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Dehydrogenation of Hydrocarbons with Metal-Carbon Multiple Bonds and Trapping of a Titanium(II) Intermediate.

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ABSTRACT: Reacting (PNP)Ti=CH^tBu(CH₂^tBu) with 2,2'-bipyridine (bipy) in cyclohexane or heptane results in dehydrogenation of the solvent, cleanly producing cyclohexene and 1-heptene, respectively, and a Ti^{II} intermediate that is trapped by bipy to produce [(PNP)Ti^{III}(CH₂^tBu)(bipy^{•-})] (1). This titanium (II) intermediate reduces the bipy ligand upon coordination to form a Ti^{III} center, where the unpaired electron is antiferromagnetically coupled to the electron of the reduced [bipy^{•-}] π -radical moiety, giving an overall diamagnetic species. Complex 1 has been characterized by NMR and UV-vis spectroscopies as well as single crystal X-ray diffraction studies.

2,2'-Bipyridine (bipy) is a ubiquitous ligand commonly used to stabilize electron-rich metal centers. Likewise, bipy has also proven to be a non-innocent redox ligand upon chelation to a variety of electron-rich metals.¹ Reduction of the bipy ligand has been studied with a variety of transition metals and lanthanides.^{1,2} Several Ti-bipy complexes have also been reported in the literature, where the bipy acts as an innocent ligand.³ Our group has demonstrated that the

transient titanium complex $[(\text{PNP})\text{Ti}\equiv\text{C}'\text{Bu}]$ ($\text{PNP}' = \text{N}-[2\text{-P}(\text{CHMe}_2)_2\text{-4-methylphenyl}]_2$) (**A**) can ring open pyridine or picolines by a [2+2]-cycloaddition pathway.⁴ We examined the reactivity of **A** with bipy since chelation would be expected to disfavor further reactivity of the alkylidyne ligand, such as cyclometallation or cycloaddition. A similar strategy has been applied by our group to trap the transient $[(\text{PNP})\text{V}=\text{CH}'\text{Bu}]$ fragment to form $[(\text{PNP})\text{V}=\text{CH}'\text{Bu}(\text{bipy})]$.⁵ In this work, we report reactivity of **A** with bipy in alkane solvents. Rather than bipy trapping **A**, or being activated, the solvent medium (cyclohexane or heptane) becomes instead dehydrogenated,⁶ at room temperature, to form a transient $[(\text{PNP})\text{Ti}(\text{CH}_2'\text{Bu})(\eta^2\text{-olefin})]$ (olefin = cyclohexene or 1-heptene) which eliminates olefin to generate putative “ $[(\text{PNP})\text{Ti}^{\text{II}}(\text{CH}_2'\text{Bu})]$ ”. We demonstrate that the bipy ligand does not react with **A**, but rather instead traps the “ $[(\text{PNP})\text{Ti}^{\text{II}}(\text{CH}_2'\text{Bu})]$ ” fragment to form a coordinatively saturated complex $[(\text{PNP})\text{Ti}(\text{CH}_2'\text{Bu})(\text{bipy})]$ (**1**). Electronic spectra suggests the bipy ligand in **1** to have radical anion character, which antiferromagnetically couples to the Ti^{III} center to yield an overall close shell singlet species such as $[(\text{PNP})\text{Ti}^{\text{III}}(\text{CH}_2'\text{Bu})(\text{bipy}^{\cdot-})]$.⁷

Accordingly, complex $[(\text{PNP})\text{Ti}=\text{CH}'\text{Bu}(\text{CH}_2'\text{Bu})]$ was reacted with one equivalent of bipy in cyclohexane at room temperature over a period of a day, with the goal of trapping transient **A**. To our surprise, however, we observe trapping of a Ti^{2+} intermediate, which forms from dehydrogenation of cyclohexane. We previously have proposed that dehydrogenation of cyclohexane occurs via C-H activation of cyclohexane by **A** to form $[(\text{PNP})\text{Ti}=\text{CH}'\text{Bu}(c\text{-C}_6\text{H}_{11})]$ (**B**),⁸ and then the olefin adduct $[(\text{PNP})\text{Ti}(\text{CH}_2'\text{Bu})(\eta^2\text{-C}_6\text{H}_{10})]$ (**C**) (Scheme 1). Likewise, we have demonstrated that **C** eliminates cyclohexene (presumably via a dissociative process) to generate transient $[(\text{PNP})\text{Ti}(\text{CH}_2'\text{Bu})]$ (**D**), which becomes trapped with bipy to form **1** (Scheme 1). The generation of cyclohexene has been previously confirmed by GC-MS of the volatiles of

