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## Mutual functionalization of dinitrogen and methane mediated by heteronuclear metal cluster anions $\text{CoTaC}_2^-$ †

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The direct coupling of dinitrogen ( $\text{N}_2$ ) and methane ( $\text{CH}_4$ ) 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  $\text{N}_2$  and  $\text{CH}_4$  mediated by heteronuclear metal cluster anions  $\text{CoTaC}_2^-$ , which starts with the dissociative adsorption of  $\text{N}_2$  on  $\text{CoTaC}_2^-$  to generate a  $\text{Ta}^{\delta+}-\text{N}_t^{\delta-}$  (terminal-nitrogen) Lewis acid–base pair (LABP), followed by the further activation of  $\text{CH}_4$  by  $\text{CoTaC}_2\text{N}_2^-$  to construct the N–C bond. The  $\text{N}\equiv\text{N}$  cleavage by  $\text{CoTaC}_2^-$  affording two N atoms with strong charge buffering ability plays a key part, which facilitates the  $\text{H}_3\text{C–H}$  cleavage *via* the LABP mechanism and the N–C formation *via* a  $\text{CH}_3$  migration mechanism. A novel  $\text{N}_t$  triggering strategy to couple  $\text{N}_2$  and  $\text{CH}_4$  molecules using 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  $\text{N}_2$  offers the potential to reduce the enormous fossil-fuel consumption for the current synthesis of N-containing organic compounds through  $\text{NH}_3$ , which is mainly produced *via* the energy-intensive Haber–Bosch process ( $\text{N}_2 + \text{H}_2 \rightarrow \text{NH}_3$ ).<sup>1</sup> Considerable research efforts have been devoted to this subject since the initial observation of N–C bond formation in the reaction of  $\text{N}_2$  complexes with organic halides.<sup>2</sup> A long-sought goal for this chemistry has been the direct coupling of  $\text{N}_2$  with abundant carbon-based molecules that are viable in industry. However, activation of these stable molecules remains a challenge, and only  $\text{CO}$ ,<sup>3–5</sup>  $\text{CO}_2$ ,<sup>6–8</sup> and unsaturated hydrocarbons<sup>9,10</sup> have been reported to form N–C bonds with  $\text{N}_2$  induced by appropriate reactive species.  $\text{CH}_4$ , the major component of widely available natural gas, is closely linked to industrial  $\text{NH}_3$  synthesis in

which  $\text{H}_2$  is produced through the energy-intensive  $\text{CH}_4$ -reforming process. Therefore, the direct coupling of  $\text{N}_2$  and  $\text{CH}_4$  is of great importance for economic and environmental reasons. However, the appropriate species that can mediate the coupling of inert  $\text{N}_2$  and  $\text{CH}_4$  molecules to form an 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.<sup>11</sup> The activation and individual functionalization of  $\text{N}_2$  or  $\text{CH}_4$ ,<sup>12–18</sup> and the formation of N–C bonds<sup>19–25</sup> are also extensively studied issues in the gas-phase field. Typical examples of N–C bond formation from  $\text{N}_2$  or  $\text{CH}_4$  in gas-phase studies can be classified as follows: (i) reactions of metal carbide clusters with  $\text{N}_2$ <sup>22–25</sup> or metal nitride clusters with  $\text{CH}_4$ ,<sup>26,27</sup> and (ii) coupling reactions of  $\text{CH}_4$  with  $\text{NH}_3$ <sup>28,29</sup> or  $\text{N}_2$  with  $\text{CO}_2$ .<sup>6</sup> In addition to reactions involving  $\text{N}_2$  or  $\text{CH}_4$ , the N–C bond formation was also observed in a few other reaction systems.<sup>30–32</sup> Compared with these N–C formation processes, the direct coupling of  $\text{N}_2$  and  $\text{CH}_4$  is rather challenging and of particular interest.

Herein, we report the first example of N–C bond formation from the mutual functionalization of  $\text{N}_2$  and  $\text{CH}_4$  mediated by heteronuclear metal cluster anions  $\text{CoTaC}_2^-$  under thermal collision conditions. A terminal-nitrogen ( $\text{N}_t$ ) triggering strategy for the coupling of  $\text{N}_2$  and  $\text{CH}_4$  was accordingly proposed (Scheme 1), which starts with the dissociative adsorption of  $\text{N}_2$  on metal-based substrates to generate a  $\text{M}^{\delta+}-\text{N}_t^{\delta-}$  Lewis acid–base pair (LABP), followed by the  $\text{H}_3\text{C–H}$  cleavage of  $\text{CH}_4$  *via* the LABP mechanism and the N–C formation *via* a  $\text{CH}_3$  migration mechanism. Considering that

