

CH Bond Activation of Methane by a Transient η^2 -Cyclopropene/Metallabicyclobutane Complex of Niobium

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S Supporting Information

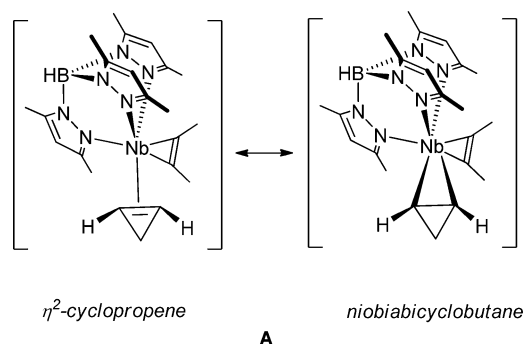
ABSTRACT: This study challenges the problem of the activation of a CH bond of methane by soluble transition metal complexes. High pressure solution NMR, isotopic labeling studies, and kinetic analyses of the degenerate exchange of methane in the methyl complex $[\text{Tp}^{\text{Me}_2}\text{NbCH}_3(c\text{-C}_3\text{H}_5)(\text{MeCCMe})]$ (**1**) are reported. Stoichiometric methane activation by the mesitylene complex $[\text{Tp}^{\text{Me}_2}\text{Nb}(\text{CH}_2\text{-}3,5\text{-C}_6\text{H}_3\text{Me}_2)(c\text{-C}_3\text{H}_5)(\text{MeCCMe})]$ (**2**) giving **1** is also realized. Evidence is provided that these reactions proceed via an intramolecular abstraction of a β -H of the cyclopropyl group to form either methane or mesitylene from **1** or **2**, respectively, yielding the transient unsaturated η^2 -cyclopropene/metallabicyclobutane intermediate $[\text{Tp}^{\text{Me}_2}\text{Nb}(\eta^2\text{-}c\text{-C}_3\text{H}_4)(\text{MeCCMe})]$ **A**. This is followed by its mechanistic reverse 1,3-CH bond addition of methane yielding the product.

Despite unabated efforts, efficient catalytic functionalization of methane by soluble metal complexes remains a long-term goal on scientific, environmental, and economic grounds.^{1–4} Oxidative pathways leading to methanol by late metal complexes face the challenge of selectivity since the CH bonds of the product are more reactive than those of the reactant although useful compounds such as acetic acid can be obtained in some instances.^{5–8} Alternative insertive pathways have been proposed.^{9,10} Understanding the key CH bond cleavage step of such a strong and inert bond remains an important issue. Early transition metal complexes, including supported organometallic complexes,¹¹ exhibit distinctive pathways for the activation of the CH bond of methane although it has led to productive catalysis only in a few cases. σ -Bond metathesis at $L_nM\text{-C}$ was the first recognized pathway^{12,13} from which catalytic hydromethylation of propene and dehydrocoupling of diphenylsilane with methane were developed.^{14,15} Four-center transition states also characterize the reactivity of many transient unsaturated, strongly polar, imido complexes $L_nM\text{=NR}$ ^{16–22} or carbon-based alkylidene complexes $L_nM\equiv\text{CR}$ ²³ toward methane. In these systems, the CH bond cleavage occurs through a 1,2-addition across the metal–heteroatom multiple bond. Kinetic studies suggested that a methane complex precedes CH bond activation, but DFT studies highlighted the low stability and kinetic lability of such species. The much less polar unsaturated η^2 -1,3-butadiene tungsten complex $[\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-CH}_2\text{=CH-CH=CH}_2)]$,

generated by neopentane abstraction from the neopentyl allyl precursor $[\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\eta^3\text{-CH}_2\text{CHCHMe})]$ is also competent for the activation of methane ($p = 70$ bar) at room temperature to give $[\text{Cp}^*\text{W}(\text{NO})(\text{CH}_3)(\eta^3\text{-CH}_2\text{CHCHMe})]$.^{24,25} It is the only case where methane activation has occurred via a 1,3-CH bond addition across a $L_nM(\eta^2\text{-alkene})$ so far. Capitalizing on related CH bond activation of arenes,^{26–28} we report herein that methane activation can be observed under mild conditions at an unsaturated transient η^2 -cyclopropene/metallabicyclobutane niobium complex by a 1,3-CH bond addition mechanism.

