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Room Temperature Dehydrogenation of Ethane to Ethylene

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S *Supporting Information*

ABSTRACT: The transient titanium alkylidyne, (PNP)Ti≡C^{t}Bu (PNP = *N*[2-P^{i}Pr$_2$-4-methylphenyl]$_2$$^-$), activates a C−H bond of ethane at room temperature, and a β-hydrogen of the resulting ethyl ligand is subsequently transferred to the adjacent alkylidene ligand to form an ethylene adduct of titanium. Treatment of the ethylene complex with two-electron oxidants such as organic azides results in extrusion of ethene concomitant with formation of a mononuclear titanium imido complex.

Whereas methane received much attention as a potential carbon feedstock, the chemistry of ethane remains relatively unexplored. This hydrocarbon, which makes up the second largest component of natural gas, after methane, is particularly interesting as a potential source of more reactive C$_2$ products, such as ethene. Although practical, the most common industrial method for the conversion of ethane to ethene, referred to as steam cracking, is very energy-intensive (Temp. >800 °C) and rather inefficient given the detrimental buildup of CO$_2$ (1.5−3 tons of CO$_2$ per ton of ethene produced).[1] The use of ethane in organometallic processes under mild conditions is fundamentally difficult because of its inferior binding affinity to typical transition metal catalysts, the inherent strength of the C−H bond of ∼101 kcal/mol[2] and extraordinarily high pK_a in the range of 50.[3] Another factor often inhibiting the dehydrogenation of ethane to ethene is the accumulation of hydrogen,[4] which can serve as a ligand or hydride source, thus, impeding catalytic turnover. Homogeneous dehydrogenation catalysts were developed in the past using iridium,[5,6] rhodium,[4,7,8] and rhenium,[9] but these require high temperatures, limiting their utility to less volatile paraffins (C$_6$ and heavier and usually in the presence of a H$_2$ acceptor). Solid-state ethane dehydrogenation catalysts are also known[10] and degenerate metathesis and cross-metathesis of ethane have been reported in surface-based organometallic catalysts,[11] but the conversion of ethane to value-added chemicals like ethene has not yet been demonstrated under mild conditions—either catalytically or stoichiometrically[12]—or in a manner allowing for a clear understanding of the underlying mechanism.

Previously, we established that the transient titanium alkylidyne complex (PNP)Ti≡C^{t}Bu (**A**) (PNP = *N*[2-P^{i}Pr$_2$-4-methylphenyl]$_2$$^-$) can activate C−H bonds of arenes and other hydrocarbons (R−H) to give alkylidene−alkyl complexes of the type (PNP)Ti=CH^{t}Bu(R), in which the alkylidene hydrogen derives from a 1,2−CH bond activation of the hydrocarbon.[13] More recently we demonstrated that methane is also a suitable CH-activation substrate.[14] It is herein reported that the stoichiometric dehydrogenation of ethane to ethene can be achieved by **A** at room temperature with good yield.

A cyclohexane solution of the alkylidyne precursor complex, (PNP)Ti=CH^{t}Bu(CH$_2$^{t}Bu), undergoes a clean conversion in the presence of ethane at 21 °C over 24 h to give a single product. Moderately elevated ethane pressure (>400 psi) is required to improve yield and avoid the side-reactions of **A** with the solvent.[14] At these higher pressures, the transformation is quantitative within the detection limit of ^{31}P NMR spectroscopy (45% isolated yield). The isolated brown solid gives, by the solution ^{31}P{^{1}H} NMR spectrum, two doublets at 27.8 and 25.9 ppm and having a $^2J_{P-P}$ = 22.2 Hz. A spectroscopically identical compound was synthesized independently by treating a diethyl ether solution of (PNP)Ti=CH^{t}Bu(OTf) with 1 equiv of ClMgC$_2$H$_5$ (or 0.5 equiv of Mg(C$_2$H$_5$)$_2$) at −35 °C.

