

Eight-Electron Reduction of CO₂ to CH₄ by a Bioinspired Mo-Fe-S Cubane Catalyst

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Title: Eight-Electron Reduction of CO₂ to CH₄ by a Bioinspired Mo-Fe-S Cubane Catalyst

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Summary paragraph: Metal-sulfur (M-S) clusters are ancient biological cofactors that catalyze CO₂ and N₂ reduction, yet no biological or synthetic M-S cluster has achieved sustained, high-turnover conversion of CO₂ to hydrocarbons at a single active site. We reasoned that effective CO₂-to-CH₄ catalysis requires not only CO₂ activation but also retention of a metal-bound CO intermediate for subsequent six-electron reduction. Here, a bioinspired [Cp*₃Mo₃S₄Fe] cubane (Cp* = C₅Me₅) catalyzes the direct eight-electron reduction of CO₂ to CH₄ under ambient conditions with turnover numbers exceeding 150,000 and only trace CO formation. A structurally characterized CO₂-derived anionic Fe-CO intermediate was identified, and a neutral Fe-CO cubane undergoes nearly quantitative conversion to CH₄ under the catalytic conditions. These results identify synthetic M-S clusters as a competent framework for advancing catalytic CO₂ reduction beyond the two-electron stage, with appropriate molecular design and reaction conditions. More broadly, they establish productive retention of a metal-bound CO intermediate as a key molecular design principle for CO₂-to-hydrocarbon catalysis.

Main Text:

Metal-sulfur (M-S) clusters are among the most ancient cofactors known to biology, with phylogenomic evidence linking them to the reductive activation of CO₂ and N₂ in the last universal common ancestor of cellular life ^{1,2}. This reductive chemistry persists in extant enzymes. Carbon monoxide dehydrogenase (CODH) catalyzes the reversible interconversion of CO₂ and CO at a Ni-Fe-S active site ^{3,4,5}, while nitrogenases reduce N₂ at intricate M-Fe-S cofactors (M = Mo, V, Fe) ^{6,7,8} and, in the case of vanadium-dependent nitrogenase, further reduce CO to CH₄, C₂H₄, and short-chain hydrocarbons ⁹. Together, these enzymes demonstrate that biological M-S clusters can catalyze both CO₂ activation and CO reduction. However, these functions remain largely separated among different enzyme systems. Although some nitrogenases can reduce CO₂ directly to hydrocarbons, their turnover numbers (TONs) are below 100 under specialized conditions ^{10,11,12}. Neither biological nor synthetic M-S clusters have achieved sustained, high-turnover catalytic conversion of CO₂ directly to hydrocarbons at a single active site (Fig. 1).

(Fig. 1, here)

Synthetic M-S clusters have long been developed as structural and functional models of enzymatic cofactors, yet molecular M-S catalysts remain largely limited to the two-electron reduction of CO₂ to CO or formate (Eq. 1) ^{13,14,15}. Direct conversion of CO₂ to CH₄ requires six additional electrons and protons to be delivered before the CO intermediate dissociates (Eq. 2). An effective molecular catalyst for this eight-electron transformation must combine a durable cluster framework with an accessible metal site that binds and activates inert small molecules under mild conditions, while retaining the CO-derived intermediate long enough for its further reduction. Our recently developed Mo-Fe-S Cubane ^{16,17}, in which the Fe site catalytically reduces N₂ under ambient conditions ¹⁸ and exhibits strong Fe-CO interaction ¹⁹, provides a molecular platform for testing this design principle.



Here we show that a Mo-Fe-S cubane cluster catalyzes the direct eight-electron reduction of CO₂ to CH₄ under ambient conditions, with TONs exceeding 150,000 and only trace CO formation (Fig. 1). This activity surpasses previous M-S cluster catalysts by approximately four orders of magnitude ^{20,21,22} and, to our knowledge, represents the highest turnover number reported to date for a homogeneous molecular catalyst for CO₂-to-CH₄ conversion. Mechanistic studies identify a persistent yet catalytically competent Fe-CO intermediate that undergoes nearly quantitative conversion to CH₄ under the catalytic conditions. These findings demonstrate that a single molecular M-S cluster can integrate CO₂ activation and complete reduction of the resulting CO intermediate, a chemistry that appears not to have been achieved at a single active site over nearly four billion years of biological evolution. The ability to retain a metal-bound CO intermediate without arresting its further reduction offers a design principle for molecular CO₂-to-hydrocarbon catalysis.