the reaction mixture,⁹ while the formation of **1** is characterized by an indigo colored solution. Complex **1** is diamagnetic and displays a distinct set of doublets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, at 38 ppm and 54 ppm ($^2J_{\text{PP}} = 48$ Hz). In the ^1H NMR spectrum, there are two highly downfield resonances above 7.9 ppm in addition to several resonances in the olefinic region (4-6 ppm), and we have assigned these signals as the protons of the reduced bipy ligand. The ^1H NMR spectrum also reveals the bipy ligand to lack any symmetry given the observation of eight different resonances, two of which are buried in the aromatic region. A highly shielded resonance at -1.2 ppm (1H) is also observed, which arises from one of the diastereotopic methylene protons of the neopentyl ligand. The other diastereotopic resonance is most likely in crowded aliphatic region of 0.5-2.0 ppm. Compound **1** was also characterized by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, and a resonance at ~ 116 ppm is diagnostic of the neopentyl methylene group. The correct hybridization and coupling of the methylene carbon was confirmed by DEPT-135 and dqf-HSQC experiments.¹⁰ Notably, the ^1H - ^{13}C (DEPT-135) gHSQC spectrum shows direct correlation of the highly shielded ^1H NMR resonance at -1.2 ppm (Ti-CH₂-^tBu) to the negative DEPT-135 resonance at 116 ppm (Figure 1). This upfielded ^1H NMR spectroscopic resonance assigned to the neopentyl ligand was confirmed as two equivalent protons by full and selective decoupling of the ^{13}C NMR at 116 ppm, with $^1J_{\text{C-H}} = 96$ Hz.¹⁰ No other carbon resonances are observed above 150 ppm and monitoring the reaction by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy does not reveal any intermediates.¹⁰ In fact, the rate for dehydrogenation of cyclohexane by [(PNP)Ti=CH^tBu(CH₂^tBu)] (based on its pseudo first-order decay) is nearly the same with ($t_{1/2} = 3.8$ hr) or without ($t_{1/2} = 5.8$ hr) bipy.

