** and **1f** were separately isolated in the crystalline form. Unfortunately, we were not able to obtain **1e** and **1g** in crystalline form. ^{31}P{^{1}H}-NMR examinations of reaction solutions also reveal the formation of different compounds mainly with newly formed P-P and P-H bonds in each reaction. In reaction 1, two compounds were found as main byproducts: *t*Bu$_2$P-P*t*Bu$_2$ [17] and *t*Bu$_2$PH [18]. Most of the resulting byproducts were observed in the reaction of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (**1**) with *i*Pr$_2$PCl. In this reaction, in addition with two complexes **1a** and **1b** following compounds are also formed: *i*Pr$_2$P-P*i*Pr$_2$,[17] (*i*Pr$_2$P)$_3$P, (*t*Bu$_2$P)(*i*Pr$_2$P)$_2$P, *i*Pr$_2$P-PH-P*i*Pr$_2$ [4a] and *t*Bu$_2$P-PH-P*i*Pr$_2$. The tetraphosphorus compound (*i*Pr$_2$P)$_3$P was earlier synthesized and characterized by Scheer and co-workers in the reaction of *i*Pr$_2$P-P(Li)-P*i*Pr$_2$ with *i*Pr$_2$PCl,[2] while the (*t*Bu$_2$P)(*i*Pr$_2$P)$_2$P is observed for the first time. To confirm that, we additionally performed reaction of *i*Pr$_2$P-P(Li)-P*i*Pr$_2$ with *t*Bu$_2$PCl and as a result we received the desired compound (*t*Bu$_2$P)(*i*Pr$_2$P)$_2$P (doublets at 43.06 ppm and 9.96 ppm and multiplet at -102.27 ppm, J_{PP} = 397.1 Hz and J_{PP} = 459.6 Hz, for all NMR spectra of the reaction see SI, Figure S63-S71). In reactions 3 and 4 as byproducts symmetrical diphosphane *t*Bu$_2$P-P*t*Bu$_2$ was found along with *t*Bu$_2$PH. Additionally in reaction 4 the weak signals of (*t*Bu$_2$P)((Cy)*t*BuP)$_2$P were observed (doublets at 57.23 ppm and 32.06 ppm and multiplet at -99.86 ppm, J_{PP} = 486.8 Hz and J_{PP} = 508.6 Hz, see SI, Figure S25-S26). In reaction 5 were found symmetrical diphosphanes *t*Bu$_2$P-P*t*Bu$_2$, (Me)*t*BuP-P(Me)*t*Bu [19] and also *t*Bu$_2$PH, ((Me)*t*BuP)$_3$P, *t*Bu$_2$P-PH-P*t*Bu$_2$ [20] and *t*Bu$_2$P-PH-P(Me)*t*Bu as byproducts. In reaction 6, except symmetrical diphosphanes *t*Bu$_2$P-P*t*Bu$_2$, (Ph)*t*BuP-P(Ph)*t*Bu [21] and other byproducts were also found including *t*Bu$_2$PH, ((Ph)*t*BuP)$_3$P and (Ph)*t*BuP-PH-P*t*Bu$_2$. In reaction 7 we observed as byproducts only *t*Bu$_2$PH, Ph$_2$P-PPh$_2$ [22] and Ph$_2$P-P*t*Bu$_2$ [23]. ^{31}P{^{1}H}-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}PCl can be considered as a reduction of R^{B}R^{C}PCl by Ti(III) compounds leading to the formation of new P-P bonds. Taking into account, the byproducts *t*Bu$_2$P-P*t*Bu$_2$, *t*Bu$_2$P-PR^{B}R^C, R^{B}R^{C}P-PR^{B}R^C and *t*Bu$_2$PH it seems very probable, that the main process is a reduction of R^{B}R^{C}PCl which proceeds according to a radical mechanism, thereby R^{B}R^{C}P· or *t*Bu$_2$P· radicals are released. Thus the first step should lead to a nearly symmetric intermediate with a ligand of formula PR^{B}R^C-P-P*t*Bu$_2$ (the optimization of the example of β-diketiminate titanium(III) complex with triphopshorus ligand (see SI, Figure S73).