We began by evaluating the catalytic performance of the chloride (Cl⁻)-bound clusters [Cp^R₃Mo₃S₄FeCl] (Cp^R = Cp* (1), Cp^L (2), Cp^{XL} (3)) ^{16,17} for CO₂ reduction. Reactions were conducted in THF using SmI₂ as a single-electron reductant and H₂O as a proton source, and the conditions were selected on the basis of our previous studies of multi-electron small-molecule reduction ²⁰⁻²² and related Mo-catalyzed N₂ reduction to ammonia ²³. Under 1 atm of CO₂, the catalytic activity depended strongly on the steric profile of the Cp^R ligands. Among the available Cp^R ligands, the least sterically hindered cluster, [Cp*₃Mo₃S₄FeCl] (1), showed

the highest activity. In the presence of 5,000 equiv. of SmI₂ and 1.5% v/v H₂O, **1** produced 216 ± 29 equiv. of CH₄, corresponding to 35 ± 5% of the consumed reducing equivalents (Table 1, entry 1 and Supplementary Fig. 2)²⁴. H₂ was formed as the main competing product (1,729 ± 60 equiv., 69 ± 10% selectivity), whereas CO formation was negligible (3.4 ± 0.9 equiv., 0.54 ± 0.14% selectivity). By contrast, the more sterically demanding clusters **2** (Cp^L) and **3** (Cp^{XL}) produced only 10 ± 1.1 and 0.4 ± 0.2 equiv. of CH₄ (Table 1, entries 2 and 3). In these reactions, 87-88% of the reducing equivalents were used for H₂ formation (2,170 ± 40 and 2,190 ± 140 equiv., respectively). These results identified **1** as the most effective catalyst among the three cluster variants and suggested that steric accessibility around the Fe site of the cubane is critical for CO₂ reduction.

(Table 1, here)

We next examined whether the observed activity could arise from iron salts, cluster fragments, or decomposition products. The individual synthetic precursors of **1**, [Cp*₃Mo₃S₄] and FeCl₂, each produced less than 2.6 equiv. of CH₄ under otherwise identical conditions (Table 1, entries 4 and 8). Common mononuclear and dinuclear iron complexes, including Fe(TPP)Cl (TPP = *meso*-tetraphenylporphyrin), Fe₂(CO)₉, and FeCp₂ (Cp = C₅H₅), were also inactive or weakly active. FeCp₂ gave at most 7 equiv. of CH₄ (Table 1, entries 5-7). Fe(TPP)Cl, despite its established activity in electro- and photocatalytic CO₂-to-CO conversion^{25,26}, did not produce appreciable CO or CH₄ under the present conditions (Table 1, entry 5). These control experiments indicate that neither simple iron species nor the separated components of the cubane account for the catalytic activity of **1**.

Isotope labelling experiments using ¹³CO₂ established the carbon source of the CH₄ product. Gas chromatography-mass spectrometry (GC-MS) analysis showed identical retention times for CH₄ generated from ¹²CO₂ and ¹³CO₂, but the molecular-ion signal shifted from *m/z* = 16 for ¹²CH₄ to *m/z* = 17 for ¹³CH₄ (Supplementary Fig. 3). The corresponding +1 *m/z* shift was also observed throughout the fragmentation pattern (Fig. 2A). These results establish that the carbon atom of CH₄ originates from CO₂.

(Fig. 2, here)

Time-course measurements under the standard conditions showed that CH₄ and H₂ were formed linearly during the initial 10 min, with initial turnover frequencies (TOFs) of 10 min⁻¹ and 148 min⁻¹, respectively (Fig. 2B and Supplementary Fig. 4). Product formation approached a plateau after approximately 30 min, by which point 97% of the SmI₂ reductant had been consumed. The termination of product formation coincided with depletion of the electron source (SmI₂), rather than with an observable loss of catalytic activity. This conclusion is further supported by the large-scale experiments discussed below, which demonstrate sustained activity in the presence of a large excess reductant. Polynuclear clusters are often prone to degradation and aggregation, but our kinetic data support the molecular nature of the catalysis. The initial rates of both CH₄ and H₂ formation were proportional to the concentration of **1** over the range of 5 - 40 μM, establishing a first-order dependence on the cluster concentration over this range (Fig. 2C and Supplementary Fig. 5). Furthermore, no induction period was observed. Although these kinetic features alone do not exclude every possible decomposition pathway, they are compatible with catalysis by a molecular species derived directly from **1** rather than by slowly formed nanoparticles or other aggregated species.

