A theoretical investigation on the activation of small molecules by a disilenide: a DFT prediction

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Abstract: Herein, we proposed several mechanistic scenarios for activation of small molecules (NH_3, CO_2, CS_2, H_2, CH_4, N_2, and N_2O) by a disilicon analogue of a vinyl anion (**1H**) using density functional theory (DFT) calculations. The DFT results established that all the possible reactions to yield a variety of potential products have an exergonic nature except for the activation of N_2 with the obtained overall energy of $\Delta G = 33.6$ kcal mol^{-1}. Moreover, the highest exergonic character was $\Delta G = -95.8$ kcal mol^{-1} for N_2O. Therefore, the findings reveal that **1H** can be considered a suitable candidate for activation of NH_3, CO_2, CS_2, H_2, CH_4, and N_2O under metal-free conditions.

Key words: Silicon chemistry, disilenide, DFT, reaction mechanism

1. Introduction

The considerable interest and concentrated experimental and theoretical research efforts in the study of small molecule activation arise from the fact that important practical applications for molecules depend to a great extent on catalytic phenomena.[1,2] One of the fascinating applications of small molecules is their activation for chemical transformation into chemical feedstocks.[3−8] Numerous synthetic and computational studies have been documented on the activation of small molecules by employing heterogeneous and homogeneous transition-metal catalysis at elevated temperatures.[9−15] Alternatively, metal-free systems have been considered actively for the processes. Since the discovery of frustrated Lewis pairs (FLPs) by Stephan and coworkers, several metal-free systems capable of activating small molecules under ambient conditions have been reported.[16−20] In recent years, it was also discovered that the multiple bonded or low coordinated main-group species have a similar reactivity to transition-metal complexes for such reactions owing to their energetically accessible occupied and unoccupied frontier orbitals.[21−27] In this regard, the first activation of H_2 by an unsaturated main-group compound digermyne $ArGe \equiv GeAr$ ($Ar = C_6H_3$-$2,6(C_6H_3$-$2,6$-$Pr_2^i)_2$) was accomplished by Power and coworkers.[21] Robinson and coworkers reported stable silicon oxides Si_2O_3 and Si_2O_4 from the reactions of an N-heterocyclic carbene-stabilized $Si(0)$ compound with N_2O and O_2.[22] The oxidative addition of NH_3 to an N-heterocyclic silylene (NHSi) was explored by Roesky and coworkers.[23] An early report by Sita and coworkers detailed the ability of bis(triorganosilyl)amido stannylenes for activation of CO_2 to yield organic isocyanates and carbodiimides.[24−26] The activation of CS_2 by silylene compounds was extensively studied by Tacke and coworkers.[27]

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Disilenides, the silicon analogues of vinyl anions, have considerable diversity and have attracted growing attention as transfer reagents to Si–Si fragments.[28−34] The Scheschkewitz group have shown the use of a disilenide ($Tip_2Si=SiTipLi$, Tip = 2,4,6-triisopropylphenyl) compound in an efficient manner for activation of CO results in the full reductive cleavage of the C–O triple bond in CO under ambient conditions (Figure 1).[28] In a collaboration with the Scheschkewitz group, we have also theoretically investigated the ability of different permutations of heavier vinyl anions for the activation of CO.[29] To the best of our knowledge, however, to date there has been no other report on the activation of NH_3, CO_2, CS_2, H_2, CH_4, N_2, or N_2O across anionic Si=Si bonded systems.
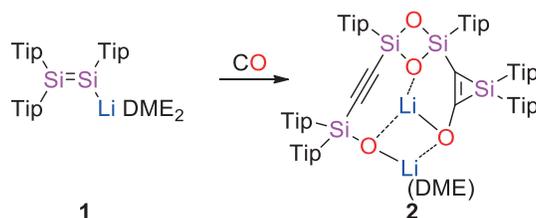

Figure 1. Full reduction of carbon monoxide by disilenide (Tip = 2,4,6-$^i Pr_3 C_6 H_3$).

Inspired by the previous studies regarding the activation of small molecules by metal-free catalysts, herein we examined the ability of **1H** ($[H_2Si=SiH]^-$; simplified form of **1**, H group replaced with Tip in **1**) on the processes of the small molecule activations considered. Oxidative additions of the small molecules lead to the formation of several product models. All the proposed reactions are determined to have an exergonic nature except for the process of N_2. The endothermicity of N_2 activation is found to be $\Delta G = 33.6$ kcal mol^{-1}, showing that the reaction is not spontaneous. The DFT analyses on this fascinating topic will lead to a much deeper understanding of small molecule activation by disilicon analogues of vinyl anions for further experimental and theoretical studies.