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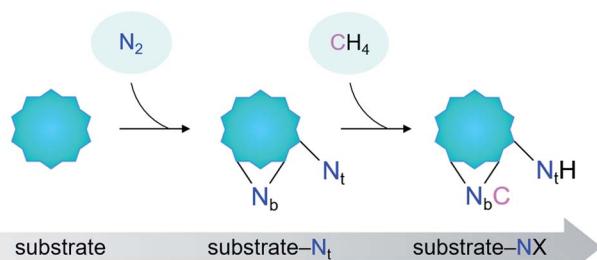
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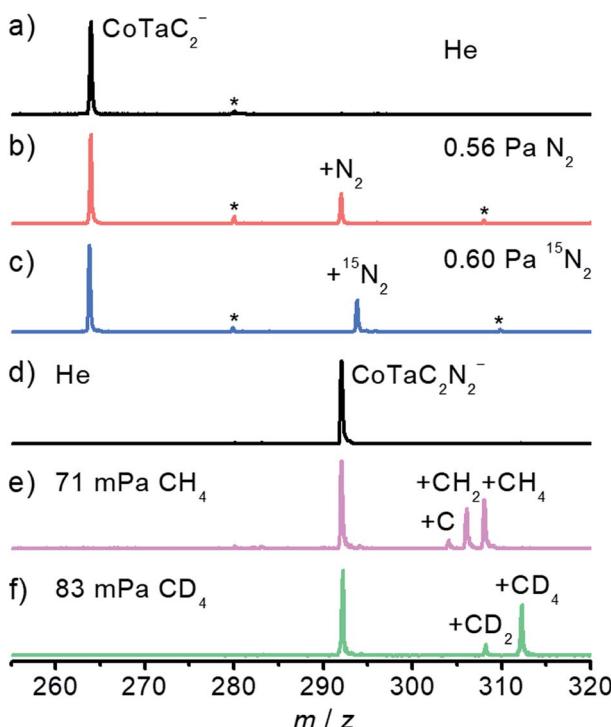
**Scheme 1** The proposed terminal-nitrogen ( $N_t$ ) triggering strategy for the coupling of  $N_2$  and  $CH_4$ . The key to this strategy is the predissociation of  $N_2$  on an appropriate substrate to generate a  $N_t$  and a bridging- $N$  ( $N_b$ ).

the activation of  $CH_4$  by some metal nitrides follows the LABP mechanism,<sup>26,27</sup> we infer that the proposed strategy can be quite general, which is confirmed by the study on the  $FeTaC_2^-/N_2/CH_4$  reaction system. The important roles of producing substrate- $N_t$  complexes in the coupling of  $N_2$  and  $CH_4$ , as well as the strength of M- $N_t$  bonds in the activity of the  $N_t$  complexes were discussed.

## 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



**Fig. 1** Time-of-flight mass spectra of the reactions of  $CoTaC_2^-$  with (a) He, (b)  $N_2$ , and (c)  $^{15}N_2$ , and  $CoTaC_2N_2^-$  with (d) He, (e)  $CH_4$ , and (f)  $CD_4$ . The reaction times are 4.8 ms for (b and 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.

the reactions of  $CoTaC_2^-$  ( $m/z = 264$ ) with  $N_2$  and  $CoTaC_2N_2^-$  ( $m/z = 292$ ) with  $CH_4$ . 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  $N_2$  in a linear ion trap (LIT) reactor. As shown in Fig. 1b, on pulsing 0.56 Pa  $N_2$  into the LIT reactor, a strong product peak assigned as  $CoTaC_2N_2^-$  appeared, suggesting the following reaction channel:



The isotopic labeling experiment using  $^{15}N_2$  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  $TaC_2N_2^-$  was also observed (Fig. S1a-c†). Based on a least-squares fitting procedure (Fig. S2a†), the rate constant  $k_1(CoTaC_2^-/N_2)$  of the pseudo first-order reaction between  $CoTaC_2^-$  and  $N_2$  was estimated to be  $(8.0 \pm 1.6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , corresponding to a reaction efficiency ( $\Phi = k_1/k_c$ ) of about 0.1% relative to the theoretical collision rate ( $k_c$ ).<sup>33</sup>

