

# A new and selective cycle for dehydrogenation of linear and cyclic alkanes under mild conditions using a base metal

Douglas P. Solowey<sup>1</sup>, Manoj V. Mane<sup>2,3</sup>, Takashi Kurogi<sup>1</sup>, Patrick J. Carroll<sup>1</sup>, Brian C. Manor<sup>1</sup>, Mu-Hyun Baik<sup>2,3\*</sup> and Daniel J. Mindiola<sup>1\*</sup>

Selectively converting linear alkanes to  $\alpha$ -olefins under mild conditions is a highly desirable transformation given the abundance of alkanes as well as the use of olefins as building blocks in the chemical community. Until now, this reaction has been primarily the remit of noble-metal catalysts, despite extensive work showing that base-metal alkylidenes can mediate the reaction in a stoichiometric fashion. Here, we show how the presence of a hydrogen acceptor, such as the phosphorus ylide, when combined with the alkylidene complex (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>3</sub>) (PNP=N[2-P(CHMe)<sub>2</sub>-4-methylphenyl]<sub>2</sub><sup>-</sup>), catalyses the dehydrogenation of cycloalkanes to cyclic alkenes, and linear alkanes with chain lengths of C<sub>4</sub> to C<sub>8</sub> to terminal olefins under mild conditions. This Article represents the first example of a homogeneous and selective alkane dehydrogenation reaction using a base-metal titanium catalyst. We also propose a unique mechanism for the transfer dehydrogenation of hydrocarbons to olefins and discuss a complete cycle based on a combined experimental and computational study.

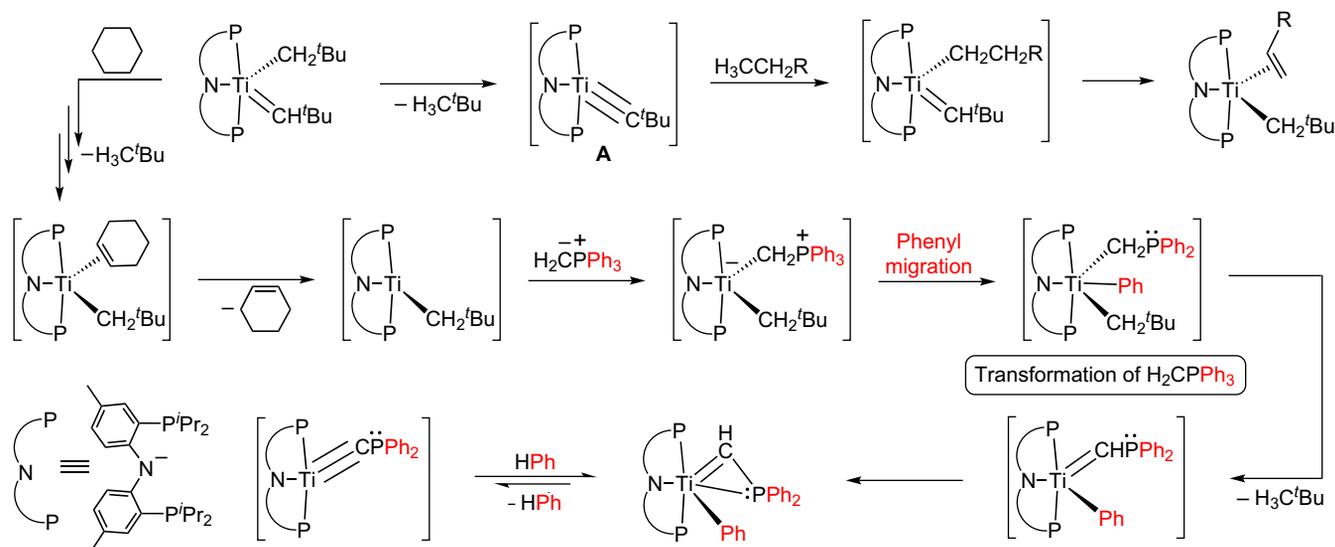
Steam cracking (SC) of ethane and other hydrocarbons is an important industrial process in which C–C bonds are cleaved to produce radicals that ultimately form olefin mixtures and other hydrocarbons<sup>1,2</sup>. This process accounts for well over 90% of the ethylene and  $\alpha$ -olefins (for example, 1-butene, 1-hexene and 1-octene) produced in North America<sup>3,4</sup>. Unfortunately, SC produces mixtures of hydrocarbons and olefins and is energy-intensive, typically requiring reaction temperatures above 800 °C. In addition, the methane produced during SC inevitably results in side reactions that produce CO<sub>2</sub> through steam reforming. Given these problems, methods that are more energy-efficient and selective are highly desirable. Over past decades, significant advances have been made in homogeneous alkane dehydrogenation<sup>5–7</sup> using rhodium<sup>8–10</sup>, ruthenium<sup>11–13</sup> and iridium-based catalysts<sup>14–17</sup>. Rhenium<sup>18,19</sup> and osmium<sup>20</sup> complexes have also been reported to be active for such reactions. Notably, the recent work of Goldman *et al.* demonstrated the versatility of iridium-catalysed alkane dehydrogenation in alkane metathesis<sup>21</sup>, dehydroaromatization<sup>22</sup> and, more recently, in heterogeneous-like catalytic processes<sup>23</sup>. Typically, the proposed iridium-catalysed alkane dehydrogenation mechanism relies on oxidative addition of the C–H bond to a 14-electron iridium complex, followed by a  $\beta$ -hydride elimination to produce a dihydride species, (L)IrH<sub>2</sub>, that subsequently regenerates the unsaturated (L)Ir fragment after liberating H<sub>2</sub> as part of the reductive elimination step. Inadvertently, the formation of hydrides can result in olefin isomerization processes that convert terminal to internal forms. In an effort to use base metals in C–H bond activation and functionalization of hydrocarbons<sup>24</sup> we turned our attention to (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) (PNP=N[2-P(CHMe)<sub>2</sub>-4-methylphenyl]<sub>2</sub><sup>-</sup>), because this species is known to dehydrogenate linear hydrocarbons C<sub>1</sub>–C<sub>8</sub> (refs 25–28), as well as cyclohexane<sup>28,29</sup>, at room temperature without the formation of hydrides, albeit not catalytically. When

C<sub>4</sub>–C<sub>8</sub> hydrocarbons are dehydrogenated, terminal olefins are formed selectively via  $\alpha$ -hydrogen abstraction to form [(PNP)Ti $\equiv$ C<sup>t</sup>Bu] (A), followed by 1,2-CH bond addition of the alkane H<sub>3</sub>CCH<sub>2</sub>R (R=H, CH<sub>3</sub>, Et, <sup>n</sup>Pr, <sup>n</sup>Bu, <sup>n</sup>Hex) to produce the alkylidene-alkyl (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub>CH<sub>2</sub>R), which then undergoes  $\beta$ -hydrogen abstraction to form the titanium olefin complex (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)(H<sub>2</sub>C=CHR) (Fig. 1)<sup>28</sup>.

In this work, we present a novel and selective catalytic cycle for the transfer dehydrogenation of volatile alkanes using a titanium catalyst in combination with a methylene transfer reagent as both an oxidant and hydrogen acceptor. A transient titanium alkylidyne A (Fig. 1) is proposed to be the active catalyst for the dehydrogenation of small linear and cyclic hydrocarbons. By using a unique phosphorus ylide H<sub>2</sub>CP(C<sub>12</sub>H<sub>8</sub>)Ph as a stoichiometric carbene ‘CH<sub>2</sub>’ transfer reagent, not only can we shut down other transformative pathways, but we can also enable the catalytic transfer-dehydrogenation of cyclohexane, cyclooctane and linear alkanes with four to eight carbons, resulting, selectively, in  $\alpha$ -olefins. A complete mechanism for the catalytic cycle for the dehydrogenation is proposed based on a combination of isotopic labelling studies, reactivity studies and extensive computer simulations using density functional theory.

