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Communication

Titanium Phosphinidene and Phosphide Moieties from Oxidative Phosphorylation and Desilylation

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ABSTRACT: A unique entry into mononuclear titanium complexes bearing phosphinidene and phosphide ligand moieties is reported. Reaction of $[K(crypt)][(PN)_2TiCl]$ (**1**, crypt = 2.2.2-cryptand) with $[Na(OCP)]$ results in $[K(crypt)][(PN)_2Ti(OCP)]$ (**2**) and such species can be oxidized to the derivative $[(PN)_2Ti(OCP)]$ (**3**), both of which do not undergo decarbonylation. However, the reaction of **1** and $[NaP(SiMe_3)_2]$ leads to an unprecedented Ti^{III} phosphinidene, $[K(crypt)][(PN)_2Ti{=}PSiMe_3]$ (**4**), through an oxidative phosphorylation reaction. To promote the formation of a Ti≡P bond, complex **4** was treated with 0.5 equivalent XeF_2, resulting in an oxidative desilylation step forming a molecular titanium phosphide complex, $[K(crypt)][(PN)_2Ti{\equiv}P]$ (**5**), which showed a characteristic downfield chemical shift at 1449.8 pmm in the ^{31}P NMR spectrum. Complex **5** can be further functionalized to generate a terminal Ti^{IV} phosphinidene, $[(PN)_2Ti{=}PSiMe_3]$ (**6**), and the latter can be independently accessed through oxidation of **4**. All new complexes were characterized structurally and as appropriate by multinuclear NMR, CW X-band EPR (for Ti^{III}), and HFEPR (for Ti^{II}) spectroscopies.

Despite the growing utility of transition metal phosphide materials in electrochemistry and battery technologies,[1−10] only a handful of terminal, molecular, transition metal phosphidos (M≡P) bearing a metal phosphorus triple bond have been isolated and structurally characterized.[11−24] Much of the early work regarding the synthesis of M≡P was established on group 6 metals (Mo and W) by Cummins, Schrock, and Scheer[11−13,17,18,21] utilizing P_4 (Figure 1A)[11−14,19] and LiPHPh or $LiP(SiMe_3)_2$ (Figure 1D)[17,18,21] as P atom transfer reagents. While these P atom sources enabled the synthesis of M≡P bonds to extend to group 5 metals (Nb) by Cummins[14] and Wolczanski,[19] it was not until a recent resurgence in the synthesis of other P atom transfer reagents[25−30] that M≡P bonding was extended to group 7 (Re) by Schneider[22] via decarbonylation of [NaOCP] or by Agapie via anthracene extrusion to form Mo^{IV} and Mo^{V} phosphides (Figure 1B,C). Despite these recent strides made in the synthesis of M≡P bonds, first row transition metals and group 4 metals remain underexplored. Group 4 elements pose an even greater challenge due to their propensity to have d^0 valencies, the lack of suitable low-valent metal precursors, and low electronegativity (high energy d-orbitals), thus making it difficult for them to accept a P^{3-} fragment.[31−35] Due to our group's recent success in the synthesis of Nb≡P,[24] $[Ti{\equiv}N]^-$,[31] and more recently $[Ti{\equiv}As]^-$ moieties,[32] we sought to synthesize a molecular example of a Ti-complex bound to a single P atom bearing a triple bond. In this study, we explore reactions of a Ti^{II} precursor $[K(crypt)][(PN)_2TiCl]$[32] (**1**), with $[Na(OCP)]$ and $[NaP(SiMe_3)_2]$, the latter of which allowed us to isolate an unprecedented Ti^{III} phosphinidene, a molecular Ti^{IV} phosphide, and its Ti^{IV} phosphinidene derivative (Figure 1).