Additional evidence for persistence of the [Cp*₃Mo₃S₄Fe] cubane core came from post-catalytic mass spectrometry (MS) analysis. The MS spectrum of the reaction mixture after CO₂

reduction displayed four major mono-cationic signals (i-iv in Supplementary Fig. 7). Signal (i), with its most intense peak at $m/z = 1003.7$, matched the calculated isotope pattern of $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{FeI}]^+$, and no prominent signals attributable to decomposition products of the $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Fe}]$ core were detected. Signals (ii)-(iv) were assigned on the basis of their isotope patterns to oxidized and oligomerized SmI_2 -derived species, $[\text{Sm}_2\text{I}_5(\text{OH})(\text{THF})_3]^+$ (ii), $[\text{Sm}_2\text{I}_5(\text{OH})(\text{THF})_3(\text{H}_2\text{O})_3]^+$ (iii), and $[\text{Sm}_3\text{I}_8(\text{OH})(\text{THF})_3(\text{H}_2\text{O})_3]^+$ (iv). Related oligomeric products of oxidized SmI_2 have been structurally characterized previously²³. Overall, these results support retention of the $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Fe}]$ core during catalysis.

Attempts to observe catalytic intermediates directly under turnover conditions were unsuccessful, consistent with their low steady-state concentrations. We therefore sought to intercept intermediates under stoichiometric conditions. When cluster **1** was reduced with 10 equiv. of KC_8 under a CO_2 atmosphere (1 atm), the anionic CO-adduct $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Fe}(\text{CO})]^-$ (**4**) was formed in 32% NMR yield (Fig. 2D and Supplementary Fig. 8). This reaction was carried out under anhydrous conditions to arrest the reduction at an intermediate stage. The absence of a proton source, which would otherwise promote further reduction of the Fe-bound CO ligand, likely contributed to the accumulation of **4**. X-ray crystallographic analysis established **4** as the potassium salt of an anionic Fe-CO cubane (Fig. 2E and Supplementary Fig. 23). The CO stretching band of **4** appeared at 1690-1692 cm^{-1} in the infrared (IR) spectra (Supplementary Figs. 9 and 17). Preparation of **4** under $^{13}\text{CO}_2$ (Supplementary Fig. 10) shifted this band to 1648 cm^{-1} ($\Delta\nu = 42\text{-}44\text{ cm}^{-1}$, Fig. 2F and Supplementary Fig. 11), in agreement with the expected isotopic shift for a ^{13}C -labeled CO ligand ($\Delta\nu = 37\text{ cm}^{-1}$). These results demonstrate that the Fe-bound CO ligand is derived from CO_2 and support the involvement of an Fe-CO intermediate in the reduction pathway.

The catalytic relevance of the Fe-CO intermediate was established independently. Both anionic cluster **4** and neutral CO cluster $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Fe}(\text{CO})]$ (**5**) catalyzed CO_2 reduction under the standard conditions, producing 273 ± 34 and 281 ± 41 equiv. of CH_4 , respectively (Table 1, entries 9 and 10). These activities were comparable to or greater than that of chloride precursor **1**. Cyclic voltammetry of **5** revealed a reversible redox couple assignable to the **5/4** couple at -1.73 V vs. Fc/Fc^+ ($\text{Fc} = \text{FeCp}_2$) (Supplementary Fig. 18), corresponding to -1.16 V vs. SCE (SCE = saturated calomel electrode) (Supplementary Fig. 19)^{27,28}. This potential is accessible by the $\text{SmI}_2/\text{H}_2\text{O}$ reducing system (-1.3 V vs. SCE)²⁹, suggesting that cluster **5** is reduced to **4** under catalytic conditions. Characterization data for independently synthesized **4** and **5** are summarized in Supplementary Figs. 12- 17, 23, 24, and Supplementary Table 4.

Most importantly, stoichiometric treatment of independently synthesized **5** with excess SmI_2 (32 equiv.) and protons (H_2O) under argon converted its Fe-bound CO into CH_4 in near-quantitative yield (0.96 ± 0.08 equiv.; Fig. 2G and Supplementary Table 2). The Fe-CO species is therefore not an off-cycle decomposition product or terminal resting state, but a chemically and catalytically competent intermediate in CH_4 formation.

The Fe-CO unit is persistent in the absence of a proton source. The CO ligand of neutral Fe-CO cluster **5** was not detectably displaced after 1 day at room temperature under CO_2 , as monitored by ^1H NMR in $\text{THF}-d_8$ (Supplementary Fig. 20). Its CO stretching frequency (ν_{CO}) of 1857 cm^{-1} is substantially lower than that of free CO (2143 cm^{-1}), whereas the anionic Fe-CO cluster **4** exhibits an even lower value of 1690-1692 cm^{-1} (Supplementary Figs. 9, 14, and 17). The ν_{CO} values of both **4** and **5** rank among the lowest reported for Fe-CO species bearing cubic metal-sulfur cores (Supplementary Fig. 21)^{19,30,31,32,33,34}. Moreover, the ν_{CO} of **4** lies at the lowest end of structurally characterized terminal Fe-CO complexes, below even that of $[\text{Fe}(\text{CO})_4]^{2-}$ (1730 cm^{-1} , Supplementary Fig. 22)^{35,36}. The unusually low ν_{CO} values of **4** point to strong $\text{Fe} \rightarrow \text{CO}$ π backdonation and substantial activation of the bound CO ligand. While strong metal-CO interactions can lead to thermodynamic trapping or catalyst inhibition, the

