Solvent Impact on the Diversity of Products in the Reaction of Lithium Diphenylphosphide and a Ti(III) Complex Supported by a tBu₂P−P(SiMe₃) Ligand

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ABSTRACT: We present two important trends in the reactivity of the titanium complex \([\text{MeNacNacTi(Cl)}\{\eta^{2}-P(\text{SiMe}_{3})-\text{P}t\text{Bu}_{2}\}]\) \((\text{MeNacNac} = \{\text{Ar}NC(\text{Me})\text{CHC}\text{(Me)}\text{N}[\text{Ar}]\}; \text{Ar} = 2,6-i\text{Pr,Ph})\) with nucleophilic reagents \(\text{RLi} (\text{R} = \text{Ph}_{2}P, \text{BuO}, (\text{Me}_{3}\text{Si})_{2}N, \text{and} \text{tBu}_{2}N)\) depending on the reaction medium. Reaction in nonpolar solvent (toluene) leads to three main products: via an autoredox process and nucleophilic substitution at the Ti-atom to a Ti(IV) complex \([\text{MeNacNacTi(R)}\{\eta^{2}-P(\text{P}t\text{Bu}_{2})\}]\) \((1 \text{ for } \text{R} = \text{P}t\text{Bu}_{2})\), via the elimination of \(\text{Me}_{3}\text{SiR}\) to afford Ti(III) complex \([\text{MeNacNacTi(Cl)}\{\eta^{2}-P(\text{P}t\text{Bu}_{2})\}]\) \((2)\), and via 2e⁻ reduction process to afford new ionic complex \([\text{ArNC(Me)-CHC(Me)}\text{N}[\text{Ar}]]\{\eta^{2}-P(\text{SiMe}_{3})-\text{P}t\text{Bu}_{2}\}]\) \((3)\). Quite differently, the complex \([\text{MeNacNacTi(Cl)}\{\eta^{2}-P(\text{SiMe}_{3})-\text{P}t\text{Bu}_{2}\}]\) reacts with \(\text{Ph}_{2}P\text{Li}\) in THF, unexpectedly yielding two new, four-coordinate Ti(IV) imido complexes \(4a\) \([\text{ArNC(Me)}\text{-CHC}((\text{Me})_{2})\text{CH}=\text{C}(\text{Me})\text{-P(}t\text{Bu}_{2})\text{]}\text{Ti=NAr(Cl)}\] \((\text{toluene})_{2}\) and \(4b\) \([\text{ArNC(CH}_{2})_{2}\text{CH}=\text{C}(\text{Me})\text{-P(}t\text{Bu}_{2})\text{]}\text{Ti=NAr(Cl)}\] \((\text{Et}_{2}\text{O})\). Complex 2 dissolved in THF converts to \(4a\) and \(4b\). \(1, 2, 3, 4a, \text{and} 4b\) were characterized by X-ray diffraction. \(1, 4a, \text{and} 4b\) were also fully characterized by multinuclear NMR spectroscopy.

1. INTRODUCTION

Recently, much attention has been dedicated to titanium carbene, nitrene and phosphinidene complexes.1−15 Due to the high oxo- and halogenophilicity of titanium in phosphinidene complexes, they exhibit significant phospha-Wittig reactivity.16 Thus, they are important synthons to introduce low-valent phosphorus fragments into organic molecules. The proper choice of auxiliary stabilizing ligands is very important for the synthesis of these complexes. Recently, \(\beta\)-diketiminate species have been widely applied as excellent stabilizing spectator ligands, especially for reactive organometallic compounds with low coordination numbers.17−20 Their additional advantages are the good crystallizing properties of the obtained complexes and the facile modification of these ligands.21 The stability of \(\beta\)-diketiminate ligands seems to be significantly overestimated and show an important contribution to reactivity. In the literature there are a wide range of processes in which the \(\beta\)-diketiminate ligands are directly involved and often present redox noninnocent behavior.22−24 Among others, two main transformations can be distinguished: electrophilic attack of the \(\gamma\)-carbon25,26 and deprotonation of the methyl group attached to the \(\beta\)-carbon of the NCCCN ring.27−32 Recently, the reductive transformation of a \(\beta\)-diketiminate ligand via migration of the imido group from the NacNac backbone to the metal center and formation of a bond between the \(\beta\)-carbon and metal center was reported.26,33−36

