

# Phosphinoalkylidene and -alkylidyne Complexes of Titanium: Intermolecular C–H Bond Activation and Dehydrogenation Reactions

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**S** Supporting Information

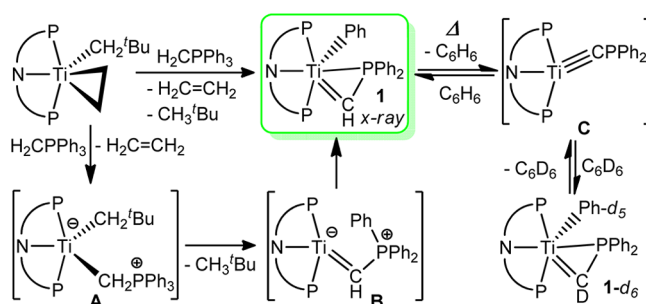
**ABSTRACT:** The ethylene complex (PNP)Ti( $\eta^2$ -H<sub>2</sub>C=CH<sub>2</sub>)(CH<sub>2</sub><sup>t</sup>Bu) or (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) (PNP<sup>-</sup> = N[2-P(CHMe<sub>2</sub>)<sub>2</sub>-4-methylphenyl]<sub>2</sub>) reacts with H<sub>2</sub>CPPH<sub>3</sub> to form the  $\kappa^2$ -phosphinoalkylidene (PNP)Ti=CHPPH<sub>2</sub>(Ph) (**1**). Compound **1** activates benzene via the transient intermediate [(PNP)Ti≡CPPH<sub>2</sub>] (**C**). By treatment of (PNP)Ti=CH<sup>t</sup>Bu(OTf) with LiCH<sub>2</sub>PPh<sub>2</sub>, **1** or its isotopologue (PNP)Ti=CDPPH<sub>2</sub>(C<sub>6</sub>D<sub>5</sub>) (**1-d<sub>6</sub>**) can be produced by an independent route involving intermediate **C**, which activates benzene or benzene-*d*<sub>6</sub> and dehydrogenates cyclohexane-*d*<sub>12</sub>. Addition of MeOTf to **1** results in elimination of benzene concomitant with the formation of the phosphinoalkylidyne complex, [(PNP)Ti≡CPPH<sub>2</sub>Me(OTf)] (**2**). Theoretical studies of **2** suggest a resonance structure having dominant Ti–C triple-bond character with some contribution also from a C–P multiple bond.

High-oxidation-state metal complexes having a phosphinoalkylidene (L<sub>n</sub>M=CR'PR<sub>2</sub>) are a relatively unexplored ligand class in which the phosphine group is attached to the alkylidene carbon, whereas the capped P(V) analogues, L<sub>n</sub>M=CR'P(X)R<sub>2</sub> (X = O, S, NR), have been more widely studied.<sup>1</sup> Examples of the phosphinoalkylidene ligand with high-valent early transition metals are somewhat common for Ta, Mo, and W, and this scaffold can sometimes chelate via the pendant phosphino group.<sup>2</sup> Surprisingly, the chemistry of heterosubstituted M–C multiple bonds is rather unexplored, and examples of group 4 transition metal complexes having a PR<sub>2</sub> substituent are unknown, which is rather remarkable since phosphorus has been regarded as the carbon copy,<sup>3</sup> with Schrock carbenes being ubiquitous in transition metal chemistry and catalysis.<sup>4</sup> Here we extend this underexplored ligand to Ti by reporting Ti–C multiple bonds in which the  $\alpha$ -carbon atom has a PPh<sub>2</sub> group. Notably, we demonstrate that the phosphinoalkylidene ligand can be a precursor to a titanium phosphinoalkylidyne,<sup>5</sup> akin to how titanium alkylidenes can undergo  $\alpha$ -hydrogen abstraction.<sup>2b,6</sup> The latter ligand can engage in a rare case of intermolecular C–H bond activation, including dehydrogenation of cyclohexane to cyclohexene. Our entry to these reactive species is depicted by several independent routes that provide convincing support for some of the proposed intermediates in

the C–H bond-splitting steps. In addition, we report structural information for a terminally bound phosphinoalkylidene ligand<sup>7,8</sup> exhibiting the shortest Ti–C bond length known to date. Theoretical studies have been applied to elucidate the structure and bonding of this scaffold.