Initial experimental kinetic modeling suggested that the unsaturated transient η^2 -cyclopropene $[\text{Tp}^{\text{Me}_2}\text{Nb}(\eta^2\text{-}c\text{-C}_3\text{H}_4)(\text{MeCCMe})]$ **A** (Chart 1), generated by the rate determining methane loss from $[\text{Tp}^{\text{Me}_2}\text{NbCH}_3(c\text{-C}_3\text{H}_5)(\text{MeCCMe})]$ (**1**), reacted significantly faster with benzene than with methane itself at 323 K.²⁷

Chart 1. Two Important Limiting Structures of Intermediate A



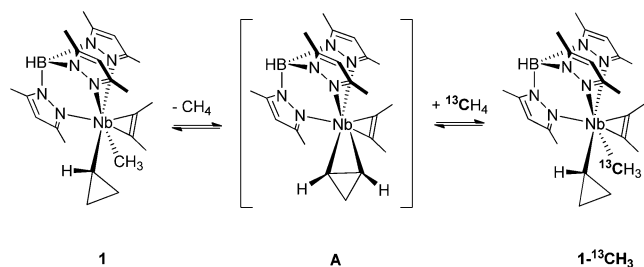
Two approaches were followed to examine whether **A** could be observed to react with methane directly. In a first set of experiments, the degenerate exchanges between **1** and different isotopomers of methane were probed. Initially a solution of **1** in cyclohexane- d_{12} was reacted with $^{13}\text{CH}_4$ (ca. 3 bar, 1.2 equiv) at 313 K in a medium-pressure NMR tube fitted with a Teflon valve. Monitoring the progress of the reaction over 19 h by ^1H NMR showed, the appearance and the growth of a doublet centered at δ 0.766 with $^1J_{\text{CH}} = 119.6$ Hz characteristic of a Nb- $^{13}\text{CH}_3$ group.

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This signal was superimposed on the singlet at δ 0.779 for the Nb– $^{12}\text{CH}_3$ group in **1**. This preliminary experiment establishes the equilibrium between **1** and **1**- $^{13}\text{CH}_3$ shown in Scheme 1 and

Scheme 1



confirms that **A** readily reacts with methane, a remarkable reaction. Under these conditions, however, signs of significant decomposition were noted after ca. 5 h precluding detailed thermodynamic or kinetic analysis of the reaction.

In a second set of experiments, **1** was reacted with CD_4 (ca. 8 bar) in C_6F_6 at 303 K and the progress of the reaction was followed by ^1H and $^2\text{H}\{^1\text{H}\}$ NMR over the course of 4 h. C_6F_6 was found to be a suitable inert solvent. Following a careful interpretation of a ^1H ROESY NMR spectrum that allowed the assignment of all diastereotopic protons of the cyclopropyl group in **1** (see Supporting Information), the stereochemical outcome of the reaction could be assessed. In addition to a Nb– CD_3 group, ^1H and $^2\text{H}\{^1\text{H}\}$ NMR spectra (Figure 1) indicated that

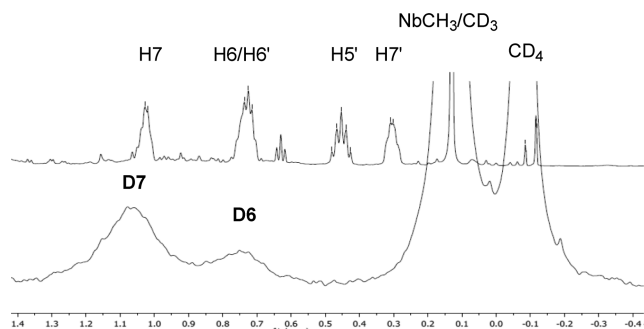
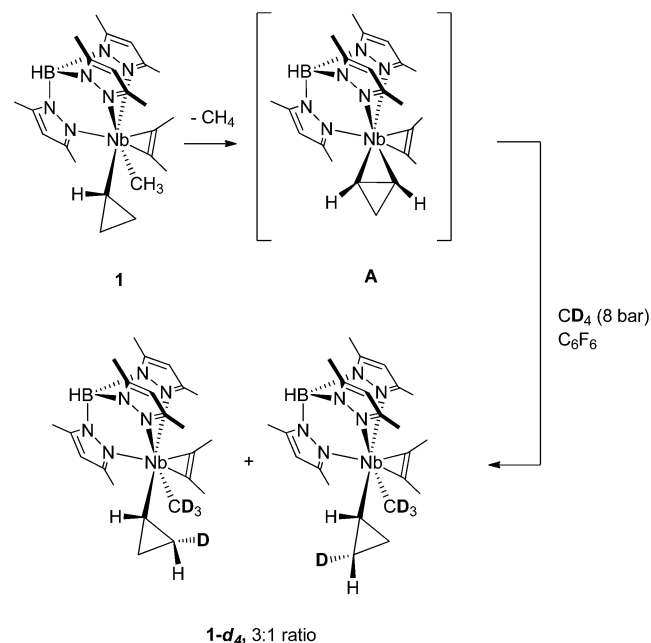