Our group has studied metathesis reactions of R′R′’P−P(\text{SiMe}_{3})\text{Li} with transition metal compounds bearing chloride ligands to introduce phosphaphosphinidene R′R′’P and phosphaphenophosphido R′R′’P(\text{SiMe}_{3}) moieties into the product complexes \((R′ = \text{tBu} \text{and} i\text{Pr}; R′′ = \text{Bu}_{2} \text{P}, i\text{Pr}, \text{and} \text{Ph})\). Phosphaphenophosphido complexes have been obtained for titanium,35−39 iron,40,41 hafnium,42 zirconium,43−47 tungsten,48 and molybdenum,49 and phosphaphenophosphido complexes have been reported for titanium,15−17 iron,18 hafnium,40,41 zirconium,43−47 tungsten,48 and molybdenum,49 and platinum.50 Among these complexes, the complexes of titanium, zirconium, and iron were stabilized using a \(\beta\)-diketiminate ligand. The reactivity of the phosphaphenophosphidene complexes of tungsten was investigated by Grubba and co-workers.51,52 Moreover, the reactivities of monophosphorus analogues M=P and P−R are also rarely reported. In part, this may be caused by the
substituents R on the phosphorus atom, which are generally alkyl or aryl groups, where the P–C bond is relatively robust. Hey-Hawkins and co-workers have made attempts to investigate reactivity of transition metal bis(trimethylsilyl)-phosphido complexes.54

The reactivity of phosphanylphosphido complexes has practically not been studied. One of our recent work shows the reactivity of the titanium(III) complex containing Bu2P-P(SiMe3) ligand toward isolated chlorophosphines (as electrophiles).55 These research resulted in new method of synthesis of titanium(IV) complexes with versatile phosphanylphosphinidene accompanied by the reduction of by-products which possess a new P–P bond, mainly symmetrical and unsymmetrical diphosphines, or a P–P bond, tBu2PH in the great majority.55

We considered it appropriate and justified to examine the reactivity toward reagents with other properties. In this report, we describe the reactions of β-diketiminate titanium(III) complex with phosphanylphosphido ligand (Bu2P–P(SiMe3)) toward lithium nucleophiles, such as Ph2PLi, (Me3Si)2NLi, and the great majority.55

For C53H91ClLiN2O8P2Ti: C, 61.41; H, 8.85; N, 2.70%. Found: C, 61.17; H, 8.68; N, 2.78%. Next, we obtained 0.13 g (0.08 mmol, 15%, only the crystalline form in all reactions).

The reactions of [MeNacNacTi(Cl)(η3-P(SiMe3)-P Bu2)] with other nucleophiles (Bu2Oli, Bu2NLi, and (Me3Si)2NLi) were carried out analogously to this reaction with Ph2PLi. In the reactions with these nucleophiles, the substitution products were not isolated in crystalline form; therefore, the reaction solutions were investigated by 31P{1H} NMR spectroscopy. Complex 2 was only isolated product in the crystalline form in all reactions.

2.1. Reactions of [MeNacNacTi(Cl)(η3-P(SiMe3)-P Bu2)] with Group 13 Elements and Alkynes.

2.1.1. Reaction with NbLi. The compounds [MeNacNacTi{N(SiMe3)2}{P(SiMe3)-P Bu2}], [MeNacNacTi(N(SiMe3)2){P(SiMe3)-P Bu2}], [MeNacNacTi{N(SiMe3)2}{P(SiMe3)-P Bu2}](Me3Si)2NLi, and tBu2NLi in the Presence of 12-crown-4 in Toluene. To a solution of [MeNacNacTi(Cl)(η3-P(SiMe3)-P Bu2)] (0.240 g, 0.305 mmol) were added 12-crown-4 (0.049 mmol), [MeNacNacTi{N(SiMe3)2}{P(SiMe3)-P Bu2}](Me3Si)2NLi, and tBu2NLi were purchased from commercial suppliers. Ph2PH and tBu2NH were isolated and identified as Ph2PLi and tBu2NLi in our laboratory.

2.1.2. Reaction with tBu2NLi. The compounds [MeNacNacTi(Cl)(η3-P(SiMe3)-P Bu2)] (0.240 g, 0.305 mmol), Bu2NLi (0.041 g, 0.305 mmol), and 12-crown-4 (0.049 mmol) were added to [MeNacNacTi(Cl)(η3-P(SiMe3)-P Bu2)] (0.194 g, 0.187 mL; 1.100 mmol; 1.087 g/mL) was added dropwise, and the reaction mixture changed from green to red. Additionally, 12-crown-4 was added to the solution. The mixture was stirred for 30 min at room temperature. The reaction mixture was then filtered, and concentrated to a solution of 0.092 g (0.9 mmol, 29%).

