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Mutual Functionalization of Dinitrogen and Methane Mediated by Heteronuclear Metal Cluster Anions CoTaC$_2^-$

Li-Hui Mou,$^a,b,c$ Yao Li,$^{b,c,d}$ Gong-Ping Wei,$^{a,b,c,d}$ Zi-Yu Li,$^{*,a,d}$ Qing-Yu Liu,$^{a,d}$ Hui Chen,$^{*,b,d}$ and Sheng-Gui He$^{*,a,c,d}$

The direct coupling of dinitrogen ($N_2$) and methane ($CH_4$) to construct the N–C bond is a fascinating but challenging approach for the energy-saving synthesis of N-containing organic compounds. Herein we identified a likely reaction pathway for N–C coupling from $N_2$ and $CH_4$ mediated by heteronuclear metal cluster anions CoTaC$_2^-$, which starts with the dissociative adsorption of $N_2$ on CoTaC$_2^-$ to generate a Ta$^{δ+}$–N$_2^-$ (terminal-nitrogen) Lewis acid-base pair (LABP), followed by the further activation of $CH_4$ by CoTaC$_2^-$ to construct the N–C bond. The N$_2$ cleavage by CoTaC$_2^-$ affording two N atoms with strong charge buffering ability plays a key part, which facilitates the H$_2$C–H cleavage via the LABP mechanism and the N–C formation via a CH$_3$ migration mechanism. A novel N$_2$ triggering strategy to couple $N_2$ and $CH_4$ molecules by metal clusters was accordingly proposed, which provides a new idea for the direct synthesis of N-containing compounds.

Introduction

The construction of N–C bonds directly from $N_2$ offers the potential to reduce the enormous fossil-fuel consumption for the current synthesis of N-containing organic compounds through NH$_3$, which is mainly produced via the energy-intensive Haber-Bosch process ($N_2$ + $H_2$ $\rightarrow$ NH$_3$). Considerable research efforts have been devoted to this subject since the initial observation of N–C bond formation in the reaction of $N_2$ complexes with organic halides.$^2$ A long-sought goal for this chemistry has been the direct coupling of $N_2$ with abundant carbon-based molecules that are viable in industry. However, activation of these stable molecules remains a challenge, and only CO$_3^{3-}$, CO$_2$,$^{6-8}$ and unsaturated hydrocarbons$^{9,10}$ have been reported to construct N–C bonds with $N_2$ induced by appropriate reactive species. $CH_4$, the major component of widely available natural gas, is closely linked to industrial NH$_3$ synthesis in which $N_2$ is produced through the energy-intensive CH$_4$-reforming process. Therefore, the direct coupling of $N_2$ and $CH_4$ is of great importance for economic and environmental reasons. However, proper species that can mediate the coupling of inert $N_2$ and $CH_4$ molecules to form the N–C bond has not been revealed.

Isolated gas-phase atomic clusters are important model systems for the precise design of desired active sites and the fundamental understanding of bond activation and formation processes.$^{11}$ The activation and individual functionalization of $N_2$ or $CH_4$$^{12-18}$, and the formation of N–C bonds$^{19-25}$ are also extensively studied issues in the gas-phase field. Typical examples of N–C bond formation from $N_2$ or $CH_4$ in gas-phase studies can be classified as follows: (i) reactions of metal carbide clusters with $N_2$$^{22-25}$ or metal nitride clusters with $CH_4$$^{26,27}$ and (ii) coupling reactions of $CH_4$ with NH$_3$$^{28,29}$ or $N_2$ with CO$_2$.$^{3}$ In addition to reactions involving $N_2$ or $CH_4$, the N–C bond formation was also observed for a few other reaction systems.$^{30-32}$ Compared with these N–C formation processes, the direct coupling of $N_2$ and $CH_4$ is rather challenging and of particular interest.