[Cp*₃Mo₃S₄Fe] framework appears to enable productive retention, maintaining the activated Fe-CO intermediate for subsequent reduction toward CH₄ rather than simply promoting CO dissociation. This behavior provides an interesting contrast with CODH, where CO is released as product, and nitrogenase, where CO can inhibit catalysis, highlighting how the surrounding metal-sulfur framework can tune the balance among CO binding, activation, and further reduction. This productive retention, rather than the strength of CO binding alone, accounts for the low yield of CO and its continued reduction to CH₄.

Based on the experimental observations and density functional theory (DFT) calculations, we propose the catalytic cycle illustrated in Fig. 3. Consistent with the observed first-order kinetics (Fig. 2C and Supplementary Fig. 5), the catalysis proceeds via a unimolecular pathway. Reduction of chloride precursor **1** induces loss of Cl[−], generating a coordinatively unsaturated Fe site capable of binding CO₂. Theoretical calculations support thermodynamically favorable binding of CO₂ to the vacant site in a side-on (η^2) fashion (see details in the Supplementary Information and Supplementary Figs. 25 and 26). The computed CO₂ binding energy is 31.4 kcal/mol for [Cp*₃Mo₃S₄Fe(CO₂)], relatively higher than the value calculated for the Cp^{XL} analog (21.4 kcal/mol). Bulkier ligands on the Mo atoms thus yield smaller CO₂ binding energy, providing a rationale for markedly lower CO₂ reduction activities of clusters **2** (Cp^R = Cp^L) and **3** (Cp^R = Cp^{XL}). Subsequent transfer of two electrons and two protons promotes C-O bond cleavage and H₂O release to form the neutral CO cluster **5**, which then undergoes one-electron reduction to give the corresponding anionic cluster **4**. The preferential binding of CO over CO₂ at **4** and **5** is also bolstered by DFT-calculated binding energies of CO (73.7 and 55.8 kcal/mol for **4** and **5**, respectively, vs. 32.3 kcal/mol for [Cp*₃Mo₃S₄Fe(CO₂)]) (see details in the Supplementary Information). Further proton- and electron-transfer steps convert the bound CO ligand into CH₄ via an Fe-CH₃ intermediate, regenerating the active species. The regenerated coordinatively unsaturated Fe site should also be competent for proton reduction. Under argon, cluster **1** produced H₂ with an initial TOF of 1,116 min^{−1}, whereas under CO₂ this value decreased to 148 min^{−1} (Supplementary Fig. 4). In contrast, the sterically congested cluster **3** (Cp^{XL}) exhibited an H₂-formation TOF exceeding 2,000 min^{−1} even under CO₂ (Supplementary Fig. 6). These observations are in line with competition between CO₂ binding and proton reduction within the same molecular catalyst. Access of CO₂ to the cubane suppresses, but does not eliminate, the competing H₂ evolution pathway. This competition parallels the intrinsic proton-reduction chemistry of nitrogenase, which obligatorily evolves H₂ during catalysis and relies on ATP-coupled electron transfer to drive difficult multielectron substrate reductions. In this context, achieving the eight-electron reduction of CO₂ to CH₄ with up to 35% selectivity under ambient conditions, without ATP-dependent protein machinery, underscores the remarkable intrinsic catalytic capability of the isolated [Cp*₃Mo₃S₄Fe] framework. This performance does not arise from a single structural or electronic property. Rather, it emerges from the interplay of an accessible reaction site, a durable metal-sulfur framework, efficient binding and activation of inert small molecules under mild conditions, and productive retention of the CO-derived intermediate.