To study the reaction of the  $N_2$  association product  $CoTaC_2N_2^-$  with  $CH_4$ , a newly-developed double ion trap apparatus (Scheme S1 in the ESI†) was used to first generate the  $CoTaC_2N_2^-$  from the reaction of  $CoTaC_2^-$  with  $N_2$  in the first LIT reactor and then mass select  $CoTaC_2N_2^-$  to interact with  $CH_4$  in the second LIT reactor. Upon the interaction of  $CoTaC_2N_2^-$  with  $CH_4$  (Fig. 1e), three product peaks assigned as  $CoTaC_2N_2CH_4^-$  ( $m/z = 308$ ),  $CoTaC_2N_2CH_2^-$  ( $m/z = 306$ ), and  $CoTaC_2N_2C^-$  ( $m/z = 304$ ) were observed, suggesting the following reaction channels:



The rate constant  $k_1(CoTaC_2N_2^-/CH_4)$  for the reaction of  $CoTaC_2N_2^-$  with  $CH_4$  was estimated to be  $(1.4 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , corresponding to a  $\Phi$  of about 1.4%. Noticeably, the reaction channel of ejecting two  $D_2$  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 isotopic effect (KIE) calculated using  $k_1(CoTaC_2N_2^-/CH_4)/k_1(CoTaC_2N_2^-/CD_4)$  was estimated to be 1.3 (Fig. S2b and c†). The loss of  $H_2$  ( $D_2$ ) in the reaction of  $CoTaC_2N_2^-$  with  $CH_4$  ( $CD_4$ ) suggests that activation of C-H bonds must have occurred. To determine the mechanisms of  $CoTaC_2^- + N_2$  and  $CoTaC_2N_2^- + CH_4$  reactions, structural characterization of the reactant cluster ions should be performed.

## Structural characterization

Photoelectron imaging spectroscopy (PEIS)<sup>34</sup> combined with quantum chemistry calculations was employed to characterize the structures of  $\text{CoTaC}_2^-$  and  $\text{CoTaC}_2\text{N}_2^-$ . The structures were optimized at the density functional theory (DFT) level,<sup>35</sup> 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.<sup>36,37</sup>

The experimental spectrum of  $\text{CoTaC}_2^-$  recorded with 670 nm photons at 10 K reveals a sharp peak centered at 1.63 eV, followed by three discernible peaks with electron binding energies of 1.70, 1.73, and 1.76 eV (Fig. 2a, top). The calculated lowest-lying isomer (<sup>2</sup>IS1) of  $\text{CoTaC}_2^-$  features a Co-Ta double bond with a Wiberg bond index (WBI) of 2.04 and a  $\text{C}_2$  ligand. The presence of two d-d bonding orbitals between Co and Ta atoms provides further evidence for the Co-Ta double bond (Fig. S12†). The Franck–Condon (FC)-simulated spectrum of the <sup>2</sup>A → <sup>3</sup>A vibrational transition for <sup>2</sup>IS1 can reasonably reproduce the experimental spectrum from 1.70 to 1.76 eV (Fig. 2a, middle),<sup>38</sup> and the calculated adiabatic electron detachment energy (ADE) of <sup>2</sup>IS1 is close to the experimental value (1.83 eV