At the beginning, we have considered the nucleophilic substitution of P-SiMe$_3$ phosphorus of **1** into the P-atom of R^{B}R^{C}PCl yielding [^{Me}NacNacTi(Cl){1,2-η-tBu$_2$P-P-PR^{B}R^C}] or [^{Me}NacNacTi(Cl)-{1,2-η-PR^{B}R^C-P-PtBu$_2$}] and Me$_3$SiCl. Unfortunately, the (iPr$_2$N)tBuPCl 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^- and Δf for these compounds. The obtained results reveal that the chlorophosphanes Ph$_2$PCl, tBu$_2$PCl, (Et$_2$N)$_2$PCl, (Ph)tBuPCl, (Me)tBuPCl, iPr$_2$PCl indicate the weak nucleophilic character (Δf < 0). The Cy$_2$PCl and (Cy)tBuPCl display stronger nucleophilic properties, while the (iPr$_2$N)tBuPCl as the only one shows the electrophilic ones. The values of f^-, f^+ and Δf are depicted in Table 3.

Table 3. Values of condensed nucleophilic f^- and electrophilic f^+ functions and Δf dual descriptor calculated based on Hirshfield population analysis (HPA).

Chlorophosphane	f^+	f^-	Δf
tBu$_2$PCl	0.242	0.317	-0.075
iPr$_2$PCl	0.264	0.332	-0.069
Cy$_2$PCl	0.032	0.320	-0.288
(Cy)tBuPCl	0.041	0,317	-0,276
(Me)tBuPCl	0.302	0.338	-0.035
(Ph)tBuPCl	0.160	0.246	-0.086
Ph$_2$PCl	0.192	0.212	-0.020
(Et$_2$N)$_2$PCl	0.048	0.101	-0.054
(iPr$_2$N)tBuPCl	0.205	0.125	0.080

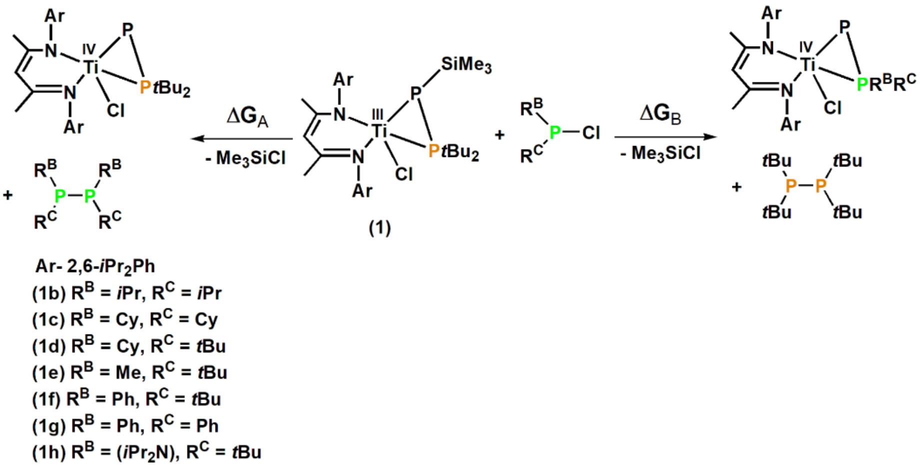
The obtained DFT results indicate a different initial stage of this reaction. It is very likely that the reaction starts with a nucleophilic attack of R^{B}R^{C}PCl on the Ti(III) center and after removal of Me$_3$SiCl leads to the same triphosphorus intermediate. Furthermore, this route is consistent with the lack of reactivity of (iPr$_2$N)tBuPCl.