Unfortunately, single crystals suitable for X-ray diffraction studies could not be obtained. In lieu of this, the structure of complex **1** was unambiguously assigned as the ethylene adduct (PNP)Ti(CH$_2$^{t}Bu)(η^2-CH$_2$CH$_2$) (**1**) and not the ethyl intermediate, (PNP)Ti=CH^{t}Bu(CH$_2$CH$_3$) (**B**) on the basis of ^{1}H, ^{13}C, HSQC, and COSY NMR spectra. A salient feature is the presence of a titanium-neopentyl group, evidenced by correlation of a ^{13}C resonance at 110.0 ppm with two diasterotopic signals in the ^{1}H NMR spectrum at 1.26 and 0.02 ppm arising from the methylene protons. The latter ^{1}H NMR signal appears as a doublet of triplets with $^2J_{H-H}$ = 11.9 Hz and $^3J_{H-P}$ = 2.9 Hz, but the former signal is overlaying with other resonances from the PNP backbone. In addition to this neopentyl group, the foremost feature is an ethylene moiety, which was identified by ^{13}C NMR spectroscopy as two moderately broad singlets at 72.8 ($\Delta\nu_{1/2}$ = 16.1 Hz) and 66.8 ($\Delta\nu_{1/2}$ = 15.8 Hz) ppm. These resonances are significantly upfield shifted when compared to free ethylene (122.9 ppm)[15] and to the analogous complex Cp*$_2$Ti(η^2-C$_2$H$_4$) reported by Bercaw,[16] but are roughly in line with the titanium−ethylene complex, (ArO)$_2$Ti(η^2-C$_2$H$_4$) published by Rothwell.[17] In addition, an HSQC NMR experiment reveals correlation of each ethylene ^{13}C NMR signal with a set of two multiplet resonances in the ^{1}H NMR spectrum: the more downfield-shifted carbon (72.8 ppm) with signals at 2.30 (1H, $^1J_{CH}$ = 151 Hz) and 0.94 ppm (1H, $^1J_{CH}$ = 148 Hz), and the more upfield ^{13}C signal (66.8 ppm) with a broad resonance at 1.96 ppm (2H, $^1J_{CH}$ = 151 Hz). The COSY NMR spectrum shows clearly that the latter resonance arises from two overlaying multiplets, and reveals coupling between all four proton resonances,[18] allowing for the conclusive assignment of the titanium-ethylene moiety.

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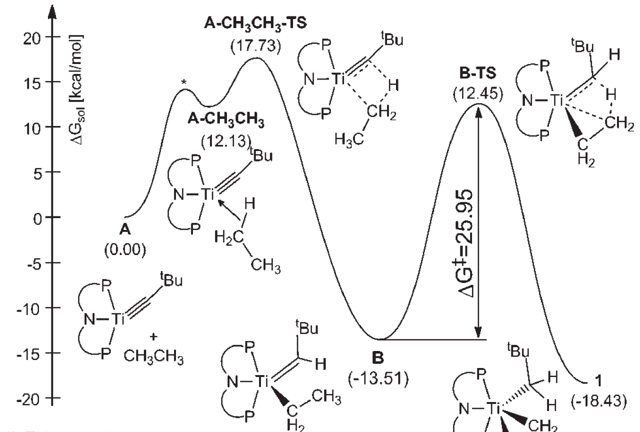


(*: This transition state was not located and shown only for illustration.)

Figure 1. Computed reaction profile for C−H activation of ethane and conversion to the titanacyclopropane **1**.

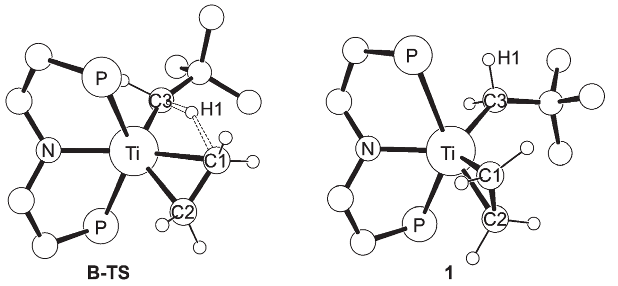
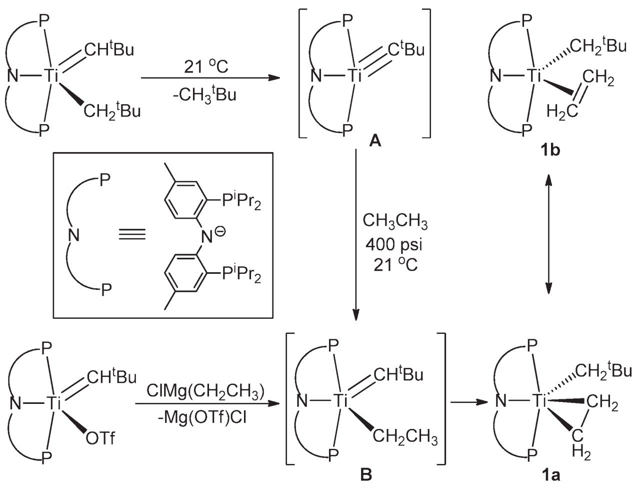


Figure 2. Optimized structures of the transition state **B-TS** and titanacyclopropane **1**.

