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Reactions of Lithiated Diphosphanes $R_2P-P(SiMe_3)Li$ (R = *t*Bu and *i*Pr) with [^{Me}NacnacTiCl₂·THF] and [^{Me}NacnacTiCl₃]. Formation and Structure of Titanium^{III} and Titanium^{IV} β -Diketiminato Complexes Bearing the Side-on Phosphanylphosphido and Phosphanylphosphinidene Functionalities

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S Supporting Information

ABSTRACT: β-Diketiminate complexes of Ti^{III}-containing phosphanylphosphido ligands [^{Me}NacnacTi(Cl){ η^2 -P(SiMe₃)-PR₂}] (^{Me}Nacnac⁻ = [Ar]NC(Me)CHC(Me)N[Ar]; Ar = 2,6-*i*Pr₂C₆H₃) were prepared by reactions of [^{Me}NacnacTiCl₂·THF] with lithium derivatives of diphosphanes R₂P–P(SiMe₃) Li (R = *t*Bu, *i*Pr) in toluene solutions. Surprisingly, reactions of [^{Me}NacnacTiCl₂·THF] with R₂P–P(SiMe₃)Li in THF solutions led to Ti^{IV} complexes containing phosphanylphosphinidene ligands [^{Me}NacnacTi(Cl)(η^2 -P-PtBu₂)] via an autoredox path involving a migration of a nitrene NAr from the Nacnac skeleton to the Ti centers. Solid-state structures of [^{Me}NacnacTi(Cl)(η^2 -P-PtBu₂]] (1a) and [^{Me}NacnacTi(Cl)(η^2 -P-PtBu₂]] (1a) and [^{Me}NacnacTi(Cl)(η^2 -P-PtBu₂]] (1b)



and $[^{Me}NacnacTi(Cl)(\eta^2-P-PiPr_2)]$ (2b) were established by the single-crystal X-ray diffraction and display clearly side-on geometry of the (Me₃Si)P-PR₂ and P-PR₂ moieties in the solid state. Phosphanylphosphinidene complexes $[^{Me}NacnacTi-(Cl)(\eta^2-P-PR_2)]$ indicate that the ³¹P NMR resonances of phosphinidene P atoms appear at a very low field in solution and in the solid state.

1. INTRODUCTION

Stable phosphinidene complexes of transition metals have been intensively explored mainly because of their role as P-R transfer reagents in synthetic organic chemistry.¹ Nevertheless, they are less studied than analogous nitrene complexes.² The stable phosphinidene complexes of these metals display evident nucleophilic properties.³⁻⁶ The phosphinidene complexes of tantalum stabilized by N_3N ligand (N_3N = (Me₃SiNCH₂CH₂)₃N) and phosphinidene complexes of zirconium stabilized by Cp (η^5 -C₅H₅) ligands with bulky R groups on the P-R ligand display phospha-Wittig reactivity and have been thoroughly investigated by Schrock's,⁷ Stephan's and Protasiewicz's groups.^{1,8–13} Our group has studied the metathesis reactions of $R_2P-P(SiMe_3)Li$ with transition-metal compounds bearing chloride ligands to introduce the phosphanylphosphinidene moiety (R₂P-P) into the resulting complexes. The group 4 complexes with Cp ancillary ligands display diverse reactivity that is metal-dependent. Thus, $[Cp_2ZrCl_2]$ reacts with $tBu_2P-P(SiMe_3)Li$ in the presence of PMe₂Ph to yield $[Cp_2Zr(PPhMe_2)(\eta^1-P-PtBu_2)]$ —the only complex of a transition metal with the terminal phosphanylphosphinidene ligand.¹³ The reactions of R₂P-P(SiMe₃)Li with $[Ind_2ZrCl_2]$ (Ind = C₉H₇) and PMe₂Ph do not yield related phosphanylphosphinidene complexes but the phosphido derivatives $[Ind_2Zr(Cl){(Me_3Si)P-PR_2-\kappa P^1}]$ as the main products.¹⁴ There is only one known phosphinidene complex of hafnium [Cp₂(PMe₃)Hf=P-Mes*].¹⁵ Reactivity of $[Cp_2HfCl_2]$ was much lower than that of $[Cp_2ZrCl_2]$, and the main products of its reactions with *t*Bu₂P-P(SiMe₃)Li were monophosphido complexes [Cp₂Hf(Cl){(Me₃Si)P- $PR_2 - \kappa P^1$].¹⁶ The formation of phosphido and phosphinidene complexes of titanium^{IV} with Cp spectator ligands via a metathesis route (vide infra) is not possible due to oxidative dimerization of phosphido groups and formation of titanium^{III} compounds.^{17–19} The reactions of $tBu_2P-P(SiMe_3)Li$ with [Cp₂TiCl₂] or with [CpCp*TiCl₂] in the presence of tertiary phosphines do not yield Ti^{IV} phosphanylphosphido and phosphanylphosphinidene complexes but instead afforded several Ti^{III} compounds without phosphorus ligands.²⁰ The

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essential breakthrough in the chemistry of phosphinidene complexes of Ti^{IV} was achieved by Mindiola and co-workers. The use of sterically encumbered β -diketiminate ancillary ligands^{21–24} or pincer PNP²⁵ ligands and the oxidation of these Ti^{III} complexes with Ag^I salts^{25,26} afforded the formation of Ti^{IV} phosphinidene complexes. At present we are investigating the synthesis and reactivity of phosphanylphosphinidene complexes of Mo^{VI} and W^{VI} with ancillary imido ligands²⁷⁻³⁰ and Fe^{II} complexes with β -diketiminate ancillary ligands.³¹ All the resulting phosphanylphosphinidene complexes revealed the side-on coordination for incoming R₂P-P groups with little phospha-Wittig character.²⁹ Therefore, we extended our studies to Ti^{III} and Ti^{IV} complexes to determine the geometry of resulting complexes and to obtain reagents with the expected high phospha-Wittig reactivity. Herein we describe novel synthetic routes to phosphanylphosphido Ti^{III} and phosphanylphosphinidene Ti^{IV} complexes bearing β -diketiminate and chlorido spectator ligands. [Ar]NC(Me)CHC(Me)N[Ar] (^{Me}Nacnac⁻; Ar = $2,6-iPr_2C_6H_3$) was chosen as an ancillary ligand because of its robust and "non-innocent" character and because of its ability to stabilize reactive metal fragments.^{32,33} Moreover the very recent report of Bertrand and co-workers of the synthesis and properties of a "bottle-able" phosphanylphosphinidene has allowed a direct comparison of the free and ligated phosphanylphosphinidene. This species can be isolated only because of the electronic stabilization by a phosphanyl group bearing two nitrogen substituents and the steric protection by the substituents on nitrogen atoms.^{34,35}