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 $[^{Me}NacNacTi(Cl)\{tBu_2P\text{-}P\text{-}PR^BR^C\}]$ is +III and tendency to reach oxidation number +IV causes destabilization of the triphosphorus unit and generates radicals: $tBu_2P\cdot$ or/and $R^BR^CP\cdot$. Comparison of amounts of $tBu_2P\text{-}PtBu_2$, $R^BR^CP\text{-}PR^BR^C$, $R^BR^CP\text{-}PtBu_2$, R^BR^CPH, and tBu_2PH in reaction solutions may assume, that in reaction 3 (**1** + Cy_2PCl) and in reaction 4 (**1** + $(Cy)tBuPCl$) $tBu_2P\cdot$ radicals are released and in reaction 7 (**1** + Ph_2PCl) almost entirely $Ph_2P\cdot$ radicals are released. In reactions 2, 4, 5, and 6 we observed releasing $tBu_2P\cdot$ and $R^BR^CP\cdot$. 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 $(tBu_2P)(R^BR^CP)_2P$ and/or $(R^BR^CP)_3P$, $R^BR^CP\text{-}PH\text{-}PR^BR^C$, $tBu_2P\text{-}PH\text{-}PR^BR^C$ and $tBu_2P\text{-}PH\text{-}PtBu_2$

Experimental data indicate that the substituents on the P-atoms in chlorophosphanes determine their reactivity towards **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 ΔG values we also determined the values of the equilibrium constants K_A and K_B and then the molar ratio between the reaction products **1a** and new titanium complexes with $R^BR^CP\text{-}P$ ligand (Scheme 3 and Table 4).



Scheme 3. Possible reactions of $[^{Me}NacNacTi(Cl)\{\eta^2\text{-}P(SiMe_3)\text{-}PtBu_2\}]$ (**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** $[^{Me}NacNacTi(Cl)\{\eta^2\text{-}P\text{-}PR^BR^C\}]$). Hence, the differences in the composition of reaction products may be explained on the grounds of thermodynamics.

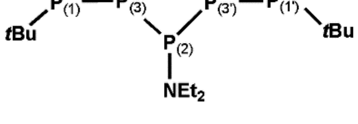
Table 4. Calculated and experimental data of the reactions of complex $[^{Me}NacNacTi(Cl)\{\eta^2\text{-}P(SiMe_3)\text{-}PtBu_2\}]$ (**1**) with selected chlorophosphanes: ΔG_A, ΔG_B – values of calculated free energies of reactions A and B; K_A, K_B – values of calculated equilibrium constants of reactions A and B, X_{CALC} – calculated molar ration of complexes obtained after A route and obtained after B route, X_{EXP} – experimental molar ration of complexes obtained after A route and obtained after B route.

RR'PCl	**ΔG_A [kJ.mol^{-1}]**	**ΔG_B [kJ.mol^{-1}]**	**K_A**	**K_B**	**x_{CALC} [% mol]**		**x_{EXP} [% mol]**	
					Product in A reaction	Product in B reaction	Product in A reaction	Product in B reaction
iPr_2PCl	-31.1	-24.7	2.1E+04	2.8E+05	53.3	46.7	55	45
Cy_2PCl	-38.2	-48.9	3.7E+08	4.9E+06	1.3	98.7	40	60
(Cy)*t*BuPCl	-16.5	-32.7	5.4E+05	7.8E+02	0.1	99.9	40	60
(Me)*t*BuPCl	-29.6	-26.7	4.7E+04	1.5E+05	76.4	23.6	79	21
(Ph)*t*BuPCl	-170.9	-171.1	9.9E+29	8.9E+29	47.4	52.6	70	30
Ph_2PCl	-47.6	-44.1	5.5E+07	2.2E+08	80.0	20.0	90	10
$(iPr_2N)tBuPCl$	14.1	25.2	3.8E-05	3.4E-03	0.0	0.0	0.0	0.0

DFT calculations indicate smaller values of product according to the A reaction. Especially, this is clearly visible in the slow reactions with Cy_2PCl and (Cy)*t*BuPCl. These results may indicate that in these cases the spontaneous decomposition of **1** is significant. The P-P bond cleavage according to the radical mechanism may depend on two main factors:

