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Main-group compounds selectively activate natural gas alkanes under room temperature and atmospheric pressure

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Most C–H bond activations of natural gas alkanes rely on transition metal complexes. Activations by using main-group systems have been reported but required heating or photo-irradiation under high atmospheric pressure with rather low regioselectivity. Here we report that Lewis acid-carbene adducts facilely undergo oxidative additions to C–H bonds of ethane, propane and *n*-butane with high selectivity under room temperature and atmospheric pressure. The Lewis acids can be moved by the addition of a base and the carbene-derived products can be easily converted into aldehydes. This work offers a route for main-group element compounds to selectively functionalise C–H bonds of natural gas alkanes and other small molecules.

Natural gas, particularly from shale, has substantial amounts of ethane, propane and *n*-butane, though it is primarily methane. These natural gas alkanes have been serving as low-cost hydrocarbon feedstocks. The efficient and selective activation of their C–H bonds can directly convert them into value-added chemicals and fuels for the needs of the industry[1–4]. Most of the C–H bond activations of natural gas alkanes rely on transition metal complexes (Fig. 1a)[5–9]. Alternative activations by main-group materials have been reported, such as superacids, main-group metal complexes, hexagonal boron nitrides, and frustrated radical pairs, etc. (Fig. 1b)[10–13], but require high pressure upon heating or photo-irradiation. Moreover, the activation regioselectivity in many main-group cases is rather low, with little discrimination of primary and secondary C–H bonds of these light alkanes[14–17]. Notably, main-group compounds with unique structural and bonding behaviours have attracted extensive interest as potential alternatives to transition metals in recent years[18–22]. While activation of small molecules such as H_2, N_2, NH_3, CO, C_2H_4, and P_4 has emerged by main-group systems under mild conditions (Fig. 1c)[23–31], natural gas alkanes are absent in the list for their strong undirected $C(sp^3)$–H bonds and poor solubility in many solvents.

Carbenes are species featuring a divalent carbon centre with a six-electron valence shell and normally considered reaction intermediates[32–34]. Since Bertrand et al. successfully synthesised stable carbenes and Arduengo et al. obtained isolable N-heterocyclic carbene (NHC)[35,36], stable carbenes have attracted extensive attention in the fields of organic synthesis, organometallic chemistry, materials science and main-group chemistry[37–39]. Stable carbenes with strong electrophilicity such as cyclic (alkyl) (amino) carbenes (cAACs)[40–42] and *N*, *N*′-diamidocarbenes (DACs)[43–45], are capable of activating small molecules under mild conditions. Stable carbenes were also reported to insert into inert C–F, B–H, N–H bonds and C–H bonds in some acidic substrates, including PhC≡CH, C_6F_5H and Cl_3CH at room temperature[46]. They may even cleave the $C(sp^3)$–H bonds of much less acidic toluene[47] ($pK_a = 41.2$ in cyclohexylamine) upon heating up to 80–100 °C and liquid alkanes such as cyclohexane upon photo-irradiation[48].

Recently we found that the electrophilicity of a *N,N*′-diamidocarbene (DAC_1)[47] could be considerably strengthened by the coordination with Lewis acid $B(C_6F_5)_3$ (BCF)[49]. The BCF–DAC_1 adduct has a significantly lower LUMO energy level compared to DAC_1, accelerating its activation towards small molecules and inert bonds[49]. The work demonstrated the feasibility of regulating electron properties of stable carbenes with strong Lewis acids instead of designing a new carbene structure. Here we report that the BCF–DAC_1 adduct facilely