2. EXPERIMENTAL SECTION

Toluene and tetrahydrofuran (THF) were dried over Na/benzophenone and distilled under argon. Pentane was dried over Na/benzophenone/diglyme and distilled under argon. All manipulations were performed in flame-dried Schlenk-type glassware on a vacuum line. ³¹P, ¹³C, and ¹H spectra in solution were recorded on Bruker AV300 MHz and Bruker AV400 MHz (external standard tetramethylsilane for ¹H, ¹³C; 85% H₃PO₄ for ³¹P). Literature methods were used to prepare $tBu_2P-P(SiMe_3)Li\cdot nTHF,^{36}$ $iPr_2P-P(SiMe_3)Li\cdot nTHF,^{37}$ [NacnacTiCl₂·THF],²¹ [NacnacTiCl₂],³⁸ and [NacnacTiCl₃].³⁹ The yields of the reactions leading to phosphanylphosphinidene complexes **2a1**, **2a2**, and **2b** are calculated in comparison to amount of used [^{Me}NacnacTiCl₂·THF].

2.1. Preparation of [MeNacnacTi(CI)(η^2 -P-PtBu₂)] 2a1 (Method 1). A suspension of [MeNacnacTiCl₃] (0.200 g, 0.349 mmol) in 5 mL of THF was slowly added to the solution of tBu₂P-P(SiMe₃)Li-2.5 THF (0.303 g, 0.694 mmol) in 5 mL of THF at -35 °C. After 20 h at room temperature THF was removed from the green-brown solution, and pentane was added to the solid product. The resulting solution was filtrated, and the filtrate was concentrated. After 2 d homogeneous green crystals were isolated. For the crystals the unit cell was investigated by the X-ray method and characterized as 2a1 complex (0.078 g, yield 33%). NMR data for **2a1**: ¹H NMR (C_6D_6) δ 7.04 (m, 6H, C_6H_3 , 4.64 (s, 1H, γ -CH), 3.76 (sept. 2H, J = 6.72 Hz, CHMe₂), 3.18 (sept. 2H, J = 6.72 Hz, CHMe₂), 1.57 (d, 6H, CHMe₂, J = 6.72Hz), 1.32 (s, 6H, C(Me)CHC(Me)), 1.317 (d, 6H, CHMe₂, J = 6.72Hz), 1.04 (d, 18H, tBu, $J_{\rm P-H}$ = 14.67 Hz), 0.98 (d, 6H, J = 6.72 Hz, CHMe), 0.96 (d, 6H, J = 6.72 Hz, CHMe₂); ¹³C NMR (C₆D₆) δ 166.27 (C(Me)CHC(Me)), 142.71 (s, $i-C_6H_3$), 141.61 (s, $o-C_6H_3$), 127.00 (s, p-C₆H₃), 124.64 (s, m-C₆H₃), 124.00 (s, m-C₆H₃), 96.86 (C(Me)CHC(Me)), 40.04 $(PCMe_3)$, 32.45 $(d, J = 5.87, Me_3CP)$, 29.25 (CHMe₂), 28.32 (CHMe₂), 26.02 (CHMe₂), 25.14 (CHMe₂), 24.31 (C(Me)CHC(Me)), 24.29 (CHMe₂), 23.61 (CHMe₂); ³¹P NMR (C₆D₆) 843.8 (d, P-PtBu₂, J_{P-P} = 457.76 Hz), 143.6 (d, P-PtBu₂, $J_{\rm P-P} = 457.76$ Hz).

2.2. Preparation of [^{Me}NacnacTi(Cl){ η^2 -P(SiMe₃)-PtBu₂]] 1a. [^{Me}NacnacTiCl, THF] (0.547 g, 0.9 mmol) in 5 mL of toluene was

slowly added to the solution of $tBu_2P-P(SiMe_3)Li\cdot2.5THF$ (0.449 g, 1 mmol) in 5 mL of toluene at -35 °C. After addition the reaction mixture was stirred for 2 h at room temperature. The solvent was then evaporated under reduced pressure, and a green solid residue was extracted with 30 mL of pentane. The solution was filtered, concentrated to 20 mL, and stored at +4 °C. After 2 h, light green crystals of 1a were obtained (0.428 g, yield 60.4%). Anal. Calcd for C_{42.5}H₇₄C₁₁N₂P₂Ti₁: C, 64.91; H, 9.48; N, 3.56. Found: C, 64.12; H, 9.33; N, 3.63%.

2.3. Preparation of [^{Me}NacnacTi(Cl){ η^2 -P(SiMe₃)-PiPr₂}] 1b. [^{Me}NacnacTiCl₂·THF] (0.250 g, 0.411 mmol) in 5 mL of toluene was added at -30 °C to a solution of iPr_2P -P(SiMe₃)Li·2.0THF (0.170 g, 0.457 mmol) in 5 mL of toluene. The mixture was then stirred for 2 h at room temperature. The solvent was evaporated under reduced pressure, and the green solid residue was dissolved in 30 mL of pentane. The resulting solution was filtered and concentrated to 20 mL. After 1 h at +4 °C green crystals of 1b were obtained (0.193 g, yield 65%). Anal. Calcd for C₃₈H₆₄ClN₂P₂Si₁Ti: C, 63.19; H, 8.93; N, 3.88. Found: C, 63.20; H, 9.05; N, 3.79%.