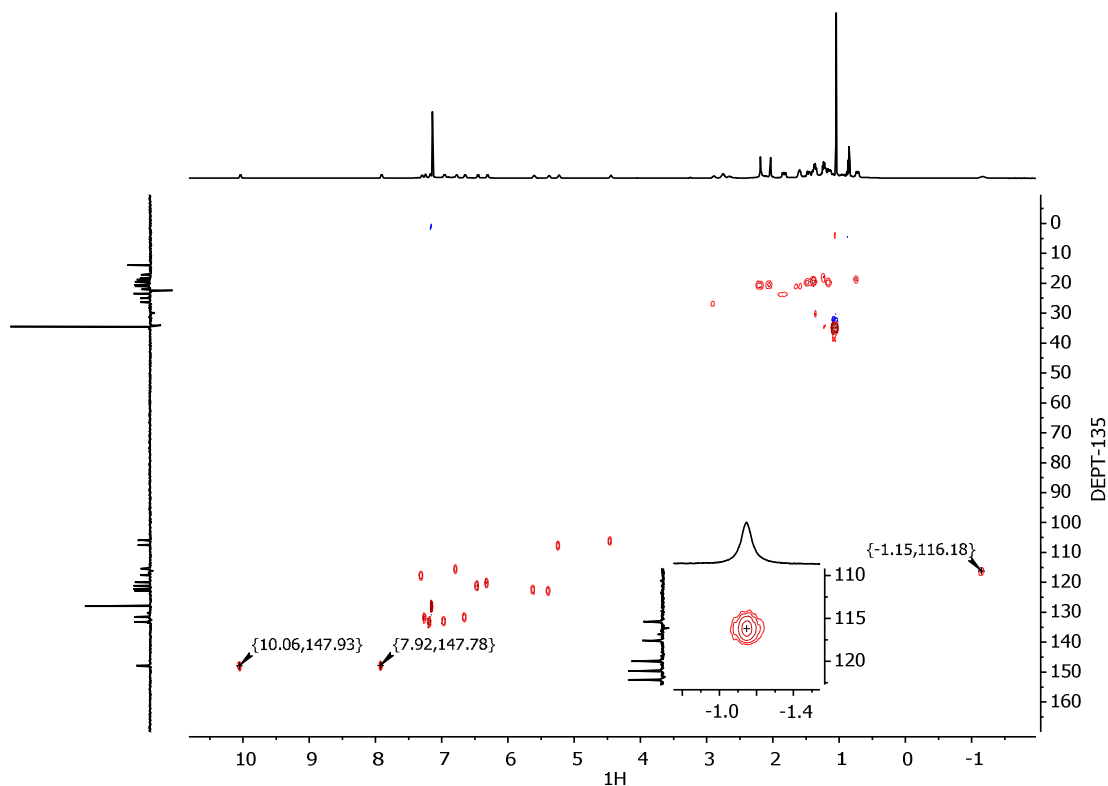


Figure 1. ^1H - ^{13}C (DEPT-135) gHSQC spectrum of **1** in C_6D_6 at $25\text{ }^\circ\text{C}$. The DEPT-135 spectrum is used to show a correlation (inset) of the proton at -1.15 ppm to the Ti-CH_2 - $t\text{Bu}$ carbon.

Small purple crystals of **1** were grown from an ether solution cooled to $-35\text{ }^\circ\text{C}$ for three days. From the X-ray diffraction data of a single crystal, the geometry at titanium is best described as pseudo octahedral with the phosphines of the PNP ligand situated transoid ($149.94(3)^\circ$) relative to the titanium center (See Figure 2 below for additional bond angles). This feature places the bipy and neopentyl ligands in the *mer* configurations. Another notable characteristic in **1** is the rather wide Ti1-C27-C28 bond angle of the neopentyl fragment ($168.5(2)^\circ$) indicating some distortion from ideal sp^3 . However, we have observed such distortion for a neopentylidene moiety in the similar complex, $[(\text{PNP})\text{V}=\text{CH}^t\text{Bu}(\text{bipy})]$.⁵ This

type of deformation most likely arises as a consequence of accommodating the pseudo octahedral geometry around titanium, while also avoiding steric clash with the PNP isopropyl groups. Regardless of this distortion, the Ti-C bond distance of 2.106(3) Å, which corroborated by the NMR spectroscopic data unambiguously confirms the presence of an alkyl group. In addition, the X-ray structural data indicates that the bond lengths of the [bipy^{•-}] ligand are distorted compared to that for free bipy (Figure 2, right).¹¹ In particular, the 2,2'-C-C bond distances, normally at 1.480 Å in free bipy, is contracted to 1.416 Å in **1**, which is consistent of a one-electron reduction.¹ Since the LUMO of bipy is augmented with significant π -bonding orbital character at 2,2'-C-C positions, a contraction in bond length of C32 and C31 would be expected when this orbital is housed by one or two electrons.¹