To gain insight about the mechanism of forming **1**, we computed several possible reaction trajectories, and the most likely pathway is illustrated in Figure 1. As anticipated, the titanium alkylidyne intermediate **A** and ethane first form the adduct **A-CH$_3$CH$_3$**, a σ-complex calculated to be 12.1 kcal·mol^{-1} higher in energy than **A** and free ethane. A 1,2-addition of the C−H bond across the highly reactive Ti≡C linkage yields the ethyl-neopentylidene intermediate **B** with a relative solution phase free energy of −13.5 kcal·mol^{-1}. Finally, a concerted β-hydrogen migration from the ethyl moiety to the neopentylidene ligand gives the final product complex **1**, traversing the transition state **B-TS**, which is best envisioned as containing a [4,3]-metallabicyclic framework. This last step is associated with a barrier of 25.9 kcal·mol^{-1}.[19] The computed structure of **B-TS**, depicted in Figure 2, adopts a trigonal-bipyramidal geometry in which the migrating hydrogen H1 is located midway between the donor carbon C1 and the acceptor carbon C3 with C−H distances of 1.59 and 1.53 Å, respectively. The relatively short Ti···H1 distance of 1.72 Å, a Wiberg bond order of 0.23, and Natural Population Analysis electron density of 0.74 at H1 in this transition state suggest that this step can be described as a metal mediated hydrogen atom transfer.[20] The ethylene product **1** lies 4.9 kcal·mol^{-1} lower in energy than intermediate **B**, rendering the last step irreversible within plausible reaction conditions and in good agreement with our experimental observations. The computed reaction profile suggests that intermediate **B** should in principle be detectable, as it should display a finite lifetime. We have made significant efforts to do so, but were unsuccessful.[18,21]

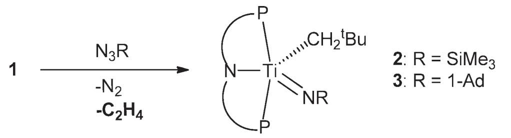
Scheme 1. Synthesis of the Ethane Complex 1 via Dehydrogenation of CH$_3$CH$_3$ and Independent Synthesis of This Complex via Salt Metathesis



Complex **1** is calculated to adopt a trigonal-bipyramidal geometry in which the C$_2$H$_4$ ligand is oriented parallel to the plane defined by the PNP ligand (Figure 2). Although it is reasonable to interpret the short Ti−C1 and Ti−C2 distances of 2.13 and 2.14 Å, respectively, and the long C−C distance of 1.44 Å as a strong indicator of a Ti(IV)-cyclopropane moiety,[22] which we denote as **1a**, the alternative assignment of a Ti(II)−ethene π-complex **1b** is equally plausible, as highlighted in Scheme 1. Distinguishing these two resonance structures is potentially helpful, as fundamentally different reactivities may be expected: The titanacyclopropane **1a** may undergo migratory insertion reactions, while in the π-complex **1b**, the olefin ligand may be preactivated toward nucleophilic attack in addition to the metal being more vulnerable toward oxidation.[22] One plausible way of estimating the weight of these resonance extremes is to quantify the metal character in the molecular orbital corresponding to the metal to ethene−π^* interaction. Our calculations indicate that the HOMO represents a metal−π^* interaction consisting of a 56% contribution by the metal-d orbitals,[18] thus positioning the electronic structure around the median of **1a**−**1b** range. Consequently, we expect **1** to display chemical reactivities reminiscent of both canonical forms.

Complex **1** is thermally stable up to 60 °C, but transforms slowly over several days to intractable products. Unfortunately, ethylene was not found to be one of the products. Two-electron oxidation of **1** by N$_3$R (R = SiMe$_3$ or 1-adamantyl) at room temperature, however, rapidly and quantitatively afforded the titanium−neopentyl imido complexes (PNP)Ti═NR(CH$_2$^{t}Bu) shown in Scheme 2 (**2**: R = SiMe$_3$; **3**: R = 1-adamantyl). Ethylene extrusion via oxidation of a titanium−ethylene complex Cp*$_2$Ti-(η^2-C$_2$H$_4$) with N$_3$Ph was previously observed by Bergman and Andersen.[23] When these reactions are performed in a sealed, J-Young NMR tube in THF-d_8, free ethylene (~0.5 equiv measured in solution using an internal standard) is formed displaying a characteristic ^{1}H NMR signal at 5.36 ppm. The presence of free ethylene was further confirmed by bubbling it into a THF-d_8 solution having compounds **2** or **3**. Imido complexes **2** and **3** are both stable at room temperature which