2.4. Preparation of [^{Me}NacnacTi(Cl)(η^2 -P-PtBu₂)] 2a1 (Method 2) and Isolation of [{ArNC(Me)CHC(Me)}Ti(NAr){P(SiMe3)-PtBu₂}]⁻[Li(THF)₄]⁺ 3a. [^{Me}NacnacTiCl₂·THF] (0.332 g, 0.561 mmol) in 5 mL of THF was added to a cold solution (-30 °C) of tBu₂P-P(SiMe₃)Li·2.8THF (0.514 g, 1.123 mmol) in 5 mL of THF. The solution was stirred at room temperature for 1 d. Then the solvent was removed under reduced pressure, and the green-red oily residue was extracted with 25 mL of pentane. The resulting solution was filtered, concentrated to 5 mL, and stored at +4 °C. After 4 d the green crystals of 2a1 were obtained (0.150 g, 39%). Anal. Calcd for C37H59Cl1N2P2Ti1: C, 65.63; H, 8.78; N, 4.14. Found: C, 65.55; H, 8.92; N, 3.92. All NMR spectra for 2a1 compound are described in the Section 2.1. The mother liquor remaining after separation of 2a1 was concentrated to 2 mL. After several hours red oil separated and crystallized a few days later yielding dark red crystals of 3a (0.086 g). Anal. Calcd for C₅₆H₁₀₃TiN₂P₂O₄SiLi: C, 66.38; H, 10.25; N, 2.76. Found: C, 64.39; H, 9.49; N, 2.64%. **2.5. Preparation of** [^{Me}NacnacTi(Cl)(η²-P-PtBu₂)] 2a2. A

2.5. Preparation of [^{Me}**NacnacTi(Cl)**(η^2 -**P-PtBu**₂)] **2a2.** A solution of $tBu_2P-P(SiMe_3)Li\cdot 3THF$ (0.54 g, 1.143 mmol) in 5 mL of THF was added dropwise to a solution of [^{Me}NacnacTiCl₂] (0.306 g, 0.572 mmol) in 5 mL of THF cooled to -40 °C. The mixture was heated to room temperature and kept at this temperature for 2 d. Then the solvent was evaporated under the reduced pressure, and the greenyellow oily residue was extracted with pentane (20 mL). The resulting solution was filtered, concentrated to 3 mL, and stored at -30 °C. After one week, green crystals (plates) of **2a2** were separated (0.032 g, yield 5.4%). Anal. Calcd for C₃₇H₅₉ClN₂P₂Ti: C, 65.63; H, 8.78; N, 4.14. Found: C, 65.54; H, 8.88; N, 3.95%.

2.6. Preparation of [^{Me}NacnacTi(Cl)(η^2 -P-PiPr₂)] 2b. $\left[^{Me}NacnacTiCl_{2}{\cdot}THF\right]$ (0.182 g, 0.309 mmol) in 5 mL of THF was added dropwise to a solution of iPr₂P-P(SiMe₃)Li·2.0THF (0.230 g, 0.618 mmol) in 5 mL of THF cooled to -30 °C. The mixture was then stirred overnight at room temperature. The solvent was evaporated under reduced pressure; the oily residue was dissolved in pentane, and the resulting solution was filtered. The filtrate was concentrated to 2 mL and stored at -30 °C. After 6 d, dark green crystals of 2b were separated (0.138 g, yield 35%). Anal. Calcd for C₅₇H₅₅ClN₂P₂Ti: C, 64.76; H, 8.54; N, 4.32. Found: C, 64.74; H, 8.57; N, 4.30%. ¹H NMR (C_6D_6) δ 7.14 (m, 6H, C_6H_3), 4.67 (s, 1H, γ -CH), 3.96 (sept. 2H, J = 6.72 Hz, CHMe₂), 3.12 (sept. 2H, J = 6.72 Hz, $CHMe_2$), 1.88 (m, 2 H, PCHMe₂), 1.60 (d, 6H, J = 6.72 Hz, $CHMe_2$), 1.42 (d, 6H, J = 6.72 Hz, CHMe₂), 1.41 (s, 6H, C(Me)CHC(Me)), 1.29 (dd, 6H, ${}^{3}J_{PCCH} = 16.14$ Hz, ${}^{3}J_{HCCH} = 7.09$, PCHMe₃), 1.09 (d, 6H, J = 6.72 Hz, CHMe₂), 1.08 (d, 6H, J = 6.72 Hz, CHMe₂), 0.92 (dd, 6H, ${}^{3}J_{PCCH} = 16.14 \text{ Hz}, {}^{3}J_{HCCH} = 7.09, \text{PCH}Me_{2}$; ${}^{13}\text{C} \text{ NMR} 166.28 (C(Me)CHC(Me)), 142.82 (s,$ *i* $-C_{6}H_{3}), 141.42 (s,$ *o* $-C_{6}H_{3}), 127.09 (s,$ p-C₆H₃), 124.67 (s, m-C₆H₃), 124.05 (s, m-C₆H₃), 96.10 (C(Me) CHC(Me)), 29.77 (d, J_{P-C} = 7.89 Hz, PCHMe₂), 29.08 (CHMe₂), 28.13 (CHMe2), 26.16 (CHMe2), 24.71 (CHMe2), 24.43 (C(Me)-CHC(Me)), 24.11 ($CHMe_2$), 23.55 ($CHMe_2$), 22.52 ($PCHMe_2$),

Scheme 1. Reaction of $[MeNacnacTiCl_3]$ with $tBu_2P-P(SiMe_3)Li$ in Toluene



Ar = 2,6-*i*Pr₂Ph

Scheme 2. Reaction of [MeNacnacTiCl₃] with R₂P-P(SiMe₃)Li in THF



Scheme 3. Reaction of [^{Me}NacnacTiCl₂·THF] with 1 equiv of $R_2P-P(SiMe_3)Li\cdot nTHF$ in Toluene (R = tBu, iPr)



21.54 (PCHMe₂); ³¹P NMR (C_6D_6) 823.8 (d, P-PtBu₂, $J_{P-P} = 443.23$ Hz), 118.4 (d, P-PtBu₂, $J_{P-P} = 443.23$ Hz). **2.7. Preparation of [^{Me}NacnacTi(Cl)(\eta^2-P-PtBu₂)] 2a1 (Method**

2.7. Preparation of [^{Me}NacnacTi(Cl)(η^2 -P-PtBu₂)] **2a1** (Method **3**). A solution of [iBu_3PAgCl]₄ (0.069 g, 0.05 mmol) in 1 mL of toluene was added to a solution of **1a** (0.150 g, 0.200 mmol) in 3 mL of toluene cooled to -30 °C. Then the reaction mixture was stirred for 3 h at room temperature. The green solution turned green-brown. The solvent was removed under vacuum. The solid product was dissolved in 20 mL of pentane and filtered. The filtrate was concentrated to 2 mL and left at +4 °C. Dark green crystals of **2a1** were obtained after a few hours (0.064 g, yield 49.23%).

