Postprint of: Ziółkowska A., Szynkiewicz N., Pikies J., Ponikiewski Ł.: Synthesis of compounds with C-P-P and C=P-P bond systems based on the phospha-Wittig reaction DALTON TRANSACTIONS (2020) DOI: 10.1039/D0DT02728F

Synthesis of compounds with C-P-P and C=P-P bond systems based on the phospha-Wittig reaction

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A reactivity study of a β-diketiminate titanium(III) phosphanylphosphido complex [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (**1**) towards ketones such as benzophenone, 9-fluorenone, acetophenone, cyclopentanone, cyclohexanone and cycloheptanone is reported. The reactions of **1** with aromatic ketones (without α-protons) directly lead to the Ti(III) complex [^{Me}NacNacTi(μ^2-Cl)(OSiMe$_3$)] (**5**) as well as Ti(IV) complexes with the pinacol condensation product [^{Me}NacNacTi(OSiMe$_3$)(η^2-pinacolate)] (**3**), and phosphanylphosphaalkenes Ph$_2$C=P-P*t*Bu$_2$ (**2**) and (fluorenyl)C=P-P*t*Bu$_2$ (**6**), respectively. The reaction with acetophenone leads to the titanium(III) complex with the aldol condensation product as ligand [^{Me}NacNacTi(Cl){OC{Me(Ph)}CH$_2$(C=O)Ph] (**8**) and in parallel to phosphanylphosphaalkene (Ph)MeC=P-P*t*Bu$_2$ (**9**) and **5**. The reactions of **1** with cyclic ketones (cyclopentanone and cyclohexanone) lead to Ti(III) complexes [{(ArN=C(Me)CHC(Me)=NAr)((CH$_2$)$_4$CO)}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)((CH$_2$)$_4$CO)}] (**10**) and [{(ArN=C(Me)CHC(Me)=NAr)((CH$_2$)$_5$CO)}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)((CH$_2$)$_5$CO)}] (**11**), which are formed via successive insertion of two molecules of ketone to one molecules of **1**. The stability investigation of complexes **10** and **11** in a polar solvent (THF) revealed that under these conditions, the complexes decompose, resulting in titanium(III) complexes with aldol condensation products and the expected phosphanylphosphaalkenes (CH$_2$)$_4$C=P-P*t*Bu$_2$ (**10a**) and (CH$_2$)$_5$C=P-P*t*Bu$_2$ (**11a**). In the reaction of **1** with cycloheptanone only the Ti(III) complex with the aldol condensation product [^{Me}NacNacTi(Cl){OC(CH$_2$)$_5$}CH(C=O)(CH$_2$)$_6$] (**12**) was isolated. The structures **3, 5**, **8**, **10**, **11**, **11b** and **12** were characterized by X-ray spectroscopy, while all the phosphanylphosphaalkenes were characterized by NMR spectroscopy.

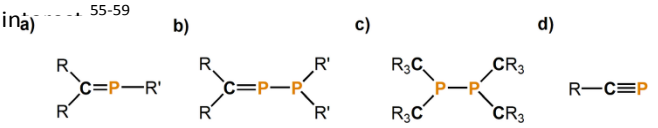
Introduction

The field of C-P, C=P and C≡P bond formation has been of great interest for many years and still has much to offer. Low-valent organophosphorus compounds are primarily of importance as scientific materials, particularly those that can serve as π-acceptors. This property is especially important for building blocks used to construct organic and inorganic macromolecules possessing phosphorus atoms.[1-4] Although species containing C-P single bonds have been thoroughly studied, new routes towards functionalized phosphines are still being reported.[5-8] Among acquiring methods of C-P species, such as the reaction of organometallic complexes with halophosphines or the reaction of metal phosphides with alkyl halides, the catalytic synthesis of phosphines is of considerable importance.[9-12] Palladium complexes have been successfully used as catalysts for such reactions for many years.[11, 13-15] Waterman and co-workers are highly active in this field and have introduced catalysts based on other transition metals as well.[16-19] Their recent works also described an improvement in catalytic hydrophosphination under photolysis and visible light irradiation or thermal conditions.[20, 21] Except for the above methods in the literature, there are few examples of reactions of P$_4$ molecules in which C-P bonds are formed.[22, 23] On the other hand, considering phosphorus-carbon multiple bonds, it should be noted that the amount of reports about phosphaalkenes (C=P) and phosphaalkynes (C≡P), including their reactivity, are rather limited; however, several examples of the synthesis such systems can be found in the literature.[24-29] The most common methods for preparing phosphaalkenes are reactions of phospha-Wittig reagents (metal-assisted: X(M)P=PR$_3$; free XP=PR$_3$).[30-32] Free phosphanylidenephospharanes had limited use due to difficult isolation, this problem was eliminated by Protasiewicz and co-workers. They relied on Mathey's work, and demonstrated one-pot reaction of RPCl$_2$ with zinc powder or magnesium in the presence of PR$_3$ which has proven successful for appropriately steric substituents R on dichlorophosphine.[33-38] Others synthetic approaches are the phospha-Peterson reaction, condensations and eliminations.[39-41] The procedures involving metal-phospha-Wittig reagents (phosphinidene complexes of transition metals) were studied only briefly.[42-44] Titanium phosphinidenes used by Mindiola and co-workers as

catalytic species in hydrophosphination of alkynes with primary phosphines led to secondary vinylphosphine which tautomerize to the phosphaalkene.[45] At this point it should be mentioned that the phosphido complexes have never been used and tested as potential phospha-Wittig reagents. Carbon-phosphorus compounds containing π-systems are attractive materials in polymer synthesis. Gates demonstrated the polymerizability of phosphaalkenes using VAZO (4-(vinyloxy-ethyloxy)azobenzene) to afford poly(methylenephosphine).[46-48]

Furthermore, Gates and Protasiewicz described π-conjugated P-C polymers, further elucidating PPV analogues.[49-51]

PPV-type polymers are used in electrical and optical devices. The insertion of a phosphorus atoms in the structure of these compounds may alter the function of these devices, broadening their applicability.[52-54] From another hand, compounds with C-P bonds bearing additional phosphorus atoms, such as diphosphanes, have also attracted increasing in[55-59]



Scheme 1. Low-valent phosphorus compounds with different C-P bond motifs: a) phosphaalkene, b) phosphanylphosphaalkene, c) diphosphane, and d) phosphaalkyne

Notably, among compounds with C=P bonds, there are a negligible number of reports available on phosphanylphosphaalkenes (C=**P-P**). This is probably because the synthesis of these compounds remains difficult and problematic. Organophosphorus compounds with C=P-P motifs are relatively unknown, and only a few articles have presented methods for obtaining such systems.[60-62] Additionally, the series of phosphanylphosphaalkenes $(R_2N)(R'_2N)C{=}P{-}PtBu_2$ were synthetized and characterized. ^{31}P- and ^{13}C-NMR spectra of these compounds reveal the reverse polarity due to R_2N groups which are powerful π-donors in β-position to $\lambda^3\sigma^2$-P-atom.[63]

Our research group has been investigating the synthesis and properties of titanium complexes with phosphanylphosphido ligands for several years. We have synthesized a wide range of new compounds, such as [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}],[64] [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*i*Pr$_2$}],[64] [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P(Ph)*t*Bu}],[65] [(PNP)Ti(Cl){η^1-P(SiMe$_3$)-P*t*Bu$_2$}][66] and [(PNP)Ti(Cl){η^2-P(SiMe$_3$)-P*i*Pr$_2$}].[66] In addition, we have examined the properties of β-diketiminate titanium(III) complexes with phosphanylphosphido ligands towards electrophilic, nucleophilic and oxidizing reagents. Importantly, one of our previous reactivity studies demonstrated for the first time that two β-diketiminate titanium(III) complexes with a phosphanylphosphido ligands ([^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}], [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P(Ph)*t*Bu}] could undergo reaction with acetone. The preliminary research revealed that the phosphanylphosphido Ti(III) complexes indicated a phospha-Wittig reactivity and may be very good precursors of phosphanylphosphaalkenes via reactions with ketones. The reaction with acetone generated two new phosphanylphosphaalkenes, $Me_2C{=}P{-}PtBu_2$ and $Me_2C{=}P{-}P(Ph)tBu$, of which the first was isolated in pure form.[67]

Herein, as continuation of our previous research, we present the reactivity of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (**1**) towards selected ketones, such as benzophenone, 9-fluorenone, acetophenone, cyclopentanone, cyclohexanone, and cycloheptanone leading to compounds with a new C-P-P, C=P-P and C-C bonds.

Results and discussion

Reactions of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$] (1) with selected aromatic ketones.