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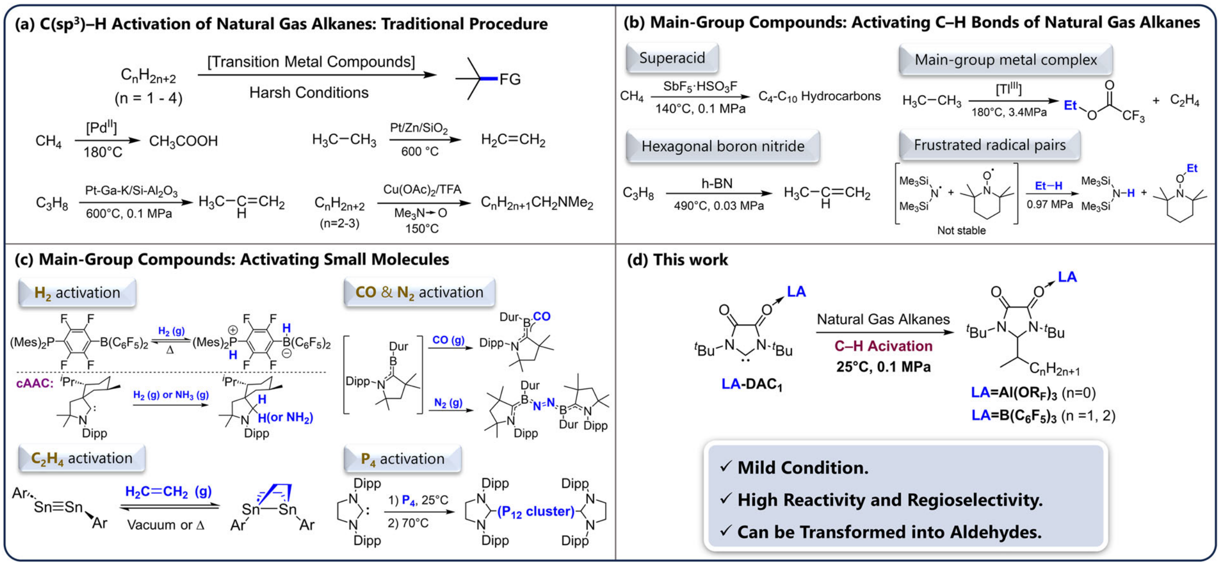


Fig. 1 | Activation strategies of natural gas C(sp^3)–H bonds and small molecules by transition metal or main-group compounds. a Transition metal complexes activating C(sp^3)–H bonds of natural gas alkanes. **b** Representative examples of activating C–H bonds of natural gas alkanes by main-group compounds. **c** Representative examples of small molecular activation by main-group compounds. **d** Reactions of Lewis acid-carbene adducts with C–H bonds of natural gas alkanes. Mes = mesityl; Dipp = 2, 6-diisopropylphenyl; Dur = 2, 3, 5, 6-tetramethylphenyl; OR$_F$ = OC(CF$_3$)$_3$.