2. Results and discussion

2.1. Activation of ammonia (NH_3)

There are very few studies on the activation of the $N-H$ bond in NH_3 under metal-free conditions. The first report associated with NH_3 fragmentation mediated by transition metal catalysis was published by Hartwig et al.[35] On the other hand, the activation of NH_3 by an N-heterocyclic silylene (NHSi) in the absence of a transition metal was accomplished by Roesky et al.[23] In this regard, the proposed pathway for the reaction of **1H** with NH_3 is mapped out in Figure 2. The activation can occur via initial attack of NH_3 to the anionic silicon center of **1H** via **TS1−NH$_3$** to form the possible intermediate **1−NH$_3$** by an energy barrier of $\Delta G^{\neq} = 15.4$ kcal mol^{-1} at the wB97XD/6-31+G(d,p) level of theory. Coordination of NH_3 to the silicon atom reduces the Si=Si double bond character of **1H** and features an ammonia-stabilized silylene structure **1−NH$_3$**, as manifested by elongation of the $Si-Si$ bond about 0.195 Å. A comparison of the $Si-Si$ bonding orbitals in **1H** and **1−HN$_3$** can also confirm the silylene character due to the increase in the p character of mono- and dihydrogen substituted silicon atoms ($sp^{1.2}$ and $sp^{4.13}$ for **1H**; $sp^{3.7}$ and $sp^{4.43}$ for **1−HN$_3$**), respectively. Furthermore, the increase in the negative charge accumulation of the tricoordinate silicon atom (-0.586) in **1−NH$_3$** can serve as another criterion of silyene character as compared to that in **1H** (-0.258). Subsequently, the intramolecular rearrangement of **1−NH$_3$** via **TS2−NH$_3$** results in the formation of **2−NH$_3$**. The required energy barrier

for this step is determined to be $\Delta G^{\neq} = 8.4$ kcal mol^{-1}. In this case, the overall pathway for $\mathbf{2-NH_3}$ is strongly exergonic by $\Delta G = -22.2$ kcal mol^{-1}, showing that the reaction is spontaneous and could be realized under mild conditions. The free energy barriers of $\mathbf{TS1-NH_3}$ and $\mathbf{TS2-NH_3}$ are predicted to be lower than the highest energy barrier of the previously proposed mechanism ($\Delta G^{\neq} = 36.6$ kcal mol^{-1} to generate a four-membered ring) for the reaction of $Tip_2Si=SiTipLi$ (Tip = 2,4,6-triisopropylphenyl) with CO.[28,29] As can be seen in Figure 2, the proposed pathway for the activation of $\mathbf{NH_3}$ was calculated at DFT and CCSD(T) levels of theories (wB97XD/6-31+G(d,p), wB97XD/cc-pVTZ, and CCSD(T)/6-31+G(d,p)). In general, all the methods used herein predict very similar trends.
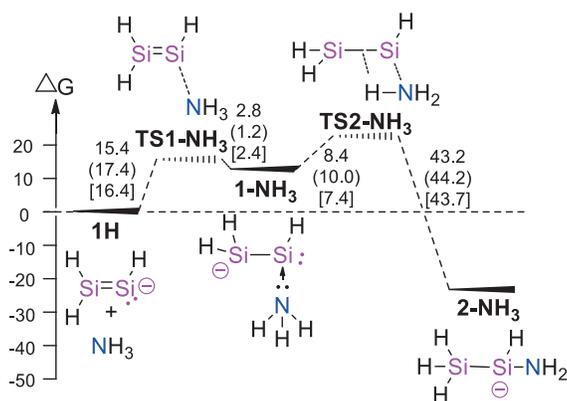

Figure 2. The proposed reaction path for activation of ammonia at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.

2.2. Activation of carbon dioxide (CO$_2$) and carbon disulfide (CS$_2$)

Carbon dioxide (CO$_2$) is one of the actively used starting materials for conversion into chemical feedstocks, alternative fuels, and organic building blocks.[3,5] The application of metal catalyst has an obvious role for the related activations and transformations.[36−41] The use of main group species, however, has just started to garner attention for the processes.[42−45] Recently, the reduction of CO$_2$ to CO by an amido-digermyne was reported by the collaboration of Frenking and Jones.[42] Furthermore, carbon disulfide (CS$_2$), as isoelectronic of CO$_2$, can also serve as a similar system for CO$_2$. To the best of our knowledge, there is no report on the activation and reduction of CO$_2$ and CS$_2$ to CO and CS through the anionic Si−Si double bonded systems, respectively. With this incentive, we have suggested the possible reactions of $\mathbf{1H}$ with CO$_2$ and CS$_2$ by using the DFT method. Several types of pathways have been proposed for the reactions (see Supplementary Information Figure S1−S5). The results indicate that, among the proposed pathways, the lowest initial energy barrier belongs to $\mathbf{TS1-CO_2}$, which includes the initial interaction between CO$_2$ and the tricoordinate silicon atom in $\mathbf{1H}$ (Figure 3). In the case of CS$_2$, however, the concerted 1,3-dipolar cycloaddition of CS$_2$ to $\mathbf{1H}$ is more prominent (Figure 4).