In the first reaction, to the complex [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (**1**) was added benzophenone dissolved in toluene (molar ratio 1:2). The ^{31}P{^{1}H}-NMR analysis conducted 24 hours after initiation of the reaction did not reveal signals indicative of phospha-Wittig reaction products, namely, a phosphanylphosphaalkene. The reaction was performed again, but in a polar solvent, THF. The ^{31}P{^{1}H}-NMR spectrum obtained after 24 hours of reaction showed weak signals of the expected product, the phosphanylphosphaalkene; therefore, the reaction mixture was stirred for 1 month, and after this time, the signals of phosphanylphosphaalkene were more intense. The ^{31}P{^{1}H}-NMR spectrum of the reaction mixture indicated that the product of the phospha-Wittig reaction, which had the formula $Ph_2C{=}P{-}PtBu_2$ (**2**), was present in solution (AX pattern, d, 277.32 ppm and 27.38 ppm, J_{PP} = 232.5 Hz, see ESI, Figure S1). The ^{1}H/^{31}P-NMR spectrum showed that the phosphorus atoms coupled with the expected protons; the signal observed at 277.32 ppm correlates with the aromatic protons at 7.65 ppm and 7.04 (broad multiplets), while the signal observed at 27.38 ppm correlates with protons at 1.19 ppm from the *tert*-butyl groups (J_{PP} = 11.0 Hz). Additionally, the signals of [^{Me}NacNacTiCl{η^2-P-P*t*Bu$_2$}] (**4**) are visible in the ^{31}P{^{1}H}-NMR spectrum. The obtained NMR spectra may indicate that the benzophenone reacts very slowly with the β-diketiminate titanium(III) complex with a phosphanylphosphido ligand. The titanium(IV) complex (**4**) bearing P-P*t*Bu$_2$ may come from the spontaneous decomposition of the starting titanium(III) complex, as was previously described by us.[64]

Due to the above results, 9-fluorenone was tested in the next step. The reaction of **1** with 9-fluorenone was also conducted in toluene at a molar ratio of 1:2. In contrast to the reaction with benzophenone, in this case, the colour of the reaction solution changed from green to raspberry-pink after 1 hour. The ^{31}P{^{1}H}-NMR spectrum of the reaction mixture revealed two doublets near 297.91 ppm and 9.64 ppm (J_{PP} = 232.5 Hz, see ESI, Figure S2). Additionally, the ^{1}H/^{31}P-HMBC spectrum showed that the phosphorus atom appearing at 297.91 ppm is coupled with the aromatic protons appearing at 9.71 ppm (m), 8.23 ppm (m), 7.33 ppm (m) and 7.08 ppm (m), while the signal of the phosphanyl phosphorus atom (9.64 ppm) showed a correlation with the *tert*-butyl protons (d, 1.26

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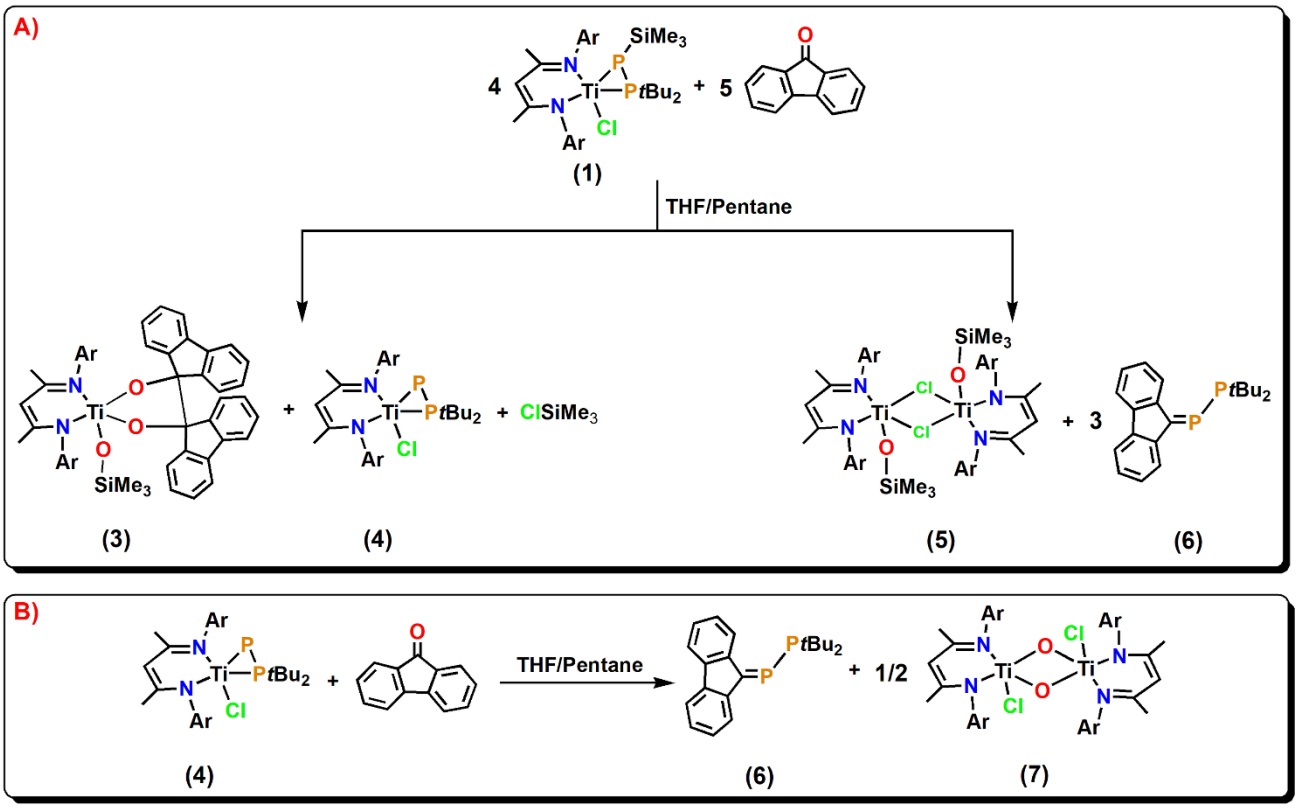
ppm, J_{PP} = 11.6 Hz) and a weak correlation with some of the aromatic protons on the fluorenone (7.08 ppm and 9.71 ppm). The obtained results indicate that one of the products of the reaction is a phosphanylphosphaalkene, (fluorenyl)C=P-P*t*Bu$_2$ (**6**). The isolation of the obtained phosphanylphosphaalkene by using a Kugelrohr apparatus failed because no material distilled below 260 °C, and above this temperature, we observed decomposition (change of the colour of the distilled material). Crystallization from a pentane solution of the reaction mixture afforded red crystals, which were characterized as new dimeric titanium complex with the formula [^{Me}NacNacTi(OSiMe$_3$)(μ^2-Cl)]$_2$ (**5**). The second crop of crystals obtained after the isolation of **5** (-30 °C, 24 hours) was a mixture of orange crystals and a small amount of yellow crystals. Both crystals were characterized by X-ray crystallography as titanium(IV) complexes; the yellow crystals were a β-diketiminate titanium(IV) complex with the pinacol condensation product [^{Me}NacNacTi(OSiMe$_3$)(η^2-pinacolate)] (**3**) and the orange crystals were the known complex [^{Me}NacNacTi(Cl)(μ^2-O)]$_2$ (**7**).[68] These results suggest that the reaction of **1** with 9-fluoreneone can run according to two parallel reactions (see Scheme 2A). One of which leads to phospha-Wittig product **6** and complex **5**, while the second one leads to titanium(IV) complexes (**3** and **4**). The formation of the pinacol ligand is related to the one-electron reduction of 9-fluorenone and the creation of a ketyl ligand bound to the titanium atom. Wakatsuki and co-workers described a similar redox process for alkoxy lanthanide complexes with 9-fluorenone.[69] They also demonstrated that the reaction of samarium with 9-fluorenone under the appropriate conditions leads to a samarium complex with ketyl ligands which makes the pinacol-coupling process leading to pinacol condensation products or a samarium complex with pinacol condensation products.[70] To create a new C-C bond in our reaction, two ketyl ligands are needed, therefore; two titanium atoms are oxidized. Increased amounts of substrates have enabled us to isolation of titanium(IV) complex with the formula [^{Me}NacNacTi(Cl)(μ^2-O)]$_2$ (**7**).[68]



Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Scheme 2. Overall reaction of **1** with 9-fluorenone showing all the reactants and products. Part A, shows two parallel reactions, including the resulting titanium(IV) complex (**4**) in one of them. Part B, shows the reaction of the resulting complex **4** with an excess of ketone in solution.

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Due to that the first reaction of **1** with 9-fluorenone was conducted at a molar ratio of 1:2 (excess 9-fluorenone), we performed a testing reaction at a 1:1 stoichiometric ratio. The $^{31}P\{^1H\}$-NMR spectrum carried out from the reaction mixture revealed that at this stoichiometry, β-diketiminate titanium(IV) complex with phosphanylphosphinidene ligand is created (**4**) (d, 843.31 ppm, 143.63 ppm, J_{PP} = 450.5 Hz, see ESI, Figure S3). The obtained results may indicate that in reaction of **1** with 9-fluorenone with molar ratio 1:2, the complex **4** is formed, but in the presence of excess of 9-fluorenone reacts further with the ketone and consequently the complex **7**, and phosphanylphosphaalkene are created (See Scheme 2B). It can be concluded that an excess of 9-fluorenone in the reaction leads to an increase in the final yield of phosphanylphosphaalkene. To clarify this process we synthetized the β-diketiminate titanium(IV) complex with phosphanylphosphinidene ligand,[64] and performed a test reaction with 9-fluorenone in molar ratio 1:1 in THF. $^{31}P\{^1H\}$-NMR spectrum conducted from the reaction mixture revealed the presence of phosphanylphosphaalkene (fluorenyl)C=P-P*t*Bu$_2$ (**6**) (d, 297.84 ppm, 9.61 ppm, J_{PP} = 232.7 Hz, see ESI, Figure S29). Additionally, the crystallisation performed from the pentane (24 hours, -30 °C) allowed us to obtain the dimeric titanium complex **7**. The obtained crystals were isolated and the remaining solution was concentrated and stored at -30 °C. Unfortunately, we no longer observed the formation of crystals.