Our first attempts at the synthesis of a Ti≡P moiety involved the use of the P atom transfer reagent $[Na(OCP)]$ given the analogous direct As-atom transfer from $[Na(OCAs)]$ to Ti^{II} to generate the first molecular $[Ti{\equiv}As]^-$.[32] Complex **1** reacts with $[Na(OCP)(dioxane)_{2.5}]$ in THF at RT to yield $[K(crypt)][(PN)_2Ti(OCP)]$ (**2**) in 76% yield (Figure 2). In contrast to the reaction of **1** with $[Na(OCAs)]$,[32] **2** does not undergo decarbonylation likely in part due to the stronger P−CO bond as compared to the As−CO bond.[33,34] Compound **2** can be readily oxidized with $[(PN)_2TiCl]$ or $[FeCp_2][OTf]$ to generate $[(PN)_2Ti(OCP)]$ (**3**, Figure 2) in 73% or 36% yield, respectively, along with formation of **1** or $FeCp_2$ and KOTf.[35]

scXRD studies of **2** and **3** (Figure 3A,B) revealed the phosphaethynolate to be O-bound in each with a Ti−O bond of 2.070(3) (**2**; Figure 3A) and 1.978(2) (**3**; Figure 3B) Å. The decrease of ∼0.092 Å from **2** to **3** is consistent with the decrease in atomic radius and increase in covalency from Ti^{II} (**2**) to Ti^{III} (**3**).[36,37] The geometry of **3** (τ_5 = 0.80) is nearly identical with that of **2** (τ_5 = 0.77) with O-binding of $[OCP]^-$ being especially surprising since P-bound phosphaethynolate was proposed in low-valent Ti and isolated in V^{III}.[39−42] IR spectroscopy (KBr pellet) revealed vibrational stretching frequencies of $\nu(C{\equiv}P)$ as 1770 and 1655 cm^{-1} for **2** and **3**, respectively,[43] and suggest the dominant resonance structure in

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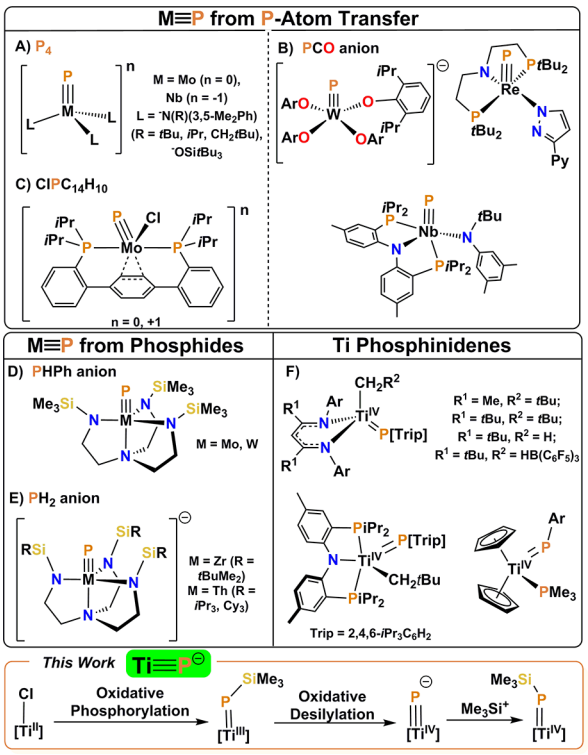

Figure 1. Pathways to metal phosphide and phosphido complexes (A–E) along with examples of titanium phosphinidenes (F). Below: Our work describing the synthesis of Ti phosphinidene and phosphide complexes.