Figure 1. Superimposed ^1H and $^2\text{H}\{^1\text{H}\}$ NMR spectra of a mixture of **1** and CD_4 in C_6F_6 .

deuterium was found selectively at the β -positions D6 and D7 on the same enantioface of the cyclopropyl group as the niobium. Integration of those two signals translated to 3:1 mixture of two diastereomers of $[\text{Tp}^{\text{Me}_2}\text{NbCD}_3(c\text{-C}_3\text{H}_4\text{D})(\text{MeCCMe})]$ **1-d**₄ (Scheme 2). These results confirm that **A** is generated by a rate-determining intramolecular abstraction of a β -H of the cyclopropyl group by the niobium bound methyl group to form methane from **1** followed by its microscopic reverse, a stereospecific 1,3-CH/D bond addition of CH_4/CD_4 across a Nb–C bond of Nb(η^2 - $c\text{-C}_3\text{H}_4$). **A** is known to activate benzene/benzene- d_6 in a similar manner, but the ratio of the two phenyl cyclopropyl diastereomers was ca. 2:1 in similar experimental circumstances.²⁸

We next sought to investigate methane elimination/addition more quantitatively. ^1H NMR spin saturation transfer (SST)²⁹ experiments at intermediate pressures of methane (ca. 10 bar, 4 equiv vs **1**) were carried out at 500 MHz at 341 K in C_6F_6 (with one drop of cyclohexane- d_{12} for the lock of the spectrometer). Saturation of the Nb CH_3 resonance at δ 0.59 was followed by

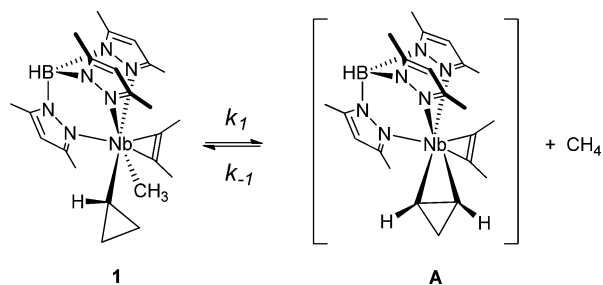
Scheme 2



observation of the CH_4 resonance at δ 0.14 after the probe pulse. Integration of the CH_4 resonance before and after the saturation revealed a ca. 10% decrease. However, a closer look at the ^1H NMR spectrum revealed significant decomposition at this temperature. Most probably, the intermediate **A** decomposes more rapidly than it reacts with methane under these conditions. In order to get quantitative results with a higher concentration of methane, we resorted to high pressure (HP) NMR techniques (400 MHz instrument). Compound **1** (0.100 g, 0.200 mmol) was charged in a 1 cm (outside diameter) sapphire HP NMR tube and dissolved in a 1:1 mixture of C_6F_6 /cyclohexane- d_{12} (2 mL). The HP NMR tube was then pressurized at ca. 60 bar at room temperature and carefully shaken to ensure homogeneous methane dissolution. SST were carried out at 351 K ($[\text{CH}_4]/[\mathbf{1}]$ ratio of 29). Saturation of the Nb CH_3 resonance at δ 0.59 was followed by observation of the CH_4 resonance at δ 0.14 after the probe pulse. Integration of the CH_4 resonance before and after the saturation revealed a 12% decrease, which translated to a rate constant $k_{\text{obs}} = (2.67 \pm 0.23) \times 10^{-2} \text{ s}^{-1}$. However, insignificant changes in the intensity of the niobium bound methyl signal at δ 0.59 in **1** were noted when the methane signal at δ 0.14 was saturated.