These results suggest that in the reaction of **1** with benzophenone, the titanium(IV) complex with a phosphanylphosphinide ligand observed in the $^{31}P\{^1H\}$-NMR spectrum may be created not only by the spontaneous decomposition of **1** but can be also related with formation of a pinacol condensation product. Unfortunately, all attempts to isolate crystals of the titanium(IV) complex with the pinacol condensation product after the reaction of **1** with benzophenone failed. Interestingly, the reaction of [^{Me}NacNacTi(Cl){η^2-P-P*t*Bu$_2$}] (**4**) with benzophenone in THF proceeded very slowly, and after two months, the starting titanium(IV) complex was still visible in the reaction solution, and the amount of phosphanylphosphaalkene generated was negligible.

In the next reaction, we decided to use a ketone with one aromatic group and one aliphatic group, namely, acetophenone. The introduction of an aliphatic group into ketone completely changes the composition of the obtained products. The presence of α-protons in the ketone causes the reaction to proceed via an aldol condensation instead of a pinacol condensation. Crystallization from pentane allowed us to isolate and characterize the β-diketiminate titanium(III) complex with the aldol condensation product [^{Me}NacNacTi(Cl){OC{Me(Ph)}CH$_2$(C=O)Ph] (**8**). The second crop of crystals revealed the presence of complex **5**. The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture showed that two isomers of the phospha-Wittig product (Ph)MeC=P-P*t*Bu$_2$ (**9**) (263.93 ppm, 21.90 ppm, J_{PP} = 234.9 Hz, *E* isomer and 252.92 ppm, 24.59 ppm, J_{PP} = 222.8 Hz, *Z* isomer) are formed in this reaction (see ESI, Figure S4 and S5). The integration of the methyl proton signals of both isomers indicated that the *E* isomer is the major product (84 %). The mixture of isomers was isolated using a Kugelrohr apparatus. The ^{1}H-NMR spectrum shows that under the influence of temperature (160 °C), the ratio of the two isomers changed (60 % of the *E* isomer and 40 % of the *Z* isomer). The obtained results show that at high temperature, the *E* derivative isomerizes to the *Z* species. The $^1H/^{31}P$-NMR spectrum shows that the methyl proton signals of the two isomers appear at 2.94 ppm (dd, J_{PH} = 11.4 Hz and 1.6 Hz, *E* isomer) and 2.64 ppm (dd, J_{PH} = 21.4 Hz and 0.9 Hz, *Z* isomer), while the protons of *tert*-butyl groups afford doublets at 1.32 ppm (J_{PH} = 11.4 Hz, *E* isomer) and 1.19 ppm (J_{PH} = 10.9 Hz, *Z* isomer). Additionally, the signals at 19.09 ppm and -197.19 ppm (J_{PP} = 190.7 Hz) were attributed to the diphosphane with the formula *t*Bu$_2$P-P(SiMe$_3$)H.[71] The presence of the diphosphorus compound (generated by protonation of the phosphorus atom) explains the creation of the titanium(III) complex with the aldol condensation product. The obtained NMR and X-ray results imply that in this case also two parallel reactions take place. The first one is the formation of Ti(III) complex with aldol condensation product (**8**) and diphosphane, while the second one is the formation of the phosphanylphosphaalkene (**9**) and titanium complex **5** (Scheme 3). For comparison, reaction of β-diketiminate titanium(IV) complex with phosphanylphosphinidene ligand (P-P*t*Bu$_2$) with acetophenone leads only to the phosphanylphosphaalkene **9** and dimeric complex **5**. In the case of using the titanium(IV) complex, formation of aldol condensation product and diphosphane was not observed (See ESI, Figure S30)

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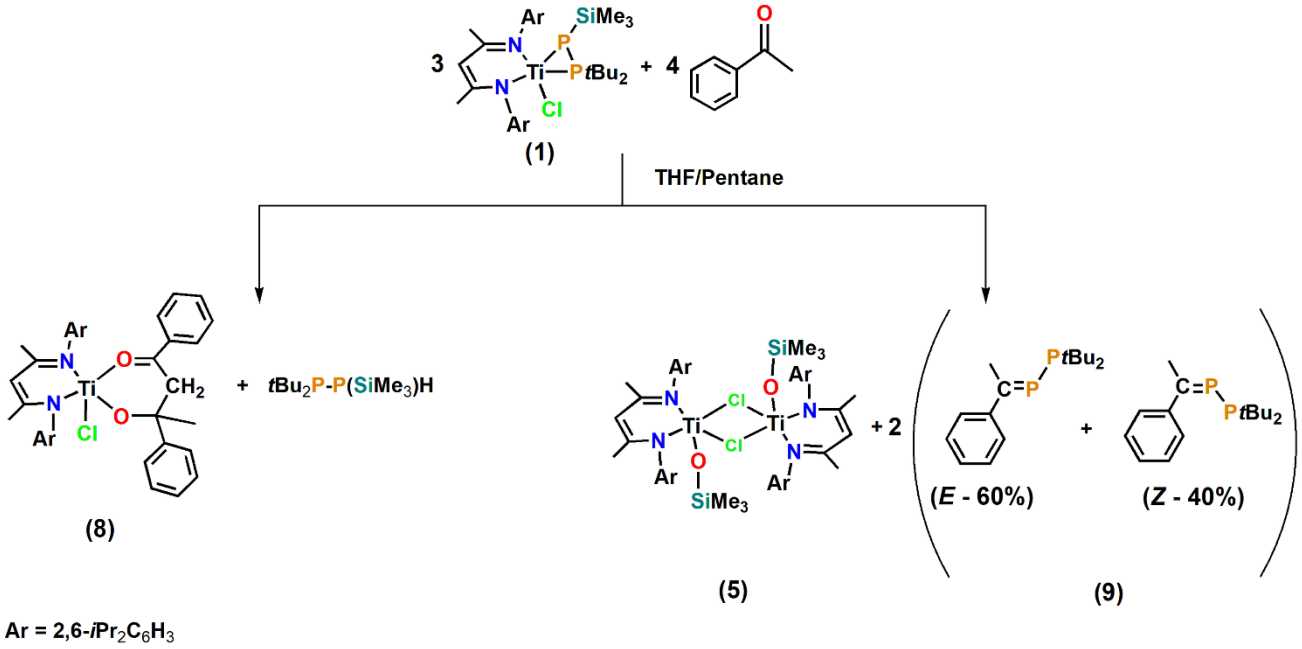

Scheme 3. Summary of the reagents and products in the reaction of **1** with acetophenone.

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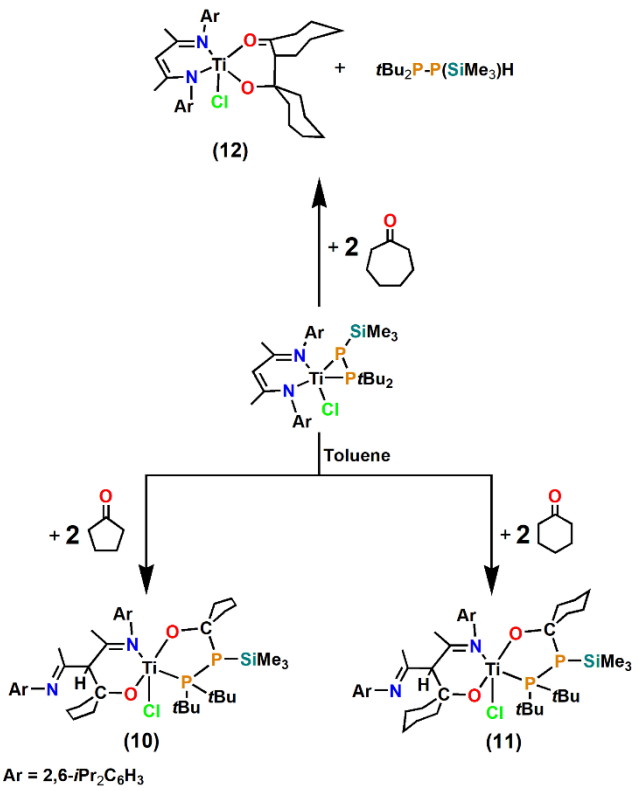
Reactions of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (1) with cyclic ketones.