(Fig. 3, here)

Finally, to demonstrate the exceptional durability of the [Cp*₃Mo₃S₄Fe] framework, we scaled up the catalytic reaction using a massive excess of reductant (4 million equiv. of SmI₂) with chloride precursor **1** and neutral Fe-CO cluster **5**. Optimization studies revealed that the reaction temperature strongly influenced CH₄ production. At room temperature, cluster **1** produced only 19,000 ± 2,100 equiv. of CH₄ (Supplementary Table 3, entry 1). At 0 °C, however, cluster **1** produced 127,000 ± 5,000 equiv. of CH₄, whereas neutral Fe-CO cluster **5** reached 157,000 ± 5,000 equiv. with no apparent catalyst deactivation before depletion of the

available reducing equivalents (Table 1, entries 11 and 12 and Supplementary Table 3, entries 2 and 3). These turnover numbers exceed those of previously reported M-S cluster catalysts for hydrocarbon formation by approximately four orders of magnitude. Our earlier [Fe₄S₄]-based systems, for example, were limited to fewer than 25 turnovers under related chemically reducing conditions²⁰⁻²². More broadly, homogeneous molecular catalysts for CO₂ reduction predominantly produce the two-electron reduction products, such as CO and formate^{37,38}, and molecular CO₂-to-CH₄ conversion catalysis remains uncommon. Among the reported systems, a nickel macrocyclic complex achieved 29,000 turnovers of CH₄ over 72 hours, although CO (130,000 turnovers) was the dominant product under photochemical conditions³⁹. A trimethylammonium-substituted iron tetraphenylporphyrin complex afforded 79 turnovers of CH₄ together with 367 turnovers of CO under photocatalytic conditions^{40, 41}. Direct comparison between chemical and photochemical systems requires caution because reductants, energy inputs, and efficiency metrics differ. Nevertheless, the combination of more than 150,000 turnovers and only trace CO formation distinguishes the present Mo-Fe-S cubane from previously reported homogeneous molecular catalysts.

In conclusion, a bioinspired [Cp*₃Mo₃S₄Fe] cubane catalyzes the direct eight-electron reduction of CO₂ to CH₄ under ambient pressure with turnover numbers exceeding 150,000. A single molecular metal-sulfur cluster can mediate both CO₂-to-CO conversion and the subsequent six-electron reduction of the resulting Fe-bound CO intermediate with exceptional durability. A structurally characterized CO₂-derived anionic Fe-CO intermediate and the near-quantitative conversion of an independently synthesized neutral Fe-CO cluster to CH₄ collectively establish the catalytic competence of the Fe-CO intermediate. These findings identify productive retention of a metal-bound CO intermediate, coupled with its continued reduction rather than CO release, as an important molecular design principle for CO₂-to-hydrocarbon catalysis. Moreover, unlike metalloenzymes, which use structured hydrogen-bonding networks and proton relays to control proton delivery, the [Cp*₃Mo₃S₄Fe] system sustains effective multi-electron/multi-proton reduction using only H₂O in THF. This behavior highlights the intrinsic ability of the metal-sulfur framework to coordinate proton and electron transfer without a protein scaffold. Future incorporation of pendant proton relays or other secondary-sphere features could provide additional control over proton delivery and potentially suppress competing H₂ evolution.

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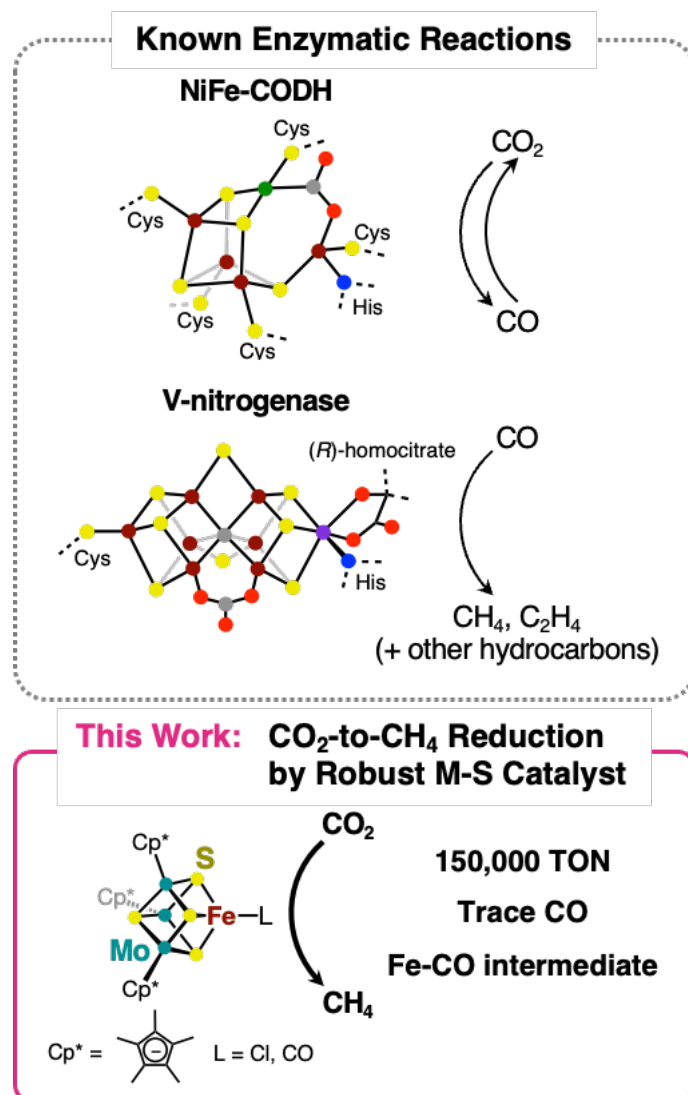
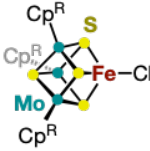