2.2. Reactions of [MeNacNacTi(Cl)(η3-P(SiMe3)-P Bu2)] with Ph2PLi in the Presence of 12-crown-4 in THF. Crystals of [MeNacNacTi(Cl)(η3-P(SiMe3)-P Bu2)] (0.320 g; 0.407 mmol) were dissolved in 10 mL of THF, and Ph2PLi (0.078 g; 0.407 mmol) in 10 mL of THF was added at −15 °C. After approximately 5 min at room temperature, the green-red solution was slowly added 12-crown-4 (0.112 mL; 0.814 mmol, 1.089 g/mL). The mixture changed color to deep-red. The mixture was stirred for 16 h, after which the solution was evaporated. The obtained red solid was dissolved in the diethyl ether, but after 48 h at +4 °C, no crystals had appeared. The solvent was evaporated again, and crystallization was attempted in different solution mixtures. Depending on the solutions used to dissolve the obtained solid, different complexes were isolated.

2.2.1. Crystallization from Toluene/Pentane. The solid residue was dissolved in 10 mL of toluene, filtered, and concentrated to a solution of 3 mL. Then, 0.5 mL of pentane was added, and the solution was stored at +4 °C. After 24 h, brown-red crystals of complexes 3a ([ArN(CN)(Me)═CHCH(Me)(P–P Bu2)]=NAr(12-crown-4)3]+(toluene) and 3b ([ArN(CN)(CH)−]−)}
3. RESULTS AND DISCUSSION