2.8. Preparation of [^{Me}NacnacTi(Cl)(η^2 -P-PtBu₂)] **2a1** (Method **3**). A solution of iBu_3PAgI (0.058 g, 0.033 mmol) in 2 mL of toluene was added to a cold solution ($-30 \,^{\circ}C$) of **1a** (0.100 g, 0.133 mmol) in 3 mL of toluene. The mixture was stirred for 5 d at room temperature. The green solution turned green-brown. The solvent was removed under reduced pressure, and the solid product was dissolved in 30 mL of pentane and filtered. The filtrate was evaporated to a small volume and placed at $-30 \,^{\circ}C$. Green crystals of **2a1** were obtained after 24 h (0.038 g, yield 44.18%).

3. RESULTS AND DISCUSSION

3.1. Reactivity of $tBu_2P-P(SiMe_3)Li$ and iPr_2P-P -(SiMe_3)Li with [^{Me}NacnacTiCl_3]. According to ³¹P NMR spectroscopy the reaction of $tBu_2P-P(SiMe_3)Li$ with [^{Me}NacnacTiCl_3] in molar ratio 1:1 in toluene- d_8 (NMR tube) does not lead to the formation of a putative phosphanylphosphido Ti^{IV} complex [^{Me}NacnacTiCl_{ η^1 -P-(SiMe_3)-PtBu_2]] nor to [^{Me}NacnacTi(Cl)(η^2 -P-PtBu_2)] (2a). In this run resonances of two diastereomers of tBu_2P- $P(SiMe_3)-P(SiMe_3)-PtBu_2^{40}$ were detected, which points to the dimerization of $tBu_2P-P(SiMe_3)$ groups. Additionally signals of tBu_2PH , $tBu_2P-P(SiMe_3)H$ and probably of tBu_2P-PH_2 were found. These products support a radical mechanism of the dimerization. The crystallization from pentane solution resulted in separation of [^{Me}NacnacTiCl₂] as a red solid, even if the run was conducted at -30 °C (Scheme 1).

According to the ³¹P NMR spectroscopic examination of the reaction solutions, $tBu_2P-P(SiMe_3)Li$ and $iPr_2P-P(SiMe_3)Li$ react with [^{Me}NacnacTiCl₃] in molar ratio 2:1 in THF yielding phosphanylphosphinidene complexes [^{Me}NacnacTi(Cl)(η^2 -P-PtBu_2)] (**2a**) and [^{Me}NacnacTi(Cl)(η^2 -P-PiPr_2)] (**2b**), respectively (Scheme 2).

The yields of $[^{Me}NacnacTi(Cl)(\eta^2-P-PtBu_2)]$ were modest, and the reproducibility was poor, because the runs shown in Scheme 2 were accompanied by a dimerization of $R_2P-P(SiMe_3)_2$ moieties and formation of $tBu_2P-PH-P-(SiMe_3)-PtBu_2$ or $iPr_2P(1)-P(2)H-P(3)(SiMe_3)-P(4)iPr_2$, respectively. The identity of the latest compound was established by comparison of its ³¹P NMR data: P(1) 1.70 ppm, P(2) -142.4 ppm, P(3) -177.4 ppm, P(4) 1.65 ppm, ¹J_{P(1)-P(2)} 197.3 Hz, ²J_{P(1)-P(3)} 120.3 Hz, ³J_{P(1)-P(4)} 4.7 Hz, ¹J_{P(2)-P(3)} 243.5 Hz, ²J_{P(2)-P(4)} 12.5 Hz, ¹J_{P(2)-H} 184.0 Hz, ¹J_{P(3)-P(4)} 301.4 Hz, with the known data for $tBu_2P-PH-P(SiMe_3)-PtBu_2$.¹¹ Additionally formations of $R_2P-P(SiMe_3)-H$, $R_2P-P(SiMe_3)-PR_2$, and $R_2P-PH-PR_2$ were observed. **2a** was isolated via crystallization from the pentane solution, which Scheme 4. Reaction of [MeNacnacTiCl₂·THF] with tBu₂P-P(SiMe₃)Li in THF^a



^{*a*}Molar ratio \approx 3:5.

Scheme 5. Reactions of $[^{Me}NacnacTi(Cl)\{\eta^2-P(SiMe_3)-PtBu_2\}]$ 1a with $[iBu_3PAgX]$ in Toluene



was however complicated due to the concomitant crystallization of [^{Me}NacnacTiCl₂·THF]. The attempts to isolate **2b** failed. Thus, this way to introduce R₂P–P functionalities directly to titanium^{IV} center was not efficient, and the introduction of Me₃SiP–PtBu₂ group was not possible at all.

3.2. Reactivity of $tBu_2P-P(\dot{SiMe_3})Li$ and $iPr_2P-P(\dot{SiMe_3})Li$ toward [^{Me}NacnacTiCl₂·THF]. To avoid oxidative dimerization during the metathesis reactions involving [^{Me}NacnacTiCl₃] the Ti^{III} precursor [^{Me}NacnacTiCl₂·THF] was used. The metathesis in toluene involving [^{Me}NacnacTiCl₂·THF] and R₂P-P(SiMe₃)Li·*n*THF in molar ratio 1:1 yielded paramagnetic complexes [^{Me}NacnacTi(Cl){ η^2 -P(SiMe₃)-PiBu₂}] (1a) and [^{Me}NacnacTi(Cl){ η^2 -P(SiMe₃)-PiPr₂}] (1b) as green solids with good yields (Scheme 3).

The ³¹P NMR spectroscopic examination of reaction solutions indicated the presence of additional diamagnetic compounds. A run leading to the isolation of **1a** showed signals of **2a**, $tBu_2P-P(SiMe_3)_2$, $tBu_2P-P(SiMe_3)H$, and small signals of tBu_2PH together with two unidentified AX patterns of low intensity: (a) 81.3 ppm, -123.6 ppm (¹J_{P-P} 476.8 Hz); (b) 27.4 ppm, -100.3 ppm (¹J_{P-P} 366.8 Hz). **1a** dissolved in toluene- d_8 displayed weak resonance of **2a** and a weak singlet of tBu_2PH . Similarly reaction solution from a run leading to **1b** showed signals of **2b**, $iPr_2P-P(SiMe_3)_2$, $iPr_2P-P(SiMe_3)H$, P-(SiMe₃)₂H, and unidentified AX pattern 591.9 ppm, 125.8 ppm (470.1 Hz). **1b** dissolved in toluene- d_8 displayed weak resonance of **2b**, $iPr_2P-P(SiMe_3)H$ and $P(SiMe_3)_2H$.