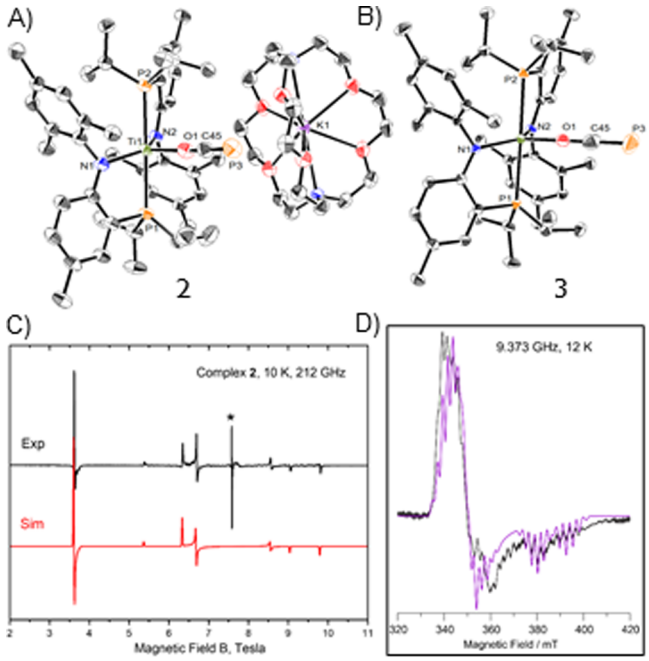

Figure 3. Solid state structures (ORTEP-III 50% probability) of **2** (A) and **3** (B) are shown with hydrogen and residual solvents omitted for clarity. C: HFEPR spectrum of **2** (212 GHz, 10 K; black trace) and its simulation (red trace; see text). The resonances appearing at ~7.5 T (*) correspond to an Ti^{III} impurity ($g \sim 1.96$) and an unidentified radical ($g \sim 2.00$) which are not simulated. D: CW-X-Band EPR spectrum (9.373 GHz, 12 K) of **3** (black trace) and its simulation (purple trace), representing the sum of two components (conformations) in equal abundance with slightly different spin Hamiltonian parameters.[48]

the solid state to be $[O{-}C{\equiv}P]^-$ (1780 $cm^{-1}$for bridging dimer versus 1755 $cm^{-1}$for the free $[OCP]^-$).[25]

Both **2** and **3** are paramagnetic and are observed to have solution magnetic moments (Evans' method; THF-d_8 (**2**), C_6D_6 (**3**), 300 K) of μ_{eff} = 2.41(2) μ_B (**2**) and μ_{eff} = 1.96(1) μ_B (**3**), consistent with a d^2, S = 1 high-spin Ti^{II} ion and d^1, S = 1/2 Ti^{III} ion, respectively.[39,44−46] Further evidence for these assignments was made utilizing HFEPR spectroscopy (**2**; Figure 3C) and CW-X-band EPR (**3**; Figure 3D). Compound **2** exhibited a characteristic spin triplet pattern (powder, 10 K, 212 GHz, Figure 3). The spectrum was simulated using S = 1 spin Hamiltonian parameters: D = +2.065(5) cm^{-1}, E = +0.125(3) cm^{-1}, and g = [1.965(2), 1.952(2), and 1.999(2)] (Figure 3C). Despite the low symmetry of **2**, the electronic system is nearly axial (E/D = 0.06; $g_x \approx g_y$, therefore $g_\perp$ = 1.9595(10)), which is in good agreement with that of the starting material **1** and the previously reported $[K(crypt)][(PN)_2Ti(NCO)]$.[35,37] Despite this apparent similarity, D of **1** (D = 2.137 cm^{-1}), **2**, and $[K(crypt)][(PN)_2Ti(NCO)]$ (D = 1.967 cm^{-1}) deviate significantly, indicating differing degrees of σ-donation and π-acceptance with $[NCO]^-$ being a stronger field ligand.[35,37] Given these differences, $[OCP]^-$ spectroscopically exhibits pseudohalide characteristics; therefore, **2** appears to have more electronic similarities to **1** than $[K(crypt)][(PN)_2Ti(NCO)]$. CW-X-band EPR of **3** (9.373 GHz, 50 K, glassy toluene; Figure 3D) revealed a highly axial system, which was modeled by two conformations each with super hyperfine coupling (hfc) to two ^{14}N and two ^{31}P atoms.[47,48]

Remarkably, reduction of **3** with KC_8 and cryptand also failed to promote decarbonylation but, instead, reforms **2** in 77% yield (Figure 2) in contrast to previous observations with Sc where reduction leads to P−P bond formation without decarbonylation.[49] Likewise, subjecting **2** or **3** to thermal and photolytic conditions does not lead to decarbonylation or formation of the target molecule: Ti≡P or any titanium based P-coupled product.[38] With the reductive decarbonylation of

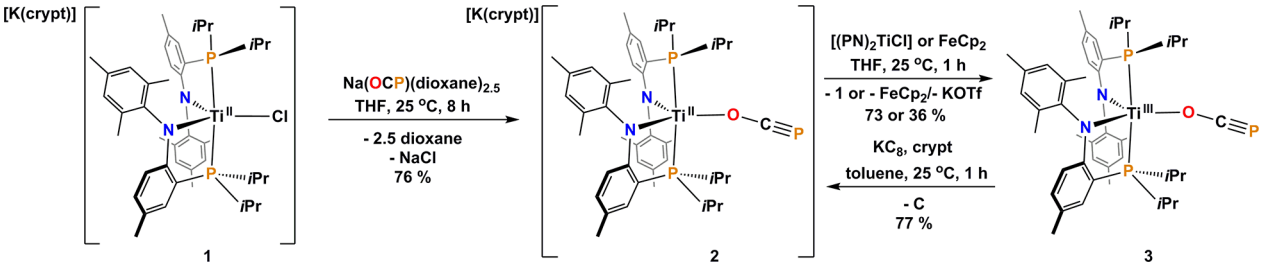

Figure 2. Reactivity studies involving complex **1** and [Na(OCP)] to form complex **2** and oxidized **3**.