Recently, we have reported that the ylide H<sub>2</sub>CPPh<sub>3</sub> reacts cleanly with (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) in cyclohexane to form the phosphino alkylidene complex (PNP)Ti=CHPPh<sub>2</sub>(Ph), H<sub>3</sub>C<sup>t</sup>Bu and cyclohexene, without eliminating free phosphine<sup>30</sup>. Under thermolytic conditions, the complex (PNP)Ti=CHPPh<sub>2</sub>(Ph) extrudes benzene to produce a transient phosphino alkylidyne, [(PNP)Ti $\equiv$ CPPh<sub>2</sub>], which reversibly adds the C–H bond of benzene across the Ti $\equiv$ C multiple bond. Although [(PNP)Ti $\equiv$ CPPh<sub>2</sub>] could, in principle, dehydrogenate alkanes to olefins akin to A, attempts to regenerate such species from (PNP)Ti=CHPPh<sub>2</sub>(Ph) by adding excess amounts of the ylide in the presence of alkanes

<sup>1</sup>Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104, USA. <sup>2</sup>Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 34141, Republic of Korea. <sup>3</sup>Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea. \*e-mail: mbaik2805@kaist.ac.kr; mindiola@sas.upenn.edu



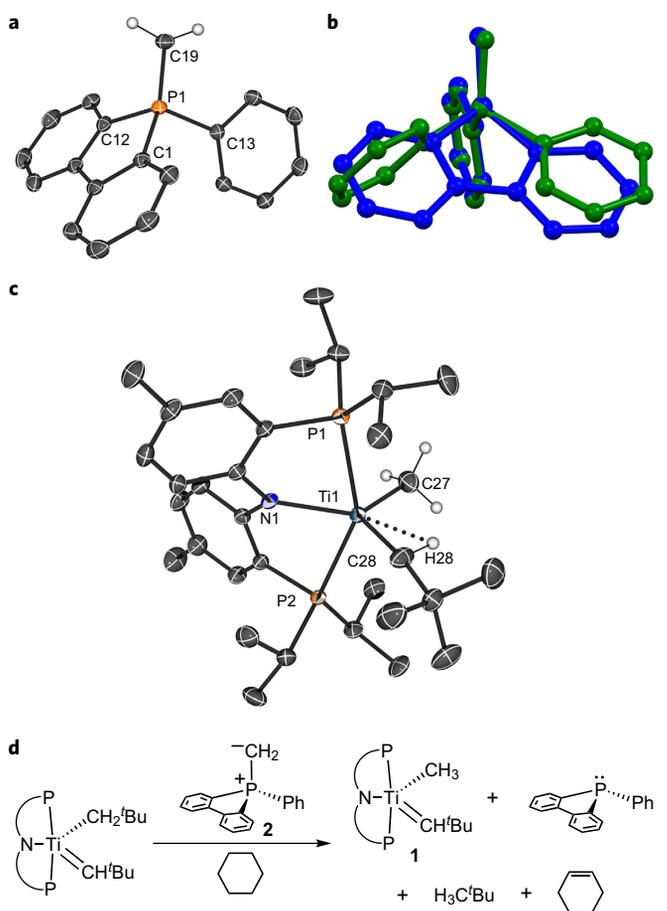
**Figure 1 | Dehydrogenation of cyclohexane using the alkylidyne precursor (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu), along with a proposed mode for the decomposition of the phosphorus ylide H<sub>2</sub>CPPh<sub>3</sub>.** Proposed pathway (from the top) describing how (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) can eliminate H<sub>3</sub>C<sup>t</sup>Bu and form alkylidyne intermediate **A**, which then dehydrogenates linear alkane H<sub>3</sub>CCH<sub>2</sub>R (R=H, CH<sub>3</sub>, ethyl, propyl (<sup>n</sup>Pr), butyl (<sup>n</sup>Bu), pentyl (<sup>n</sup>Pen), hexyl (<sup>n</sup>Hex)) via the alkylidene intermediate (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub>CH<sub>2</sub>R), followed by β-hydrogen abstraction to produce a stable complex with bound olefin (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)(H<sub>2</sub>C=CHR). For linear alkanes, only the α-olefin adduct is formed. When (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) is treated with cyclohexane, dehydrogenation also occurs by a similar set of steps (not shown for clarity) to form the unstable cyclohexene adduct (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)(C<sub>6</sub>H<sub>10</sub>), which dissociates cyclohexene (C<sub>6</sub>H<sub>10</sub>) to form transient (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu). In the presence of phosphorus ylide H<sub>2</sub>CPPh<sub>3</sub>, coordination probably occurs to form (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)(CH<sub>2</sub>CPPh<sub>3</sub>), but the bound ylide becomes activated via phenyl migration and α-hydrogen abstraction to form the phosphino alkylidene (PNP)Ti=CHPPh<sub>2</sub>(Ph) and H<sub>3</sub>C<sup>t</sup>Bu. The phenyl groups of the phosphorus ylide are highlighted in red to emphasize how the H<sub>2</sub>CPPh<sub>3</sub> becomes activated and transformed. Although (PNP)Ti=CHPPh<sub>2</sub>(Ph) can be a source of a phosphino-alkylidyne (PNP)Ti≡CPh<sub>2</sub> (by losing benzene HPh), this process requires forcing conditions. Bottom left: caricature of the PNP, which represents pincer ligand N[2-P(CHMe<sub>2</sub>)<sub>2</sub>-4-methyl phenyl]<sub>2</sub><sup>-</sup>.

gave a mixture of decomposition products including the phospho-lyde [PC<sub>12</sub>H<sub>8</sub>]<sup>-</sup>. Given the chelation of the phosphino group on the alkylidene in (PNP)Ti=CHPPh<sub>2</sub>(Ph) and its difficulty to eliminate benzene, we explored the reactions of other ylide reagents with (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu). As illustrated in Fig. 1, the decomposition of the phosphorus ylide H<sub>2</sub>CPPh<sub>3</sub> may be promoted by the transient Ti(II) intermediate [(PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)] formed after the cyclohexane dehydrogenation is completed<sup>29</sup>. The mechanism probably involves phenyl migration in the Ti-phosphine adduct [(PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)(CH<sub>2</sub>PPh<sub>3</sub>)], which formally constitutes an oxidative addition, to form a hypothetical Ti(IV) species [(PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)(CH<sub>2</sub>PPh<sub>2</sub>)(Ph)]. Intermediate [(PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)(CH<sub>2</sub>PPh<sub>2</sub>)(Ph)] would then eliminate H<sub>3</sub>C<sup>t</sup>Bu to then produce (PNP)Ti=CHPPh<sub>2</sub>(Ph). In an attempt to avoid both phenyl migration and deprotonation reactions, each of which renders the reaction non-catalytic, we turned our attention to a thus far unknown but possibly highly competent methylene transfer reagent phenyldibenzophosphole methylene ylide, H<sub>2</sub>CP(C<sub>12</sub>H<sub>8</sub>)Ph (**2**), as highlighted in Fig. 2a. Because the P atom is chelated by a biphenyl moiety, the two phenyl groups are interlocked and phenyl migration should be discouraged by at least two orders of magnitude compared to H<sub>2</sub>CPPh<sub>3</sub>.