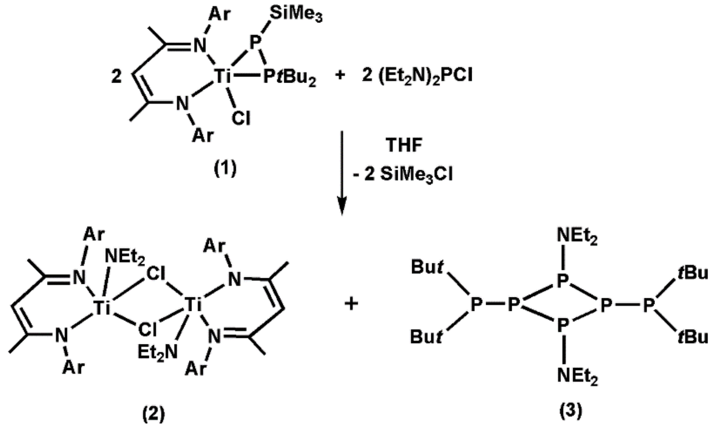
electronic properties of organic substituents on the phosphanyl phosphorus atom and consequently from their steric hindrance. Our results show that the stability of the generated $R^BR^CP\cdot$ radicals is an important factor. The particular example is reaction 7 (**1** + Ph_2PCl) in which **1a** is formed almost solely and only a small amount of [^{Me}NacNacTi(Cl){η^2P-PPh$_2$}] (**1g**) is created. Additionally in the $^{31}P\{^1H\}$-NMR spectrum, a large signal of Ph_2P-PPh_2 is visible whereas the signal of tBu$_2$P-PtBu$_2$ 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: $Ph_2P\cdot$ > (Ph)tBuP· > (iPr$_2$N)$_2$P· > tBu$_2$P·. Furthermore, the $Ph_2P\cdot$ 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 **1a** : **1x** ($x \neq a$) are the nucleophilic properties of related chlorophosphanes. For the most nucleophilic species Cy_2PCl and (Cy)tBuPCl we observe products which indicate the liberating of tBu$_2$P· radicals as tBu$_2$P-PtBu$_2$ and tBu$_2$PH. The small amount of **1a** in reaction solutions should be attributed to a spontaneous rearrangement of **1** leading to **1a**.

We also conducted the reaction of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] (**1**) with $(Et_2N)_2PCl$ in THF solution in molar ratio 1 : 1 (Δf calculated for $(Et_2N)_2PCl$ -0.054). **1** reacts with $(Et_2N)_2PCl$ yielding two different crystalline products. Both compounds were X-ray characterized as [^{Me}NacNacTiCl$_2$(THF)] (green crystals in form of blocks) and [^{Me}NacNacTi(Cl){NEt$_2$}]$_2$ (**2**) (green crystals in form of plates). The [^{Me}NacNacTiCl$_2$(THF)] was earlier reported by Mindiola and co-workers.[25] After isolation of both obtained crystalline products, the remained solution was $^{31}P\{^1H\}$-NMR investigated. Surprisingly, the NMR results revealed a formation of additional several compounds: $(Et_2N)_3P$, $(Et_2N)_2P$-$P(Et_2N)_2$, tBu$_2$P-P(SiMe$_3$)H, and a compound **3** with AA'M$_2$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 **3**, we conducted a simulation of its ^{31}P spectra (See SI, Figure S60-S62). The established ^{31}P-NMR data (See SI, Figure S53-S59) closely resemble these found earlier in a series for phosphetanes of formula A-P(μ_2-PNR$_2$)$_2$P-B where R = Et or *i*Pr; A, B = PR$_2$ or/and SiMe$_3$ which are formed in reactions of [Cp$_2$HfCl$_2$] or [CpZrCl$_3$] with (R$_2$N)$_2$P-P(SiMe$_3$)Li or *via* thermal rearrangement of [Cp$_2$Hf(Cl)(η^1-(Me$_3$Si)P-P(NEt$_2$)$_2$] [26] or in reaction of (*i*Pr$_2$)$_2$P-P(Me$_3$Si)Li with [^{Me}NacNacFeCl$_2$Li]. [27] Such phosphetanes are not formed in reactions of (R$_2$N)$_2$P-P(SiMe$_3$)Li with [L$_2$PtCl$_2$] (L = tertiary phosphanes) but [L$_2$Pt{η^2-P=P(NR$_2$)$_2$}] can be isolated.[6a] In all processes leading to phosphetanes, compounds with TM-NR$_2$ (TM – transition metals) moieties were isolated. Thus TM-NR$_2$ bonds are formed rather for early (Ti, Zr, Hf) or medium (Fe) TM than for late (Pt) ones. Scheme 5 shows the probable stoichiometry of reaction **1** with (Et$_2$N)$_2$PCl leading to **3**.