The reaction outcomes of $[^{Me}NacnacTiCl_2 \cdot THF]$ with $R_2P-P(SiMe_3)Li \cdot nTHF$ in molar ratio 1:2 in THF were quite different, and diamagnetic Ti^{IV} complexes **2a** and **2b** were isolated as green solids with good yields (Scheme 4).

[^{Me}NacnacTi(Cl)(η^2 -P-PtBu₂)] (2a) was isolated in two forms, the main isomer denoted as 2a1 and second isomer

denoted as 2a2, once isolated with low yield. The ³¹P NMR spectroscopic examination of reaction solutions leading to 2a1 and 2a2 showed the same AX patterns 842.8 ppm, 143.6 ppm (457.76 Hz; denoted as 2a), $tBu_2P-P(SiMe_3)_2$ and $tBu_2P-P(SiMe_3)H$. Isolated 2a1 and 2a2 are stable in solution, and in toluene- d_8 they displayed the same ³¹P NMR spectra (denoted as 2a) and weak resonances of tBu_2PH . Similarly reaction solution of a run leading to 2b showed AX pattern 823.8 ppm, 118.4 ppm (443.23 Hz) together with weak signals of $iPr_2P-P(SiMe_3)_2$, $iPr_2P-P(SiMe_3)H$, and $P(SiMe_3)_2H$ and not identified AX pattern 642.9 ppm, 127.6 ppm (466.0 Hz). 2b is stable in solution.

The reaction of $tBu_2P-P(SiMe_3)Li$ with [^{Me}NacnacTiCl₂· THF] in THF was also tested in molar ratio 1:1 to explain the results of runs in THF (2:1). The only product was **2a** isolated as **2a1**. In a run conducted in THF in molar ratio 2:1 in a bigger scale, a paramagnetic Ti^{III} complex **3a** was isolated and as a red solid structurally characterized. Thus, for this reaction the stoichiometry presented in Scheme 4 was suggested.

Having considered that contraction of six-membered ring {ArN-C(Me)-CH-C(Me)-NAr}Ti of 1a to five-membered ring {ArN-C(Me)-CH-C(Me)}Ti of 3a and transfer of ArN onto Ti atom (the transformation $1a \rightarrow 3a$) can be seen as $2e^{-1}$ reduction,⁴¹⁻⁴⁴ which was accompanied by the $1e^{-1}$ oxidation $1a \rightarrow 2a$ (of two molecules), the reaction presented in Scheme 4 can be interpreted as an autoredox process.

The examination of stabilities of 1a and 1b in solvents of different donor properties clearly revealed (³¹P NMR spectrum) that 1a was relatively stable in toluene and decomposed very slowly at room temperature yielding 2a, tBu_2PH , $tBu_2P-P(SiMe_3)H$, and $tBu_2P-P(SiMe_3)_2$ together with not identified compound (³¹P NMR spectrum: AX pattern 27.4 ppm and -104.3 ppm, ¹ J_{P-P} 366.5 Hz). Differently 1a and

1b were not stable in THF solution and rearranged even at low temperature (−23 °C). **1b** rearranged relatively rapidly at room temperature yielding **2b** (after one week the isolated yield \approx 37%). **1a** rearranged slower with the formation of **2a** (isolated as **2a1**, contaminated with **1a**). Even after three weeks (0.19 M **1a** in THF-*d*₈) some amounts of **1a** were observed in solution (¹H NMR broad signals). The evolution of a new AX pattern (³¹P NMR, 64.6 and −244.4 ppm, ¹*J*_{P−P} = 357.5 Hz) parallel to the formation of **2a** was also observed, but this compound decomposed within six weeks with a continuous growth of signals of *t*Bu₂P−P(SiMe₃)₂. In conclusion, the stoichiometry of the reaction of R₂P−P(SiMe₃)₁Li with [^{Me}NacnacTiCl₂·THF] in THF should be considered as accordant to Scheme 4, because the spontaneous transformations of **1** → **2** in THF solution were significantly slower.

Considering the crucial role of redox processes in the reactions of Ti^{III} complexes **1a** and **1b**, the compounds of Ag^I as external oxidants similar to oxidation by AgOTf or AgBPh₄ reported by Mindiola and co-workers^{45–47} were tested. Reactions of toluene solutions of **1a** with [*i*Bu₃PAgX] (X = Cl, I), molar ratio 1:1 at room temperature, led to formation of a silver mirror concomitant with the formation of **2a** isolated as **2a1** and *i*Bu₃P (Scheme 5). The ³¹P NMR spectroscopic studies of reaction solutions of **1a** with [*i*Bu₃PAgX] indicated that [*i*Bu₃PAgI] has reacted much slower than [*i*Bu₃PAgCl], and no traces of [^{Me}NacnacTi(I)(η^2 -P-PtBu₂)] were found. This oxidation reaction represents a very nice entrance to phosphanylphosphinidene complexes with NacnacTi^{IV} center (Scheme 5). It produces only one soluble and well-crystallizing solid **2a** [^{Me}NacnacTi(Cl)(η^2 -P-PtBu₂)] very easily and with a high purity.

The **2b** complex was also obtained successfully in the similar reaction with [*i*Bu₃PAgCl], but in the ¹H NMR spectrum the paramagnetic signals were still presented.