Preparing and fully characterizing the phosphorus ylide H<sub>2</sub>CP(C<sub>12</sub>H<sub>8</sub>)Ph (**2**) required the use of a strong base, sodium bis(trimethylsilyl)amide (Na[N(SiMe<sub>3</sub>)<sub>2</sub>]), and the phosphonium salt [H<sub>3</sub>CP(C<sub>12</sub>H<sub>8</sub>)Ph][I] (ref. 31). Ylide **2** forms as an orange-yellow solid and is thermally stable, but is moisture- and air-sensitive (see Supplementary Section ‘Experimental’ for more details). It can be stored indefinitely at -35 °C. In addition to multinuclear NMR spectroscopic data, a solid-state structure of **2** (Fig. 2b, top) revealed it to be quite similar to the well-known phosphorus ylide H<sub>2</sub>CPPh<sub>3</sub>, albeit with subtle differences in their tetrahedral structures (see Supplementary Section ‘X-ray crystallographic studies’

for more details). As illustrated in Fig. 2b, ylide **2** (shown in blue, τ<sub>4</sub> = 0.85) (τ<sub>4</sub> = (360° - (α + β))/141° as defined in ref. 32) has a slightly more distorted tetrahedral geometry than H<sub>2</sub>CPPh<sub>3</sub> (shown in green, τ<sub>4</sub> = 0.93)<sup>32</sup>. The ylide bond character in **2** is evident from the P-C<sub>methylene</sub> bond length of 1.6789(11) Å, which is similar to that found in H<sub>2</sub>CPPh<sub>3</sub> (1.662(8) Å)<sup>33</sup>. Density functional theory (DFT) calculations indicate a natural bond orbital charge of -0.604 on C and +0.810 on P, further confirming the strong ylide character. To our delight, when (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) is treated with 1 equiv. of **2** over 24 h in cyclohexane at 25 °C, we observed nearly quantitative formation of cyclohexene, H<sub>3</sub>C<sup>t</sup>Bu, phenyldibenzophosphole P(C<sub>12</sub>H<sub>8</sub>)Ph and the previously reported methyl complex (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>3</sub>) (**1**) (Fig. 2d)<sup>25</sup>. Because we know that **1** can extrude CH<sub>4</sub> via a four-centred transition state to form **A** with activation parameters ΔH<sup>‡</sup> = 29.5 kcal mol<sup>-1</sup> and ΔS<sup>‡</sup> = 4.6 cal mol<sup>-1</sup> K<sup>-1</sup> (ref. 25), our reaction could in principle be catalytic in **1**. However, given the predicted barrier of ΔG<sup>‡</sup> ≈ 28.1 kcal mol<sup>-1</sup> at 25 °C, this catalytic reaction may require elevated temperatures due to the slow elimination of CH<sub>4</sub> in complex **1**.

Although spectroscopic data for complex **1** have been reported previously<sup>25</sup>, precise structural information was not available. Thus, the solid-state structure of **1** was obtained from X-ray diffraction data of a single crystal (see Supplementary Section ‘X-ray crystallographic studies’ for more details) and we confirmed the presence of the methyl (Ti-C, 2.136(2) Å) and neopentylidene (Ti=C, 1.870(2) Å) moieties with an α-agostic interaction at the alkylidene C-H bond (Fig. 2c). The α-hydrogen was located and refined isotropically and points towards the metal in the C27-Ti1-C28 groove at a distance of 1.93(3) Å. The formation of **1** from (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu), cyclohexane and the ylide suggested that the latter reagent transfers the methylidene to the transient Ti(II) fragment [(PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)] with loss of phosphine, instead of forming a phosphino-alkylidene titanium



**Figure 2 | Crystal structures of the phosphorus ylide **2** and catalyst **1** along with reactivity of (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) with **2** and cyclohexane. **a**,**

View of the solid-state structure of phosphorus ylide **2**, depicting thermal ellipsoids at the 50% probability level. Non-methylidene hydrogen atoms are omitted for clarity. Selected metric parameters are reported as distances (Å) and angles (°): P1–C1, 1.8255(11); P1–C12, 1.8020(11); P1–C13, 1.8110(11); P1–C19, 1.6789(11); C12–P1–C1, 90.80(5); C12–P1–C13, 110.13(5); C13–P1–C1, 103.33(5); C19–P1–C1, 127.28(5); C19–P1–C12, 113.24(5); C19–P1–C13, 110.11(6). **b**, Superimposed molecular structures of ylide **2** (blue) and H<sub>2</sub>CPPH<sub>3</sub> (green)<sup>33</sup>, emphasizing the similarity of the geometry and steric crowding at the phosphorus atom. **c**, Molecular structure of alkylidene-methyl **1**, with thermal ellipsoids at the 50% probability level. Non-essential hydrogen atoms are omitted for clarity. Selected metric parameters are reported in distances (Å) and angles (°): Ti1–P1, 2.5806(7); Ti1–P2, 2.5779(7); Ti1–N1, 2.1122(17); Ti1–C27, 2.136(2); Ti1–C28, 1.870(2); P1–Ti1–P2, 149.16(2); N1–Ti1–P1, 73.96(5); N1–Ti1–P2, 75.21(5); N1–Ti1–C27, 118.21(9); N1–Ti1–C28, 130.40(10); C27–Ti1–P1, 98.47(7); C27–Ti1–P2, 95.39(7); C28–Ti1–P1, 97.15(8); C28–Ti1–P2, 103.24(8); C28–Ti1–C27, 111.33(11).

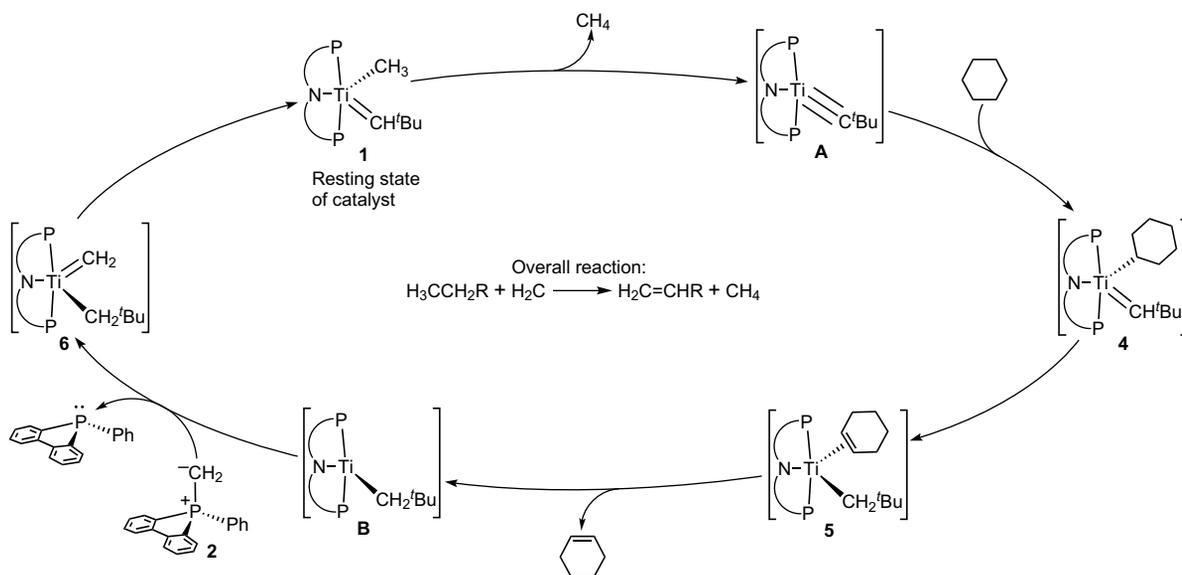
**d**, Reaction showing how compound (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) and phosphorus ylide H<sub>2</sub>CP(C<sub>12</sub>H<sub>8</sub>)Ph (**2**) in cyclohexane at 25 °C form phosphine P(C<sub>12</sub>H<sub>8</sub>)Ph, H<sub>3</sub>C<sup>t</sup>Bu and cyclohexene. This reaction demonstrates how the phosphorus ylide can deliver the CH<sub>2</sub> group to ultimately generate an alkylidene-methyl (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>3</sub>) (**1**), which can serve as a synthon to alkylidyne **A**. The reaction therefore suggests that complex **1** could, in principle, be a catalyst for the dehydrogenation of hydrocarbons using the ylide as a stoichiometric oxidant and hydrogen acceptor. The PNP caricature shows [N{2-P(CHMe)<sub>2</sub>-4-methyl phenyl}]<sub>2</sub><sup>-</sup>.