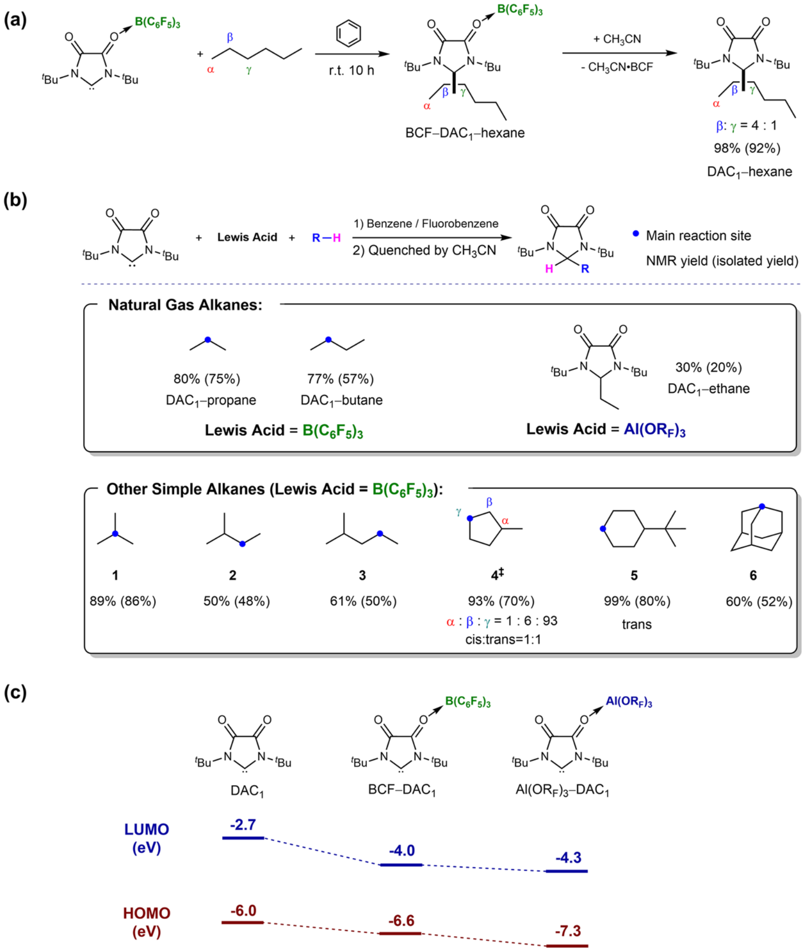


Fig. 2 | Reactions of Lewis acid-DAC$_1$ adducts with alkanes. a Reaction of BCF–DAC$_1$ and hexane in benzene. **b** Reaction of Lewis acid-DAC$_1$ adducts with natural gas alkanes and selected alkane substrates. **c** The HOMO and LUMO energy of DAC$_1$, BCF–DAC$_1$ and Al(OR$_F$)$_3$–DAC$_1$, computed with B3LYP/6-31 G(d). The yield was determined from crude ^{1}H-NMR spectra and isolated yield in the parenthesis. The structures were all confirmed by single-crystal XRD. ^{‡1}H NMR yield (see Supplementary Fig. 48). OR$_F$ = OC(CF$_3$)$_3$.

undergoes oxidative addition to C–H bonds of natural gas alkanes (ethane, propane and *n*-butane) under atmospheric pressure and at room temperature with high regioselectivity. The BCF–DAC$_1$ adduct only inserts in secondary C–H bonds of propane and *n*-butane. Primary C–H bonds of ethane could be activated by DAC$_1$ with more powerful Lewis acid Al(OR$_F$)$_3$ (OR$_F$ = OC(CF$_3$)$_3$) (Fig. 1d)[50].

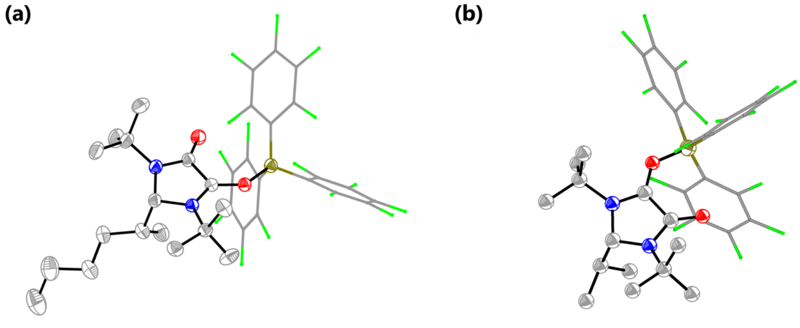
Results

DAC$_1$ is stable in *n*-hexane. As a matter of fact, many reactions of DAC$_1$ were performed in *n*-hexane. To our surprise, the red colour of the solution of the BCF–DAC$_1$ adduct in *n*-hexane immediately faded at room temperature, affording a large amount of light-yellow precipitate. Recrystallisation of the precipitate in toluene and *n*-pentane led to a BCF–DAC$_1$-derived product as a racemate with the carbon centre of the carbene inserted into the secondary C–H bond of *n*-hexane, identified by single-crystal X-ray diffraction (Fig. 2a and Fig. 3a). This reaction could also be carried out in benzene with 2.5 equivalent of *n*-hexane, indicating this reaction does not require excess amount of alkane as feedstock. One-pot reaction of BCF–DAC$_1$ with *n*-hexane directly followed by the addition of CH$_3$CN gave DAC$_1$-derived alkanes in 98% yield with a 4:1 ratio of β to γ site, tracked by ^{1}H-NMR analysis and GC-MS (Fig. 2a, Supplementary Fig. 34 and Supplementary Fig. 64). The terminal sites have C–H bonds with smallest steric hindrance, but those primary C–H bonds activated product was not observed.