The phosphinidene ³¹P resonance in solution was observed for 2a and 2b at very low field, rather typical for complexes with terminal "bent" phosphinidene ligands.¹⁴ The X-ray structures of 2a1, 2a2, and 2b indicate in the solid state a side-on bonding of R_2PP moiety (see Section 3.3). To clear these problems density functional theory (DFT) calculations to elucidate ³¹P NMR spectra for complexes 2a1 and 2a2 were run.⁴⁸⁻⁶¹ The calculated δ and ${}^{1}J_{P-P}$ values for 2a1 787 ppm, 167 ppm, and ${}^{1}J_{P-P}$ = 393 Hz and for **2a2** 725 ppm, 127 ppm, and ${}^{1}J_{P-P}$ = 423 Hz are relatively near to observed values for 2a in solution. Additionally the solid-state ³¹P NMR spectrum of 2a1 displays two resonances forming an AX pattern. The chemical shift of one doublet ($\delta = 147.0$ ppm, ${}^{1}J_{pp} = 447$ Hz) is very close to the value obtained for the tBu₂P resonances of 2a in the solution ³¹P NMR spectrum. The second signal consists of a system of side bands that spreads over the whole spectrum. The central line, which denotes the isotropic chemical shift, cannot be unambiguously established but is very probably located at $\delta \approx$ 600-900 ppm. A large shielding tensor anisotropy is additionally supported by the data calculated for 2a1 and 2a2. Principal components of shielding tensor for phosphinidene P atom (2a1) are -1654.2, -211.4, and 296.9; for tBu₂P (2a1) they are 10.8, 92.3, and 186.1. This data set indicates a very strong anisotropy for phosphinidene P atom (from 1918 ppm to -33 ppm) and the modest anisotropy for PtBu₂ (from 253 to 78 ppm) that was observed for the solid-state ³¹P NMR spectrum of 2a1. Thus, probably 2a1 and 2a2 do not adopt a terminal geometry in solution but do adopt a side-on geometry of tBu_2P-P ligand both in solution and in the solid state. The phosphinidene P atoms in these side-on bonded complexes are unusually deshielded, a feature that until now was attributed to complexes with terminal bent phosphinidene ligands. The comparison with ³¹P NMR data of a recently reported "bottle-able" phosphanylphosphinidene ($\delta_{P1} = -200.4 \text{ ppm}, \delta_{P2R2} = 80.2 \text{ ppm}, {}^{1}J_{P-P} = 884 \text{ Hz}$) has experienced an enormous downfield shift, which seems however to be dependent on electron deficiency on metal center. Thus, for complexes of electron-rich late transition metal at low oxidation state Pt⁰ in [$(pTol_3P)_2Pt\{\eta^2-P1=P2(NiPr_2)_2\}$] $\delta_{P1} = -63.1 \text{ ppm}, \delta_{P2} = 76.9 \text{ ppm}, {}^{1}J_{PP} = 662 \text{ Hz}^{62}$ this downfield shift is relatively small, but for electron-poor early transition metal in [{Ar-(Np)N}_3Nb(\eta^2-P1=P2tBu_2)] (Np = neopentyl) $\delta_{P1} = 405.5 \text{ ppm}, \delta_{P2} = 80.6 \text{ ppm}, and {}^{1}J_{PP} = 425 \text{ Hz}^{63}$ it is very significant and for **2a** $\delta_{P1} = 843.8 \text{ ppm}, \delta_{P2} = 143.6 \text{ ppm}, and {}^{1}J_{PP} = 457.76 \text{ Hz}$ this downfield shift is already enormous.

3.3. X-ray Structural Analysis. The single crystals of 1a and 1b suitable for X-ray diffraction were grown from the saturated pentane solutions. 1a crystallizes with one molecule of pentane in the unit cell in triclinic space group $P\overline{1}$. The pentane molecule lies on the *b* axis and displays disorder (occupancy 50:50, Figure S1 Supporting Information). 1a reveals a five-coordinated titanium complex in a distorted square pyramidal environment^{39,64} at the metal center, where the chloride ion occupies an axial position (Figure 1). For isostructural 1b see Supporting Information.



Figure 1. Molecular structure of $[^{Me}NacnacTi(Cl){\eta^2-P(SiMe_3)-PtBu_2}]$ (1a), hydrogen atoms omitted for clarity. Important bond lengths (Å), bond angles (deg): Ti1–N1 2.069(4), Ti1–N2 2.088(4), Ti1–Cl1 2.309(2), Ti1–P1 2.445(2), Ti1–P2 2.6759(18), P1–P2 2.125(2), P1–Si1 2.236(3); N1–Ti1–N2 88.94(16), N1–Ti1–Cl1 99.36(14), Cl1–Ti1–P1 128.52(7), Cl1–Ti1–P2 99.32(6), P1–Ti1–P2 48.78(5), P2–P1–Si1 124.17(9), P2–P1–Ti1 71.28(7), Si1–P1–Ti1 160.46(9). The sum of the angles around the P atoms: Σ P1 = 355.91, Σ P2 = 335.74.

1a contains the phosphanylphosphido ligand in a near sideon geometry, Ti1–P1 2.445(2) Å, Ti1–P2 2.6759(18) Å. The very short distance between two phosphorus atoms is 2.125(2) Å, and it is shorter than in phosphanylphosphido complexes with η^1 -coordination, that is, $[Cp_2Zr(Cl){P(SiMe_3)-PiPr_2-\kappa P^1}]$ 2.187 Å, $[Cp_2Hf(Cl){P(SiMe_3)-PiPr_2-\kappa P^1}]$ 2.185 Å, and $[Ind_2Zr(Cl){P(SiMe_3)-PiPr_2-\kappa P^1}]$ 2.201 Å.^{14,16} The geometry around P1 ($\sum P1 = 355.91^\circ$) is almost planar, and P2 ($\sum P2 = 335.74^\circ$) is more pyramidal. The Ti1–P1 distance of 2.445(2)



Figure 2. Molecular structures of [^{Me}NacnacTiCl(η^2 -Pr*B*u₂)], isomer **2a1** on the left, isomer **2a2** on the right side of the figure, hydrogen atoms omitted for clarity. Important bond lengths (Å), bond angles (deg) for **2a1**: N1–Ti1 2.0467(17), N2–Ti1 2.0774(17), P1–P2 2.1022(8), P1–Ti1 2.3160(7), P2–Ti1 2.5590(7), Cl1–Ti1 2.2894(7); P1–P2–Ti1 58.61(2), N1–Ti1–N2 92.80(7), P1–Ti1–P2 50.79(2), $\sum P2 = 329.07$; for **2a2**: Ti1–N1 2.034(7), Ti1–N2 2.072(8), Ti1–Cl1 2.329(3), Ti1–P1 2.334(3), Ti1–P2 2.523(3), P1–P2 2.112(4); N1–Ti1–N2 92.8(3), P1–Ti1–P2 51.36(10), P1–Ti1–P2 51.36(10).