complex akin to what is observed with H<sub>2</sub>CPPH<sub>3</sub> (*vide supra*, Fig. 1). An isotopic labelling experiment conducted with (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) and **2** in cyclohexane-*d*<sub>12</sub> shows that cyclohexene-*d*<sub>10</sub>, P(C<sub>12</sub>H<sub>8</sub>)Ph, H<sub>3</sub>C<sup>t</sup>Bu along with the isotopologue (PNP)Ti=CD<sup>t</sup>Bu

(CH<sub>2</sub>D) (1-*d*<sub>2</sub>) are formed (see Supplementary Section ‘Experimental’ for more details). The presence of 1-*d*<sub>2</sub> clearly indicates that the solvent was dehydrogenated by alkylidyne **A** to form a species such as [(PNP)Ti=CH<sup>t</sup>Bu(C<sub>6</sub>H<sub>11</sub>)] (**4**), which then underwent β-hydrogen abstraction to produce the cyclohexene complex [(PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)(η<sup>2</sup>-C<sub>6</sub>H<sub>10</sub>)] (**5**). Unfortunately, the dehydrogenation of C<sub>6</sub>D<sub>12</sub> in the presence of **2** also gave minor amounts of other titanium complexes, which can be detected by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, but which we have thus far been unable to unambiguously identify. Because phenyldibenzophosphole P(C<sub>12</sub>H<sub>8</sub>)Ph was formed in the reaction shown in Fig. 2d, intermediate **5** or the olefin-free species [(PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)] (**B**) must have undergone oxidation by phosphorus ylide **2** to form a transient methylene [(PNP)Ti=CH<sub>2</sub>(CH<sub>2</sub><sup>t</sup>Bu)] (**7**) species, which then tautomerized to alkylidene-methyl **1** (Fig. 3). Our isotopic labelling studies using cyclohexane-*d*<sub>12</sub> provide convincing evidence for a tautomerization process<sup>25</sup>. The transfer of a methylene group to a low-valent group **4** or **5** transition metal to form methylene complexes has been reported previously in the literature<sup>34–39</sup>. The cycle in Fig. 3 shows our proposed set of intermediates invoking **1** as the resting state.

Figure 4a shows the reaction energy profile of the catalytic cycle calculated using a quantum chemical model based on DFT, which is fully consistent with the aforementioned observations. Transient complex **A** first binds cyclohexane via σ-complex **3**, which is energetically uphill by 1.7 kcal mol<sup>-1</sup>. As found in our previous work<sup>25,27,28,40</sup>, **3** undergoes 1,2-addition of the C–H bond across the Ti≡C linkage to give cyclohexyl intermediate **4**, traversing transition state **3-TS** with a barrier of 8.0 kcal mol<sup>-1</sup>. A β-hydrogen abstraction from the cyclohexyl group in **4** leads to cyclohexene product complex **5**. Our calculations show that the transition state associated with this step, **4-TS**, gives a reaction barrier of 26.7 kcal mol<sup>-1</sup>. This barrier is slightly lower than the previously calculated barrier for methane extrusion of ~28 kcal mol<sup>-1</sup>. Given the high efficiency of this reaction, our DFT-calculated barrier may be overestimating the transition-state energy compared with the methane elimination. The computed structure of **4-TS** is also shown in Fig. 4b and exhibits parameters consistent with a distorted trigonal bipyramidal geometry, where the hydrogen abstracted is located approximately halfway between the acceptor and donor carbon, with C–H distances of 1.64 Å and 1.50 Å, respectively. The computed structure of cyclohexene adduct **5** is also shown in Fig. 4b, and the titanium centre maintains a trigonal-bipyramidal geometry in which the newly formed cyclohexene is oriented parallel to the PNP ligand plane. The short Ti–C distances are 2.14 and 2.13 Å, respectively, and the C–C distance is 1.45 Å, thus indicating that the most appropriate resonance form is that confined between the two extremes, namely a Ti(IV)–metallacyclopropene moiety and a Ti(II)–cyclohexene π-complex.

After dissociation of the cyclohexene product from **5**, intermediate complex **B** is formed. Interestingly, this process is accompanied by a spin-crossover: whereas intermediate **5** consists of a low-spin Ti(II)-*d*<sup>2</sup> centre affording a singlet ground-state configuration, liberation of the cyclohexene product cannot occur on the singlet spin-state potential energy surface, as the singlet complex **1B** is 29.2 kcal mol<sup>-1</sup> higher in energy than intermediate **5**. If the product release is accompanied by a spin-crossover into the high-spin Ti(II) triplet surface, intermediate **3B**, which is 17.0 kcal mol<sup>-1</sup> lower in energy, can be used. Thus, the cyclohexene release is only uphill by 12.3 kcal mol<sup>-1</sup>. The transition state for product release cannot be located reliably using standard quantum chemical methods, because this process is probably dominated by translational entropy changes and surface hopping, which cannot be included in standard potential energy scans. We found a surface crossing point at a relative energy of –3.3 kcal mol<sup>-1</sup>, suggesting a barrier for the cyclohexene loss of 16.2 kcal mol<sup>-1</sup>. Although this barrier appears low, the required



**Figure 3 | Proposed catalytic transfer dehydrogenation cycle using the resting state of the catalyst, namely complex 1.** The cycle shows how **1** eliminates  $\text{CH}_4$  by  $\alpha$ -hydrogen abstraction to form transient **A**. Alkyldiene **A** then activates cyclohexane ( $\text{C}_6\text{H}_{12}$ ) to form  $(\text{PNP})\text{Ti}(\text{CH}_2^t\text{Bu})(\text{C}_6\text{H}_{11})$ , which undergoes  $\beta$ -hydrogen abstraction to form the intermediate cyclohexene adduct  $(\text{PNP})\text{Ti}(\text{CH}_2^t\text{Bu})(\text{C}_6\text{H}_{10})$ . A dissociative process eliminates cyclohexene ( $\text{C}_6\text{H}_{10}$ ) to form **B**, thus allowing the ylide to deliver the methylene group ( $\text{CH}_2$ ) to form the titanium methyldiene  $(\text{PNP})\text{Ti}=\text{CH}_2(\text{CH}_2^t\text{Bu})$  (**6**) and free phenyldibenzophosphole  $\text{P}(\text{C}_{12}\text{H}_8)\text{Ph}$ . Intermediate **6** then rapidly tautomerizes to the resting state of the catalyst, namely **1**. The middle of the cycle shows the overall balanced reaction involving the conversion of a hydrocarbon ( $\text{H}_3\text{CCH}_2\text{R}$ ) to its respective olefin ( $\text{H}_2\text{C}=\text{CHR}$ ) using a carbene ( $\text{CH}_2$ ) as the hydrogen acceptor. Using cyclohexane as our substrate in this cycle we can then expand to linear hydrocarbons being converted selectively to  $\alpha$ -olefins.