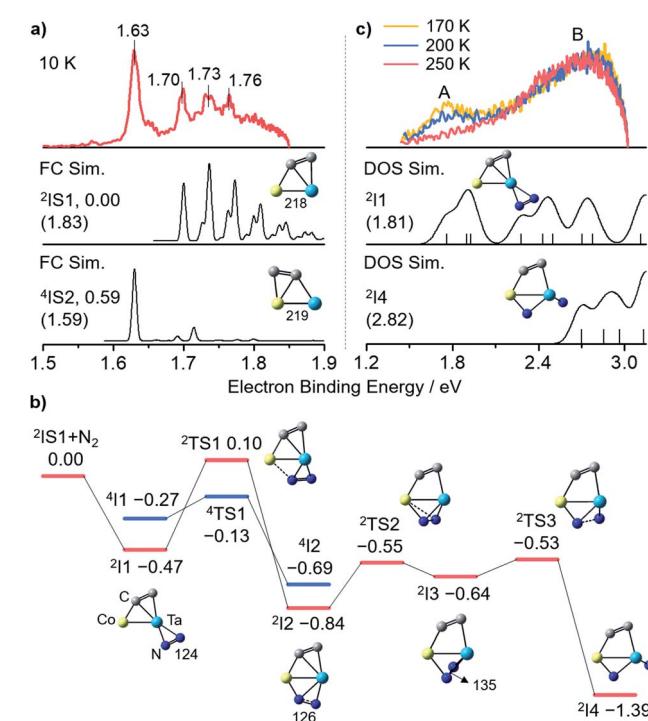


Fig. 2 (a) Experimental and Franck–Condon (FC)-simulated photoelectron spectra of  $\text{CoTaC}_2^-$ . (b) RCCSD(T)-calculated potential energy profile for the reaction of  $\text{CoTaC}_2^-$  (<sup>2</sup>IS1) with  $\text{N}_2$ . (c) Experimental and density of states (DOS)-simulated photoelectron spectra of  $\text{CoTaC}_2\text{N}_2^-$ . The 670 nm (1.85 eV) and 410 nm (3.02 eV) photons were used for  $\text{CoTaC}_2^-$  and  $\text{CoTaC}_2\text{N}_2^-$ , respectively. The relative energies, ADEs and VDEs (in brackets) are given in eV. The bond lengths are in pm. The superscripts indicate spin multiplicities. The simulated spectra of <sup>2</sup>IS1, <sup>2</sup>I1, <sup>2</sup>I4 and <sup>4</sup>IS2 are red shifted by 0.13, 0.05, 0.12 eV and blue shifted by 0.04 eV, respectively.

vs. 1.70 eV), suggesting that <sup>2</sup>IS1 is the most probable species of  $\text{CoTaC}_2^-$  generated in the experiment. The first spectral peak centered at 1.63 eV might come from the minor population of the isomer <sup>4</sup>IS2 with a relative energy of 0.59 eV higher than <sup>2</sup>IS1, considering that its calculated ADE (1.59 eV) and simulated profile of the <sup>4</sup>A → <sup>3</sup>A transition match well with the first spectral peak (Fig. 2a, bottom). A more detailed discussion of the structural assignment of  $\text{CoTaC}_2^-$  is provided in the ESI (Fig. S3†).

Reaction mechanism for the  $\text{CoTaC}_2^-/\text{N}_2$  couple

The reaction pathway of  $\text{CoTaC}_2^-$  (<sup>2</sup>IS1) with  $\text{N}_2$  calculated at the RCCSD(T) level is shown in Fig. 2b. The  $\text{N}_2$  molecule first approaches the Ta atom through a side-on ( $\eta^2$ ) mode to form the encounter complex <sup>2</sup>I1 (−0.47 eV). Further binding of  $\text{N}_2$  to Co is impeded by a high energy barrier with the doublet spin state (<sup>2</sup>TS1/0.10 eV); however, this process can be accomplished through transiting to the quartet spin state (<sup>4</sup>TS1/−0.13 eV) and then a more stable intermediate <sup>2</sup>I2 (−0.84 eV) with a side-on-end-on ( $\eta^2:\eta^1$ ) bounded  $\text{N}_2$  unit is formed. By surmounting <sup>2</sup>TS2,  $\text{N}_2$  is coordinated to the Co-Ta center in a distorted- $\eta^2:\eta^1$  mode (<sup>2</sup>I3/−0.64 eV) with an N–N bond length of 135 pm. The N–N bond is disrupted entirely after overcoming a slight energy barrier of 0.11 eV (<sup>2</sup>TS3/−0.53 eV), yielding one terminal-N ( $\text{N}_t$ ) and one bridging-N ( $\text{N}_b$ ) in <sup>2</sup>I4 (−1.39 eV). The subsequent N–C<sub>cluster</sub> coupling would encounter a highly positive energy barrier (<sup>2</sup>TS17/0.10 eV, Fig. S4†) that has little chance of being surmounted under thermal collision conditions, and thus the <sup>2</sup>I4 would be stabilized as the adsorption product  $\text{CoTaC}_2\text{N}_2^-$  through collisions with bath gas He. Note that the very minor reaction channel of generating  $\text{TaC}_2\text{N}_2^-$  in the reactivity experiment might come from the reaction of the high-lying isomer <sup>4</sup>IS2 with  $\text{N}_2$ , in which two steps of N–C<sub>cluster</sub> coupling take place before ejecting a neutral Co atom (Fig. S5†).

The PEIS characterization of  $\text{CoTaC}_2\text{N}_2^-$  at different reaction temperatures and photon energies supported the assignment of <sup>2</sup>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  $\text{CoTaC}_2^-$  signal under the condition of a long trapping time of 80 ms, so the 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  $\text{CoTaC}_2\text{N}_2^-$  at lower temperatures and accounted for the appearance of peak A. Considering that the process of <sup>2</sup>I1 → <sup>4</sup>TS1 → <sup>2</sup>I2 with the highest energy barrier and a spin crossing<sup>39</sup> is the rate-limiting step (Fig. 2b), <sup>2</sup>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 into I4. However, this situation is not the focus of this work because we aim to study the reactions of  $\text{CoTaC}_2^-/\text{N}_2$  and  $\text{CoTaC}_2\text{N}_2^-/\text{CH}_4$  couples at room temperature.