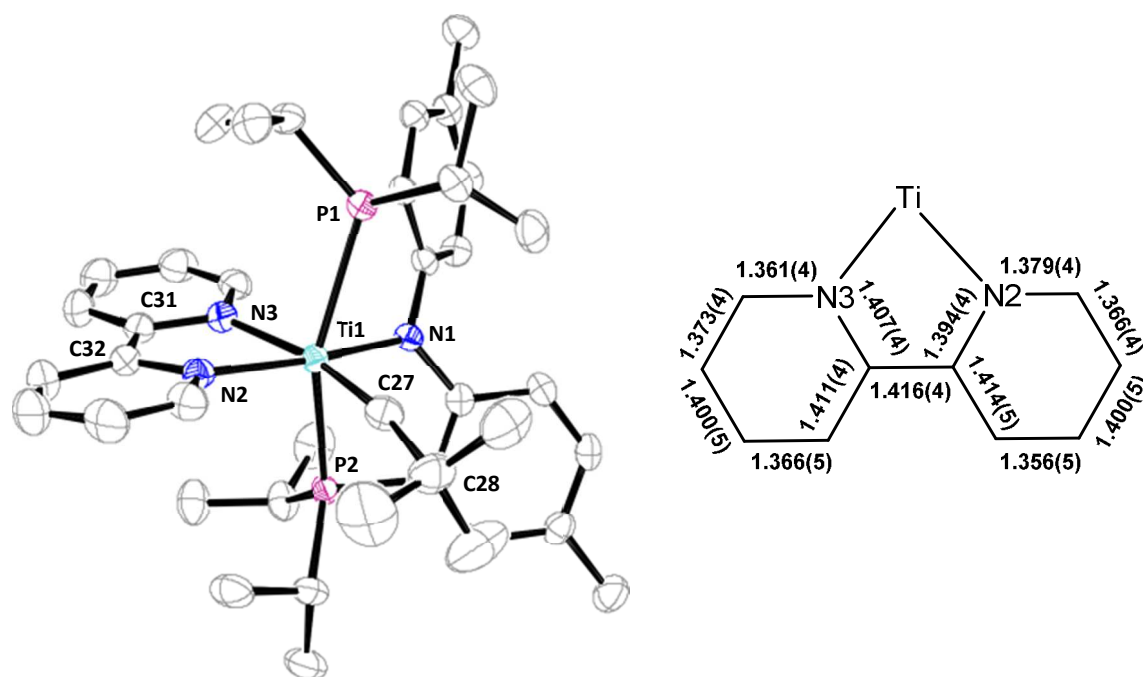


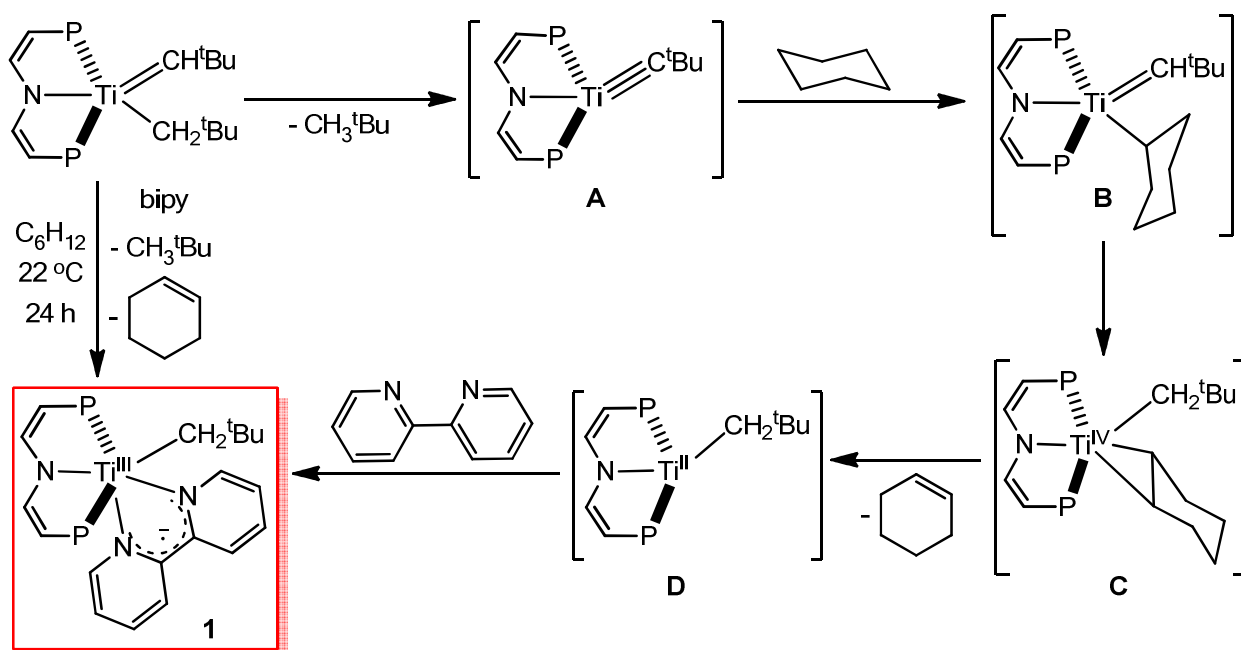
Figure 2. Left: Structure of **1** determined by X-ray diffraction, with ellipsoids shown at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles

(deg): Ti1-N1: 2.127(2); Ti1-N2: 2.117(2); Ti1-N3: 2.149(2); Ti1-C27: 2.106(3); C32-C37: 1.416(4). Ti1-C27-C28: 168.5(2); P1-Ti1-P2: 149.94(3); N1-Ti1-C27: 100.51(10); N2-Ti1-C27: 91.60(11); N2-Ti1-N3: 73.75(9); N1-Ti1-N3: 73.75(9). Right: Schematic of the titanium-bipy connectivity showing the bond lengths measured by X-ray diffraction.