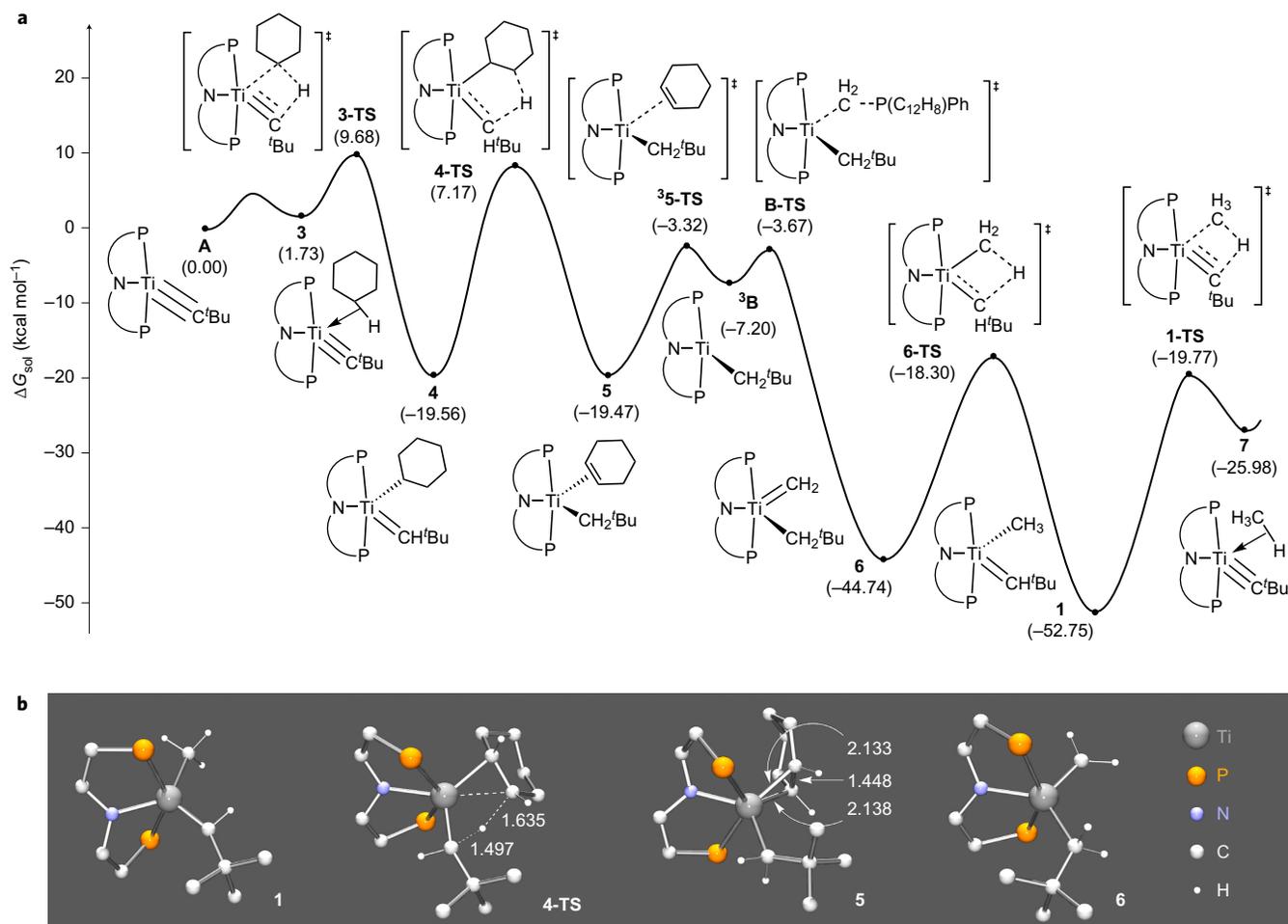
spin-crossover could pose a significant challenge to the rate of this step at higher temperature, despite the relatively low energy of the intermediate and reasonable transition-state energies. We expect, therefore, that this product release step could also be a major obstacle for the efficiency of the catalyst under our conditions.

To regenerate the active catalyst, intermediate **3B** may react with the phosphorus ylide  $\text{H}_2\text{CP}(\text{C}_{12}\text{H}_8)\text{Ph}$  to undergo a methyldiene group transfer with a barrier of  $3.5 \text{ kcal mol}^{-1}$ . The C–P bond cleavage and methylene transfer is highly exergonic, and intermediate **6** is readily formed from **3B** with a driving force of  $37.5 \text{ kcal mol}^{-1}$ . The final conversion of **6** to the resting state of the catalyst **1** has a barrier of  $26.4 \text{ kcal mol}^{-1}$ , and **1** may undergo hydrogen abstraction to afford hypothetical  $\sigma$ -complex **7**, traversing transition state **1-TS**. Dissociation of methane will regenerate the active catalyst **A**. This last step is associated with the highest barrier of  $33.0 \text{ kcal mol}^{-1}$ , but it leads to the liberation of methane, which is irreversible and therefore a non-equilibrium process. Formation of **A** by liberation of methane ( $\alpha$ -hydrogen abstraction) thus appears to be the bottleneck in our proposed reaction mechanism. Regardless, we have considered several other alternative mechanisms. For example, an associative pathway is plausible where the methyldiene transfer occurs before cyclohexene is released with or without one of the PNP arms dissociating to keep the overall coordination number constant. None of the alternatives considered gave lower-energy pathways to product. Some of these plausible mechanisms are described in the Supplementary Section ‘Computational details’.

To demonstrate that the ylide is indeed the source of the methyl unit in **1**, we prepared the deuterated phosphorus ylide  $\text{D}_2\text{CP}(\text{C}_{12}\text{H}_8)\text{Ph}$  (**2**- $d_2$ ) (see Supplementary Section ‘Experimental’ for more details) and treated it with  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2^t\text{Bu})$  in cyclohexane at  $25^\circ\text{C}$ . After 24 h we detected cyclohexene,  $\text{H}_3\text{C}^t\text{Bu}$ ,  $\text{P}(\text{C}_{12}\text{H}_8)\text{Ph}$  and the  $d_2$ -isotopologue of **1**, namely  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{CD}_2\text{H})$  (**1**- $d_2$ ). Under these conditions, deuteration of the alkyldiene  $\alpha$ -carbon is not evident based on  $^1\text{H}$  NMR spectroscopy, as the singlet resonance at 8.30 ppm is clearly visible and integrates to approximately one hydrogen when compared to

the pincer  $^i\text{Pr}$  resonances of the PNP ligand (see Supplementary Section ‘Spectroscopic data’ for more details). The fact that very little, if any, deuteration of the alkyldiene moiety in  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{CD}_2\text{H})$  is observed corroborates our computed energies and shows that the tautomerization step from **1** to **6** is essentially irreversible under these conditions. To test whether  $\alpha$ -hydrogen abstraction to form **A** is most probably the slowest step in the cycle shown in Fig. 3, we compared the rates involving the formation of **A** from  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2^t\text{Bu})$ <sup>41</sup> and **1** (ref. 28) in benzene with the rates observed for cyclohexane dehydrogenation in the presence of ylide **2** and  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2^t\text{Bu})$  and ylide **2** with **1**. Because we know that  $\alpha$ -hydrogen abstraction is the overall rate-determining step for the transformation involving benzene C–H activation, we can probe whether the formation of **A** is also the bottleneck in the dehydrogenation cycle. Comparisons show that  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2^t\text{Bu})$  forms **A** in benzene with a  $k \approx 3.0 \times 10^{-4} \text{ s}^{-1}$  at  $40^\circ\text{C}$ , whereas  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_3)$  eliminates  $\text{CH}_4$  in benzene at a much slower rate with  $k \approx 3.4 \times 10^{-6} \text{ s}^{-1}$  at  $60^\circ\text{C}$ . Monitoring cyclohexane dehydrogenation shows that  $\sim 90\%$  of the reaction is complete after 14 h at room temperature with  $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2^t\text{Bu})/2$ /cyclohexane, whereas with  $1/2$ /cyclohexane there was very little conversion at room temperature ( $<1\%$  of cyclohexane and phosphine is observed). These results corroborate our earlier reported results<sup>25</sup> with **1**, in that it is remarkably stable in  $\text{C}_6\text{D}_6$  at room temperature, with only  $<5\%$  conversion to the benzene-activated product  $(\text{PNP})\text{Ti}=\text{CD}^t\text{Bu}(\text{C}_6\text{D}_5)$  and  $\text{CH}_4$  after six weeks. As a result, these comparisons suggest that  $\alpha$ -hydrogen abstraction to form **A** greatly affect the rate (at  $25^\circ\text{C}$ ) of the overall cyclohexane dehydrogenation reaction by at least two orders of magnitude. As outlined in the mechanistic proposal above, cyclohexene was formed (entry 1, Table 1) when **1** was treated with 10 equiv. of **2** in cyclohexane at  $75^\circ\text{C}$  over 4 days.