Herein, we report the first example of N–C bond formation from the mutual functionalization of $N_2$ and $CH_4$ mediated by heteronuclear metal cluster anions CoTaC$_2^-$ under thermal collision conditions. A terminal-nitrogen ($N_2$) triggering strategy for the coupling of $N_2$ and $CH_4$ was accordingly proposed (Scheme 1), which starts with the dissociative adsorption of $N_2$ on metal-based substrates to generate a M$^{δ+}$–N$_2^-$ Lewis acid-base pair (LABP), followed by the H$_2$C–H cleavage of $CH_4$ via the LABP mechanism and the N–C formation via a CH$_3$ migration mechanism. Considering the activation of $CH_4$ by some metal nitrides follows the LABP mechanism$^{26,27}$ we infer that the proposed strategy can be quite general, which is confirmed by the study on the FeTaC$_3^-$/$N_2$/CH$_4$ reaction system. The important roles of producing substrate–$N_2$ complexes in the
coupling of \( \text{N}_2 \) and \( \text{CH}_4 \), as well as the strength of \( \text{M} \cdots \text{N}_2 \) bonds in the activity of the \( \text{N}_2 \) complexes were discussed.

![Scheme 1](image)

Scheme 1. The proposed terminal-nitrogen (\( \text{N}_1 \)) triggering strategy for the coupling of \( \text{N}_2 \) and \( \text{CH}_4 \). The key to this strategy is the predissociation of \( \text{N}_2 \) on a proper substrate to generate a \( \text{N}_1 \) and a bridging-N (\( \text{N}_0 \)).

**Results**

**Cluster Reactivity.** The spectra in Fig. 1 have been obtained by using an online time-of-flight (TOF) mass spectrometer and show the results for the reactions of CoTaC\(_2^−\) (\( m/z = 264 \)) with \( \text{N}_2 \) and CoTaC\(_2\text{N}_2^−\) (\( m/z = 292 \)) with \( \text{CH}_4 \). Reference spectra with inert He as the reactant gas were also recorded (Fig. 1a and d).

The CoTaC\(_2^−\) ions were generated by laser ablation of a mixed Co–Ta disk target (molar ratio Co/Ta = 2:1) in the presence of 0.05% CD\(_4\) diluted with He carrier gas, and then mass-selected and thermalized to room temperature to react with \( \text{N}_2 \) in a linear ion trap (LIT) reactor. As shown in Fig. 1b, on pulsing 0.56 Pa \( \text{N}_2 \) into the LIT reactor, a strong product peak assigned as CoTaC\(_2\text{N}_2\text{H}^−\) appeared, suggesting the following reaction channel:

\[
\text{CoTaC}^− + \text{N}_2 \rightarrow \text{CoTaC}2\text{N}^− \quad (1)
\]

The isotopic labeling experiment using \( ^{15}\text{N}_2 \) as the reactant gas (Fig. 1c) confirmed the above reaction channel. We should mention in passing that, a very tiny metal atom ejection channel (less than 1%) producing TaC\(_2\) was estimated to be (8.0 ± 1.6) \( \times 10^{13} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), corresponding to the \( \Phi \) of about 1.4 %.

![Fig. 1](image)

Fig. 1 Time-of-flight mass spectra for the reactions of CoTaC\(_2^−\) with (a) He, (b) \( \text{N}_2 \), and (c) \( ^{15}\text{N}_2 \), and CoTaC\(_2\text{N}_2^−\) with (d) He, (e) \( \text{CH}_4 \), and (f) CD\(_4\). The reaction times are 4.8 ms for (b, c), 1.8 ms for (e), and 1.9 ms for (f). Peaks marked with asterisks are due to water impurities in the gas handling system.

To study the reaction of the \( \text{N}_2 \) association product CoTaC\(_2\text{N}_2^−\) with \( \text{CH}_4 \), a newly-developed double ion trap apparatus (Scheme S1 in Supplementary Information) was used to first generate the CoTaC\(_2\text{N}_2^−\) from the reaction of CoTaC\(_2^−\) with \( \text{N}_2 \) in the first LIT reactor and then mass select CoTaC\(_2\text{N}_2^−\) to interact with \( \text{CH}_4 \) in the second LIT reactor. Upon the interaction of CoTaC\(_2\text{N}_2^−\) with \( \text{CH}_4 \) (Fig. 1e), three product peaks assigned as CoTaC\(_2\text{N}_2\text{CH}_4^−\) (\( m/z = 308 \)), CoTaC\(_2\text{N}_2\text{CH}_3^−\) (\( m/z = 306 \)), and CoTaC\(_2\text{N}_2\text{C}^+\) (\( m/z = 304 \)) were observed, suggesting the following reaction channels:

\[
\begin{align*}
\text{CoTaC}_2\text{N}_2^− + \text{CH}_4 & \rightarrow \text{CoTaC}_2\text{N}_2\text{CH}_4^− \quad 49\% \quad (2) \\
\rightarrow \text{CoTaC}_2\text{N}_2\text{CH}_2^+ + \text{H}_2 & \quad 41\% \quad (3) \\
\rightarrow \text{CoTaC}_2\text{N}_2\text{C}^+ + 2\text{H}_2 & \quad 10\% \quad (4)
\end{align*}
\]

The rate constant \( k_1(\text{CoTaC}_2\text{N}_2^−/\text{CH}_4) \) for the reaction of CoTaC\(_2\text{N}_2^−\) with \( \text{CH}_4 \) was estimated to be (1.4 ± 0.3) \( \times 10^{16} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), corresponding to the \( \Phi \) of about 1.4 %.

Noticeably, the reaction channel of ejecting two \( \text{D}_2 \) molecules was negligible when using isotope-labeled CD\(_4\) in place of CH\(_4\) (Fig. 1f). The branching ratio of reaction channel (2) to reaction channel (3) changed to 80:20 in the CD\(_4\) experiment, and the intermolecular kinetic isotope effect (KIE) calculated by \( k_1(\text{CoTaC}_2\text{N}_2^−/\text{CD}_4)/k_1(\text{CoTaC}_2\text{N}_2^−/\text{CH}_4) \) was estimated to be 1.3 (Fig. S2b and c). The loss of \( \text{H}_2 \) (D\(_2\)) in the reaction of CoTaC\(_2\text{N}_2^−\) with \( \text{CH}_4 \) (CD\(_4\)) suggests that activation of C–H bonds must have occurred. To determine mechanisms of CoTaC\(_2^−\) + \( \text{N}_2 \) and CoTaC\(_2\text{N}_2^−\) + \( \text{CH}_4 \) reactions, structural characterization of the reactant cluster ions should be performed.

**Structural Characterization.** Photoelectron imaging spectroscopy (PEIS) combined with quantum chemistry calculations was employed to characterize the structures of CoTaC\(_2^−\) and CoTaC\(_2\text{N}_2^−\). The structures were optimized at the density functional theory (DFT) level, and their relative energies were then refined by high-level RCCSD(T) (partially spin-adapted open-shell coupled cluster method with single, double, and perturbative triple excitations) and DMRG-SC-NEVPT2 (density matrix renormalization group strongly-contract \( n \)-electron valence perturbation theory) methods. The experimental spectrum of CoTaC\(_2^−\) recorded with 670 nm photons at 10 K reveals a sharp peak centered at 1.63 eV, followed by three discernable peaks with electron binding...
The presence of two d–d bonding orbitals between Co and Ta atoms provides further evidence for the Co–Ta double bond in the experimental spectrum from 1.70 to 1.76 eV (Fig. 2a, top). The calculated adiabatic electron detachment energy (ADE) of \(^2\)IS1 is close to the experimental value (1.83 eV vs 1.70 eV), suggesting that the \(^2\)IS1 is the most probable species of CoTaC\(_2\) generated in the experiment. The first spectral peak centered at 1.63 eV might come from the minor population of the isomer \(^4\)IS2 with relative energy of 0.59 eV higher than \(^2\)IS1, considering that its calculated ADE (1.59 eV) and simulated profile of the \(^2\)A \(\rightarrow\) \(^2\)A transition match well with the first spectral peak (Fig. 2a, bottom). A more detailed discussion of the structural assignment of CoTaC\(_2\) is provided in the Supplementary Information (Fig. S3).