The initial step of the reaction between CO$_2$ and $\mathbf{1H}$ requires an energy barrier of $\Delta G^{\neq} = 7.6$ kcal mol^{-1} for $\mathbf{TS1-CO2}$ to generate $\mathbf{1-CO_2}$, which is even lower than that of the initial energy barrier for the CO activation process.[28,29] The formation of $\mathbf{1-CO_2}$ is mildly endergonic by $\Delta G = 5.5$ kcal mol^{-1} at the
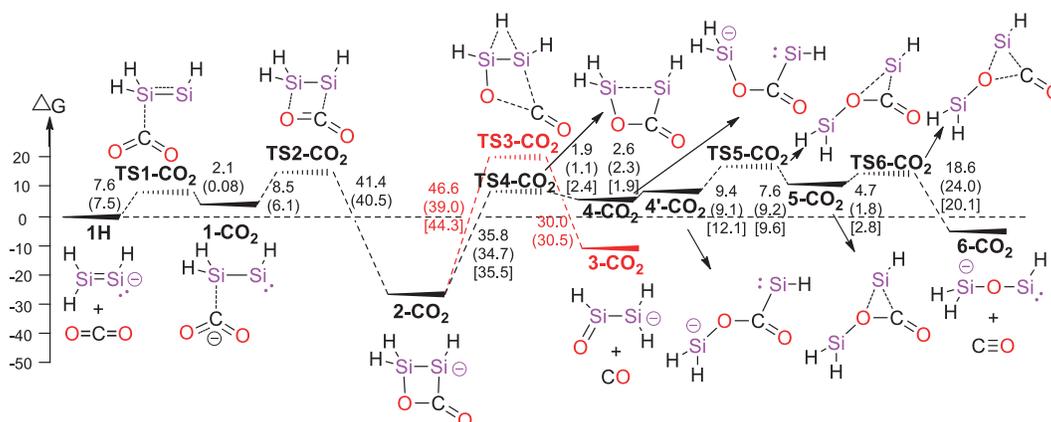
Figure 3. The proposed reaction path for activation of carbon at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.
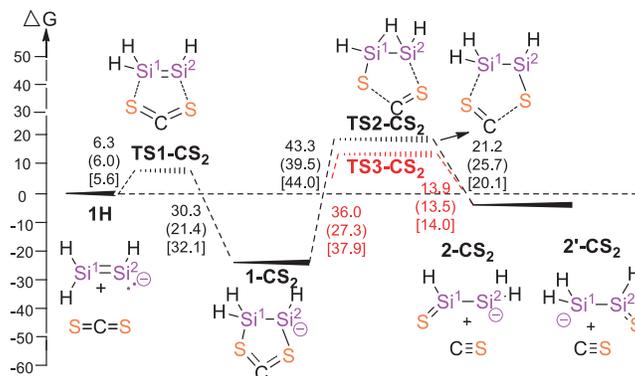

Figure 4. The proposed reaction path for activation of carbon disulfide at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.

wB97XD/6-31+G(d,p) level of theory. The intramolecular rearrangement of $\mathbf{1-CO_2}$ to the four-membered $\mathbf{2-CO_2}$ via $\mathbf{TS2-CO_2}$ needs an energy barrier of $\Delta G = 8.5$ kcal mol^{-1}. In this case, the formation of $\mathbf{2-CO_2}$ is strongly exergonic by $\Delta G^{\neq} = -27.4$ kcal mol^{-1}. Then two competitive pathways can be considered for the liberation of CO: the reaction may proceed either in a concerted fashion or stepwise. The concerted manner for the rearrangement of $\mathbf{2-CO_2}$ via $\mathbf{TS3-CO_2}$ can complete the reduction step of CO$_2$ to CO and formation of silaaldehyde $\mathbf{3-CO_2}$ by the calculated energy barrier of $\Delta G^{\neq} = 46.6$ kcal mol^{-1}. Otherwise, the initial energy barrier of the stepwise CO elimination fashion for the formation of $\mathbf{4-CO_2}$ via $\mathbf{TS4-CO_2}$ is determined to be of lower energy than the $\mathbf{TS3-CO_2}$ by $\Delta\Delta G^{\neq} = 10.8$ kcal mol^{-1}. After formation of the rotational isomer $\mathbf{4'-CO_2}$, the energy barrier for $\mathbf{TS5-CO_2}$ is calculated to be $\Delta G^{\neq} = 9.4$ kcal mol^{-1} to yield $\mathbf{5-CO_2}$. The last step is associated with the liberation of CO from $\mathbf{5-CO_2}$ via $\mathbf{TS6-CO_2}$. The predicted energy barrier to arrive at $\mathbf{TS6-CO_2}$ is observed to be very low by $\Delta G^{\neq} = 4.7$ kcal mol^{-1}. The overall pathway for $\mathbf{6-CO_2}+$ CO is slightly exergonic by $\Delta G = -3.9$ kcal mol^{-1}.