Examination of the reaction mixture by  $^1\text{H}$  NMR spectroscopy using an internal standard ( $8 \mu\text{M}$  ferrocene solution in toluene in a capillary tube) revealed that  $\sim 3$  equiv. of cyclohexene were produced, which is consistent with this process being catalytic in **1**.



**Figure 4 | Computed Gibbs free energy profile for the dehydrogenation of cyclohexane along with optimized structures.** **a**, Free energy profile for the dehydrogenation of cyclohexane using titanium alkyldiyne **A** and phosphorus ylide **2** as a carbene source. The reaction coordinate begins with alkyldiyne **A**, followed by formation of cyclohexane adduct **3**, C–H activated cyclohexyl **4** and cyclohexene adduct **5**. Dissociation of cyclohexene results in a spin-transition leading to triplet  $^3\mathbf{B}$ , which then binds phosphorus ylide **2** to yield **6** and free phosphine. Tautomerization in **6** forms **1**, which then eliminates methane via  $\sigma$ -CH<sub>4</sub> adduct **7** to reform **A**. Transition states are shown in brackets and above each barrier. **b**, Optimized structures of complex **1**, transition state **4-TS** and the product resulting from this transition state, namely cyclohexene complex **5**. Also shown is titanium methylidene **6**, resulting from CH<sub>2</sub> transfer from **2**. Only  $\alpha$ -hydrogen atoms are shown; PNP ligand peripherals have been omitted for the purpose of clarity.

Varying the amount of alkane solvent or ylide equivalents did not lead to significantly improved turnover number (TON), indicating that the activity of **1** is the limiting factor in catalytic efficiency, in good agreement with the proposed mechanism and the computed reaction energy profile. Furthermore, increasing the temperature beyond 75 °C resulted in lower yields of olefin and thus turnover number. This somewhat counter-intuitive observation suggests that other intermediates (apart from **A**) along the cycle might be decomposing, including cyclohexene release from **5**, which is coupled to spin-crossover and could pose a major challenge to catalytic turnover under more forcing conditions. The intersystem crossing process is not expected to be accelerated as much by increased temperature, while other chemical side reactions such as decomposition of **B** will become faster at higher reaction temperatures. The poor solubility of the ylide in the hydrocarbon may further deteriorate the efficiency of cleanly converting intermediates **5** or **B** to **6**.

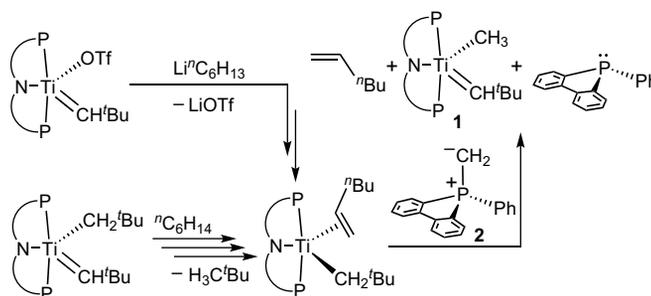
To investigate the scope of this catalytic reaction, we screened **1** and 10 equiv. of ylide **2** in various solutions of other alkanes. In the case of cyclooctane, we observe similar TON values to form only the *cis*-isomer cyclooctane, which is anticipated based on its stability relative to that of *trans*-cyclooctane (entry 2, Table 1). In the case of linear alkanes C<sub>5</sub>–C<sub>8</sub>, heating the reaction mixture for 4 days at

75 °C led to a gradual colour change from orange to dark orange-brown, and investigation of the mixture by <sup>1</sup>H NMR spectroscopy indicated selective formation of only the  $\alpha$ -olefin with 1–3 turnovers (entries 3–6). Dehydrogenation of *n*-butane proved more challenging given that the reagent and expected product (1-butene) are gases at room temperature, thus precluding **1** and the ylide from being dissolved in solution. As a result, we explored this reaction using cyclohexane as our solvent medium, under 8.5 atm of *n*-butane (~70 equiv. of *n*-butane to 470 equiv. of cyclohexane-*d*<sub>12</sub>). After 4 days at 75 °C we observed only 0.2 equiv. of 1-butene along with cyclohexene-*d*<sub>10</sub>. Unfortunately, our reaction conditions resulted in mostly the solvent cyclohexane to be the primary target of dehydrogenation, as opposed to the *n*-butane. Regardless, our approach provides a direct entry to 1-butene from the alkane without any evidence of olefin isomerization to the thermodynamically preferred product 2-butene. As a control experiment, heating a solution of **1** in alkanes C<sub>5</sub>–C<sub>8</sub> (to 75 °C) without the addition of **2** led to complete decomposition of the titanium complex within 24 h, in addition to the formation of a stoichiometric amount of olefin. Similarly, heating a solution of phosphorus ylide **2** in *n*-hexane or cyclohexane for 5 days at 100 °C in the absence of **1** resulted in only 10% degradation of the ylide as judged by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, and with no evidence of olefin formation. Thus, it is

apparent that titanium complex **1** must be responsible for dehydrogenation, whereas **2** is important for the reaction as the hydrogen acceptor but is not a source of free carbene. As noted before, the different rates for  $\alpha$ -hydrogen abstraction clearly point to our titanium **1** being responsible for these dehydrogenation reactions. To test whether trace impurities are responsible for the observed results, we conducted numerous control experiments in *n*-hexane at 75 °C over 4 days using various reagents (or side products formed in the synthesis of **1**), with or without ylide **2**. We found all these control experiments to not form 1-hexene (or isomers thereof). These reactions are described in Supplementary Section 'Control experiment'.

This approach to engineering a homogeneous catalytic alkane dehydrogenation offers several key advantages. First, complex **1** provides a mild route to the dehydrogenation of volatile alkanes, with the reaction temperature being significantly lower than that reported for most known homogeneous systems<sup>5–20,42</sup>. Second, the titanium alkylidyne **A** reacts selectively at the terminal position in the case of linear alkanes, and no evidence was found suggesting that isomerization to the thermodynamically preferred internal olefin occurs under these conditions. Such selectivity is possible in our proposed reaction cycle shown in Fig. 3, because titanium hydrides are not formed. It is important to note that some iridium catalysts can catalyse the transfer dehydrogenation of alkanes to 1-alkenes in a kinetically selective fashion, but once the 1-alkene builds up, these tend to isomerize to internal alkenes<sup>43</sup>. Although our catalyst presently shows only a few turnovers, the concept of using a methylidene group as a hydrogen acceptor in combination with a base metal such as titanium provides an unprecedented route to transfer dehydrogenation of volatile alkanes to transform these low-value feedstocks into value-added, versatile commodity chemicals, including for the selective formation of  $\alpha$ -olefins.