Our entry to the phosphinoalkylidene moiety involves the use of the masked low-valent Ti(II) reagent (PNP)Ti( $\eta^2$ -H<sub>2</sub>C=CH<sub>2</sub>)(CH<sub>2</sub><sup>t</sup>Bu)<sup>6c,d</sup> with the ylide H<sub>2</sub>CPPH<sub>3</sub> (Scheme 1). Instead

## Scheme 1. Dehydrogenation and P–C Bond Activation of the Ylide H<sub>2</sub>CPPH<sub>3</sub> via Transient Phosphinoalkylidene and -alkylidyne Intermediates

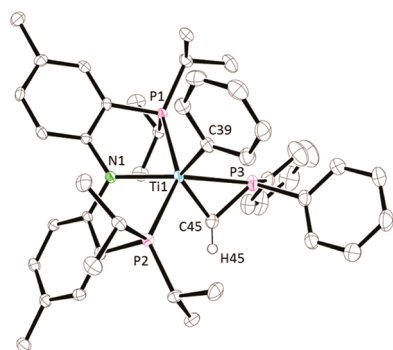


of methylidene group transfer, as one might have expected,<sup>9</sup> we observed the clean formation of a new species, (PNP)Ti=CHPPH<sub>2</sub>(Ph) (**1**),<sup>10</sup> over 7 days at 60 °C (Scheme 1). Examination of the volatiles revealed only formation of ethylene and H<sub>3</sub>C<sup>t</sup>Bu. Complex **1** can also be prepared independently over 2 days at room temperature from addition of the ylide (1 equiv) to a cyclohexane solution of (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu). CH<sub>3</sub><sup>t</sup>Bu and cyclohexene were observed as side products,<sup>10</sup> implying that the transient [(PNP)Ti≡C<sup>t</sup>Bu] intermediate dehydrogenates cyclohexane first and that a Ti(II) species is formed, presumably “(PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)”<sup>11</sup> or its cyclohexene adduct, and then reacts with the ylide H<sub>2</sub>CPPH<sub>3</sub>. In fact, monitoring the later reaction by <sup>31</sup>P NMR spectroscopy at 29 °C yielded a pseudo-first-order rate constant of 3.06 × 10<sup>-5</sup> s<sup>-1</sup>,<sup>10</sup> which is quite similar to rate constants measured for the dehydrogenation of alkanes through [(PNP)Ti≡C<sup>t</sup>Bu], implying that a similar mechanism is operative in the formation of **1**.<sup>6c,d</sup>

Received: July 5, 2015

Published: August 24, 2015

Complex **1** is characterized by three inequivalent resonances in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 27.1 ppm (dd,  $^2J_{\text{PP}} = 50.1$  Hz,  $^3J_{\text{PP}} = 16.7$  Hz), 20.9 ppm (d,  $^2J_{\text{PP}} = 49.4$  Hz), and  $-21.3$  ppm (d,  $^3J_{\text{PP}} = 17.3$  Hz). The alkylidene carbon was unambiguously assigned in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum at 248.8 ppm as a doublet of doublets (ddd,  $^1J_{\text{CP}} = 93.4$  Hz,  $^2J_{\text{CP}} = 16.9$  and  $7.1$  Hz) and correlated to the alkylidene proton at 10.59 ppm (dd,  $^2J_{\text{HP}} = 6.2$  Hz,  $^3J_{\text{HP}} = 2.2$  Hz) via an HSQC experiment.<sup>8</sup> A solid-state X-ray diffraction (XRD) study of **1** confirmed the presence of the phosphinoalkylidene ligand, confined to a  $\kappa^2$  bonding mode (Figure 1). The Ti=C bond length of 1.922(3) Å is slightly



**Figure 1.** Solid-state structure of the phosphinoalkylidene complex **1** displaying thermal ellipsoids at the 50% probability level. All H atoms except for the alkylidene  $\alpha$ -H have been omitted for clarity.