In contrast to the proposed mechanism for CO_2, the concerted 1,3-dipolar cycloaddition of CS_2 to **1H** is more likely to appear (Figure 4). The first step of the reaction has a free energy barrier of $\Delta G^{\neq} = 6.3$ kcal mol^{-1} to form the five-membered intermediate of $\mathbf{1-CS_2}$ at the wB97XD/6-31+G(d,p) level of theory. The formation process of $\mathbf{1-CS_2}$ is calculated to be heavily exergonic by $\Delta G = -24.0$ kcal mol^{-1}. The following step can be elimination of CS via $\mathbf{TS2-CS_2}$ or $\mathbf{TS3-CS_2}$ to generate silathioaldehyde $(\mathbf{2-CS_2})$ by $\Delta G^{\neq} = 43.3$ and 36.0 kcal mol^{-1}, respectively. A comparison of the computed energy barriers shows that the reaction can occur via $\mathbf{TS3-CS_2}$ due to the lower energy barrier, so that the overall pathway for $\mathbf{2-CS_2}$ is slightly exergonic by $\Delta G = -1.9$ kcal mol^{-1}.

In order to evaluate the accuracy of the wB97XD/6-31+G(d,p) level of theory, we also employed the CCSD(T)/6-31+G(d,p) and wB97XD/cc-pVTZ levels of theory to the proposed CO_2 and CS_2 systems for comparison, taking account both functional and basis set effects. In the case of CO_2, the use of CCSD(T) functional with 6-31+G(d,p) does not have a significant effect on the energy barriers. The calculations at the wB97XD/cc-pVTZ level show that identical mechanistic scenario is valid for the formation of $\mathbf{2-CO_2}$ via concerted manner rather than stepwise by an energy barrier of $\Delta G^{\neq} = 17.6$ kcal mol^{-1} for $\mathbf{TS2'-CO_2}$ (Figure S1). As for the CS_2 system, the energy barriers for $\mathbf{TS1-CS_2}$ at the levels of theory used herein do not significantly differ. However, on the one hand, the CCSD(T)/6-31+G(d,p) level predicts a lower energy barrier $(\Delta G^{\neq} = 27.3$ kcal mol$^{-1})$; on the other hand, the energy barrier is found to be higher $(\Delta G^{\neq} = 37.9$ kcal mol$^{-1})$ at the wB97XD/cc-pVTZ level for $\mathbf{TS3-CS_2}$ as compared to the wB97XD/6-31+G(d,p) level $(\Delta G^{\neq} = 36.0$ kcal mol$^{-1})$.

2.3. Activation of hydrogen (H_2)

Learning from the preceding theoretical and experimental studies, the interaction of the σ-bonding orbitals σ_{H-H} and σ_{C-H} in H_2 and CH_4 with unoccupied orbitals plays significant roles.[46] Considering this phenomenon, the proposed reaction is modeled in a stepwise fashion (Figure 5). The interaction between the unoccupied p orbital of the anionic silicon atom in **1H** and the sigma bonding orbital in H_2 weakens the H–H bond to enable the addition. This first step leads to the formation of hydrogen-bridged species $\mathbf{1-H_2}$ by an initial energy barrier of $\Delta G^{\neq} = 25.4$ kcal mol^{-1} for $\mathbf{TS1-H_2}$. Subsequently, the H^1 can migrate to the anionic silicon atom to yield related product $\mathbf{2-H_2}$ via $\mathbf{TS2-H_2}$ with a very small energy barrier of $\Delta G^{\neq} = 2.7$ kcal mol^{-1}. Overall, the reaction is determined to be strongly exergonic by $\Delta G = -27.8$ kcal mol^{-1}. The proposed energy values can be adequate and could be lower in the experimental with bulky substituents. As can be seen from our earlier results, the reaction of $Tip_2Si=SiTipLi$ (Tip = 2,4,6-triisopropylphenyl) with CO indeed proceeds smoothly at room temperature although some of the proposed barriers are too high with up to 30.5 kcal mol^{-1}.[28] Consequently, the DFT calculations depict the possibility of H_2 activation by **1H** from the obtained energy profile. In general, the energy barriers at the wB97XD/6-31+G(d,p) level of theory are anticipated to be very similar to the calculations at the wB97XD/cc-pVTZ level of theory. The only significant difference was found in the energy barrier of $\mathbf{TS1-H_2}$ $(\Delta G^{\neq} = 34.6$ kcal mol$^{-1})$ at the CCSD(T)/6-31+G(d,p) level of theory as compared to the observed value $(\Delta G^{\neq} = 25.4$ kcal mol$^{-1})$ at the wB97XD/6-31+G(d,p) level of theory.
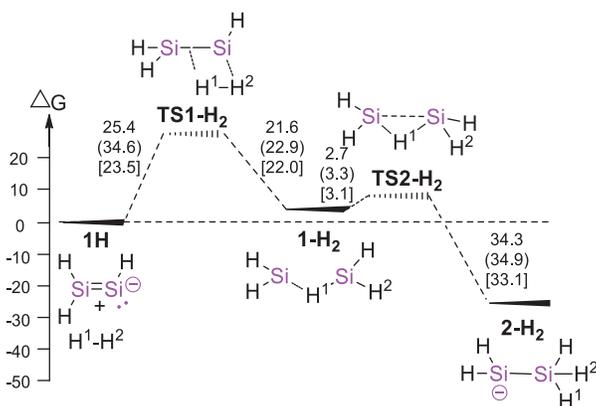
Figure 5. The stepwise proposed reaction path for activation of hydrogen at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.