These SST experiments can best be accounted for with the help of the kinetic scheme described in Scheme 3. The forward reaction (rate constant k_1) is the monomolecular methane elimination that yields **A** and methane as shown previously. The

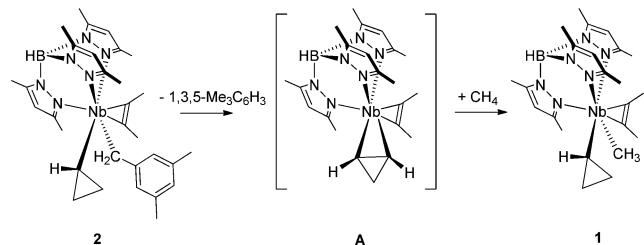
Scheme 3



reverse reaction (rate constant k_{-1}) is the bimolecular reaction of **A** with methane that yields **1**, the CH bond activation of methane. Following the rate derivation presented in the [Supporting Information](#), we have therefore measured $k_{\text{obs}} = k_{-1\text{obs}} = k_{-1} [\text{A}]$, with the reactive intermediate **A** in a steady-state concentration. Note this does not allow us to discuss the ability of **A** to activate methane since k_{-1} cannot be determined here. The failure to observe an intensity change of the NbCH₃ resonance when saturating the methane resonance unfortunately precluded the measurement of k_1 . This can be ascribed to the difference in relaxation times T_1 for the protons of the niobium bound methyl group [$T_1(\text{NbCH}_3) = 1.34 \text{ s}$] and those of methane [$T_1(\text{CH}_4) = 4.95 \text{ s}$] with respect to the actual rate constant k_1 . From the activation parameters previously determined for the β -H intramolecular abstraction of methane from **1** ($\Delta H^\ddagger = 99 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -6 \pm 10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$),²⁷ $\Delta G^\ddagger(351)$ is $101 \text{ kJ}\cdot\text{mol}^{-1}$ at 351 K, which corresponds to a $k_1(351)$ value of $6.6 \times 10^{-3} \text{ s}^{-1}$. In that case, only a variation of less than 1% of the NbCH₃ signal intensity would be expected upon saturation of the CH₄ signal (see [Supporting Information](#)).

We have realized a productive activation of methane. Along the lines established by Jones³⁰ and Wolczanski,²¹ we surmised that the reaction of a weak Nb–1-mesityl bond with a strong CH bond in methane would yield a stronger Nb–methyl bond and a weaker CH bond in mesitylene. An excess of methane should make the reaction even more favorable thermodynamically. Indeed, reaction of the 1-mesityl complex²⁶ [$\text{Tp}^{\text{Me}_2}\text{Nb}(\text{CH}_2\text{-}3\text{-C}_6\text{H}_3\text{Me}_2)(\text{c-C}_3\text{H}_5)(\text{MeCCMe})$] (**2**) with CH₄ (ca. 40 bar, 12 to 29 equiv) in 1:1 mixture of C₆F₆/cyclohexane-*d*₁₂ was found to go to completion forming **1** and mesitylene ([Scheme 4](#)). Kinetic

Scheme 4



analysis for the disappearance of **2** in the $T = 290\text{--}321 \text{ K}$ range ($E_a = 78 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H^\ddagger = 76 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -84 \pm 10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) revealed a first-order dependence in **2** and a zeroth order in methane, which together with a highly ordered transition state are consistent with a rate-determining intramolecular loss of mesitylene forming **A** followed by fast reaction with CH₄ yielding **1** as expected. The more negative entropy of activation for the elimination of mesitylene from **2** as compared to that of methane from **1** is likely due to substantial conformational changes involving the mesityl ligand needed to reach the ordered transition state.

Whereas the generation of intermediate **A** and its ability to activate methane via a rare 1,3-CH bond addition pathway constitute a remarkable result, the intermediacy of a methane adduct along the reaction coordinate remained an open question. In several low-valent late-transition metal systems methane complexes have been inferred from kinetic analyses,³¹ directly observed by time-resolved spectroscopy³² or matrix trapping experiments³³ and even characterized by NMR in solution more recently.³⁴ In high oxidation state early transition metal systems, however, methane adducts have eluded direct characterization.¹⁹

DFT modeling has yielded structures and energetic data suggesting little thermodynamic stability and high kinetic lability of these adducts,²³ significantly smaller than those for a directly observed rhodium complex.³⁴ This is confirmed here ([Figure 2a](#)) since only a loose van der Waals complex **A-CH**₄ could be located separated from **A** and CH₄ by an enthalpy of only $13 \text{ kJ}\cdot\text{mol}^{-1}$.