To probe whether a titanium olefin complex such as **5** was really formed and whether such species could be oxidized by phosphorus ylide **2**, we examined stable olefin derivatives of **5**. Olefin complex (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)( $\eta^2$ -H<sub>2</sub>C=CH<sup>n</sup>Bu) was prepared either by salt metathesis between (PNP)Ti=CH<sup>t</sup>Bu(OTf) and *n*-hexyllithium



**Figure 5** | Scheme showing how phosphorus ylide **2** can react with stable titanium 1-hexene adduct (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)(H<sub>2</sub>C=CH<sup>n</sup>Bu) to form catalyst **1**, free phosphine P(C<sub>12</sub>H<sub>8</sub>)Ph and release the  $\alpha$ -olefin 1-hexene. This reaction suggests that an olefin adduct such as (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)(H<sub>2</sub>C=CHR) is probably formed under our catalytic conditions and also demonstrates that carbene transfer (from the phosphorus ylide) and tautomerization steps (invoking (PNP)Ti=CH<sub>2</sub>(CH<sub>2</sub><sup>t</sup>Bu)) leading to **1** are probably not the slowest steps in the catalytic cycle.

(Li<sup>n</sup>C<sub>6</sub>H<sub>13</sub>) or by *n*-hexane dehydrogenation with precursor (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) (Fig. 5)<sup>28,41</sup>. Heating a diastereomeric mixture of (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)( $\eta^2$ -H<sub>2</sub>C=CH<sup>n</sup>Bu) with **2** in cyclohexane solution for 15 min at 75 °C led to the formation of **1**, 1-hexene and the phosphine PhP(C<sub>12</sub>H<sub>8</sub>) (Fig. 5). This independent synthesis of a derivative of **5** confirms that dehydrogenation by **A** precedes methylidene group transfer by **2** to the titanium centre, and suggests that olefin dissociation to form **B** is not the rate-determining step. Unfortunately, attempts to form **1** using the ethylene complex (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)( $\eta^2$ -H<sub>2</sub>C=CH<sub>2</sub>) and **2** at 75 °C were unsuccessful and instead yielded free phosphine and a myriad of titanium products that we were unable to precisely identify. We suspect that the stability of (PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)( $\eta^2$ -H<sub>2</sub>C=CH<sub>2</sub>) to the release of ethylene and form **B** prevents clean oxidation by **2**.

In conclusion, we have demonstrated that the phenyldibenzophosphole methylene ylide **2** can oxidize the transient and high-spin titanium(II) fragment [(PNP)Ti(CH<sub>2</sub><sup>t</sup>Bu)] (**B**), which is generated after alkane dehydrogenation and dissociation of the olefin (or  $\alpha$ -olefin in the case of linear alkanes), to form a transient titanium methylidene that tautomerizes quickly to a stable resting state, namely neopentylidene-methyl **1**. This catalytic process represents a new route for selective transfer dehydrogenation of alkanes C<sub>4</sub>–C<sub>8</sub> to  $\alpha$ -olefins as well as for cyclic alkanes C<sub>6</sub> and C<sub>8</sub>. Our proposed pathway invokes non-oxidative C–H activation reactions, which prevent olefin isomerization. Although the present conditions only allow for a few turnovers, we are now in a position to optimize the few turnovers in this reaction because we can readily control the rate to the formation of **A** and, in principle, the source of the methylidene transfer reagent. The poor solubility of **2** in hydrocarbon, the high barrier associated with the  $\alpha$ -hydrogen abstraction from **1** to **A** and the spin-crossover needed for the olefin release are probably the main causes of low turnover efficiency under our reported conditions.

**Data availability.** Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition nos. CCDC 1529334 (**1**) and 1529335 (**2**). Copies of these data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). All other data supporting the findings of this study are available within the Article and its Supplementary Information, or from the corresponding author on reasonable request.

Received 25 January 2017; accepted 5 May 2017; published online 26 June 2017

**Table 1** | Catalytic dehydrogenation of various alkanes using **1** and phosphorus ylide **2**.

Entry	Alkane	Alkene	TON*
1			2.8(2)
2			2.5(2) (cis)
3			1.5(7)
4			3.2(8)
5			3.0(2)
6			2.7(2)
7			0.2 <sup>†</sup>

\*Turnover numbers were determined in reference to an internal standard of ferrocene in toluene (in a capillary tube). Each experiment (with the exception of entry 7) was performed at least twice to ensure consistency. TONs are reported as an average, with the number in parenthesis corresponding to the margin of error of experiments. <sup>†</sup>The formation of 1-butene is accompanied by the formation of cyclohexene, which is used as the solvent medium (see Supplementary Section 'Dehydrogenation of 'butane' for more details).