2.4. Activation of methane (CH_4)

In a similar fashion to H_2 activation, we have proposed the possible pathways for the activation of CH_4. The proposed reaction can start by breaking of the C–H bond and subsequent Si–C bond formation in the H bridged intermediate of $1-CH_4$ via $TS1-CH_4$ (Figure 6). The required energy barrier for this step is too high for a reaction considered at room temperature by $\Delta G^{\neq} = 45.6$ kcal mol^{-1} at the wB97XD/6-31+G(d,p) level of theory. Moreover, the intermediate of $1-CH_4$ is found to be thermodynamically very unstable, lying $\Delta G = 15.6$ kcal mol^{-1} higher in free energy than the reactants. The relatively easy intramolecular rearrangement of $1-CH_4$ implies that two competitive pathways are operative to form the thermodynamic and kinetic final potential products of $2-CH_4$ and $2'-CH_4$ via $TS2-CH_4$ and $TS2'-CH_4$, respectively. The calculated energy barriers are predicted to be $\Delta G\text{Å}^{\neq} = 3.6$ and 2.4 kcal mol^{-1} for $TS2-CH_4$ and $TS2'-CH_4$, respectively. The overall pathways for $2-CH_4$ and $2'-CH_4$ are calculated to be exergonic by $\Delta G = -19.2$
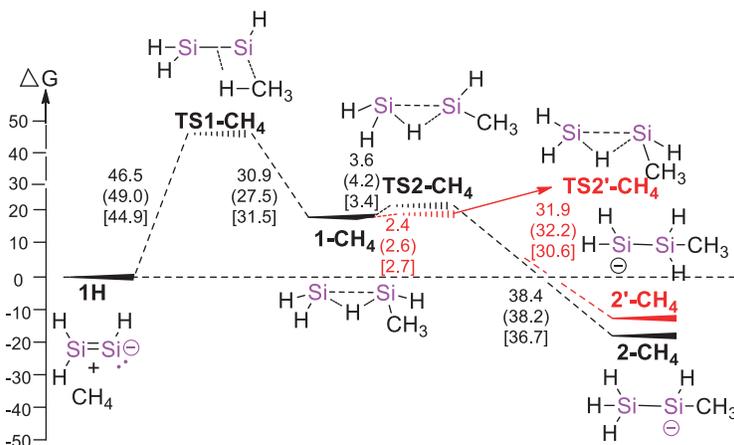

Figure 6. The proposed reaction path for activation of methane at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.

kcal mol^{-1} and -13.9 kcal mol^{-1}, respectively. Additionally, the influence of the basis set and functional on the calculated thermodynamic parameters does not lead to major differences.

2.5. Activation of nitrogen (N_2)

N_2 activation is a problematic task in chemistry. The extremely strong N–N triple bond causes difficulty in converting N_2 to useful chemical feedstocks due to the very strong bonding energy. The first metal-catalyzed dinitrogen activation with $[Ru-(NH_3)_5(N_2)]^{2+}$ was reported by Allen and Senoff in 1965.[47] Inspired by this, the activation of N_2 with transition-metal complexes has been widely investigated.[48−51] The activation and conversion of N_2 to ammonia from the active center of nitrogenase enzyme (which contains Fe and Mo) under ambient conditions has been studied several times.[52−54] To the best of our knowledge, the only report on the activation of N_2 by a main group compound under metal-free conditions was published very recently by Braunschweig et al.[55]