longer than those in prototypical Schrock-like titanium alkylidenes such as  $\text{L}_n\text{Ti}=\text{CHR}$  ( $\text{R} = \text{aryl or alkyl group}$ )<sup>4</sup> but significantly shorter than those in ligands such as  $\text{Ti}-\text{CH}_2\text{PPh}_2$  (i.e., 2.203(3) and 2.183(3) Å),<sup>12</sup> suggesting that such species might contain a three-centered bonding topology at Ti–C–P but with significant Ti=C character. Interestingly, the Ti–C distance is quite similar to the only known titanium phosphinoalkylidene complex,  $\text{Cp}^*\text{Ti}=\text{CHPPh}_3(\text{Cl})_2$ , reported by Li and co-workers.<sup>13</sup> The bonding mode of the  $[\text{CHPPh}_2]^{2-}$  ligand in **1** could be also construed as a phosphoalkyne,  $\text{HCPPh}_2$ , that coordinates in an  $\eta^2$  fashion, and indeed, such canonical forms have been discussed.<sup>2</sup>

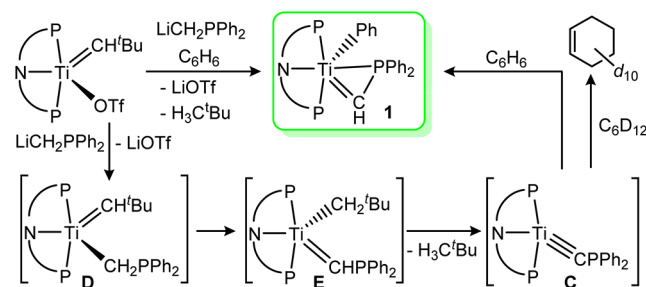
The assembly of **1** clearly implies that C–H and P–C bond activation processes involving the ylide  $\text{H}_2\text{C}=\text{C}(\text{PPh}_2)_2$  take place. Scheme 1 depicts our proposed mechanism to account for the formation of the phosphinoalkylidene ligand in **1**. A dissociative mechanism involving ethylene release from  $(\text{PNP})\text{Ti}(\eta^2\text{-H}_2\text{C}=\text{CH}_2)(\text{CH}_2^t\text{Bu})$  and trapping of the Ti(II) fragment “ $(\text{PNP})\text{Ti}(\text{CH}_2^t\text{Bu})$ ”<sup>11</sup> by the ylide forms the adduct intermediate  $[(\text{PNP})\text{Ti}(\text{CH}_2\text{PPh}_2)(\text{CH}_2^t\text{Bu})]$  (**A**), which then undergoes  $\alpha$ -hydrogen abstraction to produce the phosphinoalkylidene zwitterion  $[(\text{PNP})\text{Ti}=\text{CHPPh}_3]$  (**B**).<sup>14</sup> The highly reducing nature of this formally Ti(II) zwitterionic intermediate could promote the migration of a  $\text{P}^+$  group to produce **1** (Scheme 1). Alternatively, formation of **1** from **B** could be also interpreted as an oxidative addition of the P–Ph bond of the phosphonio group. At this point we cannot rule out methylidene transfer and  $\text{PPh}_3$  release followed by coordination of this Lewis base at a later stage of the reaction. However, we discourage this route since a strong C–P bond is broken and later reformed.<sup>15</sup>

It is noteworthy that complex **1** is remarkably stable, akin to the alkylidene–phenyl derivative  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{C}_6\text{H}_5)$  previously reported by our group.<sup>6a</sup> Nevertheless, heating a  $\text{C}_6\text{D}_6$  solution of **1** for 16 h at 80 °C resulted in the formation of

$(\text{PNP})\text{Ti}=\text{CDPPh}_2(\text{C}_6\text{D}_5)$  (**1-*d*<sub>6</sub>**), depicted in Scheme 1.<sup>10</sup> This result implies that a phosphinoalkylidene,  $[(\text{PNP})\text{Ti}\equiv\text{CPh}_2]$  (**C**), is responsible for the activation of a C–D bond of  $\text{C}_6\text{D}_6$  through a 1,2-addition step (Scheme 1), similar to how the transient neopentylidene  $[(\text{PNP})\text{Ti}\equiv\text{C}^t\text{Bu}]$  derivative activates arenes and other hydrocarbons.<sup>6</sup>