Scheme 5. The reaction of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (**1**) with (Et$_2$N)$_2$PCl.

3.2. X-ray studies

X-ray suitable crystals of [^{Me}NacNacTi(Cl){η^2-P-PCy$_2$}] (**1c**) grow from a saturated pentane solution and crystallize in monoclinic space group $P2_1/n$ with four molecules in the unit cell. The metal center of (**1c**) adopts a pseudo-trigonal-bipyramidal geometry with one nitrogen atom of β-diketiminate ligand, phosphinidene phosphorus atom and chloride atoms in the equatorial position. The axial position is occupied by one nitrogen atom of *β*-diketiminate ligand and phosphanyl phosphorus atom of the Cy$_2$P-P ligand.

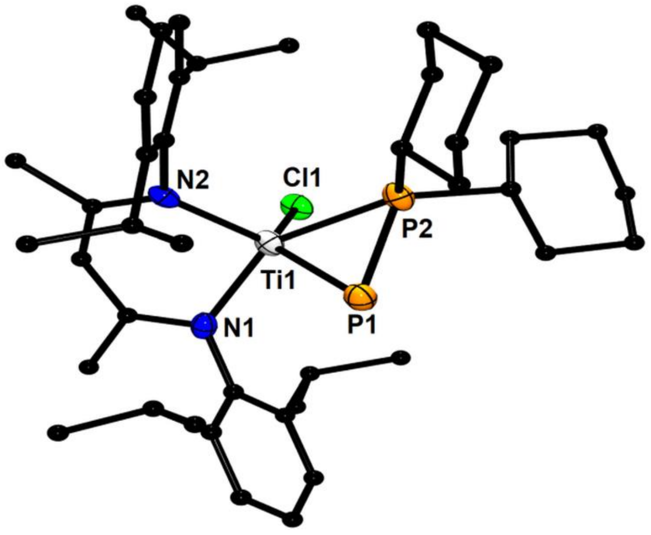


Figure 1. Molecular structure of [^{Me}NacNacTi(Cl){η^2-P-PCy$_2$}] (**1c**), (hydrogen atoms omitted for clarity). Important bond lengths (Å), bond angles (deg): N1-Ti1 2.031(10), N2-Ti1 1.984(9), P1-P2 2.114(5), P1-Ti1 2.322(4), P2-Ti1 2.512(4), Cl1-Ti1 2.313(3); P1-P2-Ti1 59.52(14), N1-Ti1-N2 93.9(4), P1-Ti1-P2 51.70. The sum of the angles around the P atoms: ΣP2 = 328.3(5)

The values of Ti-P bond lengths (Ti1-P1 2.322(4) Å and Ti1-P2 2.512(4) Å) indicate that the coordination of phosphanylphosphinidene ligand to the metal center is near η^2 (P2-P1-Ti1 = 68.78(16)°). The same distances and coordination were also observed in early described β-diketiminate titanium(IV) complexes with phosphanylphosphinidene ligand [^{Me}NacNacTi(Cl){η^2-P-P*t*Bu$_2$}] (**1a**) (Ti1-P1 2.334(3) Å, Ti1-P2 2.523(3) Å),[6e] [^{Me}NacNacTi(Cl){η^2-P-P*i*Pr$_2$}] (**1b**) (Ti1-P1 2.3237(7) Å, Ti1-P2 2.4933(7) Å)[6e] and [^{Me}NacNacTi(Cl){η^2-P-P(Ph)*t*Bu}] (**1f**) (Ti1-P1 2.3237(7) Å, Ti1-P2 2.5128(7) Å).[6f] The P1-P2 distance (P1-P2 2.114(5) Å) is typical for P=P double bond in side-on geometry and is comparable to the complex with the same pseudo-trigonal-bypyramidal geometry on the metal center [^{Me}NacNacTi(Cl){η^2-P-P*t*Bu$_2$}] (**1a**) (2.112(4) Å). The NCCCN unsaturated backbone of the β-diketiminate ligand is almost planar, with 0.0391(2) Å; the titanium atom is out of plane of the diamine ligand framework by 0.944(3) Å. The value of bond lengths of the N-C and C-C in the backbone of the β-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 [^{Me}NacNacTi(Cl){η^2-P-P(Cy)*t*Bu}] (**1d**) grow from a saturated pentane solution. **1d** crystallizes in monoclinic space group $P2_1/c$ with four molecules in the unit cell. The titanium atom adopts a pseudo square pyramidal geometry, where the chloride ion occupies an axial position.