In this regard, we proposed the possible reaction of N_2 with **1H** in Figure 7. The first step involves the interaction of N_2 with the anionic center of disilenide via **TS1−N$_2$** to generate **1−N$_2$** by the required activation energy $\Delta G^{\neq} = 23.6$ kcal mol^{-1} at the wB97XD/6-31+G(d,p) level of theory (Figure 7). The calculations predict that the energy profile of **1−N$_2$** does not show thermodynamic stability. Afterward, the intermediate **1−N$_2$** undergoes a cyclization step to yield possible [2+2] cycloaddition product **2−N$_2$** via **TS2−N$_2$** by an energy barrier of $\Delta G^{\neq} = 20.3$ kcal mol^{-1}. The overall energy for the formation of **2−N$_2$** is calculated to be $\Delta G = 33.6$ kcal mol^{-1}, indicating that the reaction is strongly endergonic and cannot occur spontaneously. Therefore, the calculations suggest that N_2 activation by 1H is not operative under mild conditions. The use of a different basis set and functional for the proposed mechanism does not play any obvious role in the kinetics of the reaction.
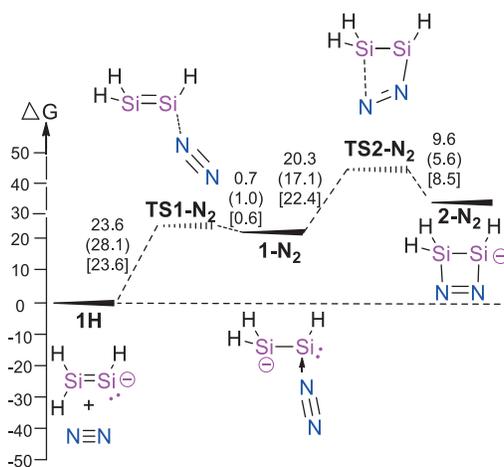

Figure 7. The proposed reaction path for activation of nitrogen at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.

2.6. Activation of nitrous oxide (N_2O)

N_2O has had a remarkable history since its first discovery in 1772.[56] The reactions in the presence of N_2O generally take place via oxygen atom transfer and liberation of N_2. However, N_2O has a very strong inert

character, resulting in difficulties for its activation under mild conditions. A predominant study for N_2O activation was described by West and coworkers.[57] In a very recent study, we proposed several pathways for the activation of N_2O by silagermenylidene and the concerted 1,3-dipolar cycloaddition fashion is determined to be more operative than others.[58,59]

Inspired by this, the concerted 1,3-dipolar cycloaddition mechanism via **TS1−N₂O** and its vice versa fashion (**TS1′−N₂O**) were considered in this part due to lower energy barriers (Figure 8). The activation energy barriers are found to be almost identical for **TS1−N₂O** ($\Delta G^{\neq} = 9.8$ kcal mol^{-1}) and **TS1′−N₂O** ($\Delta G^{\neq} = 9.9$ kcal mol^{-1}), and closely resemble the calculated initial energy barrier for the CO activation process ($\Delta G^{\neq} = 9.4$ kcal mol^{-1}).[28,29] In contrast to the dramatic differences in the mechanistic scenarios, however, the same product distribution is operative in both cases. The first intermediate **1−N₂O** via **TS1−N2O** is determined to be highly exergonic by $\Delta G = -43.1$ kcal mol^{-1} (Figure 8). After that, the concerted 1,3-dipolar cycloaddition intermediate **1−N₂O** is able to rearrange silaaldehyde **3−N₂O** via a ring-opening step and simultaneous N_2 elimination. The energy barrier for this step is very small by $\Delta G^{\neq} = 3.3$ kcal mol^{-1}. Alternatively, the reaction between **1H** and **N₂O** can occur via intermediacy of **2−N₂O**, by passing **TS1′−N₂O**. Subsequently, N_2 elimination and H migration in **2−N₂O** can generate the final product of **3−N₂O** via **TS3−N₂O** ($\Delta G^{\neq} = 4.2$ kcal mol^{-1}). The overall pathway for the formation of **3−N₂O** is determined to be strongly exergonic by $\Delta G = -95.8$ kcal mol^{-1}. It can be concluded that the concerted 1,3-dipolar cycloaddition reactions are operative for the oxidation of **1H** by N_2O under ambient conditions. Only minor differences are observed for the energetic of the proposed mechanisms by employing the CCSD(T) functional and cc-pVTZ basis set as compared to the wB97XD/6-31+G(d,p) level of theory.
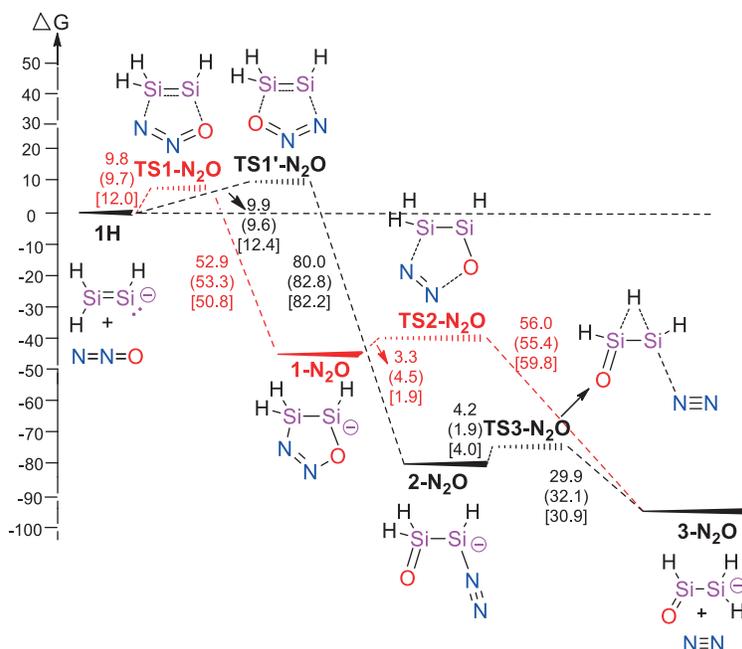

