Quadruple C–H Bond Activations of Methane by Dinuclear Rhodium Carbide Cation [Rh$_2$C$_3$]$^+$

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ABSTRACT: The structure of the [Rh$_2$C$_3$]$^+$ ion and its reaction with CH$_4$ in the gas phase have been studied by infrared photodissociation spectroscopy and mass spectrometry in conjunction with quantum chemical calculations. The [Rh$_2$C$_3$]$^+$ ion is characterized to have an unsymmetrical linear [Rh−C−C−C−Rh]$^+$ structure existing in two nearly isoenergetic spin states. The [Rh$_2$C$_3$]$^+$ ion reacts with CH$_4$ at room temperature to form [Rh$_2$C]$^+$ + C$_3$H$_4$ and [Rh$_2$C$_2$H$_2$]$^+$ + C$_2$H$_2$ as the major products. In addition to the [Rh$_2$C]$^+$ ion, the [Rh$_2$$^{13}$C]$^+$ ion is formed at about one-half of the [Rh$_2$C]$^+$ intensity when the isotopic-labeled $^{13}$CH$_4$ sample is used. The production of [Rh$_2$$^{13}$C]$^+$ indicates that the linear C$_3$ moiety of [Rh$_2$C$_3$]$^+$ can be replaced by the bare carbon atom of methane with all four C–H bonds being activated. The calculations suggest that the overall reactions are thermodynamically exothermic, and that the two Rh centers are the reactive sites for C–H bond activation and hydrogen atom transfer reactions.

KEYWORDS: methane activation, rhodium carbide, mass spectrometry, infrared photodissociation spectroscopy, quantum chemical calculation.

INTRODUCTION

Methane is a naturally abundant molecule and is one of the most potent greenhouse gases contributing to global warming. It is extremely stable with very high C−H bond strengths (439, 463, 443, and 339 kJ/mol for the four C−H bonds), negligible electron affinity, and low polarizability. Consequently, the activation and conversion of methane into value-added chemicals is very important but is quite challenging. For some chemical transformation processes, such as the conversion of methane to syngas, it needs the activation of all the four C−H bonds of methane. These reaction processes always demand high temperature and pressure. Systems that can activate methane at mild conditions are in high demand. Many examples of methane activation at transition-metal centers have been reported. To develop practical methane conversion processes, much remains to be learned about the processes and factors controlling the activity and selectivity of catalytic reactions. Gas-phase reactions of transition-metal atoms, ions, and clusters with methane serve as simple models in understanding the intrinsic mechanism of the catalytic methane conversion processes.

Mechanistic aspects of the C−H bond activation of methane by diatomic transition metal carbide cations were elucidated by quantum-chemical calculations and verified experimentally using mass spectrometry. The activation of methane by metal-carbide cations was found and proposed to proceed via different mechanisms including hydrogen atom transfer (HAT) and proton-coupled electron transfer (PCET), as well as hydride transfer (HT). Simultaneous activation of two C−H bonds of methane was identified in the reaction of the copper carbide cation. The bond dissociation energies, spin states, number of d-electrons, and charge distributions of the metal carbide cations are factors that jointly affect both the reactivity and the mechanism of C−H bond activation. Transition-metal carbide anions are usually not very reactive with methane. However, it was found that the FeC$_6$$^-$ anion can activate CH$_4$ via a dissociative adsorption manner. The large dipole moment of FeC$_6$$^-$ can induce a polarization of CH$_4$, which facilitates cleavage of the C−H bond. The FeC$_3$$^-$ anion reacts with methane under high-temperature conditions to...
form the C–C coupling product acetylene. The reactions of other metal carbide cluster ions with methane have also been reported. Most clusters show high reactivity toward CH₄ dehydrogenation at thermal conditions. The cooperation of the metal centers in the dinuclear carbide cluster reaction has been proposed. The C–H bond activation takes place predominantly around one Ta center in the initial stage of the reaction, and the second Ta center accepts the delivered H atom from the C–H bond cleavage.

In this paper, we report a combined experimental and theoretical study on the reaction of a dinuclear rhodium carbide cation [Rh₂C₃]+ with methane in the gas phase. We will show that the reactions involving the activation of all four C–H bonds of the methane and carbon atom exchange processes proceed at thermal conditions.