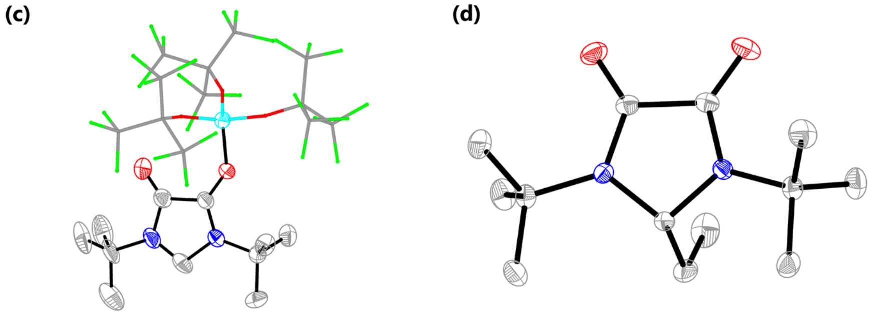
Encouraged by this initial finding, we systematically investigated reactions of the BCF–DAC$_1$ adduct with natural gas alkanes (C$_n$H$_{2n+2}$, $n = 1$–4). These gaseous alkanes (0.1 MPa) were introduced into the benzene solution of the BCF–DAC$_1$ adduct upon drying through a dehydration column filled with colour-changing silica gel and P$_2$O$_5$. The red reaction solution of BCF–DAC$_1$ with propane gradually became pale yellow after 10 h. Crystallisation led to a DAC$_1$-derived product with BCF, showing secondary C–H insertion (Fig. 2b and Fig. 3b). BCF can be removed by adding CH$_3$CN, affording a DAC$_1$–derived propane. One-pot reaction of BCF–DAC$_1$ with propane directly followed by quenching with CH$_3$CN gave same product in a ^{1}H-NMR yield of 80%, and could be purified by column chromatography on silica gel using acetone/petroleum as eluent. A similar insertion occurred in the reaction of BCF-DAC$_1$ with *n*-butane (Fig. 2b).

Resembling *n*-hexane, the C–H bond insertion at terminal position of propane and butane was not observed for higher energy barrier of primary C–H bonds compared with secondary C–H bonds[51]. For the same reason, the BCF–DAC$_1$ adduct failed to react with methane and ethane. The design of a new adduct with a stronger Lewis acid is desired. Our calculation shows that DAC$_1$ coupled with Al(OR$_F$)$_3$[50] possesses lower LUMO energy than that with BCF (Fig. 2c). Consequently, a colour change from red to purple was observed upon the addition of one equivalent of Al(OR$_F$)$_3$ into the fluorobenzene solution of DAC$_1$. Adduct Al(OR$_F$)$_3$–DAC$_1$ was isolated as dark purple crystals in a separation yield of 67% upon concentration and crystallisation at −20 °C in 1, 2-dichlorobenzene (Fig. 3c). Only one Al(OR$_F$)$_3$ is coordinated to one oxygen atom of DAC$_1$ due to steric crowding. The reaction of the Al(OR$_F$)$_3$–DAC$_1$ adduct with ethane was treated by a similar manner to the above. The C–H bond of ethane was activated within 6 h, affording DAC$_1$–derived ethane in a yield of 30% (based on ^{1}H-NMR spectroscopy) upon the addition of CH$_3$CN (Fig. 2b), which is identified by single crystal X-ray diffraction (Fig. 2b and Fig. 3d). Additionally, many other alkanes with multiple reacting sites are also compatible in our method, giving the desired products with excellent regioselectivity (Fig. 2b). It demonstrates that the secondary C–H bond in alkane was privileged in our conditions (**2**–**5**), while the tertiary C–H bond was activated in the absence of secondary C–H bond (**1**) or it has larger steric hindrance (**6**).