3.1. Reactivity Study of [MeNacNacTi(Cl)(η²-P(SiMe₃)-PtBu₄)] with Nucleophiles in the Nonpolar Solvent Toluene. Ti(III) complexes [MeNacNacTi(Cl)(η²-P(SiMe₃)-PR₂')] ([PR₂'] = tBu and iPr; R' = tBu and iPr, and Ph) contain several atoms that are prone to nucleophilic substitution. The electrophilic Fukui functions f' calculated for three complexes, [MeNacNacTi(Cl)(η²-P(SiMe₃)-PtBu₂)], [MeNacNacTiCl(Cl)(η²-P(SiMe₃)-PtBu₂)], and [MeNacNacTi(Cl)(η²-P(SiMe₃)-PtBu₂)], indicate that the most electrophilic atoms in these molecules are the hard Ti-centers (f' = 0.197, 0.189, and 0.180, respectively). Due to the theoretical results, we conducted the first reaction of [MeNacNacTi(Cl)(η²-P(SiMe₃)-PtBu₂)] with Ph₃P₂La at a 1:1 molar ratio in toluene. The reaction was started at −15 °C and then stirred for 8 h at 0 °C. The 31P{1H} NMR spectrum acquired 1 h after initiation of the reaction indicates that Ph₃P₂(SiMe₃) ([ς = −56.7 ppm] is the dominant species in the reaction solution. The presence of this compound clearly indicates that nucleophilic substitution takes place at the softer silicon atom and that the SiMe₃ group is removed from the phosphido moiety. Surprisingly, the 31P{1H} NMR spectrum obtained 7 h later revealed that except for the signal of Ph₃P₂(SiMe₃) a weaker set of resonances is visible. Additionally, a singlet at −14.9 ppm from the symmetrical diphosphane Ph₃P₂Ph₃ is observed. The other signals observed in the spectrum can be confidently assigned to those of the new Ti(IV) complex [MeNacNacTi(η²-PPh₂)(η²-P(SiMe₃)-PtBu₂)]1 (d, 676.7 ppm), J₁P₂ = 472.3 Hz, J₂P₂ = 14.5 Hz, J₃P₂ = 1.4 Hz; dд, 207.7 ppm, J₁P₂ = 65.4 Hz, J₂P₂ = 14.5 Hz, J₃P₂ = 1.4 Hz, dд, 104.0 ppm, J₁P₂ = 472.3 Hz, J₂P₂ = 65.4 Hz, J₃P₂ = 1.4 Hz (for 31P{1H} NMR spectrum of reaction mixture, see Figure S2). The 31P{1H} NMR spectrum confirms the nucleophilic attack of Ph₃P on the titanium center and the elimination of the chloride ion as LiCl. Additionally, during this reaction, the titanium atom is oxidized (1e oxidation). All attempts to isolate the compounds observed in the NMR spectra failed. To obtain the complexes in a crystalline form, the reaction of [MeNacNacTi(Cl)(η²-P(SiMe₃)-PtBu₂)] with Ph₃PLi in toluene was conducted in the presence of 12-crown-4 (molar ratio 1:1.2). Importantly, 12-crown-4 was added only 10 min before the end of the reaction. This modification allowed us to isolate the ionic Ti(III) complex [MeNacNacTi(Cl)(η²-P(SiMe₃)-PtBu₂)] [Li(12-crown-4)]₂ (2) in a crystalline form. After the isolation of 2, the reaction solution was investigated by NMR spectroscopy. 31P{1H} NMR revealed that the Ti(IV) complex [MeNacNacTi(η²-PPh₂)(η²-P(SiMe₃)-PtBu₂)] (1) was still present in the reaction mixture; therefore, the solution was concentrated and stored at −25 °C. After 24 h, dark red crystals had appeared and were characterized as complex 1 by 31P{1H} NMR spectroscopy. H⁻/31P-HMBE examinations of 1 revealed that the phosphanyl phosphorus atom (104.0 ppm) is only correlated with the tert-butyl groups (0.88 ppm, J₁P₂ = 14.8 Hz, 18H), while the phosphido phosphorus atom (at 207.7 ppm) correlates with the protons at 8.29 ppm (broad signal), 6.59 ppm (broad signal), 5.89 ppm (s), 2.89 ppm (weak correlation, J₁P₂ = 6.7 Hz, 18H), and 1.87 ppm (s). The integrations of the above-mentioned proton signals indicate 1 H in the signal at 1.87 ppm, 1 H in the signal at 5.89 ppm and 2 H in the signal at 2.89 ppm (methyl group, γ-proton, and isopropyl group of the Me₅Nac skeleton, respectively) (for the spectra of complex 1, see Figures S3–S10). In the next step, the crystals of 1 were isolated, and the solvent was
removed under vacuum. The obtained dark orange-red oily residue was dissolved in the mixture of diethyl ether and small amount of pentane. Storage at −40 °C for 1 month allowed us to obtain the oily residue in crystalline form. The X-ray measurement revealed that the complex \([\text{ArNC(Me)CHC(Me)}\text{Ti} \equiv \text{NAr} \{\eta^1-\text{P(SiMe}_3\)-\text{P}t\text{Bu}_2\}]^{-}[\text{Li(12-crown-4)}_2]^+ (3)\) was also created (for the molecular structure of complex 3, see Figure S1). NMR and X-ray results indicated that the reaction of \([\text{MeNacNacTi(Cl)}\{\eta^2-\text{P(SiMe}_3\)-\text{P}t\text{Bu}_2\}]\) with \(\text{Ph}_2\text{PLi}\) in the presence of 12-crown-4 in toluene probably leads to two independent and competitive reactions. The first reaction can be recognized as a lithiation of the phosphido phosphorus atom of the starting titanium(III) complex and proceeds without changing of the oxidation state of the titanium atom. The second reaction can be recognized as the redox reaction in which the new complexes 1, 3, and \(\text{Ph}_2\text{P-PPh}_2\) are created. The molecular structure of complex 3 indicates that it is a product of 2e\(^{-}\) reduction of \([\text{MeNacNacTi(Cl)}\{\eta^2-\text{P(SiMe}_3\)-\text{P}t\text{Bu}_2\}]\). Mindiola and co-workers observed similar 2e\(^{-}\) reduction process of \(\text{ArNC(Me)CHC(Me)}\text{Ti} \equiv \text{NAr} \{\eta^1-\text{P(SiMe}_3\)-\text{P}t\text{Bu}_2\}]^{-}[\text{Li(12-crown-4)}]^+\) in the reactions with \(\text{KCl}\) or \(\text{Ph}_2\text{P-SiMe}_3\) and \(\text{LiCl}\) are also formed. The above-described results are summarized in Scheme 1.

It should be emphasized that the employed reaction conditions aimed to optimize the preparation of compound 1. The reaction carried out in room temperature showed that the dominant processes were the elimination reaction of the \(\text{SiMe}_3\) group and lithiation of phosphorus atom. In this case, compound 1 was formed in trace amounts, and its isolation in crystalline form was impossible. The key element in this case was also the time of addition of a crown ether. The addition of a 12-crown-4 at the beginning of the reaction favors the formation of complex 2; therefore, a crown ether was added almost at the end of the reaction.