**Reaction Mechanism for the CoTaC\(_2\)/N\(_2\) Couple.** The reaction pathway of CoTaC\(_2\) (\(^2\)IS1) with N\(_2\) calculated at the RCCSD(T) level is shown in Fig. 2b. The N\(_2\) molecule first approaches the Ta atom through a side-on (\(\eta^5\)) mode to form the encounter complex \(^1\)I1 (\(-0.47\) eV). Further binding of N\(_2\) to Co is impeded by a high energy barrier with the doublet spin state \(^2\)TS1/0.10 eV), however, this process can be accomplished through transiting to the quartet spin state \(^4\)TS1/0.13 eV) and then a more stable intermediate \(^4\)I2 (\(-0.84\) eV) with a side-on-end-on (\(\eta^5:\eta^1\)) bounded N\(_2\) unit is formed. By surmounting \(^4\)TS2, N\(_2\) is coordinated to the Co–Ta center in a distorted-\(\eta^5:\eta^1\) mode (\(-0.64\) eV) with the N–N bond length of 135 pm. The N–N bond is disrupted entirely after overcoming a slight energy barrier of 0.11 eV \(^2\)TS3/0.53 eV), yielding one terminal-N (N\(_t\)) and one bridging-N (N\(_b\)) in the \(^4\)I4 (\(-1.39\) eV). The subsequent N–C\(_\text{cluster}\) coupling would encounter a highly positive energy barrier \(^4\)TS17/0.10 eV, Fig. 5a) that has little chance to be surmounted under thermal collision conditions, and thus the \(^4\)I4 would be stabilized as the adsorption product CoTaC\(_2\)N\(_2\) through collisions with bath gas He. Note that the very minor reaction channel of generating TaC\(_2\)N\(_2\) in the reactivity experiment might come from the reaction of the high-lying isomer \(^4\)I2 with N\(_2\) in which two steps of N–C\(_\text{cluster}\) coupling take place before ejecting a neutral Co atom (Fig. S5).

The PEIS characterization of CoTaC\(_2\)N\(_2\) at different reaction temperatures and photon energies supported the assignation of \(^4\)I4 as the adsorption product and also proved the reliability of our RCCSD(T) calculations. As shown in Fig. 2c, only one spectral peak (B) was observed in the experimental spectrum recorded with 410 nm photons at 250 K (Note that the residual water in the room-temperature ion trap will deplete the CoTaC\(_2\) signal under the condition of long trapping time of 80 ms, so room-temperature reaction was not performed in the PEIS experiment), however, two spectral peaks (A and B) could be observed when the reaction temperature decreased to 200 K and 170 K. This implies that an additional intermediate was stabilized as the adsorption product CoTaC\(_2\)N\(_2\) at lower temperatures and accounted for the appearance of peak A. Considering that the process of \(^2\)I1 \(\rightarrow\) \(^4\)TS1 \(\rightarrow\) \(^4\)I2 with the highest energy barrier and a spin crossing is the rate-limiting step (Fig. 2b), the \(^2\)I1 is the most probable species that could be stabilized at lower temperatures. When the temperature is decreased to a certain value, all of the I1 might be stabilized and cannot transform to I4. However, this situation is not the focus of this work because we aim to study the reactions of CoTaC\(_2\)N\(_2\)/N\(_2\) and CoTaC\(_2\)N\(_2\)/CH\(_4\) couples at room temperature. The simulated spectra of CoTaC\(_2\)N\(_2\) isomers based on density of states (DOS) simulations\(^{10}\) confirmed the contribution of \(^2\)I1 to peak A, and indicated that the peak B in the 250 K spectrum was contributed by the \(^4\)I4 (Fig. 2c). Moreover, the employment of 365 nm photons for the PEIS characterization of CoTaC\(_2\)N\(_2\) provides further evidence for the agreement of DOS-simulated spectrum of \(^4\)I4 with the experimental one (Fig. S6b and d). Other CoTaC\(_2\)N\(_2\) isomers with the N–N or N–C bonds should be excluded due to their mismatched VDE values and spectral patterns with the experimental spectrum (Fig. S6e–k) and their theoretically predicted inertness toward CH\(_4\) (Fig. S7). Therefore, a N-containing complex was successfully prepared through the dissociative adsorption of N\(_2\) on CoTaC\(_2\) at room temperature.
and 4IS2 are red shifted by 0.13, 0.05, 0.12 eV and blue shifted by 0.04 eV, respectively.