We studied the reactivity of **1** with cyclic ketones using three compounds: cyclopentanone, cyclohexanone and cycloheptanone. All reactions were conducted in toluene solution at a molar ratio of 1:2 (selecting the stoichiometry we were guided by our first reaction of acetone).[67] In all cases, the colour of the solution changed from green to blue or violet-blue. Crystallization from pentane afforded crystalline products from all three reactions. The crystals obtained from the reaction of **1** with cyclopentanone were characterized as new complex [{(ArN=C(Me)CHC(Me)=NAr)((CH$_2$)$_4$CO)}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)((CH$_2$)$_4$CO)}] (**10**), while the crystals from the reaction with cyclohexanone were characterized as complex [{(ArN=C(Me)CHC(Me)=NAr)((CH$_2$)$_5$CO)}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)((CH$_2$)$_5$CO)}] (**11**), an analogue of **10**. Surprisingly, the navy-blue crystals obtained after the reaction of **1** with cycloheptanone were characterized as a β-diketiminate titanium(III) complex with an aldol condensation product [^{Me}NacNacTi(Cl){OC(CH$_2$)$_5$}CH(C=O)(CH$_2$)$_6$] (**12**). The ^{31}P{^{1}H}-NMR spectrum obtained from the reaction mixture (reaction with cycloheptanone) showed only the signals of *t*Bu$_2$P-P(SiMe$_3$)H (see ESI, Figure S21). Both the X-ray measurements and NMR spectra clearly indicate that only an aldol condensation takes place during this reaction. The overall reactions of **1** with cyclic ketones are depicted in Scheme 4.



Scheme 4. Reactions of **1** with cyclopentanone, cyclohexanone and cycloheptanone.

On the other hand, a previously reported study of the reactivity of **1** and acetone revealed that the complex generated by the insertion of two molecules of ketone is only an intermediate in the way to phosphanylphosphaalkene. Therefore, we tested the stability of complexes **10** and **11** in a polar solvent (THF). Complex **10** was dissolved in THF and stirred for 48 hours at RT. During this time, the colour of solution changed from violet-blue to light-violet. In the next step, the solvent was evaporated, and an NMR spectrum of the solid residue was acquired in C$_6$D$_6$. The ^{31}P{^{1}H}-NMR spectrum revealed AX pattern typical for phosphanylphosphaalkenes (212.67 ppm and 26.18 ppm, J_{PP} = 220.1 Hz, see ESI, Figure S11). The obtained shifts for the phosphorus atom bound to the sp^2 carbon atom (double bond) are very similar to those observed in our previous report on the synthesis of phosphanylphosphaalkene and to those reported in the literature.[43, 44] Additionally, the ^{1}H/^{31}P-HMBC spectrum revealed that the phosphorus atom appearing at 212.74 ppm correlates with four protons (bm, 3.10 ppm and 2.71 ppm) from the CH$_2$ groups of the cyclopentane ring. The second phosphorus atom (26.26 ppm) strongly correlates with the protons of the *tert*-butyl groups (1.29 ppm, J_{PH} = 11.2 Hz)

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and weakly correlated with two protons observed near 3.10 ppm. The integrals of the abovementioned proton signals revealed that the resonances at 3.10 ppm and 2.71 ppm each represent two protons, while the resonance at 1.29 ppm represents 18 H. Additionally, the COSY spectrum indicates that the other protons on the cyclopentane ring appear near 1.48 ppm (4H). The obtained NMR spectra clearly indicate that complex **10** decomposes in the polar environment and that one of the products is a phosphanylphosphaalkene with the formula $(CH_2)_4C{=}P\text{-}PtBu_2$ (**10a**). Complex **11** was subjected to analogous stability tests. Its $^{31}P\{^1H\}$-NMR spectrum also revealed two doublets near 221.22 ppm and 17.86 ppm (with J_{PP} = 228.9 Hz, see ESI, Figure S16). The $^1H/^{31}P$-HMBC spectrum indicates that both phosphorus atoms correlate with the protons at 3.18 ppm (2H) and 2.69 ppm (2H); however, it should be noted that the correlation of the phosphanyl phosphorus atom (17.85 ppm) is slightly weaker. The COSY spectrum reveals that the other protons on the cyclohexyl ring afford signals at 1.95 (bm, 4H) and 1.35 (bm, 2H). The NMR spectra suggest the generation of phosphanylphosphaalkene $(CH_2)_5C{=}P\text{-}PtBu_2$ (**11a**). Distillation with Kugelrohr apparatus allowed us to obtain **10a** (145 °C, 0.01 Torr) and **11a** (160 °C, 0.01 Torr) in pure form. Additionally, under these conditions, the sublimation of NacNacH was observed (colourless crystals characterized by X-ray crystallography).

Furthermore, we carried out DFT calculations on the expected phosphanylphosphaalkenes, and we obtained theoretical chemical shift values for the lowest energy conformers of the optimized structures of compounds **2**, **6**, **9_*E***, **9w_*Z***, **10a** and **11a** in THF. The experimental and theoretical shifts are presented below (Table 1).

Table 1. The $^{31}P\{1H\}$-NMR experimental and theoretical shifts of phosphorus atoms in the obtained phosphanylphosphaalkene compounds.

	Experimental data		Theoretical data	
RC=P(1)-P(2)tBu$_2$	P(1)	P(2)	P(1)	P(2)
R = Ph_2 (**2**)	277.32	27.38	282.3	35.0
R = fluorene (**6**)	297.91	9.64	304.5	3.7
R = (Ph)Me (*E* isomer) (**9_*E***)	263.92	21.90	262.6	23.5
R = (Ph)Me (*Z* isomer) (**9_*Z***)	252.92	24.59	255.5	24.0
R = $(CH_2)_4$ (**10a**)	212.74	26.26	213.2	24.2
R = $(CH_2)_5$ (**11a**)	221.19	17.85	219.6	16.8

X-ray analysis

Suitable crystals of **5** were grown in a pentane solution. Complex **5** crystalizes in a monoclinic space group *C*2/*c* with four molecules in the unit cell. Both titanium atoms in the complex adopt a disordered square pyramidal geometry with $OSiMe_3$ groups in the axial position (see Figure 1). The geometrical index τ_5 calculated for the titanium atom is 0.071(12).[72] Complex **5** has C_2 symmetry; therefore, the independent unit contains half of one molecule.

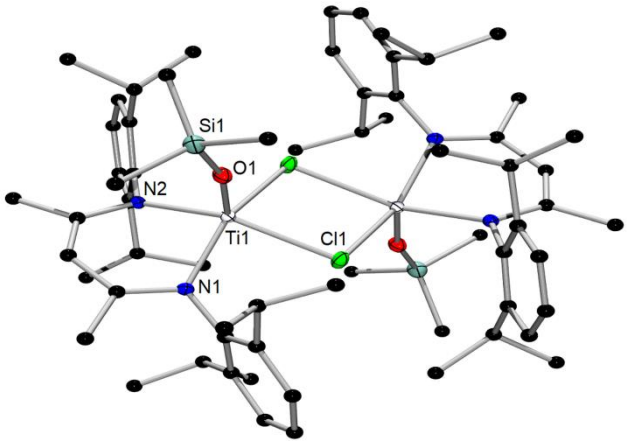

Figure 1. Molecular structure of $[^{Me}NacNacTi(OSiMe_3)(\mu^2\text{-}Cl)]_2$ (**5**) (ellipsoids 50 %, H atoms have been omitted for clarity). Important bond lengths (Å) and bond angles (°): Ti1-O1 1.817(3), Ti1-N1 2.115(3), Ti1-N2 2.117(3), Ti1-Cl1 2.460(12), Ti1-Cl1A 2.462(12); N1-Ti1-N2 88.32(12), N1-Ti-Cl1 86.97(9), N1-Ti1-O1 104.18(14), Cl1-Ti-Cl1A 78.26(4), Cl1-Ti1-O1 109.97(10).

The molecular structure of **5** confirms the migration of the $SiMe_3$ group from the phosphido phosphorus atom to the oxygen atom. The Ti1-O1 distance (1.817(3) Å) is longer than that observed in $[\eta5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(OSiMe_3)\text{-}Cl$ (1.755(3) Å),[73] shorter than that observed in $[(H_2CSiMe_2)(\eta^5\text{-}C_5Me_4)_2Ti(OSiMe_3)(CHCHSiMe_3)]$ (1.897(2) Å),[74] and lies in the range of single bonds between titanium and oxygen atoms. The Ti1-O1-Si1 angle (163.80(19)°) is comparable to that observed in $[(H_2CSiMe_2)(\eta^5\text{-}C_5Me_4)_2Ti(OSiMe_3)(CHCHSiMe_3)]$ (165.83(5)°) and may suggest the presence of O(pπ)-Si(dπ) and O(pπ)-Ti(dπ) interactions.[75] The Ti1-Cl1 bond distance (2.460(12) Å) is typical for a single bond and is comparable to the distance observed in $[^{Me}NacNacTiCl_2]_2$ (2.439(1) Å).[76] The molecular structure of **5** shows that the NCCCN atoms in the β-diketiminate ligand are planar (rms deviation 0.0408). The titanium atom lies out of the plane by approximately 0.898(2) Å.