### EXPERIMENTAL AND COMPUTATIONAL METHODS

The infrared photodissociation spectrum of the [Rh₂C₃Ar]+ ions was measured using a collinear tandem time-of-flight mass spectrometer as described in detail previously. The rhodium carbide cations were generated in the gas phase using a pulsed laser vaporization-supersonic expansion ion source. The fundamental of a Nd:YAG laser with 10–20 mJ/pulse was employed to ablating a rhodium + graphite (1:4) target. The cation complexes were produced during the laser ablation process in supersonic expansions of helium or Ar gas mixtures at about 1.0 MPa backing pressure. After free expansion and cooling, the ions were extracted and analyzed using a time-of-flight mass spectrometer. The [Rh₂C₃Ar]+ ions were mass-selected, deaccelerated, and subjected to IR photodissociation by a tunable IR laser. The fragment and undissociated parent ions were reaccelerated and mass analyzed by a second collinear time-of-flight mass spectrometer. Infrared photodissociation spectrum was obtained by monitoring the fragment ion yield (the intensity of fragment ions divided by the sum of intensities of the fragment ions and the undissociated parent ions) as a function of the dissociation IR laser wavelength. The tunable infrared source is generated by an KTP/KTA/AgGaSe₂ optical parametric oscillator/amplifier system (OPO/OA, Laser Vision) pumped by a Continuum Surelite Nd:YAG laser, which is tunable in the range of 800–5000 cm⁻¹ with an approximate line width of 2 cm⁻¹. Typical spectra were recorded by scanning the dissociation laser in steps of 2 cm⁻¹ and averaging over 250 laser shots at each wavelength. The laser pulse energy ranges from 0.2 to 1.5 mJ/pulse.

The reaction of [Rh₂C₃]+ ions with methane was studied using an ion trap mass spectrometer. The [Rh₂C₃Ar]+ ions were mass-selected, deaccelerated, and subjected to IR photodissociation by a tunable IR laser. The fragment and undissociated parent ions were reaccelerated and mass analyzed by a second collinear time-of-flight mass spectrometer. Infrared photodissociation spectrum was obtained by monitoring the fragment ion yield (the intensity of fragment ions divided by the sum of intensities of the fragment ions and the undissociated parent ions) as a function of the dissociation IR laser wavelength. The tunable infrared source is generated by an KTP/KTA/AgGaSe₂ optical parametric oscillator/amplifier system (OPO/OA, Laser Vision) pumped by a Continuum Surelite Nd:YAG laser, which is tunable in the range of 800–5000 cm⁻¹ with an approximate line width of 2 cm⁻¹. Typical spectra were recorded by scanning the dissociation laser in steps of 2 cm⁻¹ and averaging over 250 laser shots at each wavelength. The laser pulse energy ranges from 0.2 to 1.5 mJ/pulse.

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### RESULTS AND DISCUSSION

To determine the geometric and electronic structures of the [Rh₂C₃]+ cation, infrared photodissociation spectroscopy is employed to obtain the vibrational spectrum of [Rh₂C₃]+. The dissociation energies of the [Rh₂C₃]+ cation are calculated to be 504, 690, 578, and 393 kJ/mol, respectively, with respect to the [RhCCC]+ + Rh, [RhCC]+ + RhC, [RhC]+ + RhCC, and [Rh]+ + RhCCC dissociation channels at the B3LYP-D3/def2TZVP level. Because the dissociation energies of the [Rh₂C₃]+ cation are predicted to be significantly greater than the infrared photon energies in the C–C and Rh–C stretching frequency region, the method of rare-gas atom predissociation is employed. The Ar-tagged complex [Rh₂C₃Ar]+ is generated and mass-selected for infrared photodissociation. When the infrared laser is in resonance with one of the vibrational fundamentals of the [Rh₂C₃Ar]+ complex, it photodissociates by eliminating an argon atom. The resulting infrared spectrum is shown in Figure 1a. Two close-lying bands centered at 1984 and 2011 cm⁻¹ together with a weak broad band centered at 1384 cm⁻¹ are observed. The two bands around 2000 cm⁻¹ are very close to the antisymmetric stretching mode of linear C₃ molecule at 2040 cm⁻¹. The Ar-tagged complex [Rh₂C₃Ar]+ involves a C₁ subunit. The 1384 cm⁻¹ band can be attributed to the symmetric stretching vibration of the C₃ unit. The observation of the symmetric stretching mode suggests that the C₃ subunit is either bent or asymmetric.