To better understand the mechanism of this C–H activation, we performed DFT calculations on the reaction using propane and DAC$_1$ in the presence or absence of BCF (Fig. 4a). The calculations indicate that the activation barriers for concerted carbene insertion into the internal and terminal C–H bonds of propane by DAC$_1$ were prohibitively high at



BCF–DAC$_1$–hexane BCF–DAC$_1$–propane



Al(OR$_F$)$_3$–DAC$_1$ DAC$_1$–ethane

Fig. 3 | Crystal structures. a The main product from the reaction of BCF-DAC$_1$ with *n*-hexane; **b** The product from the reaction of BCF–DAC$_1$ with propane; **c** Al(OR$_F$)$_3$–DAC$_1$; **d** The product from the reaction of Al(OR$_F$)$_3$–DAC$_1$ with ethane followed by quenching by addition of CH$_3$CN. OR$_F$ = OC(CF$_3$)$_3$. Thermal ellipsoid and stick drawings are set at 30% probability and hydrogen atoms are omitted for clarity. Colour codes: carbon (grey); boron (brown); nitrogen (navy blue); oxygen (red); aluminium (light blue); fluorine (green sticks).

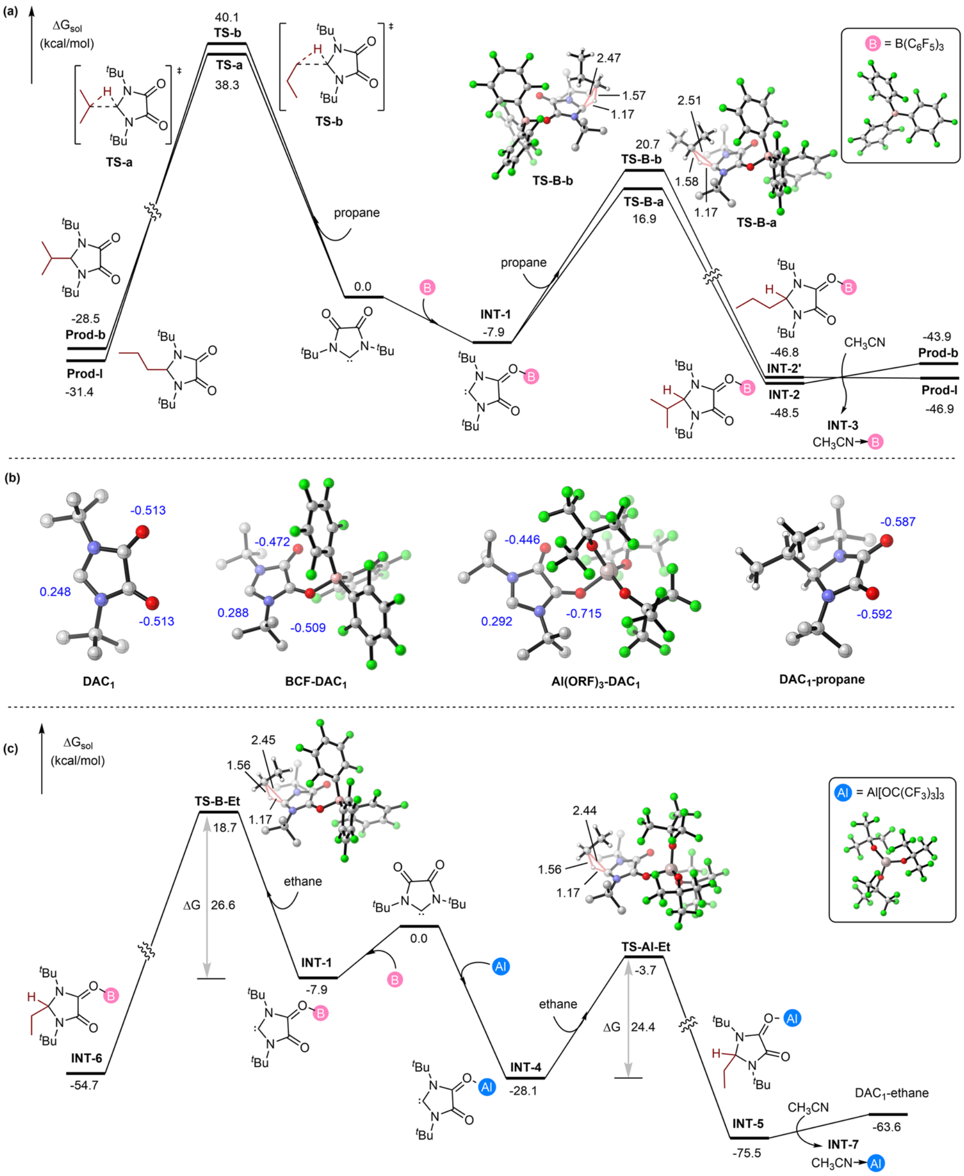


Fig. 4 | DFT-Computed free energies for C−H functionalization of gaseous alkanes with Lewis acid-carbene adducts. a Reaction of BCF−DAC$_1$ and propane. **b** The NPA charge of carbon and oxygen atoms in free carbene, adducts and products. **c** Reaction of Al(OR$_F$)$_3$−DAC$_1$ and ethane. All calculations were carried out at SMD(benzene)-M06-2X/6-311 + G(d,p)//B3LYP-D3/6-31 G(d) level of theory. Most hydrogen atoms are omitted for clarity. All distances are in Å. Colour codes: hydrogen (white); boron (pink); carbon (grey); nitrogen (blue); oxygen (red); fluorine (green); aluminium (tawny).

38.3 kcal/mol (**TS-a**) and 40.1 kcal/mol (**TS-b**), respectively. These barriers suggest that such processes cannot occur under typical reaction conditions, consistent with experimental findings. However, in the presence of Lewis acid, the coordination of carbene DAC$_1$ and BCF is found to be an exergonic process, resulting in the formation of stable adduct **INT-1**, which has been previously