After isolation of complex **5**, a concentrated solution was prepared and again stored at -30 °C. After 24 hours, a mixture of red and yellow crystals appeared. The red crystals were characterized as known complex **5**, while the yellow crystals were characterized as new complex $[^{Me}NacNacTi(OSiMe_3)(\eta^2\text{-}pinacolate)]$ (**3**). **3** crystalizes in the triclinic space group *P*-1, with four molecules in the unit cell (two molecules in the independent unit). The titanium atom in the complex **3** adopts a disordered square pyramidal geometry with the OSiMe3 group in the axial position and two nitrogen atoms and two oxygen atoms in the equatorial positions (Figure 2).

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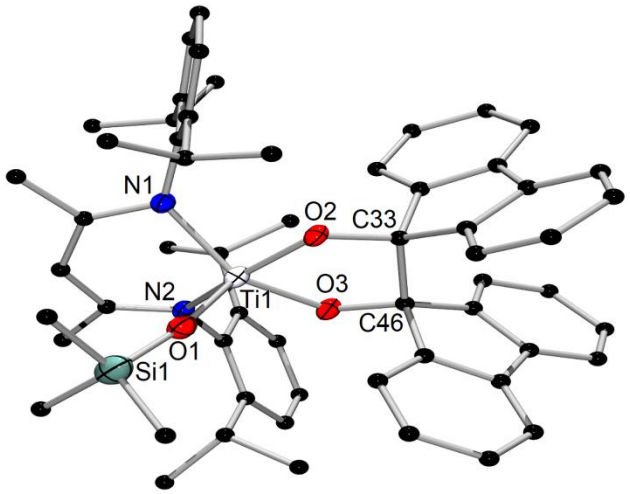

Figure 2. Molecular structure of [^{Me}NacNacTi(OSiMe$_3$)(η^2-pinacolate)] (**3**) (ellipsoids 50 %, H atoms have been omitted for clarity). Important bond lengths (Å) and bond angles (°): Ti-O1 1.832(3), Ti1-O2 1.844(3), Ti1-O3 1.875(3), Ti1-N1 2.059(4), Ti1-N2 2.125(4), Si1-O1 1.617(4), O2-C33 1.426(5), O3-C46 1.417(5), C33-C46 1.620(7); O1-Ti1-O2 106.13(14), O1-Ti1-O3 116.40(14), O2-Ti1-O3 80.44(13), O1-Ti1-N1 103.18(15), O2-Ti1-N1 93.58(14), O3-Ti1-N1 140.14(15), O1-Ti1-N2 97.09(15), O2-Ti1-N2 155.63(14), O3-Ti1-N2 82.70(14), N1-Ti1-N2 88.16(14); (τ_5 = 0.171(15) and 0.130(15)).[72]

In **3**, the C-O distances (1.426(5) Å, 1.417(5) Å, 1.409(6) Å and 1.399(5) Å) are typical of C-O single bonds. The C33-C46 (1.620(7) Å) and C91-C104 (1.637(7) Å, in a second molecule) bond distances are notably longer than typical C-C single bonds (1.54 Å) but are comparable to the length of the corresponding bond in (dpp-BIAN)Al[μ-O$_2$(C$_{13}$H$_8$)$_2$] (1.631 Å).[77] Other bond lengths in **3** are analogous to those observed in complex **5**. The NCCCN skeleton is planar with an rms deviation from planarity of 0.0559 (0.0365 for second molecule). In the two molecules, the titanium atoms are above the plane by 1.106(5) Å and 1.036(3) Å.

Suitable crystals of **8** were obtained from a pentane solution. **8** crystalizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The titanium atom in **8** adopts a disordered square pyramidal geometry with a chloride ion in the axial position (τ_5 = 0.163(7)) (Figure 3).

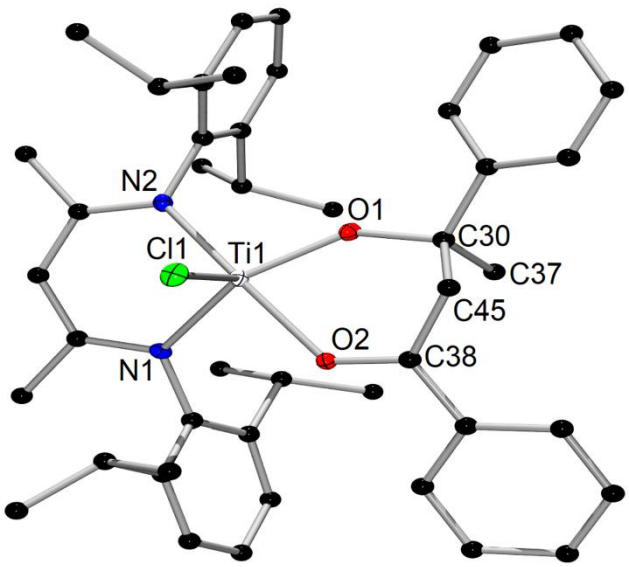

Figure 3. Molecular structure of [^{Me}NacNacTi(Cl){OC{Me(Ph)}CH$_2$(C=O)Ph] (**8**) (ellipsoids 50 %, H atoms have been omitted for clarity). The second disorder component of the {OC{Me(Ph)}CH$_2$(C=O)Ph ligand (site-occupancy factor = 0.212) have been omitted. Important bond lengths (Å) and bond angles (°): Ti-Cl1 2.3412(8), Ti1-N1 2.089(2), Ti-N2 2.105(2), Ti1-O1 1.853(3), Ti1-O2 2.098(3), O1-C30 1.411(4), O2-C38 1.248(4); O1-Ti1-N1 139.25(10), O1-Ti1-O2 83.13(10), N1-Ti1-O2 87.10(9), O1-Ti1-N2 93.70(10), O2-Ti1-N2 168.50(9), O1-Ti1-Cl1 114.47(8), N1-Ti1-Cl1 104.71(7), O2-Ti1-Cl1 88.74(7), N2-Ti1-Cl1 102.61(7); (τ_5 = 0.171(15) and 0.130(15)).

The obtained molecular structure of complex **8** confirms that the titanium(III) complex with the aldol condensation product is generated. The Ti1-O1 bond length (1.853(3) Å) is comparable to that observed in complex **3** and lies in the range of Ti-O single bonds. The Ti1-O2 distance is much longer (2.089(3) Å) than that observed for the Ti1-O1 atom and is associated with short C38-O2 bond (1.248(4) Å) (range of C-O double bond). Comparable bond lengths were observed in an analogous titanium complex, ([(PhCO)PhC(O)C(Me$_2$)C(OMe)OTi(Cl)$_2$]$_2$(μ-Cl)$_2$ (Ti-O: 1.773(4) Å, 2.106(4) Å).[78] The Ti-N distances and bond lengths in the NCCCN skeleton are typical of delocalized double bonds in similar systems.

Suitable crystals of **10** and **11** were grown from pentane solutions. Complex **10** crystalizes in a monoclinic space group $P2_1/c$ with four molecules in the unit cell, while complex **11** crystalizes in a triclinic space group P-1 with two molecules in its unit cell. In both complexes, the titanium atom adopts a distorted square pyramidal geometry with chloride in the axial position (τ_5 = 0.028(6) for **10** and τ_5 = 0.163(7) for **11**).[72]

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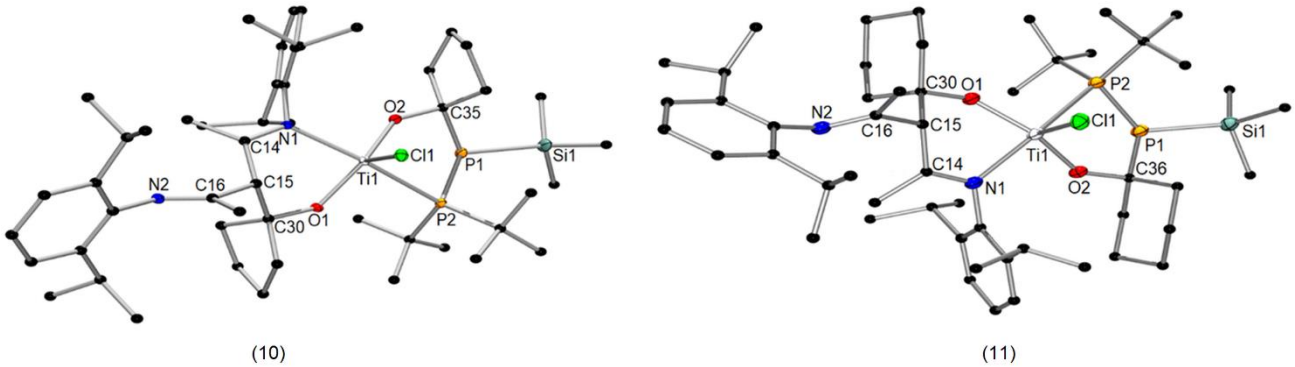