**Reaction Mechanism for the CoTaC\textsubscript{2}N\textsubscript{2}/CH\textsubscript{4} Couple.** As shown in Fig. 3, the CoTaC\textsubscript{2}N\textsubscript{2} (1\text{PI}) interacts with CH\textsubscript{4} by first anchoring it on the Ta atom to form 1\text{IS} with a binding energy of 0.44 eV. The first H\textsubscript{2}C-H bond cleavage preferably proceeds via the cooperative mechanism of a LABP composed of Ta (natural charge: 1.31 e) and N\textsubscript{4} (natural charge: -0.79 e) atoms, generating a N\textsubscript{4}-H bond and a Ta-CH\textsubscript{3} moiety in the 1\text{I6} (-2.52 eV). After that, the CH\textsubscript{3} group tends to migrate from Ta to N\textsubscript{6} to liberate the Ta site (1\text{I6} \rightarrow 2\text{TS5} \rightarrow 1\text{I7}). On the basis of Rice–Ramsperger–Kassel–Marcus (RRKM) theory,\textsuperscript{41} the conversion rate of 1\text{I6} \rightarrow 2\text{TS5} is estimated to be 6.9 \times 10^4 s\textsuperscript{-1}, which is one order of magnitude smaller than the collision rate (6.7 \times 10^5 s\textsuperscript{-1}) that a cluster experiences with the bath gas He in the LIT reactor. This suggests that only a small part of the 1\text{I6} could overcome 2\text{TS5} to form 1\text{I7}, while most of the 1\text{I6} would be stabilized as the adsorption product CoTaC\textsubscript{2}N\textsubscript{2}CH\textsubscript{3} through collisions with bath gas. If the barrier height of 2\text{TS5} is decreased by 0.1 eV that could be the uncertainty of RCCSD(T) calculations,\textsuperscript{42} the rate of 1\text{I6} \rightarrow 2\text{TS5} is increased to 3.3 \times 10^5 s\textsuperscript{-1}, which is at the same order of magnitude as the collision rate and can lead to the stabilization of about half of the 1\text{I6} (P1) as CoTaC\textsubscript{2}N\textsubscript{2}CH\textsubscript{3}. This agrees well with the ratio of CoTaC\textsubscript{2}N\textsubscript{2}CH\textsubscript{3} to CoTaC\textsubscript{2}N\textsubscript{2}H\textsubscript{2}O in the reactivity experiment (Fig. 1).

After the formation of 1\text{I7}, the reaction proceeds with a H atom of the CH\textsubscript{3} group transfer to the Ta atom to form 1\text{I8}. The resultant CH\textsubscript{2} unit then makes a chemical bond with the Co atom, enabling the consecutive activation of the remaining two C-H bonds via the transfer of H atoms to Co (1\text{I9} \rightarrow 1\text{I10} \rightarrow 1\text{I11}). Along with two steps of structural rearrangements (1\text{I11} \rightarrow 1\text{I12} \rightarrow 1\text{I13}), two H atoms on Co make a H\textsubscript{2} unit to generate the lowest-lying isomer (1\text{I5}) of CoTaC\textsubscript{2}N\textsubscript{2}CH\textsubscript{2} concomitant with loss of H\textsubscript{2}. The RRKM-theory calculated rates of traversing 2TS6-2TS11 and H\textsubscript{2} desorption from 1\text{I3} are at least two orders of magnitude larger than the collision rate (Supplementary Table 3), indicating the impossible stabilization of intermediates 1\text{I7}-1\text{I13} and the facile formation of 1\text{I5}. The generation of P2 (1\text{I5} + H\textsubscript{2}) is highly exothermic (-2.71 eV), so the 1\text{I5} has enough internal energy to undergo further transformation to evaporate the second H\textsubscript{2} molecule and yield the lowest-lying isomer (1\text{I4}) of CoTaC\textsubscript{2}N\textsubscript{2}C (Fig. S8). The most favorable pathway to generate P3 (1\text{I4} + H\textsubscript{2}) from 1\text{I5} involves a Co–NH bond-forming process (1\text{I4} \rightarrow 1\text{I5}) and a Co–CN bond-breaking process (1\text{I5} \rightarrow 1\text{I6}), followed by the transfer of a H atom from N to Ta to generate 1\text{I7}, from which a H\textsubscript{2} molecule can be evaporated. The above high-level RCCSD(T) calculations indicate that the N–C\textsubscript{CH\textsubscript{4}} bond is formed in the dehydrogenation products CoTaC\textsubscript{2}N\textsubscript{2}H\textsubscript{2}O\textsubscript{2}. Note that it is very difficult to perform the PEIS characterization of CoTaC\textsubscript{2}N\textsubscript{2}H\textsubscript{2}O\textsubscript{2} with the current apparatus due to the very weak signals of these species and the mass overlap with other species such as CoTaC\textsubscript{2}H\textsubscript{4} and CoTaC\textsubscript{2}ON\textsubscript{2}\textsuperscript{−} (Fig. S9). Quantum chemistry calculations confirmed that the formation of N–C\textsubscript{CH\textsubscript{4}} bond is necessary for the experimentally observed reactions and the migration of CH\textsubscript{3} group from Ta to N\textsubscript{6} is the most favorable pathway.
Fig. 3 Potential energy profile for the reaction of CoTaC$_2$N$_2^-$ with CH$_4$. The structures are optimized at the DFT level. The zero-point vibration corrected energies in eV relative to the separated reactants are calculated at the RCCSD(T) level. The C atoms from CoTaC$_2$ and CH$_4$ are shown in different colours.