The simulated spectra of  $\text{CoTaC}_2\text{N}_2^-$  isomers based on density of states (DOS) simulations<sup>40</sup> confirmed the contribution of  $^2\text{I}1$  to peak A and indicated that peak B in the 250 K spectrum was contributed by  $^2\text{I}4$  (Fig. 2c). Moreover, the employment of 365 nm photons for the PEIS characterization of  $\text{CoTaC}_2\text{N}_2^-$  provides further evidence for the agreement of the DOS-simulated spectrum of  $^2\text{I}4$  with the experimental one (Fig. S6b and d†). Other  $\text{CoTaC}_2\text{N}_2^-$  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  $\text{CH}_4$  (Fig. S7†). Therefore, a  $\text{N}_t$ -containing complex was successfully prepared through the dissociative adsorption of  $\text{N}_2$  on  $\text{CoTaC}_2^-$  at room temperature.

### Reaction mechanism for the $\text{CoTaC}_2\text{N}_2^-/\text{CH}_4$ couple

As shown in Fig. 3, the  $\text{CoTaC}_2\text{N}_2^-$  ( $^2\text{I}4$ ) interacts with  $\text{CH}_4$  by first anchoring it on the Ta atom to form  $^2\text{I}5$  with a binding energy of 0.44 eV. The first  $\text{H}_3\text{C–H}$  bond cleavage preferably proceeds *via* the cooperative mechanism of a LABP composed of Ta (natural charge: 1.31e) and  $\text{N}_t$  (natural charge: −0.79e) atoms, generating a  $\text{N}_t\text{–H}$  bond and a  $\text{Ta–CH}_3$  moiety in  $^2\text{I}6$  (−2.52 eV). After that, the  $\text{CH}_3$  group tends to migrate from Ta to  $\text{N}_b$  to liberate the Ta site ( $^2\text{I}6 \rightarrow ^2\text{TS}5 \rightarrow ^2\text{I}7$ ). On the basis of Rice–Ramsperger–Kassel–Marcus (RRKM) theory,<sup>41</sup> the conversion rate of  $^2\text{I}6 \rightarrow ^2\text{TS}5$  is estimated to be  $6.9 \times 10^4 \text{ s}^{-1}$ , which is

one order of magnitude smaller than the collision rate ( $6.7 \times 10^5 \text{ s}^{-1}$ ) that a cluster experiences with the bath gas He in the LIT reactor. This suggests that only a small part of  $^2\text{I}6$  could overcome  $^2\text{TS}5$  to form  $^2\text{I}7$ , while most of the  $^2\text{I}6$  would be stabilized as the adsorption product  $\text{CoTaC}_2\text{N}_2\text{CH}_4^-$  through collisions with bath gas. If the barrier height of  $^2\text{TS}5$  is decreased by 0.1 eV, which could be the uncertainty of RCCSD(T) calculations,<sup>42</sup> the rate of  $^2\text{I}6 \rightarrow ^2\text{TS}5$  is increased to  $3.3 \times 10^5 \text{ s}^{-1}$ , which is of the same order of magnitude as the collision rate and can lead to the stabilization of about half of the  $^2\text{I}6$  (P1) as  $\text{CoTaC}_2\text{N}_2\text{CH}_4^-$ . This agrees well with the ratio of  $\text{CoTaC}_2\text{N}_2\text{CH}_4^-$  to  $\text{CoTaC}_2\text{N}_2\text{CH}_{2,0}^-$  (49 : 51) in the reactivity experiment (Fig. 1).

After the formation of  $^2\text{I}7$ , the reaction proceeds with a H atom of the  $\text{CH}_3$  group transferred to the Ta atom to form  $^2\text{I}8$ . The resultant  $\text{CH}_2$  unit then forms 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 ( $^2\text{I}9 \rightarrow ^2\text{I}10 \rightarrow ^2\text{I}11$ ). Along with two steps of structural rearrangements ( $^2\text{I}11 \rightarrow ^2\text{I}12 \rightarrow ^2\text{I}13$ ), two H atoms on Co make a  $\text{H}_2$  unit to generate the lowest-lying isomer ( $^2\text{IS}3$ ) of  $\text{CoTaC}_2\text{N}_2\text{CH}_2^-$  concomitant with loss of  $\text{H}_2$ . The RRKM-theory calculated rates of traversing  $^2\text{TS}6$ – $^2\text{TS}11$  and  $\text{H}_2$  desorption from  $^2\text{I}13$  are at least two orders of magnitude larger than the collision rate (ESI Table 3†), indicating the impossible stabilization of intermediates  $^2\text{I}7$ – $^2\text{I}13$  and the facile formation of  $^2\text{IS}3$ . The generation of P2