Figure 4. Molecular structures of [{(ArN=C(Me)CHC(Me)=NAr)((CH$_2$)$_4$CO)}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)((CH$_2$)$_4$CO)}] (**10**), and [{(ArN=C(Me)CHC(Me)=NAr)((CH$_2$)$_5$CO)}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)((CH$_2$)$_5$CO)}] (**11**) (ellipsoids 50 %, H atoms have been omitted for clarity). Important bond lengths (Å) and bond angles (°) for **10**: Ti1-O1 1.8689(16), Ti-O2 1.8479(17), Ti1-Cl1 2.3604(7), Ti1-P2 2.7191(7), Ti1-N1 2.2005(19), P1-P2 2.1927(9), P1-Si1 2.2651(10), O1-C30 1.407(3), O2-C35 1.406(3), N1-C14 1.294(3), C14-C15 1.524(3), C15-C16 1.526(3), N2-C16 1.272(3); O1-Ti1-O2 145.07(8), N1-Ti1-P2 160.45(5), O1-Ti1-N1 84.58(7), O2-Ti1-P2 78.49(5), P2-Ti1-Cl1 105.51(2), O2-Ti1-Cl1 108.31(6), Ti1-P2-P1 96.56(3); ΣC15 = 340.2(6); for **11**: Ti1-O1 1.864(3), Ti-O2 1.860(3), Ti1-Cl1 2.3649(12), Ti1-P2 2.7685(13), Ti1-N1 2.225(4), P1-P2 2.1883(15), P1-Si1 2.2742(18), O1-C30 1.420(5), O2-C36 1.404(5), N1-C14 1.287(5), C14-C15 1.527(5), C15-C16 1.528(6), N2-C16 1.279(6); O1-Ti1-O2 142.62(13), N1-Ti1-P2 164.79(9), O1-Ti1-N1 84.32(13), O2-Ti1-P2 76.96(9), P2-Ti1-Cl1 102.49(4), O2-Ti1-Cl1 110.54(10), Ti1-P2-P1 98.15(5); ΣC15 = 342.0(3);

The XRD results show that in the reaction, one ketone molecule is inserted between the phosphido phosphorus and titanium atoms. The formation of Ti-O bond in the first step causes a positive charge at carbonyl carbon atom in the connected ketone and may result in the nucleophilic attack of this carbon atom by the phosphido phosphorus atom. This process generates the Ti-P-P-C-O ring and may be considered a transitional step in the phospha-Wittig reaction. To date, only Stephan and co-workers have described the individual steps in the reactions of [Cp$_2$Zr=PR*(PMe$_3$)] (R* = C$_6$H$_2$-2,4,6-*t*Bu$_3$) with benzaldehyde, benzophenone and isophtalaldehyde.[43] Our previous studies on the reactivity of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] and [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P(Ph)*t*Bu}] with acetone confirmed the formation the Ti-P-P-C-O ring. Additionally, for the abovementioned reactions, the intermediates (**10** and **11)** could be crystalized, and they were characterized by X-ray crystallography for the first time.[67] The insertion of a second molecule of ketone resulted in a new coordination of β-diketiminate ligand (η^1 manner) and creation of a new C-C bond (between the γ-carbon of the NCCCN skeleton and carbon atom of the ketone).

The Ti-O distances observed in **10** (1.8689(16) Å and 1.8479(17) Å) and **11** (1.864(3) Å and 1.860(3) Å) are typical of single bonds between titanium and oxygen atoms and are comparable to the distances observed in complexes with acetone, [{(ArN=C(Me)CHC(Me)=NAr)(C(Me)$_2$O}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)C(Me)$_2$O}] (1.856(2) Å and 1.849(2) Å) and [{(ArN=C(Me)CHC(Me)=NAr)(C(Me)$_2$O}Ti(Cl){P(Ph)*t*Bu-P(SiMe$_3$)C(Me)$_2$O}] (1.860(19) Å and 1.843(19) Å).[67] The Ti-P (phosphanyl phosphorus atoms) bond lengths (2.7191(7) Å and 2.7685(13) Å) are comparable to the distances observed in the above described complexes with acetone (2.715(10) Å and 2.715(8) Å) and are slightly longer than those observed in the titanium(III) complexes with phosphanylphoshido ligands, (η^2-coordination) [^{Me}NacnacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (2.675(10) Å) and [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (2.676(2) Å).[64, 65] The observed P-P distances in **10** and **11** (2.1927(9) Å and 2.1883(15) Å) are typical of P-P single bonds. In the NacNac skeleton, the N-C distances (1.294(3) Å and 1.272(3) Å for **10** and 1.287(5) Å and 1.279(6) Å for **11**) clearly indicate the presence of a double bond between the nitrogen and carbon atoms and are comparable to the distances observed in the complex with η^1 coordination of the NacNac ligand, [MesNC(Me)CH(S)C(Me)NMes]$_2$Zn (1.285(3) Å, 1.278(3) Å, 1.268(3) Å and 1.269(3) Å).[79] In complexes with a bidentate-coordinated NacNac ligand, the γ-carbon is sp^2 hybridized, while in complexes **10** and **11** (monodentate coordination of NacNac), the analogous carbon is sp^3 hybridized. The sums of the angles around C15 (γ-carbon) atom in both complexes indicate geometries between planar and pyramidal (340.2(6)° and 342.0(3)°, respectively). On the other hand, the sums of the angles around P1 in **10** and **11** indicate pyramidal geometry. For comparison, in the starting complex (**1**) the phosphorus phosphido atom is planar with ΣP 355.9(1)°.

After the reactions of **1** with cyclohexanone and cycloheptanone, titanium(III) complexes with the

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corresponding aldol condensation products were isolated and characterized (the molecular structures are shown in the ESI, Figures S31 and S32).

Experimental section

All steps were carried out under an argon atmosphere using Schlenk technique. Toluene and THF were dried over Na/benzophenone, pentane and petroleum ether were dried over Na/K alloy, and all other solvents were distilled under argon. Solution-phase ^{1}H, ^{31}P and ^{13}C NMR spectra in solution were recorded on a Bruker AV400 MHz (tetramethylsilane as the external standard for ^{1}H and ^{13}C; 85 % H_3PO_4 for ^{31}P). [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (**1**) was prepared according to a procedure in the literature.[66] Benzophenone, 9-fluorenone, acetophenone, cyclopentanone, cyclohexanone and cycloheptanone were purchased from commercial suppliers.

Reaction of 1 with benzophenone

Benzophenone (0.046 g; 0.254 mmol) was dissolved in 2 mL of THF, and this solution was added to **1** dissolved (0.100 g; 0.127 mmol) in 2 mL of THF. There was no colour change (the solution retained the green colour of the starting complex) even after 24 hours. After this time, the control ^{31}P{^{1}H}-NMR spectrum was performed. No colour change was observed over the next month. The solvent was evaporated, and the NMR spectra of the oily residue were acquired in C_6D_6. ^{31}P{^{1}H}-NMR data of reaction mixture (298 K, C_6D_6): 843.83 (d, J_{PP} = 450.5 Hz, [^{Me}NacNacTi(Cl){η^2-**P**-P*t*Bu$_2$}], **4**), 277.32 (d, J_{PP} = 232.5 Hz, Ph$_2$C=**P**-P*t*Bu$_2$, **2**), 143.60 (d, J_{PP} = 450.5 Hz, [^{Me}NacNacTi(Cl){η^2-P-**P***t*Bu$_2$}], **4**), 44.27 (d, J_{PP} = 399.6 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)$_2$), 27.38 (d, J_{PP} = 232.5 Hz, Ph$_2$C=P-**P***t*Bu$_2$, **2**), 19.47 (s, *t*Bu$_2$**P**H), 19.11 (d, J_{PP} = 196.2 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H), -197.20 (d, J_{PP} = 196.2 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)H), -201.01 (d, J_{PP} = 399.6 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)$_2$) ppm.

Reaction of 1 with 9-fluorenone

9-Fluorenone (0.137 g; 0.759 mmol) was dissolved in 5 mL of THF, and this solution was added to **1** (0.400 g; 0.509 mmol) dissolved in 5 mL of THF. After approximately 1 hour, the solution turned raspberry-pink. Next, the solvent was evaporated, and the precipitate was treated with 15 mL of pentane. The solution was filtered, the filtrate was concentrated to half its initial volume, and the concentrated solution was stored at -30 °C. After 2-3 hours, red crystals appeared, and they were characterized as [^{Me}NacNacTi(OSiMe$_3$)(μ^2-Cl)]$_2$ (**5**) (0.150 g, 0.127 mmol, yield 25 %) Anal. Calcd for $C_{64}H_{100}Cl_2N_4O_2Si_2Ti_2$ (**5**): C, 65.12; H, 8.54; N, 4.75 %. Found: C, 65.04; H, 9.02; N, 3.18 %. The crystals were isolated, and the remaining solution was concentrated to half its initial volume and placed at -30 °C. After 24 hours, the mixture of small yellow and orange crystals was obtained. The yellow crystals were characterized as [^{Me}NacNacTi(OSiMe$_3$)(η^2-pinacolate)] (**3**) (0.097 g, 0.098 mmol, yield 19 %). Anal. Calcd for $C_{58}H_{66}N_2O_3SiTi$ (**3**) without pentane molecules: C, 76.12; H, 7.27; N, 3.06 %. Found: C, 76.25; H, 7.32; N, 3.00 %. NMR data of isolated crystals of **3**: ^{1}H-NMR (298 K, Toluene-d$_8$): δ 7.58 – 6.80 (22 H, aromatic protons from NacNac and pinacol ligands), 5.58 (s, 1H, C(Me)C*H*C(Me), 4.04 (sept, 2H, J_{HH} = 6.6 Hz, C*H*Me$_2$), 3.14 (sept, 2H, J_{HH} = 6.8 Hz, C*H*Me$_2$), 1.82 (s, 6H, C(*Me*)CHC(*Me*)), 1.39 (d, 6H, J_{HH} = 6.8 Hz, CH*Me*$_2$), 1.33 (d, 6H, J_{HH} = 6.6 Hz, CH*Me*$_2$), 1.24 (d, 6H, J_{HH} = 6.7 Hz, CH*Me*$_2$), (d, 6H, J_{HH} = 6.7 Hz, CH*Me*$_2$), 0.92 (s, 9H, OSi*Me*$_3$); ^{13}C{^{1}H}-NMR (298 K, Toluene-d8): δ 168.24 (s, *C*(Me)CH*C*(Me)), 148.17, 147.98, 143.14, 140.08, 138.69, 126.96 126.10, 125.46, 122.61, 118.72, 116.52 (s, Ar-*C*) 102.04 (s, C(Me)*C*HC(Me)), 28.98 and 28.21 (s, *C*HMe$_2$), 25.50 (s, C(*Me*)CHC(*Me*)), 25.09, 25.01, 23.74, 22.41 (s, CH*Me*$_2$), 13.89 (s, OSi*Me*$_3$) ppm.