Moreover, this reaction was also conducted with other nucleophilic reagents: \(\text{tBuOLi}, \text{Me}_3\text{Si}_2\text{NLi}, \text{and tBu}_2\text{NLi}\). After each of these reactions, we only isolated paramagnetic complex 2. Furthermore, the formation of 2 was accompanied by the formation of products containing \(\text{SiMe}_3\) groups (visible in the \(^1\text{H}\) NMR spectrum as \(\text{tBuOSiMe}_3\) at 1.25 ppm) and
0.05 ppm (s); \(\text{Me}_4\text{Si})_2\text{N}\) at 0.11 ppm (s); and \(\text{Bu}_3\text{N} (\text{SiMe}_3)\) at 1.32 ppm (s), 1.24 ppm (s) and 0.1 ppm (s), respectively). Additionally, \(\text{P}^{31}(\text{H})\) NMR examination of the reaction solution also revealed the formation of Ti(IV) complexes due to nucleophilic substitution of the \(\text{Cl}\) functionality on Ti atom by the RLi nucleophile \((R = \text{N} [\text{SiMe}_3]_2, \text{Bu}_2\text{O}, \text{and} \text{Bu}_3\text{N})\) : \(\{\text{MeNacNacTi} (\text{OBu}) (\text{η}^2-\text{P}^1(\text{P}^2)\text{Bu}_2)]\) (d, (P1) 669.6 ppm and (P2) 868.8 ppm, \(\text{J}_{PP} = 446.4 \text{ Hz}\)), \(\{\text{MeNacNacTi} (\eta^2\text{P}(\text{P}^1(\text{P}^2)\text{Bu}_2)]\) (d, (P1) 539.3 ppm and (P2) 87.7 ppm, \(\text{J}_{PP} = 485.1 \text{ Hz}\)), and \(\{\text{MeNacNacTi} (\text{N}[\text{SiMe}_3]_2) (\text{η}^2-\text{P}^1(\text{P}^2)\text{Bu}_2)]\) (d, (P1) 669.4 ppm and (P2) 86.8 ppm, \(\text{J}_{PP} = 441.4 \text{ Hz}\) for the \(\text{P}^{31}(\text{H})\) NMR spectra of the reaction mixture, see Figures S14–S16). Unfortunately, the amounts of the titanium(IV) complexes were much smaller than what was generated in the reaction with Ph\(_2\)PLi. Additionally, modification of the reaction conditions did not increase the amounts of the nucleophilic substitution products. We also observed the formation of diphasphane \(\text{Bu}_2\text{P}=\text{P} (\text{SiMe}_3)_2\) in the reaction with \(\text{Me}_4\text{Si})_2\text{N} \text{Li} \) and \(\text{Bu}_3\text{N} \text{Li} \), which may indicate that in these reactions, the starting complex decomposes.

3.2. Reactivity Study of \(\{\text{MeNacNacTi(NO)} (\text{Cl}) (\eta^2\text{P}(\text{SiMe}_3)\text{B(u)}_2)]\) with Nucleophiles in the Polar Solvent: THF. In view of the above obtained results for reactivity in a nonpolar solvent, we used only Ph\(_2\)PLi for reactivity in a polar solvent. The reaction of \(\{\text{MeNacNacTi} (\text{Cl}) (\eta^2-\text{P}(\text{SiMe}_3)\text{B(u)}_2)]\) with Ph\(_2\)PLi was also studied in THF in the presence of 12-crown-4 and a molar ratio of 1:1:2. Surprisingly, \(\{\text{MeNacNacTi} (\text{Cl}) (\eta^2-\text{P}(\text{SiMe}_3)\text{B(u)}_2)]\) reacts with Ph\(_2\)PLi quite differently under these conditions. The \(\text{P}^{31}(\text{H})\) NMR spectrum of the reaction mixture shows two AX patterns from two separate complexes: \(4\text{a}\) (34.4 ppm and −16.4 ppm, \(\text{J}_{PP} = 382.1 \text{ Hz}\)) and \(4\text{b}\) (41.0 ppm and 28.5 ppm, \(\text{J}_{PP} = 307.1 \text{ Hz}\)). The observed signals indicate that in this reaction, the titanium oxidation state is changed from +3 to +4. Crystallization from toluene/pentane solution, we used only Ph\(_2\)PLi for reactivity in a polar solvent.