As shown in Figure 2, the most stable structure of the [Rh₂C₃]+ cation is predicted to have a linear asymmetric structure [Rh–C–C–C–Rharga] with two different Rh–C bonds of 1.90 and 1.72 Å, respectively. The other C–C bonds are not the same with a shorter bond distance of 1.24 Å and a longer bond distance of 1.32 Å. The doublet ¹Δ state and the quartet ³Δ state are nearly isoenergetic and have essentially the same geometric parameters and valence electron configuration of π⁺δ¹σ⁺σ*. The unpaired electrons occupy the rhodium-based molecular orbitals as shown in Figure 3. The quartet state, in which the unpaired electrons at the terminal rhodium atoms are ferromagnetically coupled is predicted to be 1 kJ/mol higher in energy than the doublet state with antiferromagnetic coupling of the unpaired electrons at the terminal rhodium atoms at the B3LYP level (Table 1). The quartet state is predicted to be 2 kJ/mol more stable than the doublet state at the CCSD(T)//B3LYP-D3//def2TZVP level. The other nonlinear structures are predicted to lie more than 98 kJ/mol higher in energy than the most stable linear structure as shown in Figure S1. The argon-tagged complexes of the linear [Rh₂C₃]+ ions are also calculated at the B3LYP-D3//def2TZVP level. The results show that the argon atom prefers to coordinate to the terminal rhodium atom with two unpaired electrons (with longer Rh–C bond) for both the quartet and doublet spin states (see Figure S1 and Table S3). The calculations also show that the energetic ordering of the
doublet and quartet spin states is not affected by weak argon coordination. The Rh–Ar distances are quite large (2.64 and 2.67 Å) and the [Rh₂C₃]⁺ moiety in [Rh₂C₃·Ar]⁺ has essentially the same structure as the free cation as shown in Figure 2. The antisymmetric and symmetric C₃ stretching modes of the doublet state [Rh₂C₃·Ar]⁺ ion are calculated at 2042 and 1388 cm⁻¹, whereas these two modes of the quartet spin state are predicted at 2054 and 1393 cm⁻¹ (Table 1). On the basis of the comparison between the simulated and experimental infrared spectra (Figure 1), the experimentally observed [Rh₂C₃]⁺ ion can be attributed to have the unsymmetrical linear [Rh–C=C=C–Rh]⁺ structure coexisting in the two nearly isoenergetic doublet and quartet spin states. The observed 1984 and 2011 cm⁻¹ bands separated by 27 cm⁻¹ are assigned to the antisymmetric C₃ stretching modes of the ions in the doublet and quartet spin states, respectively. The symmetric stretching modes of the doublet spin state are predicted to be separated by only 5 cm⁻¹, and thus cannot be resolved experimentally. The coexistence of two spin states has been reported for other ions previously.34,39

Figure 2. Optimized structures (bond lengths in Å) of the linear [Rh₂C₃]⁺ ion and its Ar-tagged [Rh₂C₃·Ar]⁺ complex at the B3LYP-D3/def2TZVP level of theory. The relative energies are given in kJ/mol. Purple, Rh; gray, C; light blue, Ar.

Figure 3. Frontier molecular orbitals of [Rh₂C₃]⁺ in the doublet and quartet spin states. (SOMO − 1, HOMO, and HOMO − 1 are doubly degenerate, and only one orbital is shown).