characterised crystallographically[49]. The corresponding activation barriers can be dramatically lowered to 24.8 kcal/mol (**TS-B-a**) and 28.6 kcal/mol (**TS-B-b**), respectively, in the presence of BCF. Analysis of the carbene's electrophilicity revealed that the charge on the carbon atom increased from 0.248 for free DAC$_1$ to 0.288 in the BCF−DAC$_1$ adduct (Fig. 4b). This increased electrophilicity enhances the carbene's ability to abstract a hydride from the alkane, thereby reducing the energy barrier for the reaction (**TS-B-a** vs. **TS-a**). Given that the barriers depend heavily on the electrophilicity of the carbene adduct, we propose that insertion proceeds initially via hydride transfer from the alkane to the carbene, generating a partial positive charge on the alkane carbon. This results in the selectivity relating to the stability of the corresponding alkyl carbocation, and therefore a preference for internal C−H bonds and predominant formation of branched isomers.

Furthermore, the carbon atom in **INT-4** possesses a charge of 0.292, indicating higher reactivity compared to BCF-DAC$_1$ under the reaction conditions. Ethane, being a more challenging substrate for C−H activation, was examined. In the presence of Al(OR$_F$)$_3$, the activation of ethane required a free energy of 24.4 kcal/mol via **TS-Al-Et**, whereas with BCF, the energy barrier increased to 26.6 kcal/mol via **TS-B-Et** (Fig. 4c). Notably, we successfully achieved the desired product using ethane only when **INT-4** was present. These findings underscore the critical role of adduct electrophilicity in determining the reactivity of simple alkanes.

Derivatizations were conducted to further evaluate the synthetic utilisation and practicality of this methodology. The DAC$_1$-derived alkanes were treated with LiAlH$_4$/HCl (aq) at room temperature. After 10 h, corresponding aldehydes elongated by one carbon atom were obtained in 34-50% yield, achieving transformation from natural gas alkanes to aldehydes under mild condition (Fig. 5a–c). As shown in