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Figure 1. HMQC spectrum (\(\text{H}/^{13}\text{C}-\text{DEPT}-135\)) showing the correlation of the sp\(^3\)-hybridized carbon atom with protons.
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P(Ph)2]3 complex was stirred with Ph2PLi and 12-crown-4 in THF at −15 °C. The 31P{1H} NMR spectrum obtained immediately after mixing reveals only a strong singlet for Ph3P(SiMe3). 31P{1H} NMR spectra were acquired after 1, 2, 24, 48, and 72 h, 7 days, and 2 months (see Figures S39–S41). At 1 hour after initiation of the reaction at ambient temperature, the 31P{1H} NMR spectrum showed weak signals of 4a and 4b. Between 1 and 48 h, we observed the amplification of the signals of 4a and 4b, and maximum signals of 4a and 4b were observed 48 h after the initiation of the reaction. Further measurements revealed a decrease in the intensity of the signals for 4a and complete disappearance after 2 months. Unlike 4a, complex 4b is stable in THF solution. Interestingly, we observed that the singlets at 196.1 ppm (J_{P-H} = 14.5 Hz, determined from the 31P NMR spectrum) and 19.6 ppm (tBu2PH) increase with the reaction time, very likely due to the decomposition of 4a. The 1H/31P-HMBC spectrum indicates that the atom appearing at 196.1 ppm is conjugated to the protons observed at 6.42 ppm (d, J_{PH} = 5.9 Hz, 1H), 2.34 ppm (d, J_{PH} = 13.8 Hz, 3H), and 1.8 ppm (d, J_{PH} = 1.8 Hz, 3H). The integration of the above-mentioned protons reveals the following: Only 1 H is located at 6.42 ppm (d, J_{PH} = 5.9 Hz, 1H), 2.34 ppm (d, J_{PH} = 13.8 Hz, 3H), and 1.8 ppm (d, J_{PH} = 1.8 Hz, 3H). Additionally, in the 1H/13C-HMBC spectrum, we observe the correlations of the protons located at 6.42 ppm with the carbon atom appearing at 118.2 ppm (d, J_{CP} = 6.3 Hz) and of the protons visible at 2.34 and 1.8 ppm with the carbons appearing at 13.5 ppm (d, J_{PC} = 10.6 Hz) and 14.4 ppm (d, J_{PC} = 4.3 Hz), respectively. The 1H/13C-HMBC spectrum indicates that the protons at 2.34 and 1.8 ppm correlate with the carbon at 118.2 ppm. All NMR results show a signal near 196.1 ppm, which theoretically confirms the presence of a titanium(IV) complex with a PN ligand similar to that of 4a. Unfortunately, all attempts to isolate this complex failed. In order to investigate the influence of temperature on the reaction route, we have carried out the above-described reaction again. The substrates were also mixed at −15 °C and immediately after mixing, the 31P{1H} NMR spectrum was measured and singlet from Ph3P(SiMe3) was observed. The NMR tube was heated in the oily bath at +50 °C. Next, spectra were acquired after 1, 2, 24, 48, and 72 h and 7 days. The conducted experiment revealed that the temperature has an impact on the reaction rate. Higher temperature causes the reaction proceeded rapidly but no other products are formed. Moreover, after 7 days, complex 4a is no longer visible in the solution.

To better identify the differences between the reactions in polar and nonpolar solvents, we also carried out reactions with the same amounts of substrates and under the same conditions (RT). In both reactions, 12-crown-4 was added at the beginning of the reactions. One reaction was carried out in toluene-d8, while the other was carried out in THF-d8. Reaction mixtures were sealed in NMR tubes and measured cyclically. Measurements were performed after 1, 24, and 48 h and 5 days from the initiation of the reactions. The conducted experiments revealed that in nonpolar solvent only complex 1 was visible in the 31P{1H} NMR spectrum, while the high signal of Ph3P(SiMe3) indicated on the presence of complex 2 in the reaction mixture. Importantly, the 31P{1H} NMR measurement conducted after 5 days revealed no signals from 4a and 4b (see Figure S42). The obtained results clearly show, that both complexes 1 and 2 are stable in the nonpolar solvent. In the reaction carried out in THF-d8 formation of complexes 4a and 4b was observed, while the formation of complex 1 was not observed (see Figure S43). These experiments clearly prove that the polarity of the solvents is very important in the reaction of [MeNacNacTi(Cl)(η2-P(SiMe3)-PhBu2)] with Ph2PLi and 12-crown-4 and has a direct impact on the resulting products.

Finally, we also examined the stability of isolated crystals of 2 in THF at room temperature over 24 h. Therefore, the crystals of 2 were dissolved in THF-d8 and investigated via NMR. The 31P{1H} NMR spectrum revealed the formation of complexes 4a and 4b (Scheme 1). Additionally, in the 1H NMR spectrum the proton connected to the β-carbon was also visible (see Figures S44 and S45). Obtained results may indicate that the protonation of the β-carbon in 4a is directly connected with deprotonation process observed in complex 4b. In this intermolecular process of two molecules of complex 2, in the “phosha-Staudinger”, protonation and deprotonation reactions, the one molecule of complex 4a and one molecule of complex 4b are created.