The mass spectra from the reactions of mass-selected [Rh₂C₃]⁺ ions (m/z = 242) with He, CH₄, ¹³CH₄, and CD₄ in the ion trap at room temperature are shown in Figure 4. No product ion is observed in the mass spectrum using pure He as reactant gas (Figure 4a), while two mass peaks at m/z = 218 and 232, which can be attributed to the product ions with chemical formulas of [Rh₂C⁺] and [Rh₂C₂H₂]⁺, are observed to be the major reaction products (Figure 4b). A very weak mass peak at m/z = 256 is also observed, which is assigned to the ion with chemical formula of [Rh₂C₄H₂]⁺ (Figure 4b). The mass spectrum suggests that three reaction channels are observed for the [Rh₂C₃]⁺ and CH₄ reactions. The first channel is the formation of the [Rh₂C]⁺ cation with the release
The generation of the \([\text{Rh}_2\text{C}_2\text{H}_2]+\) ion with the release of a neutral \(\text{C}_3\text{H}_4\) molecule (reaction 1). According to the thermochemical data, the heat of formation of propyne \(\text{CH}_3\text{CCH}\) \((185.71 \pm 0.24 \text{ kJ/mol})\) is only slightly lower than that of allene \(\text{CH}_2\text{CCH}_2\) \((189.93 \pm 0.25 \text{ kJ/mol})\), which suggests that both propyne and allene are formed in the reactions. The second channel is the generation of the \([\text{Rh}_2\text{C}_2\text{H}_2]+\) ion with concomitant elimination of a neutral \(\text{C}_3\text{H}_4\) molecule (reaction 2). The third channel is the generation of the \([\text{Rh}_2\text{C}_3]+\) ion, the \([\text{Rh}_2\text{C}_2\text{D}]++\) ion during the reaction (see reaction 4). The \([\text{Rh}_2\text{C}_3]^+, [\text{Rh}_2\text{C}_2\text{D}_2]^+\) and \([\text{Rh}_2\text{C}_2\text{D}_3]^+\) product ions are observed when the \(\text{CD}_4\) sample is employed (Figure 4d), which also support the proposed reactions 1–3.

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[\text{Rh}_2\text{C}_3]^+ + \text{CH}_4 \rightarrow [\text{Rh}_2\text{C}_2\text{D}]^+ + \text{C}_3\text{H}_4
\]

The variation in ion intensities of the reactant \(([\text{Rh}_2\text{C}_3]^+)\) and products \(([\text{Rh}_2\text{C}_2\text{H}_2]^+, [\text{Rh}_2\text{C}_3\text{H}_2]^+\) and \([\text{Rh}_2\text{C}_3\text{H}_2]^+\) with respect to the \(\text{CH}_4\) pressure is given in Figure S2. The relative intensity of the reactant ion decreases and those of the product ions increase gradually as the pressure of reactant molecule \(\text{CH}_4\) increases. The number of \(\text{CH}_4\) is much larger than that of the \([\text{Rh}_2\text{C}_3]^+\) ion in the ion trap, and the plots fit the pseudo-first-order kinetics. The rate constant \(k([\text{Rh}_2\text{C}_3]^+ + \text{CH}_4)\) is determined to be \(2.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}\). The collision rate is calculated to be \(9.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\) using the Langevin–Gioumousis–Stevenson model, indicating that the reaction being observed occurs with an efficiency of only 2.6%. The uncertainty on this rate constants are estimated to be accurate within a factor of 3.

To gain insight into the reaction mechanism, the potential energy profiles are calculated. All of the three reactions 1–3 leading to the most stable structures of the products are exothermic by 27, 21, and 46 kJ/mol, respectively at the B3LYP level. The most favorable pathway for the \([\text{Rh}_2\text{C}_3]^+ + \text{CH}_4\) reaction leading to the \([\text{Rh}_2\text{C}_3]^+ + \text{C}_3\text{H}_4\) products on the doublet spin state is shown in Figure S5, and the other possible pathways are given in Figures S3–S5. The most stable structure of \([\text{Rh}_2\text{C}_3]^+\) is linear with a doublet ground state \((|\text{Rh}_2\text{C}–\text{Rh}_2]|^\text{g}\), Figure S6). Both the doublet state and quartet state \([\text{Rh}_2\text{C}_3]^+\) ions can involve in the reaction with methane. All of the intermediates and transition states along the reaction pathways on the quartet state surface are about the same or higher in energy than those in the doublet state surface (Table S4). On the doublet state surface, the reaction proceeds with the initial formation of the adsorption complex \((|\text{F}|\)), which is 39 kJ/mol lower in energy than the doublet ground-state reactants. The complex has a \(C_2\) symmetric structure with the \(\text{CH}_4\) molecule coordinated to the \([\text{Rh}_2\text{C}_3]^+\) ion via two
The two most favorable pathways for generating the [Rh\textsubscript{2}C\textsubscript{4}H\textsubscript{2}]\textsuperscript{+} + C\textsubscript{2}H\textsubscript{2} (acetylene) products (reaction 2) are shown in Figure S7. The most stable structure of [Rh\textsubscript{2}C\textsubscript{3}H\textsubscript{2}]\textsuperscript{+} has a doublet ground state with C\textsubscript{2v} symmetry, in which the C\textsubscript{3}H\textsubscript{2} moiety is side-on bonded to the Rh\textsuperscript{+} dimer with the C\textsubscript{2}H\textsubscript{2} plane perpendicular to the Rh—Rh bond (Figure S6). As shown in Figure S7, the reaction pathways from the reactants to the \textsuperscript{2}19 and \textsuperscript{2}21 intermediates are the same as that shown in Figure S5. Starting from either the \textsuperscript{2}19 or \textsuperscript{2}21 intermediate, the reactions proceed via multiple steps including rearrangement, C—H bond activation, and hydrogen atom transfer. The intermediate \textsuperscript{2}38 involves two equivalent C\textsubscript{2}H\textsubscript{2} moieties; either one can be liberated to form the final product P3. This explains the experimental observation that the peaks of [Rh\textsubscript{2}C\textsubscript{3}H\textsubscript{2}]\textsuperscript{+} and [Rh\textsubscript{2}C\textsubscript{3}CH\textsubscript{3}]\textsuperscript{+} have about the same intensity as shown in Figure 4.