Fig. 4 Key events and mechanisms for the coupling reaction of N$_2$ with CH$_4$ mediated by CoTaC$_2^-$ cluster anions.

Discussion

As shown in Fig. 4, the coupling reaction of N$_2$ with CH$_4$ mediated by CoTaC$_2^-$ starts with cleavage of the Ni$_3$N bond by CoTaC$_2^-$ to generate CoTaC$_2$N$_2^-$ with a Ta$^{5+}$–N$_2^-$ LABP, followed by further activation of CH$_4$ by CoTaC$_2$N$_2^-$, in which the first C–H bond is cleaved via a Ta$^{5+}$–N$_2^-$ LABP mechanism and the N–C coupling is subsequently achieved via a CH$_3$ migration mechanism. The order to activate the two molecules is crucial to this coupling reaction, as reflected by the low reactivity of CoTaC$_2$ toward CH$_4$ to produce CoTaC$_2$H$_2^-$ (Fig. S11d and e, $k_1$ = 1.2 × 10$^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) and the theoretically predicted impossibility of functionalizing N$_2$ by CoTaC$_2$H$_2^-$ (Fig. S10c). Comparative studies on CoTaC$_2^-$/CH$_4$ and CoTaC$_2$N$_2^-$/CH$_4$ reaction couples indicate that the approach of CH$_4$ to CoTaC$_2^-$ encounters a positive energy barrier of 0.05 eV (Fig. S10a). Moreover, cleavage of H$_2$C–H bond by CoTaC$_2^-$ follows the oxidative addition mechanism, which is kinetically less favorable than the LABP mechanism in CoTaC$_2$N$_2^-$/CH$_4$ couple (Fig. S10b). Therefore, the design of first activating N$_2$ not only constrains a Ta$^{5+}$–N$_2^-$ LABP to facilitate the initial activation of CH$_4$, but also generates a sufficiently reactive N atom that can accept the migrating CH$_3$ group to form the N–C bond.

Natural charge analysis on the CoTaC$_2$N$_2^-$/CH$_4$ reaction system reveals that the two N atoms in CoTaC$_2$N$_2^-$ exhibit strong charge buffering ability throughout the activation of CH$_4$: they store a large number of negative charges ($\Delta Q = -0.47$ e) during the processes of H$_2$C–H cleavage (N$_2$–H formation) and N$_2$–H formation, while release all of the stored negative charges ($\Delta Q = 0.52$ e) during the activation of remaining three C–H bonds (Fig. S11). Such charge buffering behavior largely reduces the kinetic barriers of rate-limiting steps and thus drives the N–C bond formation. Noticeably, the N–C bond formation from N$_2$ outlined here differs fundamentally from that in previous gas-phase studies. Generally, the carbon ligands in transition metal carbide clusters, such as FeTaC$_2^-$, FeV$_2$C$_7^-$, V$_2$C$_7^-$, and Ta$_3$C$_4^-$, were employed to construct N–C$_{\text{clust}}$ bonds after the Ni$_3$N bond was completely cleaved by the metal center.22–25 This study provides a likely pathway for N–C bond formation from the product of N$_2$ cleavage through migrating a CH$_4$-derived CH$_3$ group to a N$_2$-derived N atom, which opens a new window for the reactions of N$_2$-derived metal nitrides.