The deep indigo color of **1** is atypical among high-valent titanium complexes, which prompted us to examine solutions of this species via UV-Vis spectroscopy. In benzene, a shoulder can be observed around 410 nm ($24,000\text{ cm}^{-1}$, $\epsilon = 6,500\text{ M}^{-1}\text{ cm}^{-1}$), which has been assigned to a $\pi\text{-}\pi^*$ transition of the bipy ligand. A strong absorption bands is also observed at 554 nm ($18,000\text{ cm}^{-1}$, $\epsilon = 8,200\text{ M}^{-1}\text{ cm}^{-1}$),¹⁰ giving rise to the deep blue-purple color in solution that is common for organometallic complexes containing a π -radical bipy ligand. This band has been assigned as a MLCT, in accord with reduction of the bipy ligand by titanium (II).

To determine how important the dehydrogenation of solvent medium (as well as olefin formation) is with respect to formation of the titanium (II) species **C** or **D**, we performed the reaction using heptane¹² as the solvent and with a stoichiometric amount of bipy. The reason for choosing heptane was based on the fact that the olefin [(PNP)Ti(CH₂^tBu)(η^2 -H₂C=CH(CH₂)₄CH₃)], is more stable than **C**, but can slowly undergo loss of 1-heptene. Unfortunately, the olefin complexes generated from ethane, butane, pentane, and hexane dehydrogenation are too stable to undergo exchange with bipy at room temperature.⁸ Accordingly, monitoring the reaction by ³¹P{¹H} NMR spectroscopy revealed partial formation of **1**,¹⁰ but only after ten days of mixing at room temperature ($t_{1/2} \sim 192\text{ h}$). This large discrepancy in reaction time is likely attributed to the greater stability of the olefin complex [(PNP)Ti(CH₂^tBu)(η^2 -H₂C=CH(CH₂)₄CH₃)]⁸ in solution as opposed to **C** which forms over a period of 24 hours at room temperature. Comparatively, the stability of the olefin complex

$[(\text{PNP})\text{Ti}(\text{CH}_2^t\text{Bu})(\eta^2\text{-C}_6\text{H}_{10})]$ is on the order of hours, making the formation of **1** much faster when cyclohexane is used as the solvent. Alternatively, when benzene is used as the solvent with one equiv of bipy, only $[(\text{PNP})\text{Ti}(\text{CH}_2^t\text{Bu})(\text{C}_6\text{H}_5)]^{13}$ is the only product formed as a result of the 1,2-CH bond addition of C_6H_6 across the alkyldiene ligand in **A**. This result demonstrates that two C-H activation events are necessary to form **D**, which is then eventually trapped by bipy to yield **1**.



Scheme 1: Proposed mechanism for formation of **1** in cyclohexane. For clarity, the aryl moiety of the PNP and ^iPr groups on P are not shown.

In conclusion, this work demonstrates that the reactive intermediate **C** is most likely formed via the dehydrogenation of linear and cyclic alkanes, and that such species can be trapped by a π -accepting ligand such as bipyridine. Complex **1** is presumably formed via a dissociative mechanism involving loss of the olefin from **C** or $[(\text{PNP})\text{Ti}(\text{CH}_2^t\text{Bu})(\eta^2\text{-H}_2\text{C}=\text{CH}(\text{CH}_2)_4\text{CH}_3)]$,

and then trapping of the unsaturated Ti(II) fragment **D** by bipy. Complex **1** has been characterized by ^1H , $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and other NMR spectroscopic experiments, X-ray diffraction studies, and UV-Vis spectroscopy. Mechanistic studies showed that other alkanes may be used to access intermediates such as **D**, resulting still in formation of **1** when bipy is present in solution. This vital knowledge can be applied to reducing other substrates, including redox-active ligands. The fact that the Ti(II) fragment can be trapped is promising in our quest to find mild catalytic process for alkane dehydrogenation.

ASSOCIATED CONTENT

Supporting Information

Experimental preparation of **1**, kinetic data (converting $(\text{PNP})\text{Ti}=\text{CH}'\text{Bu}(\text{CH}_2'\text{Bu})$ to **1**), crystallographic data for **1**, and UV-Vis spectroscopy data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

Dedicated to Prof. Bill Kaska, an organometallic innovator and terrific scientist. We thank the US National Science Foundation (CHE-0848248 and CHE-1152123) and the University of Pennsylvania for financial support of this research.

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