The most favorable pathway for generating [Rh\textsubscript{2}C\textsubscript{4}H\textsubscript{2}]\textsuperscript{+} + H\textsubscript{2} (reaction 3) and the optimized geometries of [Rh\textsubscript{2}C\textsubscript{3}H\textsubscript{2}]\textsuperscript{+} are shown in Figures S8 and S9, respectively. The most stable structure of [Rh\textsubscript{2}C\textsubscript{3}H\textsubscript{2}]\textsuperscript{+} has a C\textsubscript{2v} symmetry structure, in which the C\textsubscript{3}H\textsubscript{2} moiety is side-on bonded to the Rh\textsuperscript{+} dimer via two C atoms with the C\textsubscript{2}H\textsubscript{2} plane perpendicular to the Rh—Rh bond (Figure S9). The reaction pathway from the reactants to the \textsuperscript{8} intermediate is the same as that shown in Figure S5. From the \textsuperscript{2}8 intermediate, the reaction further proceeds via three additional intermediates and three transition states in forming the final products [Rh\textsubscript{2}C\textsubscript{4}H\textsubscript{2}]\textsuperscript{+} + H\textsubscript{2} with the highest transition state (\textsuperscript{2}TS44) lying 8 kJ/mol below the initial reactants.

The above-mentioned calculation results indicate that all of the three reaction channels are exothermic and all of the intermediates and transition states are about the same or lower in energy than the ground state reactants. Therefore, reactions 1–3 are all thermodynamically exothermic but with low reaction efficiency. The rate-limiting transition state is \textsuperscript{2}TS2 for all three reactions. The transition state past \textsuperscript{2}TS2 that limits the loss of C\textsubscript{3}H\textsubscript{4} is the same as that limits the loss of C\textsubscript{2}H\textsubscript{2} (\textsuperscript{2}TS6, -17 kJ/mol). In contrast, the transition state past \textsuperscript{2}TS2 that limits the loss of H\textsubscript{2} is \textsuperscript{2}TS44, which lies only 8 kJ/mol lower in energy than the reactants. These results are consistent with the experimental observation that the [Rh\textsubscript{2}C\textsubscript{3}]\textsuperscript{+} and [Rh\textsubscript{2}C\textsubscript{3}H\textsubscript{2}]\textsuperscript{+} product ions have comparable intensities, in contrast, the [Rh\textsubscript{2}C\textsubscript{4}H\textsubscript{2}]\textsuperscript{+} product ion is much weaker than [Rh\textsubscript{2}C\textsubscript{3}]\textsuperscript{+} and [Rh\textsubscript{2}C\textsubscript{3}H\textsubscript{2}]\textsuperscript{+} in the mass spectrum (Figure 4).