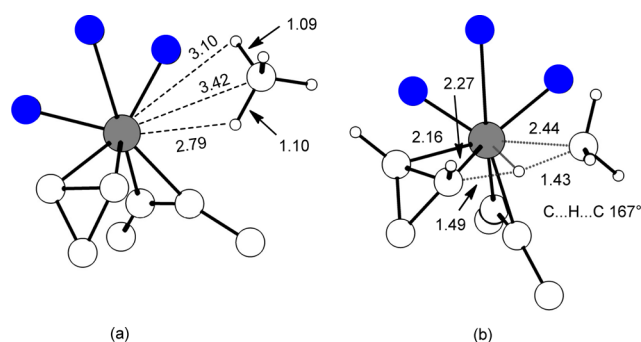


Figure 2. Plots of the DFT computed structures [wB97XD functional SDD (Nb)/TZVP (others)] of (a) **A-CH**₄ and (b) **1-TS** (distances in Å). Color code: Nb, gray; N, blue; C, large white; H, small white. Only atoms of ancillary ligands bound to Nb are shown for clarity.

The optimized transition state **1-TS** for the CH bond elimination/activation of CH₄ ([Figure 2b](#)) exhibits a relatively symmetrical situation with an almost linear C···H···C arrangement (167°). [Figure 3](#) presents an analysis of the electronic

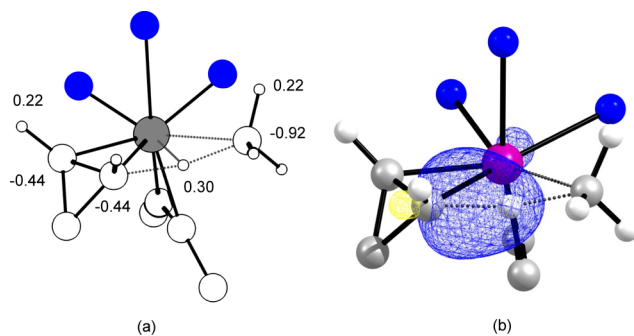


Figure 3. (a) Natural charges and (b) NLMO for **1-TS**.

structure of **1-TS** following the NPA NBO approach.³⁵ There is a slight excess of positive charge on the hydrogen being transferred between the two Nb bound carbons. The methyl carbon bears a strong negative charge; in contrast, the negative charge on the incipient cyclopropene ligand is shared equally between the two carbon atoms. The NLMO describing the interaction in the transition state is mainly delocalized on the niobium and the β -CH, but some tails on the α -C and the methyl carbon are also seen. Overall the bonding picture is that of a σ -bond metathesis^{36–38} but with a distinctive involvement of both niobium-bound carbons of the η^2 -cyclopropene ligand engaged in the hydrogen transfer. This highlights the structural and electronic differences with the more common α -abstraction/1,2-CH addition mechanism.³⁸

In this communication, we have shown that a transient unsaturated η^2 -cyclopropene complex of niobium was able to cleave a CH bond of methane via a 1,3-CH bond addition pathway under mild conditions, and we have provided mechanistic insights about this remarkable reaction. The only

previous example of such a reaction was found for an η^2 -butadiene tungsten complex.²⁴ Undoubtedly ring strain and double bond conjugation of the bound hydrocarbon ligands in the niobium and the tungsten case, respectively, increase the lifetime of these reactive intermediates. The transient η^2 -cyclopropene zirconocene [$\text{Cp}_2\text{Zr}(\eta^2\text{-cyclopropene})$] does activate a CH bond of selected heteroaromatics³⁹ but has failed to cleave the CH bond of methane. We are actively looking for other examples of such processes.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07859.

Full details of the experimental procedures including NMR spectra, SST, and other kinetic experiments, and computational results (PDF)

All computed molecule Cartesian coordinates (XYZ)

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Notes

The authors declare no competing financial interest.

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