### 3.3. X-ray Structural Analysis

Complex 1 crystallized in the orthorhombic space group Pnma with four molecules in the unit cell. 1 displays a five-coordinate titanium complex with pseudosquare pyramidal geometry (τ5 = 0.350(6)) (Figure 2).

The obtained molecular structure confirms the nucleophilic attack of the Ph3P ion on the titanium center, resulting in the elimination of the chloride ion as LiCl. The Ti1–P1 and Ti1–P2 distances (2.308 and 2.573(5) Å) are typical for Ti–P bonds in side-on coordination and are comparable to the distances observed in [MeNacNacTi(Cl)(η2-P(PhBu2))] (2.3160(7) and 2.5590(7) Å)67 and [MeNacNacTiCl(η2-P-P(PhBu2))] (2.3237(7) and 2.5128(7) Å).65 The Ti1–P3 bond (2.384(9) Å) lies in the range between single and double Ti–P bonds and is comparable to the distance (Ti–P(Pr2)) observed in [(PNP)Ti2(μ2-Pr2)(η2-H2)] (2.385(3) Å) and dramatically shorter than the Ti–P distances observed in complexes: C2TiPPPh2(PMe3) (2.681(3) Å) and [Li–(TMEDA)2][C2Ti(PPPh3)2] (2.709(1) and 2.676(1) Å).64 The planar coordination of the P3 phosphorus atom (ΣP =...
adopts an ionic structure. The titanium atom is \((\text{CO})(\text{PET})_3\) and \(2.1644(7)\) Å for \([\text{Ti}(2,4-	ext{Cl})_2(\text{PET})_3]\). The NCCCN unsaturated backbone of the \(\beta\)-diketiminate ligand is almost planar, with a deviation of 0.3107 Å from planarity. The P1, P2, N1, and N2 atoms lie in the plane (rms deviation from the plane of the diamine ligand framework by 0.236(7) Å), while the chloride ion occupies an axial position (Figure 3).

Crystals of 2 suitable for X-ray diffraction were grown from a diethyl ether solution and crystallized in the monoclinic space group \(P2_1/n\). An X-ray diffraction study established that 2 adopts an ionic structure. The titanium atom is five-coordinate and adopts a pseudosquare pyramidal geometry. The P1, P2, N1, and N2 atoms lie in the plane (rms deviation from the planarity for the P1, P2, N1, and N2 atoms is 0.3107 Å), while the chloride ion occupies an axial position (Figure 3).

The crystallographic structure shows that the phosphanylphosphinidene ligand coordinates side-on to the metal center. The Ti1–P1 distance (2.3353(17) Å) lies in the range between single and double Ti–P bonds. The reported distances of single Ti–P bonds are 2.585(1) Å for \([\text{CP}_2\text{Ti}(\text{CO})(\text{PET})_3]\) and 2.6060(7) Å for \([\text{Ti}(2,4-	ext{C}_3\text{H}_3)_2(\text{PET})_3]\), while double Ti–P bond distances are 2.1644(7) Å in \([\text{BusNacNacTi}:=\text{P}(\text{Trip})(\text{Me})]\) and 2.1831(4) Å in \([\text{McNacNacTi}:=\text{PMe}_{\text{c}}(\text{CH}_2\text{Bu})]\). The Ti–P bond lengths are comparable to those observed for the \(\beta\)-diketiminate complexes with phosphanylphosphinidene ligands \((\text{McNacNacTi}(\text{Cl})\{\eta^2-\text{P-PBu}_2\})\) (2.3160(7) Å) and \([\text{McNacNacTi}(\text{Cl})\{\eta^2-\text{P-PrP}2\}]\) (2.3182(7) Å).