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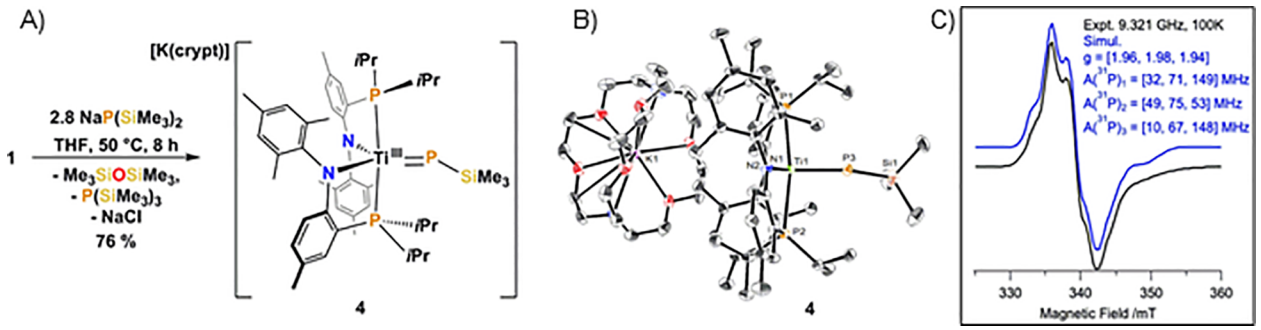

Figure 4. A: Reaction scheme of **1** and $[NaP(SiMe_3)_2]$ to form the Ti^{III} phosphinidene **4** via oxidative phosphorylation. B: ORTEP-III (50% thermal ellipsoid probability) for **4** with hydrogens and residual solvents omitted. C: CW-X-band EPR (9.321 GHz, 100 K) of **4** (black) in glassy toluene and its simulation (blue) including hyperfine coupling to three ^{31}P atoms.

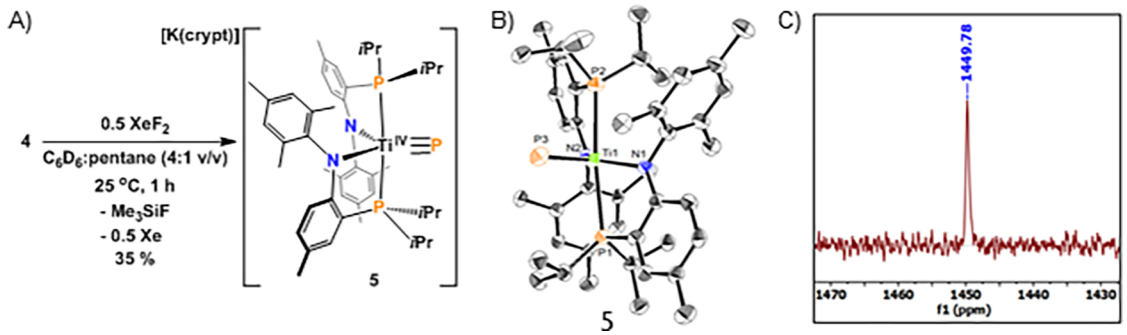

Figure 5. A: Reaction scheme of **4** to **5** was via oxidative desilylation. B: ORTEP-III (50% probability thermal ellipsoid) of **5**. All hydrogens, K(crypt) counteranion, and cocrystallized solvent molecules have been omitted for clarity. C: Room temperature (300 K) $^{31}P\{^1H\}$ NMR spectrum of **5** in THF-d_8.

$[OCP]^-$ stalled, we sought an alternative method for the synthesis of $[Ti{\equiv}P]^-$: Phosphide desilylation.