To explore other pathways to generate the reactive species **C**, we turned to the alkylidene precursor  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{OTf})$ <sup>16</sup> and  $\text{LiCH}_2\text{PPh}_2$ .<sup>17</sup> Addition of the phosphinoalkyl-lithium to the titanium alkylidene complex in benzene (16 h at 60 °C) results in formation of **1** in 92% isolated yield (Scheme 2).<sup>10</sup>

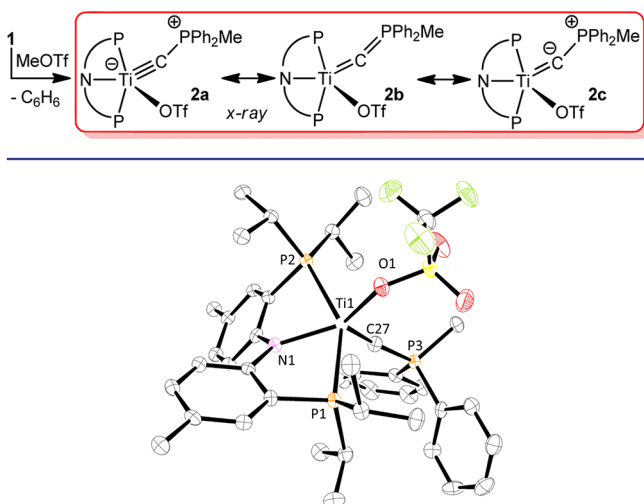
### Scheme 2. C–H Activation of Benzene and Dehydrogenation of Cyclohexane via Intermediate **C**



Generation of **1** from  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{OTf})$  and the alkylphosphine involves a salt elimination process to form  $[(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2\text{PPh}_2)]$  (**D**), which upon tautomerization produces  $[(\text{PNP})\text{Ti}=\text{CHPPh}_2(\text{CH}_2^t\text{Bu})]$  (**E**). An  $\alpha$ -H abstraction in **E** produces **C** and  $\text{H}_3\text{C}^t\text{Bu}$ , which as demonstrated above ultimately activates benzene via a 1,2-CH bond addition across the reactive  $\text{Ti}\equiv\text{CPh}_2$  moiety (Scheme 2). Conducting the same reaction in  $\text{C}_6\text{D}_6$  cleanly produces the isotopologue **1-*d*<sub>6</sub>**, while the use of cyclohexane- $d_{12}$  as the solvent forms cyclohexane- $d_{10}$  along with multiple titanium-based products that thus far we have been unable to characterize (Scheme 2).<sup>8</sup> Similar dehydrogenation chemistry has also been observed with transient  $[(\text{PNP})\text{Ti}\equiv\text{C}^t\text{Bu}]$  and cyclohexane.<sup>6c,d</sup>

Given the reactive nature of **C**, coupled with the ability of the phosphine to coordinate to the metal as in the case of **1**, we explored the use of  $\text{MeOTf}$  to produce a more reactive phosphinoalkylidene reagent. Accordingly, addition of  $\text{MeOTf}$  to **1** rapidly formed a single new product that was isolated in 85% yield, but interestingly, this was accompanied by liberation of  $\text{C}_6\text{H}_6$ .<sup>10</sup> The  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of this new product were consistent with a  $\text{C}_1$ -symmetric structure, as indicated by the presence of three inequivalent P resonances at 30.72 ppm (d,  $^2J_{\text{PP}} = 49.7$  Hz), 18.57 ppm (d,  $^2J_{\text{PP}} = 49.8$  Hz), and  $-88.07$  ppm (s);<sup>10</sup> the highly shielded signal was consistent with the formation of a phosphonio group.<sup>7,8</sup> The most salient spectroscopic feature is a highly deshielded  $^{13}\text{C}\{^1\text{H}\}$  NMR peak at 250.2 ppm that is strongly coupled to all three inequivalent P atoms (ddd,  $J_{\text{CP}} = 32.5$ , 10.0, and 6.1 Hz), suggesting that the Ti–C multiple bond was preserved (Scheme 3).<sup>10</sup>

A single-crystal XRD study allowed us to establish the precise connectivity of this new product resulting from quaternization of the phosphine moiety in **1** in addition to coordination of the triflate anion. Figure 2 shows the molecular structure of the first mononuclear titanium phosphinoalkylidene,  $[(\text{PNP})\text{Ti}\equiv\text{CPh}_2\text{Me}(\text{OTf})]$  (**2**),<sup>18</sup> having the shortest reported Ti–C distance of 1.784(3) Å. For comparison, the computed Ti–C bond length for the transient four-coordinate titanium alkylidene

Scheme 3. Synthesis of Titanium Phosphonioalkylidyne **2** (and Resonance Structures Thereof) from **1** and MeOTf

**Figure 2.** Solid-state structure of the phosphonioalkylidyne complex **2** displaying thermal ellipsoids at 50% probability level. All H atoms and a second crystallographically independent (but chemically equivalent) molecule have been omitted for clarity.