Scheme 2. Oxidative Elimination of Ethylene with Organic Azides To Give Titanium Imido Alkyls 2 and 3



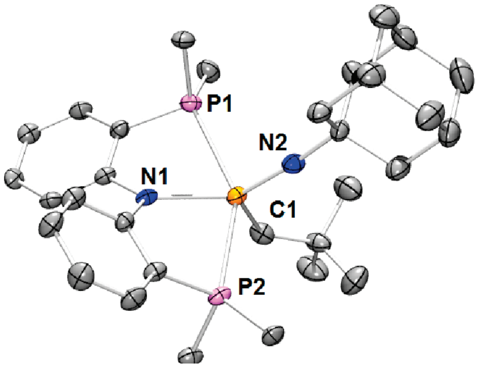


Figure 3. Single crystal X-ray diffraction structure of **3**. Hydrogen atoms, tolyl methyls, and isopropyl methyls are omitted for clarity.

is unsurprising given that a closely related imido-alkyl compound, (PNP)Ti═N[2,6-$^iPr_2C_6H_3$]($CH_2{}^tBu$) was found to be remarkably stable in solution and solid state.[24,25] Likewise, exposure of **1** to an atmosphere of N_2O also promotes ethylene elimination cleanly, but the metal-based product, presumably a metastable titanium oxo complex of the formula (PNP)Ti═O-($CH_2{}^tBu$), could not be isolated.[18]

More precise information about the structure of **3** was obtained via X-ray diffraction studies of single crystals of complex **3** grown from Et_2O at −35 °C (Figure 3). Overall, the structural parameters for the first coordination sphere of the metal in **3** resembles the previously characterized complex (PNP)Ti═N-[2,6-$^iPr_2C_6H_3$]($CH_2{}^tBu$).[24] Formation of a terminal titanium-imido ligand is further confirmed by the short Ti═N(2) bond distance of 1.714(3) Å and nearly linear Ti═N(2)−C angle of 174.7(3)°. The titanium-neopentyl has a Ti−C bond distance of 2.125(4) Å and a Ti−C1−C angle of 131.5(3)°, indicative of an sp^3 hybridized alkyl carbon singly bonded to titanium (Figure 3). The connectivity of **2** or **3** has been further inferred by a combination of ^1H, ^{31}P, ^{13}C, and HMQC NMR spectra.[18]

In addition to ethylene, we discovered that the transient titanium alkylidyne complex **A** is capable of stoichiometrically converting *n*-pentane to *n*-hexane exclusively to the terminal olefins 1-pentene and 1-hexene, respectively. These reactions proceed in neat *n*-pentane or *n*-hexane solution over the course of 24 h at room temperature to produce a mixture of isomers, and which relinquish the α-olefin exclusively upon oxidation with organic azides or N_2O along with forming the same oxo or imido products. A more detailed investigation of this reaction pathway including the selectivity of the alkylidyne for primary or secondary C−H bonds, additional details of the *β*-hydrogen migration, and the origin and nature of the observed isomeric mixture are currently underway in our laboratories.

In conclusion, we have demonstrated that the transient titanium−alkylidyne complex, **A**, is capable of activating a C−H bond of ethane and then abstracting an adjacent C−H bond to give a titanium−ethylene adduct, under ambient temperatures. Two-electron oxidation by N_3R or N_2O quantitatively releases ethylene. Although the term "oxidative" dehydrogenation of ethane is often used in the literature to illustrate the activation of the catalyst by an oxidant, the oxidant used in the present study is not involved in either activation of the titanium species or involved in the activation of two C−H bonds. Instead, the oxidant is solely used for product liberation. Therefore, this dehydrogenation process can be best described as a α,*β*-double C−H activation involving a combination of 1,2-CH bond addition and *β*-hydrogen migration. Formation of free ethylene most likely occurs by an oxidatively induced reductive elimination, that is, oxidation of the metal to promote product release.[26] The latter process may also involve insertion and retrocycloaddition steps rather than direct oxidation of the metal. To the best of our knowledge, this is the only example of a well-defined homogeneous system capable of performing this type of transformation at room temperature with a volatile paraffin such as ethane.[12,27]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, X-ray crystallographic information, computational information and spectral data are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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