Deprotection of M=PR has been previously reported with W[17] and Mo[18] utilizing LiPHPh or $LiP(SiMe_3)_2$ in which a phosphinidene intermediate was either isolated or proposed (Figure 1D). Deprotonation of M=PH has also been an effective synthetic strategy for the synthesis of terminal (Nb)[19] and bridging phosphide (U, Th)[50−52] moieties (Figure 1E). While much of the early work on group 4 M=PR was conducted on Zr,[53−57] such species with Ti are known, however, bulky R groups (Figure 1F) appear to be required for synthesis of the Ti=PR moiety.[58−63]

Complex **1** was heated and stirred at 50 °C in THF for 8 h in the presence of an excess (2.8 equiv) of $[NaP(SiMe_3)_2]$ to yield $[K(crypt)][(PN)_2Ti{=}PSiMe_3]$ (**4**) in 76% yield (Figure 4A). The scXRD study (Figure 4B) revealed a Ti=P bond length of 2.3239(8) Å, which is ∼0.15 Å longer than previously reported Ti=P bond lengths (2.1572(2)−2.2066(4) Å)[58−63] and consistent with an increased Ti^{III} ionic radius.[64,65] However, the Ti=P bond length in **4** is shorter than that reported by Hering-Junghans,[58] and the ∠Ti−P−Si bond angle of 145.22(3)° implies more double bond character unlike that for isoelectronic $[V{\equiv}O]^{2+}$ systems[66,67] and $[Ti^{III}{\equiv}NR]^+$ systems.[64,65]

Monitoring the progress of the reaction by NMR spectroscopy (^1H, ^{31}P, and ^{29}Si-INEPT) revealed resonances attributed to unreacted $[NaP(SiMe_3)_2]$, $P(SiMe_3)_3$, and $O(SiMe_3)_2$.[68] The observed loss of $P(SiMe_3)_3$ is similar to the reactivity reported by Scheer and Schrock for the synthesis of a W≡P moiety from $LiP(SiMe_3)_2$.[17,18,21] Based on their mechanism, we hypothesize that the generated highly reactive $NaSiMe_3$ reacts with O-sources by forming $O(SiMe_3)_2$. This unique oxidative phosphorylation is likely the result of the weak P−Si bond strength (86.9 kcal/mol) as a similar transformation is not observed between $[NaN(SiMe_3)_2]$ with **1** (N−Si BDE 113.1 kcal/mol).[64,65,67]

Complex **4** shows a μ_{eff} = 1.89 μ_B (Evans' method, C_6D_6, 300 K) consistent with an $S = 1/2$, d^1 system,[31,32,37,44−46] and the CW-X-band EPR (glassy toluene; Figure 4C) revealed a spectrum modeled as an $S = 1/2$ system with g values of [1.96, 1.98, 1.94] and super hfc to three ^{31}P atoms (Figure 4C). This relatively isotropic EPR spectrum is in stark contrast to complex **3**, which shows highly axial symmetry (Figure 3D). Also notable is that complex **4** is X-band EPR-visible at 100 K, whereas **3** requires temperatures below 77 K. This EPR spectral difference might be a manifestation of the flexible Ti-OCP versus the more rigid $Ti{=}PSiMe_3$ moiety.

With **4** in hand, we sought a methodology involving cleavage of the second P−Si linkage and concomitant oxidation of Ti^{III} to form a $Ti^{IV}{\equiv}P$ triple bond invoking a net loss of $\cdot SiMe_3$. Reaction of **4** with 0.5 eq of solid XeF_2 in 4:1 (v/v) C_6D_6 and pentane revealed the formation of Me_3SiF evidenced by $^{19}F\{^1H\}$ and ^1H NMR spectroscopy,[69] and the precipitation of a pink solid identified to be $[K(crypt)][(PN)_2Ti{\equiv}P]$ (**5**), in moderate yield (35%), by scXRD and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies (Figure 5A−C). This reaction involves an oxidative deprotection − here an oxidative desilylation, and such a transformation is rare for the formation of transition metal−ligand multiple bonds.[64,70−74] In fact, the same methodology failed when attempted for our previously reported mononuclear $\{Ti^{III}{\equiv}NSiMe_3\}^+$, likely partially due to the increased strength of the N−Si vs P−Si bond (*vide*

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supra).[75] A similar strategy for breaking P−Si bonds was reported using $(i\text{Bu})_3\text{PAgX}$ (X = Cl, I) by Ponikiewski for the synthesis of titanium phosphanylphosphinidene complexes $(\text{Ti}(\eta^2\text{-PPR}_2))$.[70]