Fig. 1. CO₂ reduction to CH₄ catalyzed by synthetic metal-sulfur clusters with comparison to enzymatic reactions. (Top) NiFe-carbon monoxide dehydrogenase (NiFe-CODH) catalyzes the interconversion of CO₂ and CO, while vanadium-dependent nitrogenase (V-nitrogenase) reduces CO to CH₄, C₂H₄, and other hydrocarbons. The metal-sulfur active sites are shown with atoms colored as follows: Fe, reddish brown; Mo, teal; Ni, green; V, purple; S, yellow; O, red; C, gray; N, blue. (Bottom) The cubane-type Mo-Fe-S clusters, [Cp*₃Mo₃S₄Fe(L)] (Cp* = C₅Me₅, L = Cl, CO), catalyze CO₂-to-CH₄ reduction with exceptional turnover numbers (TONs) and trace CO formation. Stoichiometric reactions and catalytic evaluations identified Fe-CO species as intermediates.

Table 1. Catalytic reduction of CO₂ to CH₄ using [Cp*₃Mo₃S₄Fe] clusters and comparison of catalytic performance with relevant cluster and iron compounds. Reaction conditions: (entries 1-10) precatalyst (10 nmol), SmI₂ (50 μmol), H₂O (1.5% v/v); (entries 11 and 12) precatalyst (0.040 nmol), SmI₂ (0.16 mmol), H₂O (6.25% v/v).

$$\text{CO}_2 \text{ (1 atm)} + 8\text{e}^- \text{ (SmI}_2\text{)} + 8\text{H}^+ \text{ (H}_2\text{O)} \xrightarrow[\text{THF, RT or 0 } ^\circ\text{C}]{\text{Precatalyst}} \text{CH}_4 + 2\text{H}_2\text{O}$$

Precatalyst

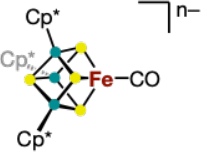


$\text{Cp}^{\text{R}} =$

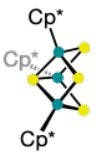

1


2


3



4 (n = 1)
5 (n = 0)


[Cp*₃Mo₃S₄]


Fe(TPP)Cl


FeCp₂

Entry	Precatalyst	SmI ₂ (equiv.) ^a	Product (equiv.) ^a [Selectivity (%)] ^b		
			CH ₄	CO	H ₂
1 ^c	1	5000	216 ± 29 [35]	3.4 ± 0.9 [0.54]	1.72·10 ³ ± 60 [69]
2 ^c	2	5000	10 ± 1.1 [1.6]	n.d.	2.17·10 ³ ± 40 [87]
3 ^c	3	5000	0.4 ± 0.2 [0.06]	n.d.	2.19·10 ³ ± 140 [88]
4	[Cp* ₃ Mo ₃ S ₄]	5000	n.d.	n.d.	2.17·10 ³ [87]
5	Fe(TPP)Cl	5000	n.d.	4.9 [0.20]	1.60·10 ³ [64]
6	FeCp ₂	5000	7.0	2.1 [0.08]	1.38·10 ³ [55]
7	Fe ₂ (CO) ₉	5000	5.9	6.3 [0.25]	1.96·10 ³ [78]
8	FeCl ₂	5000	2.6	n.d.	1.94·10 ³ [78]
9 ^c	4	5000	281 ± 41	3.7 ± 1.2 [0.15]	1.17·10 ³ ± 1.6·10 ² [47]
10 ^c	5	5000	272 ± 35	5.7 ± 3.4 [0.23]	1.25·10 ³ ± 1.1·10 ² [50]
11 ^{c,d}	1	4.0·10 ⁶	1.27·10 ⁵ ± 5·10 ³ [25]	9.3·10 ² ± 3.6·10 ² [0.05]	1.18·10 ⁶ ± 1.4·10 ⁵ [59]
12 ^{c,d}	5	4.0·10 ⁶	1.57·10 ⁵ ± 5·10 ³ [31]	1.8·10 ³ ± 2·10 ² [0.09]	1.09·10 ⁶ ± 6·10 ⁴ [55]

^a equiv. per precatalyst. ^b SmI₂-based selectivity. Selectivity was calculated on an electron-balance basis, requiring 8, 2, and 2 electrons per molecule of CH₄, CO, and H₂. Values are shown in brackets. ^c Data were obtained from three individual experiments and are presented as average ± standard deviation. ^d Reactions were performed at 0 °C.