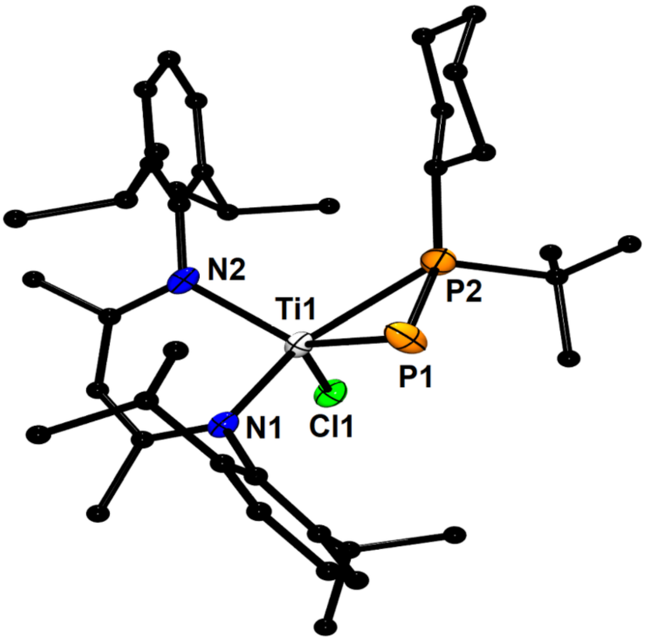


Figure 2. Molecular structure of [^{Me}NacNacTi(Cl){η^2-P-P(Cy)*t*Bu}] (**1d**), (hydrogen atoms omitted for clarity). Important bond lengths (Å), bond angles (deg): N1-Ti1 2.046(3), N2-Ti1 2.034(3), P1-P2 2.1039(19), P1-Ti1 2.3153(15), P2-Ti1 2.5079(16), Cl1-Ti1 2.3059(13); P1-P2-Ti1 59.50(5), N1-Ti1-N2 93.30(14), P1-Ti1-P2 51.54(5). The sum of the angles around the P atoms: ΣP2 = 330.2(3).

1d complex is isostructural with earlier described complex **1c**. The P-P distance in [^{Me}NacNacTi(Cl){η^2-P-P(Cy)*t*Bu}] (**1d**) (2.1039(19) Å) 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: [^{Me}NacNacTi(Cl){η^2-P-P*i*Pr$_2$}] (**1b**) (2.1038(8) Å).

Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with a four molecules in the unit cell. In the molecule the titanium atom adopts the disorder tetrahedral geometry (τ_4 = 0.88, τ_4' = 0.86) [28] (Figure 3).