The scXRD study of **5** (Figure 5B) revealed a Ti≡P bond length of 2.195(2) Å, which is nearly identical with the Nb≡P bond length of 2.194(9) Å[24] reported by our group and other M≡P bond lengths reported by Cummins (M = Nb, 2.186(2) Å)[14] and Schrock (M = W, 2.162(4) Å).[17] The Ti≡P bond length in **5** falls between the other two reported isostructural $[(\text{PN})_2\text{Ti}{\equiv}\text{E}]^-$ (E = N, P, As) of 1.719(3) Å and 2.2661(5) Å for N^{3-} and As^{3-}, respectively.[31,32] Complex **5** represents a unique example both of a group 4 metal complex containing a metal−phosphorus triple bond and a first-row transition metal phosphide.[76]

The solid state structure of **5** persists in solution as confirmed by ^{1}H NMR spectroscopy (THF-d_8, 300 K), which is quite similar to the previously reported $[\text{K(crypt)}][(\text{PN})_2\text{Ti}{\equiv}\text{E}]$ discrete salt complexes.[31,32] The $^{31}\text{P}\{^1\text{H}\}$-NMR spectrum (THF-$d_8$, 300 K) of **5** revealed two resonances: A remarkably downfield resonance at δ 1449.8 ($\nu_{1/2}$ = 104.2 Hz, Figure 5C) assigned to the Ti≡P phosphorus and a more upfield resonance at δ 21.7 assigned to the equivalent PN phosphorus atoms[23,32]. The next furthest downfield chemical shifts for M≡P systems are Agapie's $(\text{P}_2)\text{Mo}^{\text{IV}}{\equiv}\text{P}$ (Figure 1C)[23] complex and Schrock's $(\text{N}_3\text{N})\text{Mo}^{\text{VI}}{\equiv}\text{P}$ (Figure 1D),[17,18] which display phosphido ^{31}P resonances at 1300 and 1346 ppm, respectively, whereas most others fall in the 1000−1250 ppm range.[11,13−22,72,73] The large downfield ^{31}P chemical shift for terminal M≡P systems has been attributed to the breaking of the C_∞ symmetry of the M≡P unit by the ligands creating systems with lower, but axial, symmetry.[73] Judging from previous MAS ^{15}N NMR spectra for the isostructural $[\text{K(crypt)}][(\text{PN})_2\text{Ti}{\equiv}{}^{15}\text{N}]$, we expect **5** also to possess a highly axial symmetry and a large CSA.[77] The ^{31}P chemical shift of **5** is the farthest downfield chemical shift of any terminal M≡P reported, likely indicating that **5** contains a highly deshielded and electron deficient P atom.

With the addition of one drop (excess) of Me_3SiCl to **5** in THF-d_8, an immediate color change from pink to dark red-orange is observed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in THF-d_8 reveals the presence of a new resonance at δ 633.5 ($\nu_{1/2}$ = 86 Hz) as well as a doublet at 28.4 ($^2J_{\text{P-P}}$ = 24 Hz) assigned to a Ti phosphinidene and the PN ligand, respectively. Upon reaction workup, the new complex was identified to be $[(\text{PN})_2\text{Ti}{=}\text{PSiMe}_3]$ (**6**), Figure 6. The downfield chemical shift in **6** is most comparable with $[\text{Cp}_2\text{M}{=}\text{PR}(\text{PMe}_3)]$ (M = Ti,[58,59] Zr,[53,56] Hf[78]) complexes and identical chemical shifts can also be observed upon oxidation of **4** with 0.5 eq of 1,2-diiodoethane.[79] However, preparing the Ti^{IV} phosphinidene complex from **5** provides significantly higher yields than that from **4**.[80] Lastly, the scXRD of **6** revealed a Ti=P bond length of 2.2388(8) Å, which is a contraction of ∼0.08 Å compared to that of **4** (2.3239(8) Å) and likely due to the decreased size of the Ti^{IV} ion as compared to Ti^{III}, consistent with $\text{Ti}^{\text{IV/III}}{\equiv}\text{NR}$ complexes.[65] Complex **6** has a Ti=P bond length comparable to previously reported Ti=PR systems as well as to **4**.[58,61−63]

Pauling bond order calculations[81] utilizing the Schomaker-Stevenson correction[82] and the covalent radii derived from Pyykkö[83−86] corroborate the experimentally observed bond orders based on scXRD and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of triple for **5** and double for **4** and **6**. The calculations predict the