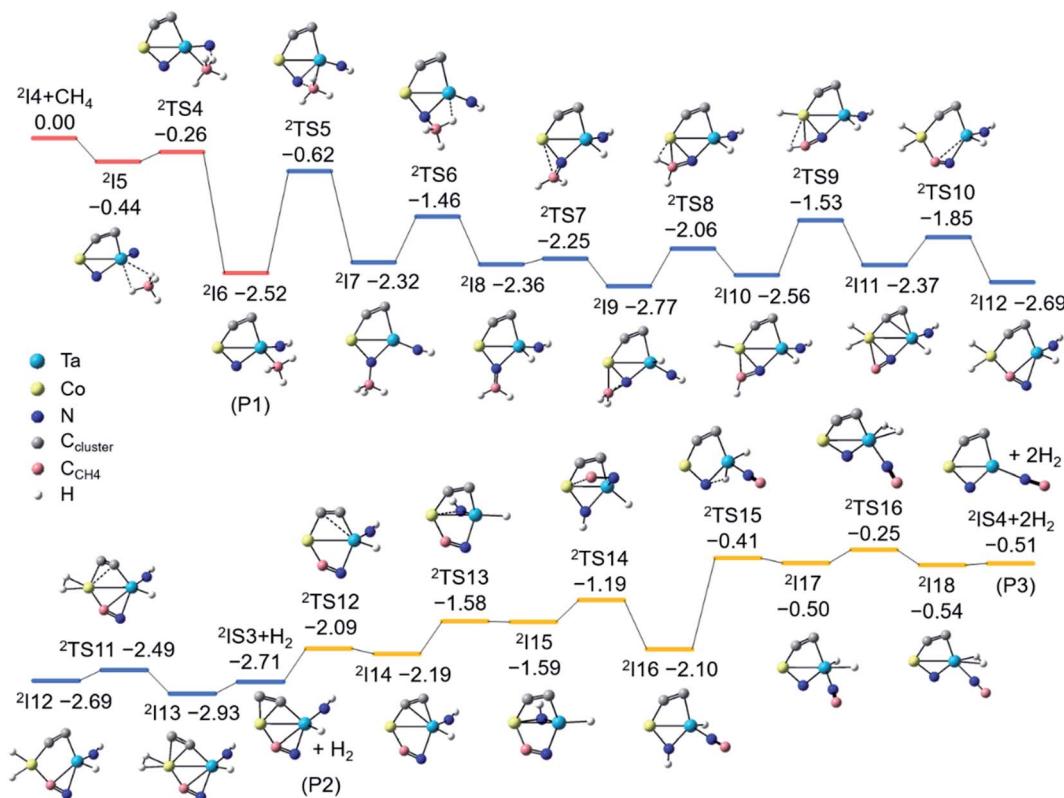


Fig. 3 Potential energy profile for the reaction of  $\text{CoTaC}_2\text{N}_2^-$  ( $^2\text{I}4$ ) with  $\text{CH}_4$ . The structures are optimized at the DFT level. The zero-point vibration corrected energies in eV relative to the separated reactants are calculated at the RCCSD(T) level. The C atoms from  $\text{CoTaC}_2^-$  and  $\text{CH}_4$  are shown in different colours.



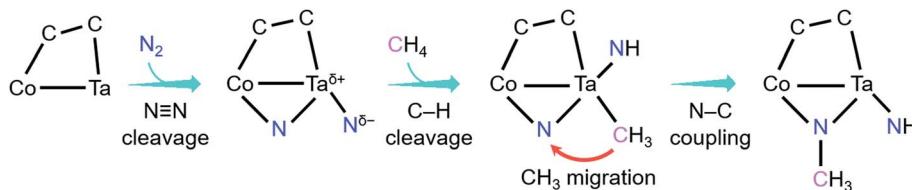


Fig. 4 Key events and mechanisms for the coupling reaction of  $\text{N}_2$  with  $\text{CH}_4$  mediated by  $\text{CoTaC}_2^-$  cluster anions.