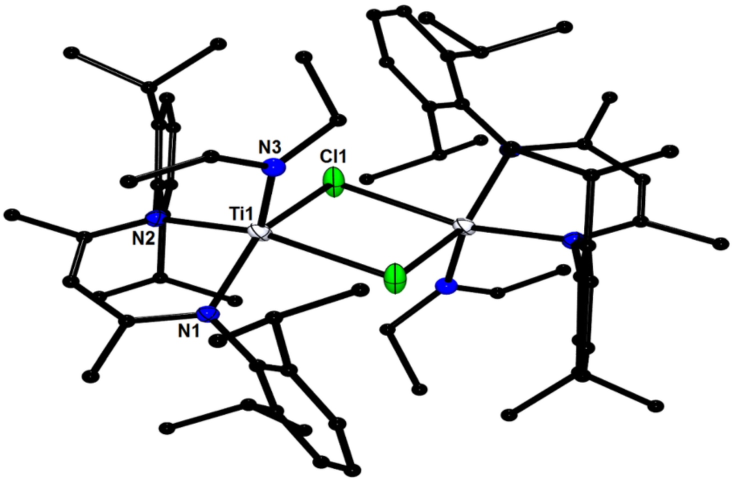


Figure 3. Molecular structure of [^{Me}NacNacTi(Cl){NEt$_2$}]$_2$ (**2**), (hydrogen atoms omitted for clarity). Important bond lengths (Å), bond angles (deg): N1-Ti1 2.101(4), N2-Ti1 2.099(4), N3-Ti1 2.009(4), Cl1-Ti1 2.4648(17); N1-Ti1-N2 87.51(15), Cl1-Ti1-N3 97.6(4). The sum of the angles around the N atoms: ΣN3 = 358.2(2).

In the obtained structure the diethylamino ligand from the $(Et_2N)_2PCl$ is observed. The Ti1-N3 distance is 2.009(4) Å and is significantly longer to these observed in [Ti(NEt$_2$)$_3$Cl] (1.864(4)Å, 1.860(4) Å and 1.860(4) Å respectively).[29] Additionally, the sum of angles around the nitrogen atom is 358.2(2)°, which may suggests multiple bonds between titanium and nitrogen atoms. The NCCCN unsaturated backbone of the ligand is almost planar with 0.0323(2) Å deviation from the planarity and the titanium atom is out of plane of the diamine ligand framework by 0.847(3) Å. The bond lengths C-N and C-C in the backbone skeleton suggest similar as in **1c** and **1d** structure the delocalization of double bond lengths. The Ti–Ti distance is 3.841(4) Å, which is definitely too long for there to be significant metal–metal bonding interaction.

4. Conclusions

Reactions of β-diketiminate Ti(III) complex with phosphanylphosphido ligand [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] (**1**) towards chlorophosphanes R^BR^CPCl were studied. These reactions can be seen as oxidation of **1** to Ti(IV) complexes with phosphanylphosphinidene ligand [^{Me}NacNacTi(Cl){η^2-P-PtBu$_2$}] (**1a**) or/and [^{Me}NacNacTi(Cl){η^2-P-PR^{B}R^C}] (**1x**). Reduction byproducts possess new P-P bond mainly tBu$_2$P-PtBu$_2$, tBu$_2$P-PR^{B}R^C, R^{B}R^{C}P-PR^{B}R^C or P-H bond, in great majority tBu$_2$PH. This composition of byproducts supports a radical mechanism of discussed redox process. The nucleophilic properties (not electrophilic) of phosphorus atoms in R^BR^CPCl 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 R^BR^CPCl in the first stage of reaction sequences – the nucleophilic addition of chlorophosphane to Ti(III) center and by the stability of liberated radicals $t\mathrm{Bu}_2\mathrm{P}\cdot$ vs $R^BR^CP\cdot$. The weak nucleophile Ph_2PCl reacts with **1** yielding **1a** almost solely and relatively stable $Ph_2P\cdot$ radicals are liberated in the oxidation stage of reaction. Quite different outcomes are observed in the case of strong nucleophiles: Cy_2PCl and (Cy)*t*BuPCl. The reactions are slow (steric hindrance) and $t\mathrm{Bu}_2\mathrm{P}\cdot$ radicals are released along with $[^{Me}\mathrm{NacNacTi(Cl)}\{\eta^2\text{-P-PR}^B\mathrm{R}^C\}]$ (**1x**) formation. $(i\mathrm{Pr}_2\mathrm{N})t\mathrm{BuPCl}$ does not react with **1** because of its very low nucleophilicity. In the reaction of $[^{Me}\mathrm{NacNacTi(Cl)}\{\eta^2\text{-P(SiMe}_3\text{)-P}t\mathrm{Bu}_2\}]$ (**1**) with $(Et_2N)_2PCl$ a formation of phosphetane **3** was observed.

APPENDIX A. Supporting information

CCDC 1898633-1898635 contains the supplementary crystallographic data for **1c**, **1d**, **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.

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