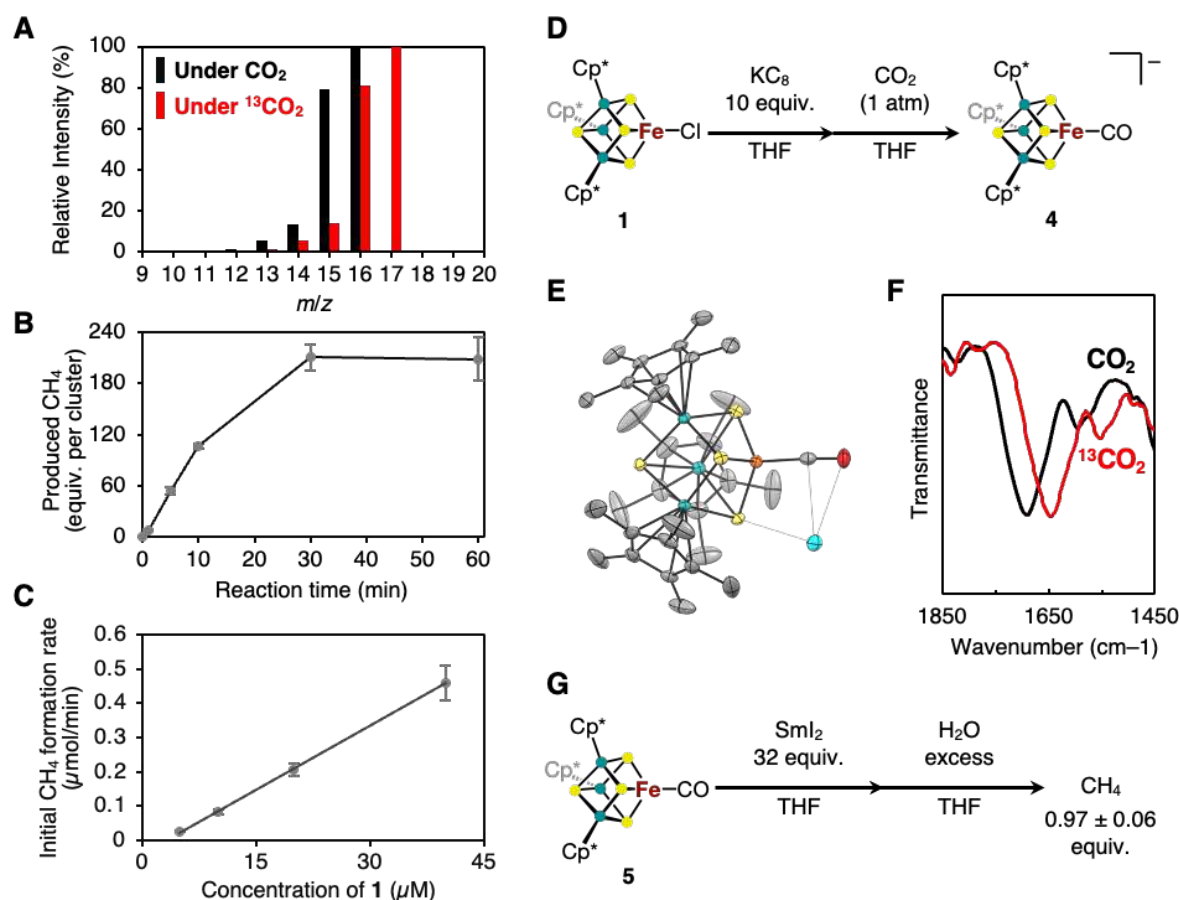


Fig. 2. Isotope labeling and kinetic characterization of the catalytic CO₂ reduction by **1 (A-C), isolation and characterization of a CO-bound intermediate (D-F), and stoichiometric conversion of bound CO to CH₄ (G).** (A) Mass spectra of CH₄ produced under unlabeled CO₂ (black) and ¹³CO₂ (red), analyzed by gas chromatograph-mass spectrometry (GC-MS). The +1 *m/z* shift under ¹³CO₂ confirms that the carbon of CH₄ originates from CO₂. (B) Time course of CH₄ formation during the reaction of **1** with SmI₂ and H₂O under CO₂. Product accumulation plateaus at approximately 30 min, coinciding with consumption of the SmI₂ reductant. (C) Initial rate of CH₄ formation as a function of the concentration of **1** (5-40 μM). The linear dependence (*R*² = 0.9997) indicates first-order kinetics with respect to cluster **1**. (D) Formation of CO-bound cluster **4** upon treatment of **1** with KC₈ under CO₂ atmosphere. (E) Crystal structure of **4** shown with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Shown is one of the two crystallographically independent pairs of **4** with a potassium cation in the asymmetric unit (For more details, see Supplementary Fig. 23). Color legend: C, grey; O, red; K, turquoise; S, yellow; Mo, teal; and Fe, orange. (F) Solid-state IR spectra of **4** in the CO-stretching region, prepared under CO₂ (black) and ¹³CO₂ (red) atmospheres. (G) Quantitative methane formation from CO-bound cluster **5** upon reaction with SmI₂ and H₂O under an Ar atmosphere.