The orange crystals were X-ray characterized as [^{Me}NacNacTi(Cl)(μ^2-O)]$_2$ (**7**) (0.086 g, 0.083 mmol, yield 8 %).

^{31}P{^{1}H}-NMR data of reaction mixture (298 K, C_6D_6): 297.91 (d, J_{PP} = 232.5 Hz, (fluorenyl)C=**P**-P*t*Bu$_2$, **6**), 9.64 (d, J_{PP} = 232.5 Hz, (fluorenyl)C=P-**P***t*Bu$_2$, **6**) ppm.

Reaction of 1 with acetophenone

Complex **1** (0.500 g; 0.637 mmol) was dissolved in 10 mL of THF, and acetophenone (0.102 g; 99 µL; 0.849 mmol) was slowly added. The resulting mixture was stirred for 48 hours, and during this time, the solution changed from green to dark green. After this time, the solvent was evaporated, and the oily residue was dissolved in 5 mL of pentane. The solution was filtered, and the filtrate was stored at +4 °C. Two days later, green-blue crystals had appeared, and they were characterized as β-diketiminate titanium(III) complex with aldol condensation product [^{Me}NacNacTi(Cl){OC{Me(Ph)}CH$_2$(C=O)Ph] (**8**). The crystals were isolated with a yield of 0.157 g (0.212 mmol, 33 %). Anal. Calcd for (**8**): C, 73.01; H, 7.62; N, 3.78 %. Found: C, 73.98; H, 7.58; N, 3.85 %. Crystals of **8** were isolated, and the filtrate was concentrated to 2 mL and stored at -30 °C for 2 days. During this time, red crystals appeared, and they were characterized as **5** (0.212 g, 0.179 mmol, yield 28 %). In the next step, the crystals were isolated, and the filtrate was concentrated. The oily residue was distilled using the Kugelrohr apparatus at 160 °C under reduced pressure (0.01 Torr). The obtained oil was characterized by NMR spectroscopy as phospha-Wittig reaction product (Ph)MeC=P-P*t*Bu$_2$ (**9**). Yield: 0.088 g (0.314 mmol, 37 %). NMR data of **9**: ^{1}H-NMR (298 K, C_6D_6): δ 8.0–7.0 (aromatic protons of both isomers of (**Ph**)MeC=P-P*t*Bu$_2$), 2.94 (dd, J_{PH} = 11.4 Hz and J_{PH} = 1.6 Hz, (Ph)**Me**C=P-P*t*Bu$_2$, *Z isomer*), 2.62 (dd, J_{PH} = 21.4 Hz and J_{PH} = 0.9 Hz, (Ph)**Me**C=P-P*t*Bu$_2$, *E isomer*), 1.32 (d, J_{PH} = 11.4 Hz, (Ph)MeC=P-P***t*Bu**$_2$, *Z isomer*), 1.19 (d, J_{PH} = 10.9 Hz, (Ph)MeC=P-P***t*Bu**$_2$, *E isomer*); ^{13}C{^{1}H}-NMR (298 K, C_6D_6): 205. 11 (dd, J_{PC} = 53.6 Hz, J_{PC} = 14.5 Hz, *t*Bu$_2$P-P=**C**Me(Ph)), 137.34, 132.18, 126.89, 126.40, 125.17, 121.82 (aromatic carbon atoms in the phenyl groups), 33.83 (dd, J_{PC} = 27.2 Hz, J_{PC} = 3.6 Hz, central carbon atoms in the *tert*-butyl groups, *Z isomer*), 33.49 (dd, J_{PC} = 18.2 Hz, J_{PC} = 3.6 Hz, central carbon atoms in the *tert*-butyl groups, *E isomer*), 30.95 (dd, J_{PC} = 13.6 Hz, J_{PC} = 5.5 Hz, methyl groups of the *tert*-butyl groups, *Z isomer*), 30.92 (dd, J_{PC} = 14.5 Hz, J_{PC} = 5.5 Hz, methyl

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groups of the *tert*-butyl groups, *E isomer*), 27.63 (broad dd, J_{PC} = 29.9 Hz, J_{PC} = 16.3 Hz, methyl group of the acetophenone, the signals from the *Z* and *E* isomers overlap); $^{31}P\{^1H\}$-NMR (298 K, C_6D_6): 263.63 (d, J_{PP} = 234.9 Hz, (Ph)MeC=**P**-P*t*Bu$_2$, *Z isomer*), 253.06 (d, J_{PP} = 222.8 Hz, (Ph)MeC=**P**-P*t*Bu$_2$, *E isomer*), 24.65 (d, J_{PP} = 222.8 Hz, (Ph)MeC=P-**P***t*Bu$_2$, *E isomer*), 21.89 (d, J_{PP} = 234.9 Hz, (Ph)MeC=P-**P** *t*Bu$_2$, *Z isomer*) ppm.

Reaction of 1 with cyclopentanone. Synthesis of [{(ArN=C(Me)CHC(Me)=NAr)((CH$_2$)$_4$CO)}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)((CH$_2$)$_4$CO)}] (10)

1 (0.350 g; 0.446 mmol) was dissolved in 5 mL of toluene, and then cyclopentanone (0.075 g; 79 µL; 0.892 mmol) was added. After a few minutes, the solution began to change from green to violet-blue. Fifteen minutes later, the toluene was removed under vacuum, and the obtained solid residue was dissolved in 10 mL of pentane. Subsequently, the solution was concentrated to 5 mL and placed at +4 °C. Twenty-four hours later, violet crystals of [{(ArN=C(Me)CHC(Me)=NAr)((CH$_2$)$_5$CO)}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)((CH$_2$)$_5$CO)}] (**10**) had appeared. Yield: 0.323 g (0.351 mmol, 79 %). Anal. Calcd for $C_{50}H_{84}Cl_1N_2O_2P_2Si_1Ti_1$ (**10**): C, 65.37; H, 9.22; N, 3.05 %. Found: C, 65.31; H, 9.07; N, 3.12 %.

Stability investigations of 10. Synthesis of (CH$_2$)$_4$C=P-P*t*Bu$_2$ (10a)

Crystals of complex **10** (0.300 g; 0.327 mmol) were dissolved in 10 mL of THF and stirred for 48 hours. During this time, the solution changed from violet-blue to light-violet. In the next step, the THF was evaporated, and the obtained oily residue was distilled using a Kugelrohr apparatus. The distillation was conducted at 145 °C under reduced pressure (0.01 Torr). The obtained oil was characterized by NMR spectroscopy as a phospha-Wittig reaction product, (CH$_2$)$_4$C=P-PtBu$_2$ (**10a**). Finally yielded: 0.041 g. NMR data of **10a**: ^{1}H-NMR (298 K, C_6D_6): δ 3.10 (bm, 2H, *t*Bu$_2$P-P=C(C**H$_2$**)$_4$), 2.71 (bm, 2H, *t*Bu$_2$P-P=C(C**H$_2$**)$_4$), 1.48 (bm, 4H, *t*Bu$_2$P-P=C(C**H$_2$**)$_4$), 1.29 (d, 18H, J_{PH} = 11.2 Hz, ***t*Bu**$_2$P-P C(CH$_2$)$_4$); $^{13}C\{^1H\}$-NMR (298 K, C_6D_6): δ 219.62 (dd, J_{PC} = 52.7 Hz, J_{PC} = 16.3 Hz, *t*Bu$_2$P-P=**C**(CH$_2$)$_4$), 42.34 (dd, J_{PC} = 39.0 Hz, J_{PC} = 6.3 Hz, *t*Bu$_2$P-P=C(**C**H$_2$)$_4$), 41.81 (d, J_{PC} = 17.2 Hz, *t*Bu$_2$P-P=C(**C**H$_2$)$_4$), 33.23 (dd, J_{PC} = 27.2 Hz, J_{PC} = 3.6 Hz, {(Me$_3$)**C**}$_2$P-P=C(CH$_2$)$_4$), 30.95 (dd, J_{PC} = 14.5 Hz, J_{PC} = 5.4 Hz, {(**Me**$_3$)C}$_2$P-P=C(CH$_2$)$_4$); $^{31}P\{^1H\}$-NMR (298 K, C_6D_6): δ 212.74 (d, $J_{P\text{-}P}$ = 220.8 Hz, *t*Bu$_2$P-**P**=C(CH$_2$)$_4$), 26.26 (d, $J_{P\text{-}P}$ = 220.8 Hz, *t*Bu$_2$**P**-P=C(CH$_2$)$_4$) ppm.