$(^2\text{IS}3 + \text{H}_2)$  is highly exothermic ( $-2.71$  eV), so  $^2\text{IS}3$  has enough internal energy to undergo further transformation to evaporate the second  $\text{H}_2$  molecule and yield the lowest-lying isomer ( $^2\text{IS}4$ ) of  $\text{CoTaC}_2\text{N}_2\text{C}^-$  (Fig. S8†). The most favorable pathway to generate P3 ( $^2\text{IS}4 + \text{H}_2$ ) from  $^2\text{IS}3$  involves a Co–NH bond-forming process ( $^2\text{I}14 \rightarrow ^2\text{I}15$ ) and a Co–CN bond-breaking process ( $^2\text{I}15 \rightarrow ^2\text{I}16$ ), followed by the transfer of a H atom from N to Ta to generate  $^2\text{I}17$ , from which a  $\text{H}_2$  molecule can be evaporated. The above high-level RCCSD(T) calculations indicate that the  $\text{N–C}_{\text{CH}_4}$  bond is formed in the dehydrogenation product  $\text{CoTaC}_2\text{N}_2\text{CH}_{4,2,0}^-$ . Note that it is very difficult to perform the PEIS characterization of  $\text{CoTaC}_2\text{N}_2\text{CH}_{4,2,0}^-$  with the current apparatus due to the very weak signals of these species and the mass overlap with other species such as  $\text{CoTaC}_4\text{H}_2\text{O}^-$  and  $\text{CoTaC}_2\text{ON}_2^-$  (Fig. S9†). Quantum chemistry calculations confirmed that the formation of the  $\text{N–C}_{\text{CH}_4}$  bond is necessary for the experimentally observed reactions and the migration of the  $\text{CH}_3$  group from Ta to  $\text{N}_b$  is the most favorable pathway.

## Discussion

As shown in Fig. 4, the coupling reaction of  $\text{N}_2$  with  $\text{CH}_4$  mediated by  $\text{CoTaC}_2^-$  starts with cleavage of the  $\text{N}\equiv\text{N}$  bond by  $\text{CoTaC}_2^-$  to generate  $\text{CoTaC}_2\text{N}_2^-$  with a  $\text{Ta}^{\delta+}\text{–N}_t^{\delta-}$  LABP, followed by further activation of  $\text{CH}_4$  by  $\text{CoTaC}_2\text{N}_2^-$ , in which the first C–H bond is cleaved *via* a  $\text{Ta}^{\delta+}\text{–N}_t^{\delta-}$  LABP mechanism and the N–C coupling is subsequently achieved *via* a  $\text{CH}_3$  migration mechanism. The order of activation of the two molecules is crucial to this coupling reaction, as reflected by the low reactivity of  $\text{CoTaC}_2^-$  toward  $\text{CH}_4$  to produce  $\text{CoTaC}_3\text{H}_2^-$  (Fig. S1d and e,†  $k_1 = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and the theoretically predicted impossibility of functionalizing  $\text{N}_2$  by  $\text{CoTaC}_3\text{H}_2^-$  (Fig. S10c†). Comparative studies on  $\text{CoTaC}_2^-/\text{CH}_4$  and  $\text{CoTaC}_2\text{N}_2^-/\text{CH}_4$  reaction couples indicate that the approach of  $\text{CH}_4$  to  $\text{CoTaC}_2\text{N}_2^-$  is overall barrierless, while the approach of  $\text{CH}_4$  to  $\text{CoTaC}_2^-$  encounters a positive energy barrier of  $0.05$  eV (Fig. S10a†). Moreover, cleavage of the  $\text{H}_3\text{C–H}$  bond by  $\text{CoTaC}_2^-$  follows the oxidative addition mechanism, which is kinetically less favorable than the LABP mechanism in the  $\text{CoTaC}_2\text{N}_2^-/\text{CH}_4$  couple (Fig. S10b†). Therefore, the design of first activating  $\text{N}_2$  not only constructs a  $\text{Ta}^{\delta+}\text{–N}_t^{\delta-}$  LABP to facilitate the initial activation of  $\text{CH}_4$ , but also generates a sufficiently reactive  $\text{N}_b$  atom that can accept the migrating  $\text{CH}_3$  group to form the N–C bond.

Natural charge analysis of the  $\text{CoTaC}_2\text{N}_2^-/\text{CH}_4$  reaction system reveals that the two N atoms in  $\text{CoTaC}_2\text{N}_2^-$  exhibit

strong charge buffering ability throughout the activation of  $\text{CH}_4$ : they store a large number of negative charges ( $\Delta Q = -0.47e$ ) during the processes of  $\text{H}_3\text{C–H}$  cleavage ( $\text{N}_t\text{–H}$  formation) and  $\text{N}_b\text{–C}$  formation, while releasing all of the stored negative charges ( $\Delta Q = 0.52e$ ) during the activation of the 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  $\text{N}_2$  outlined here differs fundamentally from that in previous gas-phase studies. Generally, the carbon ligands in transition metal carbide clusters, such as  $\text{FeTaC}_2^-$ ,  $\text{FeV}_2\text{C}_2^-$ ,  $\text{V}_3\text{C}_4^-$ , and  $\text{Ta}_2\text{C}_4^-$ , were employed to construct  $\text{N–C}_{\text{cluster}}$  bonds after the  $\text{N}\equiv\text{N}$  bond was completely cleaved by the metal center.<sup>22–25</sup> This study provides a likely pathway for N–C bond formation from the product of  $\text{N}_2$  cleavage through migrating a  $\text{CH}_3$  group to a  $\text{N}_2$ -derived N atom, which opens a new window for the reactions of  $\text{N}_2$ -derived metal nitrides.