Finally, we infer that the N$_2$-derived metal nitrides with a M–N$_2$ LABP might be promising species for further activating CH$_4$. As expected, the previously reported FeTaC$_2$N$_2^-$ with a similar Ta$^{5+}$–N$_2^-$ LABP (natural charge: 1.33 e$^-$/0.89 e) is demonstrated to react with CH$_4$ to produce FeTaC$_2$N$_2$CH$_4^+$ and FeTaC$_2$N$_2$CH$_2^-$ (ratio = 70:30) by using a newly-designed ship-lock-type reactor (Fig. S13). More interestingly, the reaction rate of FeTaC$_2$N$_2^-$/CH$_4$ couple ($k_2$ = 2.8 × 10$^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) is about four orders of magnitude smaller than that of CoTaC$_2$N$_2^-$/CH$_4$ couple, indicating large difference in the initial activation of CH$_4$ by the Ta$^{5+}$–N$_2^-$ LABP. A key difference between the two systems is that the degree of N$_2$ reduction by CoTaC$_2^-$ is properly reduced compared to FeTaC$_2^-$, as reflected by less negative charges on N atoms and smaller electron occupancy on N$_2$o orbitals in CoTaC$_2$N$_2^-$ than those in FeTaC$_2$N$_2^-$ (Fig. S14). This leads to a slightly weaker Ta–N$_2$ bond in CoTaC$_2$N$_2^-$ (WBI: 2.4) than that in FeTaC$_2$N$_2^-$ (WBI: 2.6), which has more possibility to buffer the charge variation during the initial H$_2$C–H cleavage process. This agrees with the fact that N$_2$-derived nitrides with strong M–N bonds are difficult to activate other molecules. Further research on the optimal design of highly reactive M$^{5+}$–N$_2^-$ LABP during the activation of N$_2$ to trigger efficient N–C coupling in the further activation of CH$_4$ is under progress.

Conclusions

A possible N–C bond formation from the mutual functionalization of N$_2$ and CH$_4$ mediated by heteronuclear metal cluster anions CoTaC$_2^-$ was found by using mass spectrometry, photoelectron spectroscopy and modelled reaction pathway. As verified by employing mass spectrometry, photoelectron imaging spectroscopy, and quantum chemistry calculations, the coupling reaction of N$_2$ with CH$_4$ starts with the dissociative adsorption of N$_2$ on CoTaC$_2^-$ to generate a Ta$^{5+}$–N$_2^-$ Lewis acid-base pair, which then triggers the H$_2$C–H cleavage (N$_2$–H formation) and N–C$_{\text{CH}_4}$ formation in the reaction of CoTaC$_2$N$_2^-$ with CH$_4$. Cleaving the Ni$_3$N bond to generate two N atoms with large charge buffering capacity underlies the ability of
CoTaC$_2$ to mediate the coupling of N$_2$ and CH$_4$. Based on this finding, a universal N$_2$ triggering strategy was proposed to couple inert N$_2$ and CH$_4$ molecules, which may inspire the rational design of catalysts to produce N-containing organic compounds.

Author Contributions

L.-H. M. and S.-G. H. conceived the ideas. L.-H. M. carried out the experiments and calculations and wrote the original manuscript. Y. L. and H. C. assisted with high-level quantum calculations. G.P. W. and H. C. assisted with experiments and calculations and wrote the original manuscript. Y. L., L.-H. M. and S.-G. H. conceived the ideas. L.-H. M. carried out the experiments and S.-G. H., Z.-Y. L. and H. C. supervised the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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