$[(\text{PNP})\text{Ti}\equiv\text{C}^t\text{Bu}]$  is 1.743–1.749 Å.<sup>6a,10</sup> Additionally, the Ti–C–P angle approaches linearity at 166.0(2)°. Interestingly, there are two crystallographically independent molecules in the asymmetric unit, differing primarily by the Ti–C–P angle (166.0(2) vs 176.32(19)°).<sup>10</sup> In **2** the nature of the Ti≡C bond is called into question given the reasonable canonical forms one could propose involving the phosphonio group. Scheme 3 depicts the synthesis of **2** and the three most likely resonance structures **2a–c**. While **2a** depicts a zwitterionic phosphonioalkylidyne with a legitimate Ti≡C bond, the short C–P bond length in **2** (1.690(3) Å) suggests that an ylide (i.e., a phosphoniovinyldene) resonance form such as **2b** is also operative. Another possible resonance form is **2c**, which possesses neither Ti≡C nor C=P multiple-bonded moieties but instead has ylide character.

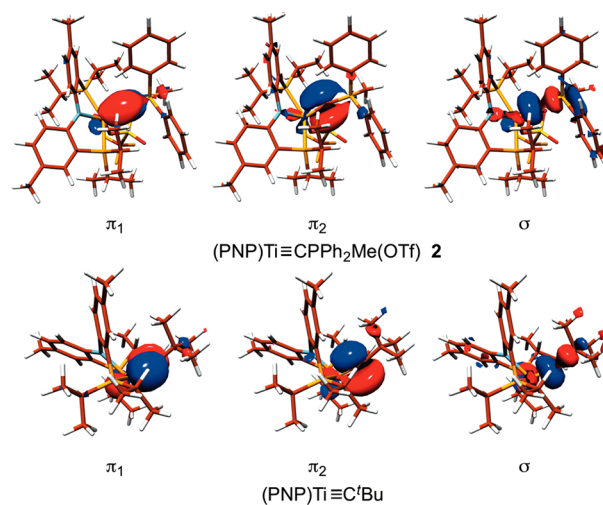
To explore which resonance form is most likely to be operative in **2**, we relied on computational studies to compare its bonding scheme with that of a more authentic Schrock alkylidyne such as  $[(\text{PNP})\text{Ti}\equiv\text{C}^t\text{Bu}]$  (**3**). From the X-ray structures, the full models of **1** and **2** were optimized with the hybrid B3LYP functional in combination with the Def2-TZVP(-f) basis set. Dispersion was also taken into account during optimizations using Grimme's D3 method.<sup>10</sup> For **2**, the two crystallographically independent structures in the asymmetric unit (vide supra) were used as initial guiding structures, but the two simulations converged to the same structure with a Ti–C–P angle of ~167°. These simulations suggest that the observed angle of 176° in one of the crystallographically independent molecules most likely arises from condensed-phase effects. Table 1 presents structural and theoretical information, including Mayer bond order (BO) analyses, for **1** and **2** as well as intermediate **3** previously investigated by our group.<sup>6a</sup> While the Ti–C bond of **3** has a BO of 2.49<sup>6a</sup> to 2.55,<sup>10</sup> a projected value for a triple bond, the corresponding BO in **2** is 2.11, indicating a notably lower degree of covalent character. The C–P BO is also quite large at 1.38, reflecting a somewhat greater degree of bonding than a traditional single bond. These values indicate that **2** has dominant **2a** character that is augmented with **2b** without too

Table 1. Experimental and Calculated Structural and Bonding Features for **1**, **2**, and  $[(\text{PNP})\text{Ti}\equiv\text{C}^t\text{Bu}]$  (**3**)