Finally, we infer that  $\text{N}_2$ -derived metal nitrides with a  $\text{M–N}_t$  LABP might be promising species for further activation of  $\text{CH}_4$ . As expected, the previously reported  $\text{FeTaC}_2\text{N}_2^-$  with a similar  $\text{Ta}^{\delta+}\text{–N}_t^{\delta-}$  LABP (natural charge:  $1.33e/-0.89e$ ) is demonstrated to react with  $\text{CH}_4$  to produce  $\text{FeTaC}_2\text{N}_2\text{CH}_4^-$  and  $\text{FeTaC}_2\text{N}_2\text{CH}_2^-$  (ratio = 70 : 30) by using a newly-designed ship-lock-type reactor (Fig. S13†).<sup>43</sup> More interestingly, the reaction rate of the  $\text{FeTaC}_2\text{N}_2^-/\text{CH}_4$  couple ( $k_1 = 2.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is about four orders of magnitude smaller than that of  $\text{CoTaC}_2\text{N}_2^-/\text{CH}_4$  couple, indicating a large difference in the initial activation of  $\text{CH}_4$  by the  $\text{Ta}^{\delta+}\text{–N}_t^{\delta-}$  LABP. A key difference between the two systems is that the degree of  $\text{N}_2$  reduction by  $\text{CoTaC}_2^-$  is properly reduced compared to  $\text{FeTaC}_2^-$ , as reflected by fewer negative charges on N atoms and smaller electron occupancy on  $\text{N}_{2p}$  orbitals in  $\text{CoTaC}_2\text{N}_2^-$  than those in  $\text{FeTaC}_2\text{N}_2^-$  (Fig. S14†). This leads to a slightly weaker  $\text{Ta–N}_t$  bond in  $\text{CoTaC}_2\text{N}_2^-$  (WBI: 2.4) than that in  $\text{FeTaC}_2\text{N}_2^-$  (WBI: 2.6), which has more possibility to buffer the charge variation during the initial  $\text{H}_3\text{C–H}$  cleavage process. This agrees with the fact that it is difficult for  $\text{N}_2$ -derived nitrides with strong M–N bonds to activate other molecules. Further research on the optimal design of highly reactive  $\text{M}^{\delta+}\text{–N}_t^{\delta-}$  LABP during the activation of  $\text{N}_2$  to trigger efficient N–C coupling in the further activation of  $\text{CH}_4$  is in progress.

## Conclusions

A possible N–C bond formation from the mutual functionalization of  $\text{N}_2$  and  $\text{CH}_4$  mediated by heteronuclear metal cluster



anions  $\text{CoTaC}_2^-$  was studied by using mass spectrometry, photoelectron spectroscopy and a modelled reaction pathway. As verified by employing mass spectrometry, photoelectron imaging spectroscopy, and quantum chemistry calculations, the coupling reaction of  $\text{N}_2$  with  $\text{CH}_4$  starts with the dissociative adsorption of  $\text{N}_2$  on  $\text{CoTaC}_2^-$  to generate a  $\text{Ta}^{\delta+}-\text{N}_t^{\delta-}$  Lewis acid-base pair, which then triggers the  $\text{H}_3\text{C}-\text{H}$  cleavage ( $\text{N}_t-\text{H}$  formation) and  $\text{N}-\text{C}_{\text{CH}_4}$  formation in the reaction of  $\text{CoTaC}_2\text{N}_2^-$  with  $\text{CH}_4$ . Cleaving the  $\text{N}\equiv\text{N}$  bond to generate two  $\text{N}$  atoms with large charge buffer capacity underlies the ability of  $\text{CoTaC}_2^-$  to mediate the coupling of  $\text{N}_2$  and  $\text{CH}_4$ . Based on this finding, a universal  $\text{N}_t$  triggering strategy was proposed to couple inert  $\text{N}_2$  and  $\text{CH}_4$  molecules, which may inspire the rational design of catalysts to produce  $\text{N}$ -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 Q.-Y. L. assisted with the experiments. 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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