Å is shorter than this seen in related complex [Cp₂TiP-(SiMe₃)₂] 2.467(1) Å,⁶⁵ while the Ti1–P2 2.6759(18) Å is comparable than those in complexes [(N₂P₂)TiMe₂] 2.6215(6) Å (N₂P₂ = *t*BuN–SiMe₂N(CH₂CH₂P*i*Pr₂))⁶⁶ and [Cp₂Ti(κ^2 -O,P-O-C₆H₄-PiPr₂)] 2.7127(8) Å.⁶⁷

The NCCCN unsaturated backbone of the ligand is almost planar, with 0.0423(2) Å deviation from planarity; the titanium atom is out of plane of the diamine ligand framework by 0.959(4) Å. The value of bond lengths of the N–C and C–C in the backbone of the β -diketiminato ligand are between single and double bond lengths. These results suggest the delocalization of the double bonds of the ligand N1–C28 1.342(7) Å, C27–C28 1.382(8) Å, C26–C27 1.405(8) Å, N2–C26 1.345(7) Å.

The deep green cubes of **2a1** were grown from a saturated pentane solution and crystallized in the monoclinic space group $P2_1/c$. This compound is similar to the five-coordinated titanium complexes with a distorted square pyramidal environment of the metal center^{39,64} where the chloride ion occupies an axial position (Figure 2).

The β -diketiminato ligand coordinates to the metal center through two nitrogen atoms. The phosphanylphosphinidene ligand coordinates side-on with Ti1-P1 = 2.3160(7) Å, Ti1-P2 = 2.5590(7) Å, and P1-P2 2.1022(8) Å. The crystallographic structure shows that the distance Ti1-P1 lies in range between single and double P-Ti bond, wherein the single bond distance Ti–P is 2.564(2) Å in $[Cp_2Ti(PMe_3)(\eta^2-P \equiv CtBu)]^{68}$ and 2.503(2) Å in $[Cp*Ti(\kappa^2 - PC(tBu)C(CH_2))]$,⁶⁹ while the double bond Ti=P distance is 2.1644(7) Å in [^{fBu}NacnacTi = P(Trip) (Me)]²⁴ and 2.1831(4) Å in [^{Me}NacnacTi = PMes*(CH₂^tBu)].²³ The bond distance Ti1–P2 is typical for single bond between titanium and phosphorus atom. The angle $P2-P1-Ti1 = 70.60(2)^{\circ}$ is a little wider than in the prototypical η^2 -phosphanylphosphinidene compounds of platinum $[(tBu_2PH)(Ph_3P)Pt(\eta^2-P-PtBu_2)]$,⁷⁰ $[(EtPh_2P)Pt(\eta^2-P-PtBu_2)]$ $PtBu_2$],⁷¹ [(dppe) $Pt(\eta^2 - P - PtBu_2)$]⁷² (62.73°, 62°, and 61.88°, respectively) described by Fritz and co-workers but is comparable to the complexes of tungsten and molybdenum: $[(2,6-iPr_2C_6H_3N)_2(Cl)W(\eta^2-tBu_2P=P)]Li\cdot 3DME^{29}$ and $[(2,6-iPr_2C_6H_3N)_2(Cl)W(\eta^2-tBu_2P=P)]Li\cdot 3DME^{29}$ $iPr_2C_6H_3N_2Mo(Cl)(\eta^2-P=PR_2)$]Li·3DME²⁸ (69.13°, 69.08°

respectively). The green plates of second isomer denoted as 2a2 from pentane solution were obtained only once. It crystallizes in triclinic space group P1. In contrast to 2a1 (Figure 2-2a1), the metal center of 2a2 adopts a pseudotrigonal-bipyramidal geometry with two nitrogen atoms of β diketiminato ligand and phosphanyl phosphorus atom in the equatorial position. The axial position is occupied by one chloride atom and phopshinidene phosphorus atom. The values of Ti-P bond lengths (Ti1-P1 2.334(3) Å, Ti1-P2 2.523(3) Å) indicate that the coordination of phosphanylphosphinidene ligand to the metal center is near η^2 (angle P2-P1-Ti1 = 68.93(12)°). The P1-P2 distances for both isomers are typical for P=P double bond in side-on geometry (2.1022(8) Å 2a1 and 2.112(4) 2a2).¹³ Similar structural properties were described by Cummins and co-workers in the phosphanylphosphinidene complexes of niobium and tungsten. 63,73,74 The NCCCN unsaturated backbones of the ligand are almost planar, with 0.043(6) Å deviation from planarity in 2a1 and 0.044(5) Å in **2a2**. The titanium atoms in both complexes are out of planes of diimine ligand frameworks by 1.077(2) Å 2a1 and 0.872(2) Å 2a2.

To clarify the charge distributions and bonding properties in **2a1** and **2a2** DFT calculations were performed.^{4\$-61} The resulting molecular coordinates are well in accordance with Xray results (Figures S5 and S6, see Supporting Information). 2a1 and 2a2 have the same energy, and therefore it was possible to obtain both isomers under similar crystallization conditions. The rotation of a tBu₂P-P moiety around an axis near perpendicular to P-P bond must be of low energy. DFT calculations have yielded following Mayer bond order (MBO) values for 2a1: P1-P2 = 0.972; Ti1-P1 = 1.60; Ti1-P2 = 0.809. Similar MBO values were obtained for 2a2: P1-P2 = 0.948; Ti1-P1 = 1.57; Ti1-P2 = 0.872. Thus, according to MBO values the P–P bonds in tBu_2PP ligands are rather single ones in both isomers. The Ti-P1 bond lengths and MBO values indicate significant π -bonding contributions. It means that tBu₂PP group does display important properties of a terminal tBu₂PP moiety; however, it is side-on bonded, and the P-P distance is short. The Hirshfeld population analysis for **2a1** yields negative charge at P1 (-0.159), which suggests some

ionic character of the P–P bond, positive at P2 (0.125) in accord with donor properties of phosphanyl part of this ligand, negative charges at N atoms (-0.128 and -0.138), and highly positive charge at Ti atom (0.339). Scheme 6 shows the Lewis structure of **2a** according to DFT results.





2b crystallizes in monoclinic space group $P2_1/n$. The X-ray structure is shown in Figure 3.