	<b>1</b>	<b>2</b>	<b>3</b> <sup>a</sup>
Ti–C <sub>exp</sub> (Å)	1.922(3)	1.784(3)/1.785(3)	–
Ti–C <sub>calc</sub> (Å)	1.918	1.761	1.743 <sup>a</sup>
Ti–P <sub>exp</sub> (Å)	2.4981(9)	–	–
Ti–P <sub>calc</sub> (Å)	2.495	–	–
C–P <sub>exp</sub> (Å)	1.726(3)	1.690(3)/1.689(3)	–
C–P <sub>calc</sub> (Å)	1.725	1.671	–
Ti–C–P <sub>exp</sub> (deg)	86.24(14)	166.0(2)	–
Ti–C–P <sub>calc</sub> (deg)	86.3	167.7	–
Ti–C Mayer BO	1.39	2.11	2.55–2.49 <sup>a</sup>
C–P Mayer BO	1.02	1.38	–
Ti–P Mayer BO	0.67	–	–

<sup>a</sup> $[(\text{PNP})\text{Ti}\equiv\text{C}^t\text{Bu}]$  (**3**) has only been studied computationally since this is a reactive intermediate. Its Mayer bond order was previously computed to be 2.49,<sup>6a</sup> and more recently we computed it to be 2.55.<sup>10</sup>

much contribution from **2c**. These conclusions are also supported by our molecular orbital (MO) analysis (Figure 3).



**Figure 3.** Important MOs of **2** (top) and  $[(\text{PNP})\text{Ti}\equiv\text{C}^t\text{Bu}]$  (bottom).

The orthogonal Ti–C  $\pi$  MOs of **2** ( $\pi_1$  and  $\pi_2$ ) are not strictly two-center-localized as in the alkylidyne analogue **3** (Figure 3 bottom) but involve the P atom of the PPh<sub>2</sub>Me group to some extent. Accordingly, these MOs are rather consistent with three-center, two-electron in-phase interactions, in accordance with resonance structure **2b** being operative, given the ability of phosphorus to be hypervalent. Similar to methylenephosphorane, H<sub>2</sub>C=PH<sub>3</sub>,<sup>19</sup> the out-of-plane p orbitals of phosphorus, which have antibonding character with the remaining substituents (Ph<sub>2</sub>Me), are involved in these three-center interactions. As a note, the **2a** character can be recognized as a shift of these  $\pi$  MOs toward the Ti–C end, which is apparent in the plotted MOs. The Ti–C  $\sigma$  bonds in **2** and **3**<sup>6a</sup> are quite similar as judged by the resemblance of the  $\sigma$  orbitals (Figure 3). Thus, the electronic structure analysis of **2** indicates a Lewis structure that can best be described as a mixture of **2a** (major) and **2b**,<sup>8</sup> but the latter should not be confused with an allene-like fragment since in **2b** the two orthogonal  $\pi$  bonds are three-centered. Akin to the delocalized nature of the bonding in **2**, the C–P BO in **1** is 1.02, which is higher than that in a typical C–P single bond, e.g., 0.91 in the PNP backbone (P–aryl).<sup>10</sup> Together with a Ti–C BO of

1.39, our analysis indicates that the Ti–C  $\pi$  bond in **1** is delocalized to the P atom to a small extent (Table 1). The MO picture corroborates our BO analysis.<sup>10</sup>

In conclusion, we have shown that alkylidene and alkylidyne scaffolds having a phosphine group can be now expanded to Ti. We have revealed that the former group can activate the C–H bond of benzene and even dehydrogenate cyclohexane to cyclohexene. Also, our titanium phosphinoalkylidene **1** can be alkylated to form a stable phosphinoalkylidyne complex of Ti. We are presently examining the ability of **1** to perform catalytic dehydrogenations since in principle the ylide could act as an acceptor of H<sub>2</sub> (formally H<sup>+</sup> and H<sup>-</sup>), and a source of a phosphinoalkylidene group.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06973.

Procedures and additional data (PDF)

Crystallographic data for **1** (CIF)

Crystallographic data for **2** (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank the U.S. NSF (CHE-0848248 and CHE-1152123) and the University of Pennsylvania for financial support. M.K. acknowledges a postdoctoral fellowship from JSPS (12J03390).

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