Figure 8. The proposed reaction path for activation of nitrous oxide at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.

2.7. Conclusion

Collectively, we have distilled a general message about the ability of **1H** in the processes of small molecule activations (NH_3, CO_2, CS_2, H_2, CH_4, N_2, and N_2O). A variety of possible product formations were reported herein. The selected energies for the proposed pathways are given in Figure 9. The only endergonic process among them is observed for N_2 activation. In the case of CO_2 and CS_2, the favorable mechanisms are predicted to have slightly exergonic natures by $\Delta G^{\neq} = -3.9$ and -1.9 kcal mol^{-1}, respectively. On the other hand, the highest exergonic pathway is determined to be $\Delta G = -95.8$ kcal mol^{-1} for the N_2O case. Depending on the theoretical findings, hence, we can suggest that the structure **1H** is a suitable precursor for activation of small molecules under metal-free conditions. We strongly believe that all the findings will prompt chemists to undertake further investigations on this fascinating topic.
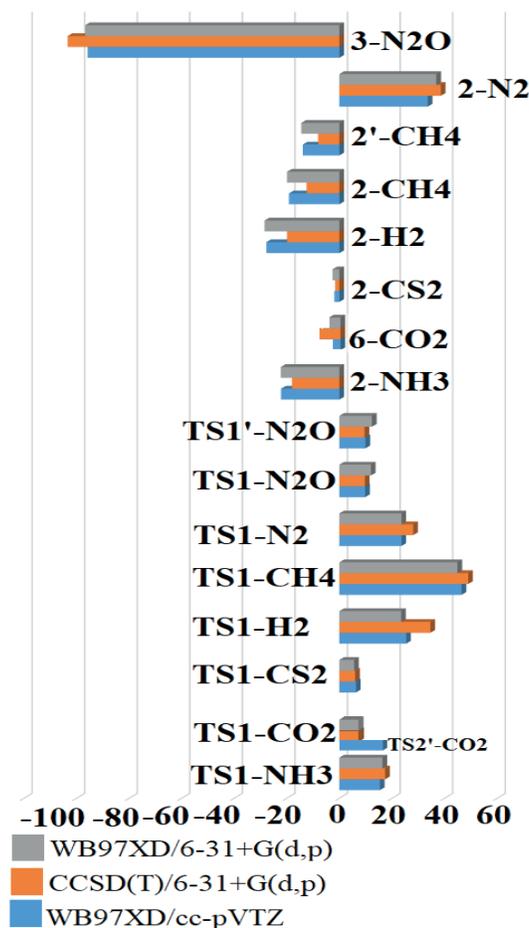

Figure 9. Graphical visualization of the initial energy barriers for activation of the small molecules by 1H and the overall energy changes of possible products at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p), and wB97XD/cc-pVTZ levels.

3. Experimental

The Gaussian 16 program was used for all the calculations in this study.[60] To optimize the title structures, the wB97XD theory was chosen with the 6-31+G(d,p) basis set due to the inclusion of long-range corrected

hybrid and dispersion correction functions.[61−64] To compare the accuracy of energy results, we also applied the CCSD(T) functional to the optimized structures using the same basis set of 6-31+G(d,p). Additionally, all the proposed systems were reoptimized at the wB97XD/cc-pVTZ level of theory to evaluate effect of the basis set on the free energies.[65,66] Natural bond order analysis was used to estimate atomic charges and hybridizations of the structures at the wB97XD/6-31+G(d,p) level of theory.[67−69] All the relative energies reported here are Gibbs free energies in kcal mol^{-1}. In order to verify the proposed pathways, the intrinsic reaction coordinate (IRC) method was employed to each transition state (see Supplementary Information Figure S6−S20).[70] All the visualizations of the title structures were performed by the GaussView 5.0 program.[71]