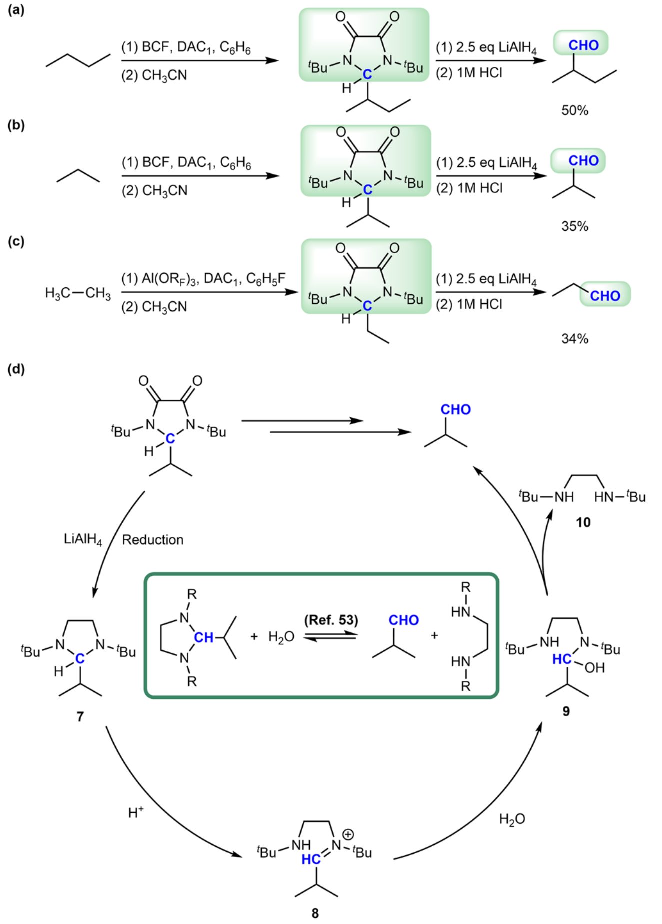


Fig. 5 | Direct carbonylation of natural gas alkanes without using transition metals and syngas. a Transformation from *n*-butane to 2-methylbutyraldehyde. **b** Transformation from propane to isobutyraldehyde. **c** Transformation from ethane to propionic aldehyde. **d** Reaction mechanism of transformation from DAC$_1$-propane to isobutyraldehyde. Yields were determined by ^{1}H-NMR spectra using 1, 3, 5-trimethoxybenzene as internal standard. OR$_F$ = OC(CF$_3$)$_3$.

Fig. 5d, the DAC$_1$-propane can be reduced by LiAlH$_4$, giving the corresponding compound **7**[52]. In the acidic conditions, compound **7** was transformed into isobutyraldehyde via intermediates **8** and **9**[53,54]. (Fig. 5d). This provides an opportunity to complete hydroformylation reactions directly from alkanes in the industry instead of using alkene and syngas (CO/H$_2$) catalysed by transition metals under high temperature and pressure[55]. Furthermore, butylene and propylene will give linear regioisomers valeraldehyde and butyraldehyde as major products in the transition metal catalysed carbonylation, respectively. However, hydroformylation of alkenes to form branched aldehydes is highly desired[56,57]. Significantly, branched 2-methylbutyraldehyde and isobutyraldehyde can be obtained from butane and propane in our conditions, which should be an importantly complementary chemistry compared with oxo-synthesis.

In conclusion, the reactivity of a stable carbene has been greatly improved to directly insert into the C–H bonds of natural gas alkanes (ethane, propane and *n*-butane) and other simple alkanes through the coordination with strong Lewis acids, offering a route for main-group element systems to C–H functionalization of natural gas alkanes. This kind of reaction only requires mild conditions at room temperature and one atmospheric pressure, without the need for excessive liquid or solid alkanes as feedstock. The work reported here indicates stable carbenes are able to mimic the behaviour of transition metals towards the activation of natural gas alkanes. It features that the electronic properties of the carbon centre of a carbene could be regulated by the strength of Lewis acids, as demonstrated by the different reactivity of Lewis acid-diamidocarbene adducts with ethane and propane. The carbene-derived products can be converted into aldehydes after reduction, achieving carbon chain growth of natural gas alkanes. This finding shows that the Lewis acid-carbene adduct is not only complementary to transition metal activation but also an exciting paradigm in transformation from natural gas alkanes to value-added chemicals.