The reactions of transition metal carbide ions with methane have previously been studied using mass spectrometric methods in the gas phase under room-temperature or even high-temperature conditions.\textsuperscript{30–41} The generation of ethylene or acetylene via C—H bond activation and C—C coupling reactions has been reported for some metal carbide cation reactions.\textsuperscript{30–32,35} C—H bond activation and dehydrogenation of methane has also been observed for metal carbide anions.\textsuperscript{38–40} The [Rh\textsubscript{2}C\textsubscript{3}]\textsuperscript{+} cation exhibits reactivity toward methane. Besides the production of acetylene, the generation of allene or propyne is also observed as a major reaction channel. The isotopic-labeled experiments reveal two different formation mechanisms of the allene or propyne product, demonstrating that the linear C\textsubscript{3} moiety of [Rh\textsubscript{2}C\textsubscript{3}]\textsuperscript{+} can be effectively replaced by the bare carbon atom of methane with all four C—H bonds being activated.

The calculations indicate that the rhodium centers in [Rh\textsubscript{2}C\textsubscript{3}]\textsuperscript{+} are the reactive sites for methane activation. Natural population analysis shows that both rhodium centers are
positively charged in the linear [Rh$_2$C$_3$]$^+$ cation (+0.80 e and +0.82 e in the doublet and quartet states for the rhodium center with longer Rh−C bond length; + 0.46 e and +0.48 e for the rhodium center with shorter Rh−C bond length, see Figure S10), which can interact with methane via ion-induced dipole interactions in forming weakly bound complex. The coordination elongates the C−H bonds of methane from 1.09 to 1.10 Å, which facilitates the C−H bond activation. Calculations indicate that the first C−H bond activation takes place on one rhodium center in forming the oxidative C−H bond insertion intermediate $^2$, from which the hydride H atom can further be transferred to the nearby carbon atom. The process from $^2$ to $^3$ is predicted to be the rate-determining step that requires overcoming the highest barrier. Thus, $^2$ serves as a key intermediate along the reaction paths. It has been shown that the ground-state neutral rhodium atom is reactive toward methane and undergoes oxidative C−H bond insertion to form the HRhCH$_3$ species even at cryogenic temperatures.$^{69}$ However, previous studies indicate that the Rh$^+$ cation is unreactive toward methane at thermal energies.$^{70}$ These studies imply that the charge of the metal center is not an important factor on the reactivity as the rate-determining step was predicted to be hydrogen/hydride transfer process. Previous investigations indicate that some dinuclear metal complexes and clusters exhibit much higher reactivity than mononuclear species toward small molecule activation such as methane and dinitrogen.$^{71-76}$ The cooperation of two metal centers could facilitate the activation processes. The investigation on methane activation by rhodium clusters implies that although the atomic Rh$^+$ is not able to dehydrogenate methane at room temperature, the dimer cation Rh$_2$$^{2+}$ reacts with methane to form the dehydrogenated product Rh$_2$C$_2$H$_2$$^{+}$.$^{24,70}$

**CONCLUSIONS**

The dinuclear metal carbide ions [Rh$_2$C$_3$]$^+$ are generated in the gas phase. It is characterized by infrared photodissociation spectroscopy as well as quantum chemical calculations to have an unsymmetrical linear [Rh−C−C−C-Rh]$^+$ structure existing in two nearly isoenergetic doublet and quartet spin states. Mass spectrometric studies on the reactions of the [Rh$_2$C$_3$]$^+$ ion with CH$_4$ in the gas phase at room temperature show that three reaction channels are observed with a quite low reaction efficiency. The first channel is the formation of the [Rh$_2$C]$^+$ cation with the release of an allene or propyne neutral C$_4$H$_4$. The second channel is the generation of the [Rh$_2$C$_2$H$_2$]$^+$ cation with the concomitant elimination of an acetylene molecule. The third channel is the generation of the [Rh$_2$C$_2$H$_2$]$^+$ ion with the release of a dihydrogen molecule. The production of [Rh$_2^{13}$C]$^+$ + C$_4$H$_4$ using isotopic-labeled $^{13}$CH$_4$ sample indicates that the linear C$_4$ moiety of the [Rh$_2$C$_3$]$^+$ reactant can be replaced by the bare carbon atom of methane with all the four C−H bonds being activated. The calculations suggest that the overall reactions are thermodynamically exothermic, and that the two Rh centers are the reactive sites for C−H bond activation and hydrogen atom transfer reactions. The results may provide useful information in understanding multifaceted mechanisms of methane activation at ambient conditions.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00265.

Experimental mass spectra, calculated geometries and potential energy profiles (PDF)

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**Notes**

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