Reaction of 1 with cyclohexanone. Synthesis of [{(ArN=C(Me)CHC(Me)=NAr)((CH$_2$)$_5$CO)}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)((CH$_2$)$_5$CO)}] (11)

Cyclohexanone (0.077 g; 82 µL; 0.790 mmol) was added to a solution of **1** (0.310 g; 0.395 mmol) in 10 mL of toluene. The solution changes from green to violet-blue. After 15 min, the solvent was removed under vacuum, and the obtained solid residue was dissolved in 10 mL of petroleum ether. The solution was concentrated to 3 mL and placed at +4 °C. After 3 hours, violet crystals of [{(ArN=C(Me)CHC(Me)=NAr)((CH$_2$)$_5$CO)}Ti(Cl){P*t*Bu$_2$-P(SiMe$_3$)((CH$_2$)$_5$CO)}] (**11**) has formed. Yield: 0.331 g (0.334 mmol, 85 %). Anal. Calcd for $C_{55}H_{95}Cl_1N_2O_2P_2Si_1Ti_1$ (**11**) (including half of a hexane molecule): C, 66.74; H, 9.68; N, 2.83 %. Found: C, 66.32; H, 9.44; N, 2.95 %.

Stability investigations of 11. Synthesis of (CH$_2$)$_5$C=P-P*t*Bu$_2$ (11a) and [^{Me}NacNacTi(Cl){OC(CH$_2$)$_5$CH(C=O)(CH$_2$)$_4$}] (11b)

Complex **11** (0.300 g; 0.303 mmol) was dissolved in 10 mL of THF, and the mixture was stirred for 48 hours. During this time, the solution changed from violet-blue to blue. Then, the THF was evaporated, and the obtained oily residue was dissolved in 5 mL of petroleum ether. This solution was filtered, and the filtrate was stored at +4 °C. Three days later, blue crystals had appeared, and they were characterized as [^{Me}NacNacTi(Cl){OC(CH$_2$)$_5$CH(C=O)(CH$_2$)$_4$}] (**11b**). Yield: 0.063 g (18 %). Anal. Calcd for $C_{44}H_{67}Cl_1N_2O_2Ti_1$ (**11b**) (including half of a hexane molecule): C, 71.46; H, 9.14; N, 3.79 %. Found: C, 71.38; H, 9.02; N, 3.86 %. Crystals of **11b** were isolated, the remaining solvent was evaporated, and the obtained oily residue was distilled using a Kugelrohr apparatus at 160 °C under reduced pressure (0.01 Torr). The obtained oil was characterized by NMR spectroscopy as a phospha-Wittig reaction product, (CH$_2$)$_5$C=P-P*t*Bu$_2$ (**11a**). Finally yielded: 0.048 g NMR data of **11a**: ^{1}H-NMR (298 K, C_6D_6): δ 3.18 (bm, 2H, *t*Bu$_2$P-P=C(C**H$_2$**)$_5$), 2.69 (dtd, 2H, J_{HH} = 4.4 Hz, $^3J_{PH}$ = 17.2 Hz, $^4J_{PH}$ = 1.5 Hz, *t*Bu$_2$P-P=C(C**H$_2$**)$_5$), 1.95 (bm, 4H, *t*Bu$_2$P-P=C(C**H$_2$**)$_5$), 1.35 (bm, 2H, *t*Bu$_2$P-P=C(C**H$_2$**)$_5$), 1.28 (d, $^3J_{PH}$ = 11.2 Hz, ***t*Bu**$_2$P-P C(CH$_2$)$_5$); $^{13}C\{^1H\}$-NMR (298 K, C_6D_6): δ 215.64 (dd, J_{PC} = 55.4 Hz, J_{PC} = 14.5 Hz, *t*Bu$_2$P-P=**C**(CH$_2$)$_5$), 43.31 (dd, J_{PC} = 40.9 Hz, J_{PC} = 5.4 Hz, *t*Bu$_2$P-P=C(**C**H$_2$)$_5$), 41.47 (s, *t*Bu$_2$P-P=C(**C**H$_2$)$_5$), 39.60 (d, J_{PC} = 29.9 Hz, J_{PC} = 17.2 Hz, *t*Bu$_2$P-P=C(**C**H$_2$)$_5$), 32.80 (dd, J_{PC} = 27.2 Hz, J_{PC} = 4.5 Hz, {(Me$_3$)**C**}$_2$P-P=C(CH$_2$)$_5$), 31.09 (dd, J_{PC} = 13.6 Hz, J_{PC} = 5.4 Hz, {(**Me**$_3$)C}$_2$P-P=C(CH$_2$)$_5$), 30.47 (d, J_{PC} = 9.9 Hz, *t*Bu$_2$P-P=C(**C**H$_2$)$_5$), 29.08 (d, J_{PC} = 6.3 Hz, *t*Bu$_2$P-P=C(**C**H$_2$)$_5$); $^{31}P\{^1H\}$-NMR (298 K, C_6D_6): δ 221.19 (d, $J_{P\text{-}P}$ = 228.9 Hz, *t*Bu$_2$P-**P**=C(CH$_2$)$_5$), 17.85 (d, $J_{P\text{-}P}$ = 228.9 Hz, *t*Bu$_2$**P**-P=C(CH$_2$)$_5$) ppm.

Reaction of 1 with cycloheptanone. Synthesis of [^{Me}NacNacTi(Cl){OC(CH$_2$)$_5$}CH(C=O)(CH$_2$)$_6$] (12)

Cycloheptanone (0.071 g, 75 µL; 0.637 mmol) was dropwise added to a solution of **1** (0.250 g; 0.319 mmol) in 10 mL of toluene. After 3 hours, the colour of the solution began to change from green to dark blue. After another hour, the solvent was evaporated, and the precipitate was dissolved in 15 mL of pentane. Afterwards, the obtained solution was concentrated to approximately 2 mL and placed at -23 °C. Forty-eight hours later, the formed navy-blue crystals were isolated and characterized as [^{Me}NacNacTi(Cl){OC(CH$_2$)$_5$}CH(C=O)(CH$_2$)$_6$] (**12**). Yield: 0.129 g (0.178 mmol, 56 %). Anal. Calcd for $C_{43}H_{64}Cl_1N_2O_2Ti_1$ (**12**): C, 71.31; H, 8.91; N, 3.87 %. Found: C, 71.24; H, 8.79; N, 3.94 %.

Conclusions

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The main aim of the present work was to study the reactivity of phosphanylphosphido titanium(III) complex [^{Me}NacNacTi(Cl){η^2-P(SiMe^3)-P*t*Bu$_2$}] (**1**) in phospha-Wittig reactions and to isolate newly formed compounds with C-P-P or C=P-P systems. The reactions of **1** with aromatic and aliphatic ketones revealed distinct reaction modes. The reactions with benzophenone and 9-fluorenone afforded phosphanylphosphaalkenes (Ph$_2$C=P-P*t*Bu$_2$ (**2**) and (fluorene)C=P-P*t*Bu$_2$ (**6**), complex **5** and titanium(IV) complexes with pinacol condensation products as ligands (**3**). Additionally, NMR spectroscopy revealed that the reaction of **1** with 9-fuorenone generates the titanium(IV) complex (**4**). Interestingly, the complex is only an intermediate in this reaction and further reacts with excess of 9-fluorenone, which increases the amount of phosphanylphosphaalkene. The presence of already one aliphatic group on the carbonyl carbon atom completely changed the reaction routes. Due to the presence of α-protons, the analogous reactions with acetophenone, cyclopentanone, and cyclohexanone accept phosphanylphosphaalkenes ((Ph)MeC=P-P*t*Bu$_2$ (**9**), (CH$_2$)$_4$C=P-P*t*Bu$_2$ (**10a**), (CH$_2$)$_5$C=P-P*t*Bu$_2$ (**11a**)), affording titanium(III) complexes with the aldol condensation products and a diphosphane (*t*Bu$_2$P-P(SiMe$_3$)H). In the reactions with cyclopentanone and cyclohexanone, new complexes generated by the insertion of two molecules of the ketone were obtained (**10** and **11**) (analogous to the intermediates in the phospha-Wittig reaction). The investigations of the stability of these two complexes revealed that in THF, a polar solvent, they decompose to phosphanylphosphaalkenes and aldol condensation products.

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