Methods

General methods for the synthesis of DAC$_1$–hexane, DAC$_1$–propane, DAC$_1$–butane, DAC$_1$–ethane, other DAC$_1$–alkane products and Al(OR$_F$)$_3$–DAC$_1$ are as follows. More details can be found in the Supplementary Information file.

General synthesis of DAC$_1$–hexane

DAC$_1$ (1 eq), B(C$_6$F$_5$)$_3$ (1 eq) and benzene were charged in a Schlenk flask. Then benzene and *n*-hexane was added into the flask. The solution was stirred for 10 h at 25°C and the solution turned from red to yellow with some yellow residue. Acetonitrile (1 mL) with a drop of water was added to quench the reaction. The product was isolated as a white solid after purification by column chromatography on silica gel.

General synthesis of DAC$_1$–propane, DAC$_1$–butane and DAC$_1$–ethane

DAC$_1$ (1 eq), Lewis Acid (B(C$_6$F$_5$)$_3$ or PhF→Al(OR$_F$)$_3$ (1 eq) and benzene were charged in a Schlenk flask. Ethane, propane or butane (0.1 MPa) was transferred into the flask via vacuum. The solution was stirred for about 10 h at 25 °C and the dark red solution turned yellow with some yellow residue. Acetonitrile (1 mL) with a drop of water was added to quench the reaction. The product was isolated as a white solid after purification by column chromatography on silica gel.

General synthesis of DAC$_1$–alkane products (1–6)

DAC$_1$ (1 eq), B(C$_6$F$_5$)$_3$ (1 eq) and benzene were charged in a Schlenk flask. Then benzene and alkanes (2.5 eq) was added into the flask. The solution was stirred for 10 h at 25 °C and the solution turned from red to yellow with some yellow residue. Acetonitrile (1 mL) with a drop of water was added to quench the reaction. The product was isolated as a white solid after purification by column chromatography on silica gel.

General synthesis of Al(OR$_F$)$_3$–DAC$_1$

DAC$_1$ (1 eq) and PhF→Al(OR$_F$)$_3$ (1 eq) were charged in a Schlenk flask, then 1 mL 1, 2-dichlorobenzene was added and stirred for 15 min. The flask was placed at −20 °C and dark purple crystals were obtained. The crystals would be fairly unstable under room temperature and are required to store in −20 °C in glove box.

Transformation from DAC$_1$–alkane products into aldehydes

DAC$_1$-alkane products (1 eq) and LiAlH$_4$ (2.5 eq) was charged in a tube with a magnetic stirring bar, and dried THF was added. After reacting for 10 h at room temperature, HCl aqueous solution was added to quench the reaction. The product was then extracted by CDCl$_3$, and the ratios and yields were determined by ^{1}H-NMR using 1, 3, 5-trimethoxybenzene as internal standard.

Data availability

The crystallographic data for compounds BCF–DAC$_1$–hexane, BCF–DAC$_1$–propane, Al(OR$_F$)–DAC$_1$, DAC$_1$–butane, DAC$_1$–ethane and other DAC$_1$–alkane products **1**–**6** have been deposited in the Cambridge Crystallographic Data Centre (CCDC) database under deposition numbers 2327624-2327628, 2332622-2332627, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Additional spectroscopic, crystallographic, and computational data generated in this study are provided in the Supplementary Information file. Source Data are included in this manuscript. All data are available from the corresponding author upon request. Source data are provided in this paper.

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Author contributions

X.W. conceived the project. R.P. performed the chemical experiments of the BCF–DAC_1 adduct. W.C. assisted in experiments and conducted theoretical calculations. L.H. performed the chemical experiments of the $Al(OR_F)_3$–DAC_1 adduct. R.P. and T.W. collected the crystallographic data. Y.Z. refined crystal structures. X.W. and Y.L. supervised the experiment work. Y.L. supervised theoretical calculations. R.P., W.C., X.W. and Y.L. wrote the first draft of the manuscript. All authors discussed the results and manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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