The X-ray structure of 4a clearly displays the migration of the phosphinylphosphinidene moiety to the \(\beta\)-carbon of the \(\text{MeNacNac}^-\) ligand, and the generation of the imide ligand N–Ar. The Ti–N\(_{\text{side}}\) distance is very short (1.724(3) Å), indicating multiple bond character. A similar migration was observed by Mendiola and co-workers in \([\text{Ar} \text{NC}(\text{Me})=\text{CH}(\text{H})\text{(CH})(\text{Me})\text{P} \text{(Trip)} \text{ Ti}=\text{NAr}(\text{CH}_2\text{Bu})]\), \([\text{Ar} \text{NC}(\text{Me})=\text{CH}(\text{Me})\text{P} \text{(Trip)} \text{ (CH}_2\text{Bu}) \text{ Ti}=\text{NAr(OEt)}_2]\), and \([\text{Ar} \text{NC}(\text{Me})=\text{CH}(\text{Me})\text{P} \text{(Cy)} \text{-(CH}_2\text{Bu}) \text{Ti}=\text{NAr(OEt)}_2]\). In 4a, the NCCCP backbone is not planar, and the reduced carbon atom C16 shows a tetrahedral coordination environment (ΣC16 = 331.40(2)°). The H16 atom was localized according to the electron density map (C–H distance is 1.000(2) Å). The N1–C14 distance of 1.416(4) Å is shorter than typical N–C single bonds (1.48 Å) but is comparable to that observed in the reduced ligand reported by Uhl (N–C 1.425(3) Å) and is significantly longer than the N–C distances in de-localized \(\pi\)-bonding systems of non-reduced \(\beta\)-diketiminate ligands \((\text{NacNacTi}(\text{OAr})\{\eta^2-\text{P-PBu}_2\})\), 1.330, 1.348, 1.367, and 1.341 Å. The C14–C15 bond length of 1.370(4) Å is slightly longer than the distances presented in the literature \((\text{MesNacNacTi(H)}\text{Ge})\) 1.344(2) Å and \((\text{Ph}_{\text{2}}\text{Me}_{\text{c}}\text{ac})\text{Al}[\text{N}(\text{Ph})\text{-C(\text{H})(\text{Me})-CH=CH(\text{Me})-N}(\text{Ph})]\) 1.332(3) Å but is still in the range of C=C double bonds, which indicates the presence of a localized C=C double bond in the NCCCP skeleton. The Ti1–P1 (2.4940(9) Å) and P1–P2
(2.1938(12) Å) bond lengths are typical for Ti–P and P–P single bonds.

Crystals of 4b suitable for X-ray analysis were grown from an diethyl ether/pentane mixture. 4b crystallizes in the triclinic system in the P1 space group with two molecules in the unit cell. The molecular structure of 4b also displays a four-coordinate titanium complex bound to two nitrogen atoms, one chloride, and one phosphorus atom (Figure 5).

4b confirms the migration of the phosphorylphosphinidene group to the β-carbon of the MeNacNac ligand and the formation of the imide ligand N–Ar (Ti–Nimide) Ti–N2 1.739(3) Å. In 4b, the C14, C15, C16, P1, and P2 atoms deviate from the plane of the C17 carbon by 1.739(3) Å. In Figure 5, the X-ray structure of 4b reveals the presence of only one set of resonances. This means that this solution contains a racemic mixture of two diastereomers or that the configuration at the Ti-center is not rigid in solution.

4. CONCLUSIONS

We demonstrated two important reaction pathways of [(MeNacNac)Ti(Cl){η^2-P(SiMe3)-P(Bu2)}] with nucleophiles (Ph,PtLi, iBuOLi, (Me3Si)2NLi, and iBu2NLi) in the presence of 12-crown-4, and the reaction outcome depends on the solvent. In toluene, substitution and simultaneous oxidation of titanium occurs with all nucleophiles. Ph,PtLi afforded the most substitution product, and [(MeNacNac)Ti(PtBu2)]{η^2-P-P(Bu2)} (1) was isolated. [(MeNacNac)Ti(Cl){η^2-P-P(Bu2)}]·[Li(12-crown-4)] (2) was isolated for all nucleophiles. Additionally, using fairly harsh crystallization, we also received a 2e− reduction product, [(ArN(COMe)CH(Me)Me)Ti=NAr(η^1-P(SiMe3)-P(Bu2))·[Li(12-crown-4)] (3), which completes the stoichiometry of the reaction and allows us to understand occurring processes in a nonpolar solvent. However, the same protocol with the same molar ratio but in THF solution led to two different Ti(IV) products, 4a and 4b. In both complexes (4a and 4b), the "phospha-Staudinger" displacement in the β-diketiminate ligand and formation of a four-coordinate titanium complexes with the NP ligands was observed. Furthermore, X-ray and NMR spectroscopic investigations revealed that the titanium atoms in both complexes are oxidized and that the organic MeNacNac ligands are reduced. The two redox processes are connected with a transfer of one hydrogen atom: In 4b, the Me group attached to the β-carbon is dehydrogenated, while in 4a, a hydrogen adds to the δ-carbon of the NP hybrid ligand. We also demonstrated that ionic complex 2 is unstable in THF solution and is transformed to complexes 4a and 4b.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00824.

NMR spectroscopic data, crystallographic data, and DFT calculations (PDF)

Accession Codes

CCDC 1859187, 1859190, 1859191, 1991067, and 2001101 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic
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**Notes**

The authors declare no competing financial interest.

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