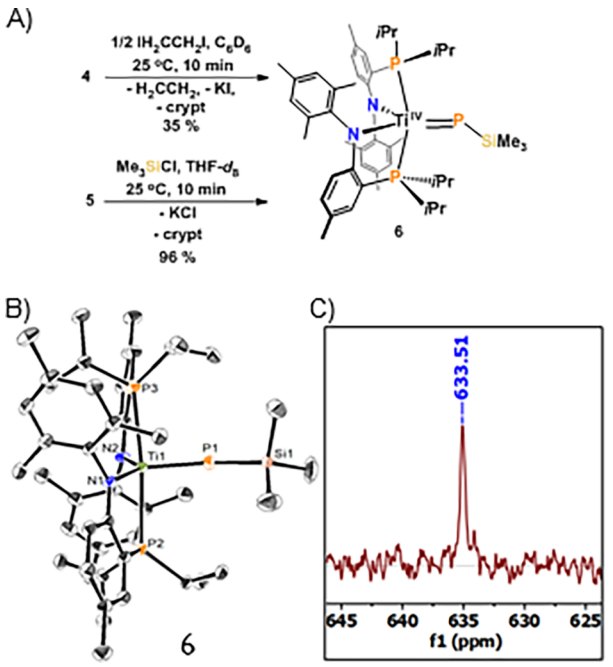

Figure 6. Top: Reaction scheme to form **6**. Bottom Left: ORTEP-III (50% thermal ellipsoid probability) of **6**. All hydrogens and cocrystallized solvents have been omitted. Bottom Right: Room temperature (300 K) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **6** in THF-d_8.

Ti−P bond distances of 2.276 and 2.206 Å for double and triple bond character, respectively. Therefore, we conclude that **5** clearly has a triple bond as the experimental bond distance (2.195(2) Å) is less than the predicted value, whereas phosphinidenes **4** and **6** may have some triple bond character but significantly less than those previously reported by our group (*vide supra*).[61−63]

In this study, we demonstrated how $[\text{NaP}(\text{SiMe}_3)_2]$ is a more effective P atom transfer reagent than [Na(OCP)], to synthesize a unique Ti^{III} phosphinidene as well as a one-coordinate and highly deshielded phosphide bound to Ti^{IV}. With these new methods in hand, we have made significant progress on the isostructural series of $[(\text{PN})_2\text{Ti}{\equiv}\text{E}]^-$ (E = N, P, or As) and can now begin comparing their bonding properties and reactivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c12242.

All relevant preparation procedures and characterization data including ^{1}H, ^{31}P, ^{19}F, ^{29}Si, and ^{13}C NMR, IR, UV−vis, EPR, and scXRD data for compounds **2**−**6** (PDF)

Accession Codes

Deposition Numbers 2380961−2380965 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

LiPHPh, lithium phenyl phosphide; P_4, white phosphorus; scXRD, single crystal X-ray diffraction; NaOCP, sodium phosphaethynolate; [A], dibenzo-7-λ^3-phosphanorbornadiene; NaOCAs, sodium arsaethynolate; THF, tetrahydrofuran; h, hours; HSAB, hard and soft acid base; NMR, nuclear magnetic resonance; MAS, magic angle spinning; EPR, electron paramagnetic resonance; HFEPR, high-frequency and -field EPR; zfs, zero-field splitting; DME, dimethoxyethane; OTf, triflate; PN, *N*-(2-(di-*iso*-propylphosphaneyl)-4-methylphenyl)-2,4,6-trimethylanilide; crypt, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2.2.2-cryptand); eq, equivalent (molar); INEPT, insensitive nuclei enhanced by polarization transfer; *t*Bu, *tert*-butyl; *i*Pr, *iso*-propyl; hfc, hyperfine coupling; PNP, bis(2-(di-*iso*-propylphosphaneyl)-4-methylphenyl)-amide; Trip, 2,4,6-tri-*iso*-propylphenyl; BDI, 1,3-diketiminide; Cp, cyclopentadienyl; P_n, pnictides or pnictido; N_3N, $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ (trisamido amine); P_2, 2,2″-bis(di-*iso*-propylphosphaneyl)-1,1′:4′,1″-terphenyl; CSA, Chemical Shift Anisotropy

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