## References

- Sadrameli, S. M. Thermal/catalytic cracking of hydrocarbons for the production of olefins: a state-of-the-art review. I: thermal cracking review. *Fuel* **140**, 102–115 (2015).
- Ren, T., Patel, M. & Blok, K. Olefins from conventional and heavy feedstocks: energy use in steam cracking and alternative processes. *Energy* **31**, 425–451 (2006).
- Tullo, A. H. Refining chemicals. *Chem. Eng. News* **85**, 27–29 (2007).
- Tullo, A. H. Ethylene from methane. *Chem. Eng. News* **89**, 20–21 (2011).
- Dobereiner, G. E. & Crabtree, R. H. Dehydrogenation as a substrate-activating strategy in homogeneous transition-metal catalysis. *Chem. Rev.* **110**, 681–703 (2010).
- Zhang, Y., Yao, W., Fang, H., Hu, A. & Huang, Z. Catalytic alkane dehydrogenations. *Sci. Bull.* **60**, 1316–1331 (2015).
- Kumar, A. & Goldman, A. S. Recent advances in alkane dehydrogenation catalyzed by pincer complexes. *Top. Organomet. Chem.* **54**, 307–334 (2015).
- Nomura, K. & Saito, Y. *n*-Alkane and dihydrogen formation from *n*-alkanes by photocatalysis using carbonyl(chloro)phosphine–rhodium complexes. *J. Chem. Soc. Chem. Commun.* 161–162 (1988).
- Maguire, J. A., Boese, W. T. & Goldman, A. S. Photochemical dehydrogenation of alkanes catalyzed by *trans*-carbonylchlorobis(trimethylphosphine)rhodium: aspects of selectivity and mechanism. *J. Am. Chem. Soc.* **111**, 7088–7093 (1989).
- Chowdhury, A. D. *et al.* Towards a practical development of light-driven acceptorless alkane dehydrogenation. *Angew. Chem. Int. Ed.* **53**, 6477–6481 (2014).
- Felkin, H., Fillebeen-Khan, T., Gault, Y., Holmes-Smith, R. & Zakrzewski, J. Activation of C–H bonds in saturated hydrocarbons. The catalytic functionalisation of cyclooctane by means of some soluble iridium and ruthenium polyhydride systems. *Tetrahedron Lett.* **25**, 1279–1282 (1984).
- Six, C. *et al.* Inter- and intramolecular thermal activation of  $sp^3$  C–H bonds with ruthenium bisallyl complexes. *Organometallics* **18**, 3316–3326 (1999).
- Gruver, B. C., Adams, J. J., Warner, S. J., Arulsamy, N. & Roddick, D. M. Acceptor pincer chemistry of ruthenium: catalytic alkane dehydrogenation by  $(^{CF_3}PCP)Ru(cod)(H)$ . *Organometallics* **30**, 5133–5140 (2011).
- Choi, J., MacArthur, A. H. R., Brookhart, M. & Goldman, A. S. Dehydrogenation and related reactions catalyzed by iridium pincer complexes. *Chem. Rev.* **111**, 1761–1779 (2011).
- Gupta, M., Hagen, C., Flesher, R. J., Kaska, W. C. & Jensen, C. M. A highly active alkane dehydrogenation catalyst: stabilization of dihydrido rhodium and iridium complexes by a P–C–P pincer ligand. *Chem. Commun.* 2083–2084 (1996).
- Gupta, M., Hagen, C., Kaska, W. C., Cramer, R. E. & Jensen, C. M. Catalytic dehydrogenation of cycloalkanes to arenes by a dihydrido iridium P–C–P pincer complex. *J. Am. Chem. Soc.* **119**, 840–841 (1997).
- Xu, W. *et al.* Thermochemical alkane dehydrogenation catalyzed in solution without the use of a hydrogen acceptor. *Chem. Commun.* 2273–2274 (1997).
- Baudry, D., Ephritikhine, M., Felkin, H. & Holmes-Smith, R. The selective catalytic conversion of cycloalkanes into cycloalkenes using a soluble rhenium polyhydride system. *J. Chem. Soc. Chem. Commun.* 788–789 (1983).
- Baudry, D., Ephritikhine, M., Felkin, H. & Zakrzewski, J. Activation of C–H bonds in saturated hydrocarbons. The formation of *bis*(triphenylphosphine) ( $\eta$ -alkadiene)rhenium trihydrides from *n*-alkanes, and their selective conversion into the corresponding 1-alkenes. *Tetrahedron Lett.* **25**, 1283–1286 (1984).
- Gruver, B. C., Adams, J. J., Arulsamy, N. & Roddick, D. M. Acceptor pincer chemistry of osmium: catalytic alkane dehydrogenation by  $(^{CF_3}PCP)Os(cod)(H)$ . *Organometallics* **32**, 6468–6475 (2013).
- Goldman, A. S. *et al.* Catalytic alkane metathesis by tandem alkane dehydrogenation–olefin metathesis. *Science* **312**, 257–261 (2006).
- Ahuja, R. *et al.* Catalytic dehydroaromatization of *n*-alkanes by pincer-ligated iridium complexes. *Nat. Chem.* **3**, 167–171 (2011).
- Kumar, A. *et al.* Dehydrogenation of *n*-alkanes by solid-phase molecular pincer-iridium catalysts. High yields of  $\alpha$ -olefin product. *J. Am. Chem. Soc.* **137**, 9894–9911 (2015).
- West, J. G., Huang, D. & Sorensen, E. J. Acceptorless dehydrogenation of small molecules through cooperative base metal catalysis. *Nat. Commun.* **6**, 1–7 (2015).
- Flores, J. A. *et al.* Methane activation and exchange by titanium–carbon multiple bonds. *Chem. Sci.* **2**, 1457–1462 (2011).
- Cavaliere, V. N. & Mendiola, D. J. Methane: a new frontier in organometallic chemistry. *Chem. Sci.* **3**, 3356–3365 (2012).
- Cavaliere, V. N. *et al.* Room temperature dehydrogenation of ethane to ethylene. *J. Am. Chem. Soc.* **133**, 10700–10703 (2011).
- Crestani, M. G. *et al.* Room temperature dehydrogenation of ethane, propane, linear alkanes C4–C8, and some cyclic alkanes by titanium–carbon multiple bonds. *J. Am. Chem. Soc.* **135**, 14754–14767 (2013).
- Hickey, A. K. *et al.* Dehydrogenation of hydrocarbons with metal–carbon multiple bonds and trapping of a titanium(II) intermediate. *Dalton Trans.* **43**, 9834–9837 (2014).
- Kamitani, M. *et al.* Phosphinoalkylidene and -alkylidyne complexes of titanium: intermolecular C–H bond activation and dehydrogenation reactions. *J. Am. Chem. Soc.* **137**, 11872–11875 (2015).
- Neumann, R. A. & Berger, S. Observation of a betaine lithium salt adduct during the course of a Wittig reaction. *Eur. J. Org. Chem.* 1085–1087 (1998).
- Yang, L., Powell, D. R. & Houser, R. P. Structural variation in copper(I) complexes with pyridylmethylamide ligands: structural analysis with a new four-coordinate geometry index,  $\tau_4$ . *Dalton Trans.* 955–964 (2007).
- Bart, J. C. J. Structure of the non-stabilized phosphonium ylid methylenetriphenylphosphorane. *J. Chem. Soc. B* 350–365 (1969).
- Schrock, R. R. High oxidation state multiple metal–carbon bonds. *Chem. Rev.* **102**, 145–180 (2002).
- Sharp, P. R. & Schrock, R. R. Multiple metal–carbon bonds: XIV. Preparation of alkylidenetantalum complexes by alkylidene transfer from phosphoranes. The first ethylidene complex and how it decomposes. *J. Organomet. Chem.* **171**, 43–51 (1979).
- Schwartz, J. & Gell, K. I. The preparation of a di(cyclopentadienyl)zirconium methylene species from a phosphorane. *J. Organomet. Chem.* **184**, C1–C2 (1980).
- Gibson, V. C., Parkin, G. & Bercaw, J. E. Synthesis and reactivity of permethyltantalocene derivatives possessing  $\eta^3$ -allyl,  $\eta^2$ -butadiene,  $\eta^2$ -methylallene, and  $\eta^1$ -alkenylidene ligands. Model studies for the role of surface vinylidenes in the Fischer–Tropsch hydrocarbon-chain-lengthening process. *Organometallics* **10**, 220–231 (1991).
- Antonelli, D. M., Schaefer, W. P., Parkin, G. & Bercaw, J. E. Synthesis and characterization of  $(\eta^3-C_5Me_5)_2TaCl(THF)$ , a useful synthetic precursor for the preparation of oxo, imido and methylidene derivatives of permethyltantalocene. *J. Organomet. Chem.* **462**, 213–220 (1993).
- Buikink, J.-K. F., Teuben, J. H., Kooijman, H. & Spek, A. L. Synthesis, molecular structure, and reactivity of a half-sandwich vanadium(III) imido complex: the first vanadium(V) alkylidene. *Organometallics* **13**, 2922–2924 (1994).
- Bailey, B. C. *et al.* Intermolecular C–H bond activation promoted by a titanium alkylidyne. *J. Am. Chem. Soc.* **127**, 16016–16017 (2005).
- Bailey, B. C., Fan, H., Huffman, J. C., Baik, M.-H. & Mendiola, D. J. Intermolecular C–H bond activation reactions promoted by transient titanium alkylidynes. synthesis, reactivity, kinetic, and theoretical studies of the  $Ti\equiv C$  linkage. *J. Am. Chem. Soc.* **129**, 8781–8793 (2007).
- Nawara-Hultsch, A. J. *et al.* Rational design of highly active “hybrid” phosphine–phosphinite pincer iridium catalysts for alkane metathesis. *ACS Catal.* **3**, 2505–2514 (2013).
- Kundu, S. *et al.* Rational design and synthesis of highly active pincer-iridium catalysts for alkane dehydrogenation. *Organometallics* **28**, 5432–5444 (2009).

## Acknowledgements

The authors thank S. Berritt, J. Gu and G. Furst for discussions. The authors acknowledge the University of Pennsylvania and the National Science Foundation (CHE30848248 and CHE31152123) for funding support. This research was supported in part by the Institute for Basic Science (IBS-R010-D1) in Korea.

## Author contributions

D.P.S. and T.K. contributed equally to the experiments conducted in this work. M.V.M. and M.-H.B. conceived and analysed the computational component in the manuscript. D.J.M. conceived the study, and D.P.S. and T.K. designed the experiments. T.K., P.J.C. and B.C.M. conducted crystallographic studies. M.-H.B. and D.J.M. co-wrote the manuscript.

## Additional information

Supplementary information is available in the [online version of the paper](#). Reprints and permissions information is available online at [www.nature.com/reprints](http://www.nature.com/reprints). Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations. Correspondence and requests for materials should be addressed to M.H.B. and D.J.M.

## Competing financial interests

The authors declare no competing financial interests.