Figure 3. Molecular structure of $[NacnacTiCl(\eta^2-P-PiPr_2)]$ (2b), hydrogen atoms omitted for clarity. Important bond lengths (Å), bond angles (deg): N1–Ti1 2.0389(18), N2–Ti1 2.0411(18), P1–P2 2.1038(8), P1–Ti1 2.3182(7), P2–Ti1 2.4933(7), Cl1–Ti1 2.2786(7); P1–P2–Ti1 59.86(2), N1–Ti1–N2 92.43(7), P1–Ti1–P2 51.70(2). The sum of the angles around the P atoms: $\sum P2 = 328.84$.

Coordination and environment on the metal center is the same as in 2a1 and 2a2; however, in 2b it was found that the location of phosphanylphosphinidene ligand is between related locations in 2a1 and 2a2. It may be caused by the different steric hindrance of substituents on the phosphorus atom (in this case *i*Pr groups). It additionally supports that the phosphanylphosphinidene group can easily rotate along an axis perpendicular to P1–P2 bond. The P1–P2 distance 2.1038(8) Å is short and is comparable to those in the structures 2a1 and 2a2.

Reaction of $[^{Me}NacnacTiCl_2 \cdot THF]$ with $R_2P-P(SiMe_3)Li$ in molar ratio 1:2 yielded also red crystals denoted as **3a**. The Xray study showed that **3a** crystallizes in the space group $P\overline{1}$ with a distorted tetrahedral geometry at the metal center. Two structurally similar independent molecules were found in the unit cell of **3a**. The molecular structure of anionic part of complex **3a** is depicted in Figure 4. Complete ionic complex, together with THF-coordinated lithium counterion, is presented in Supporting Information (see Figure S4).

Complex 3a features a four-coordinated titanium center. The molecule of 3a has a nearly linear Ti1=N2-C18 alignment 169.8(3)° similar to those reported for imido com-



Figure 4. Molecular structure of the anionic titanium-imidophosphanylphosphido complex 3a. H atoms and cation $[\text{Li}(\text{THF})_4]^+$ are omitted for clarity (complete structure see Supporting Information—Figure S4). Important bond lengths (Å), bond angles (deg): N1–Ti1 1.986(3), N2–Ti1 1.736(4), Si1–P1 2.2342(18), P1– P2 2.1799(17), P1–Ti1 2.4840(15), C16–Ti1 2.113(4); N2–Ti1–N1 114.57(16), N2–Ti1–C16 114.67(17), N1–Ti1–C16 85.86(16), N2–Ti1–P1 114.79(12), N1–Ti1–P1 113.27(11), C16–Ti1–P1 110.37(15), Ti1–N2–C18 169.8(3). The sum of the angles around the P atoms: Σ P1 = 344.14, Σ P2 = 319.01.

plexes.^{42–44,75} The C₃N ligand of 3a displays η^2 -coordination mode, although the Ti-C (ligand backbone) distances of 3a(Ti1-C14 2.798(3) Å, Ti1-C15 2.763(2) Å) are shorter than those in the C₃N ligand (Ti-C = 2.981, 2.994, 2.892, and 2.928 Å).^{42,43} The central titanium atom deviates from the C₃NTi plane by 0.0703 Å. The lengths of C15-C16 1.340(6) Å in the C₃NTi ring are close to the corresponding values of double bond lengths, whereas the C14-C15 1.487(6) Å lies in the range of single bond lengths. The distance of N1-C14 1.387(5) Å is much longer than those reported in literature (1.296–1.331 Å).^{42–44,75} P1–P2 is 2.1799(17) Å and might suggest a partial double bond character of this bond. Similar distances between P-P atom were observed in the phosphanylphosphido complexes of zirconium and hafnium.¹⁶ Thus, the $tBu_2PP(SiMe_3)$ moiety is terminally bonded to the metal center. The relatively short distance Ti1-P1 2.4840(15) Å is rather typical for Ti^{III} phosphido complexes, see, for example, $[Cp_2TiP(SiMe_3)_2] 2.467(1) Å$,⁷⁶ but it is slightly shorter than that found in $[\{(C_5Me_4)-SiMe_2-PCy\}Ti(NMe_2)]$ 2.505(3) Å.⁶⁵ The geometry around P1 $(\sum P1 = 344.14^{\circ})$ indicates significant extent of planarity, while the geometry around P2 ($\sum P2 = 319.01^\circ$) is clearly pyramidal.

4. CONCLUSIONS

Reactions of [^{Me}NacnacTiCl₂·THF] with R₂P–P(SiMe₃)Li *n*THF in toluene (molar ratio 1:1) have yielded related Ti^{III} complexes [^{Me}NacnacTi(Cl){ η^2 -P(SiMe₃)-PR₂}] (**1a**, R = *t*Bu; **1b**, R = *i*Pr) with (Me₃Si)P-PR₂ group bonded side-on to the Ti^{III} centers. Reactions of [^{Me}NacnacTiCl₂·THF] with R₂P– P(SiMe₃)Li in THF (molar ratio $\approx 2:1$) have yielded related phosphanylphosphinidene Ti^{IV} complexes [^{Me}NacnacTiCl(η^2 -P-PR₂)] (**2a1** and **2a2**, R = *t*Bu; **2b**, R = *i*Pr) with P-PR₂ group also bonded side-on to the Ti^{IV} centers. The reaction between [^{Me}NacnacTiCl₂·THF] and R₂P–P(SiMe₃)Li yielding **2a** is a 2e⁻ autoredox process connected with the contraction of ^{Me}Nacnac moiety and transfer of a nitrene Ar–N onto Ti atom with concomitant oxidation of two molecules of **1a** to **2a**. Moreover the phosphanylphosphido complexes **1a** and **1b** are not stable in THF solution and transform spontaneously into **2a** and **2b**. The best entrance to the Ti^{IV} complexes [^{Me}NacnacTiCl(η^2 -P-PR₂)] is the preparation of the related Ti^{III} complexes [^{Me}NacnacTi(Cl){ η^2 -P(SiMe₃)-PR₂}] (1) followed by their oxidation with [*i*Bu₃PAgCl]. It reacts with **1** yielding **2**, *i*Bu₃P, Me₃SiCl, and Ag.

ASSOCIATED CONTENT

Supporting Information

.The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01929.

X-ray crystallographic information (CIF)

¹H and ³¹P and ³¹P(H) NMR spectra, solid-state ³¹P NMR spectra, molecular structure of **1a**, **1b**, and **3a**, comparison of molecular structure of **2a1** and **2a2** (X-ray and optimization in the Amsterdam program) (PDF) checkCIF/PLATON report (PDF)

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Notes

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