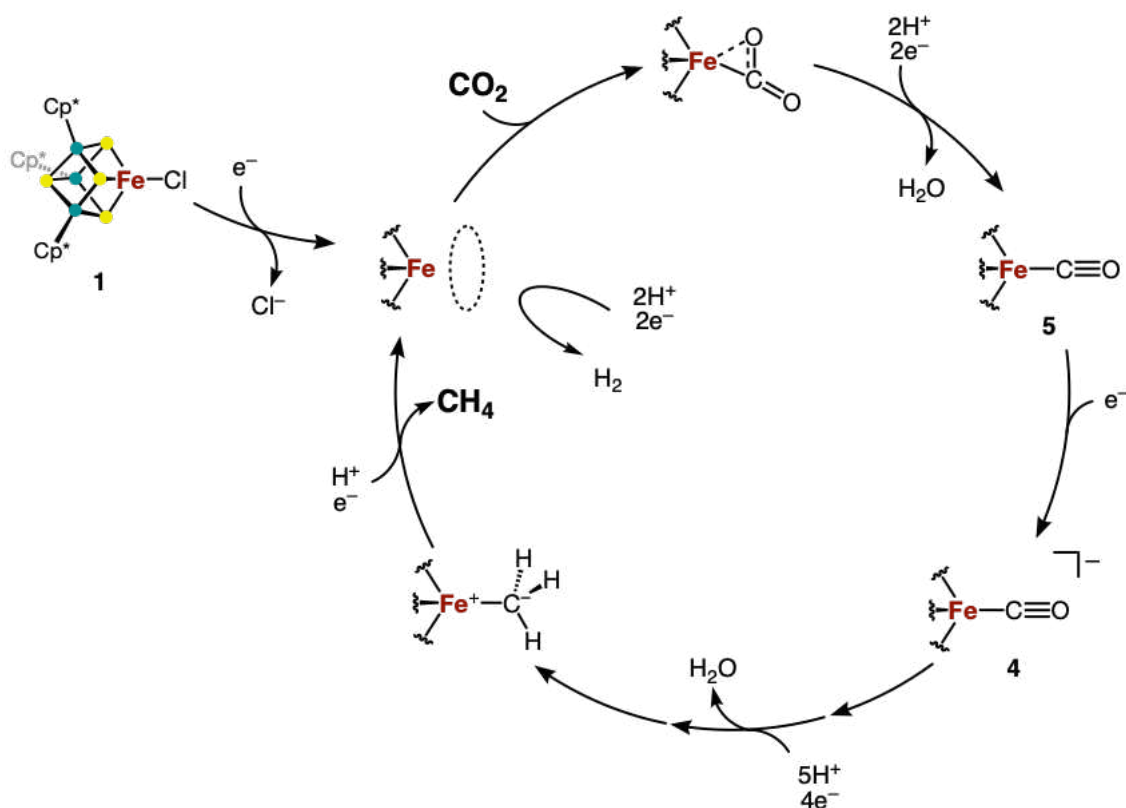


Fig. 3. Proposed catalytic cycle of CO₂-to-CH₄ conversion by the [Cp*₃Mo₃S₄Fe] cluster. Reduction of Cl-bound precatalyst **1** releases Cl⁻ and generates a coordinatively unsaturated Fe site. This site binds CO₂, which is reduced to CH₄ through Fe-CO intermediates **5** and **4** by successive electron and proton transfer. Release of CH₄ regenerates the vacant Fe site to close the cycle. The unsaturated Fe site also mediates H⁺ reduction to H₂ as a competing pathway.

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Data and materials availability: X-ray data are available free of charge from the Cambridge Crystallographic Data Centre under reference numbers CCDC 2586720 (**4**) and 2586721 (**5**). All other experimental, spectroscopic, crystallographic, and computational data are included in the supplementary materials.

Additional information

Supplementary information is available at XXXX.

Correspondence and requests for materials should be addressed K.T. or Y.O.

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