Acknowledgment

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Figure S1. The proposed concerted pathway for the formation of **2-CO$_2$** at the wB97XD/cc-pVTZ level of theory. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.
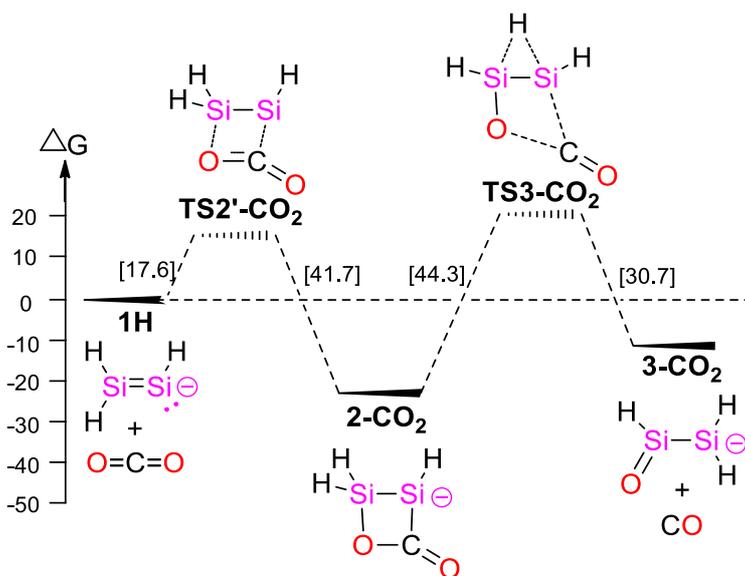

Figure S2. The proposed reaction path for activation of carbon dioxide at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.


1
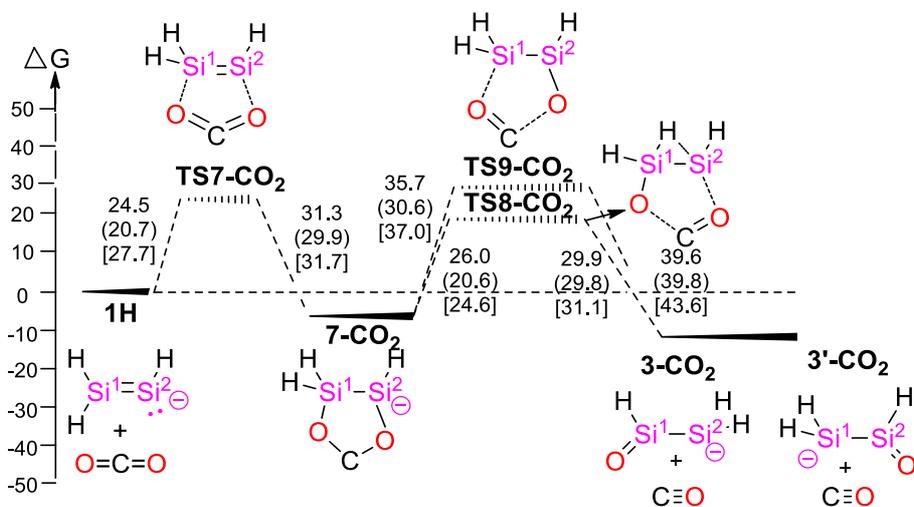
Figure S3. The proposed reaction path for activation of carbon dioxide at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.
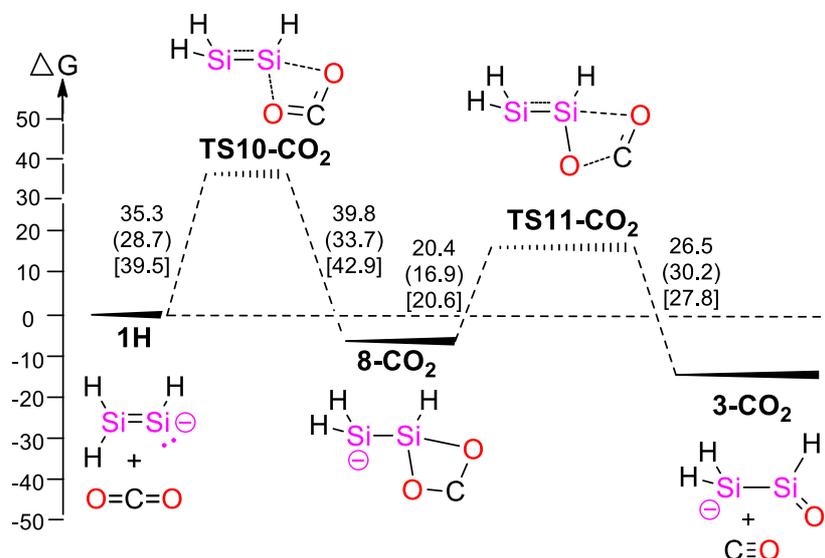
Figure S4. The proposed reaction path for activation of carbon disulfide at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.


2
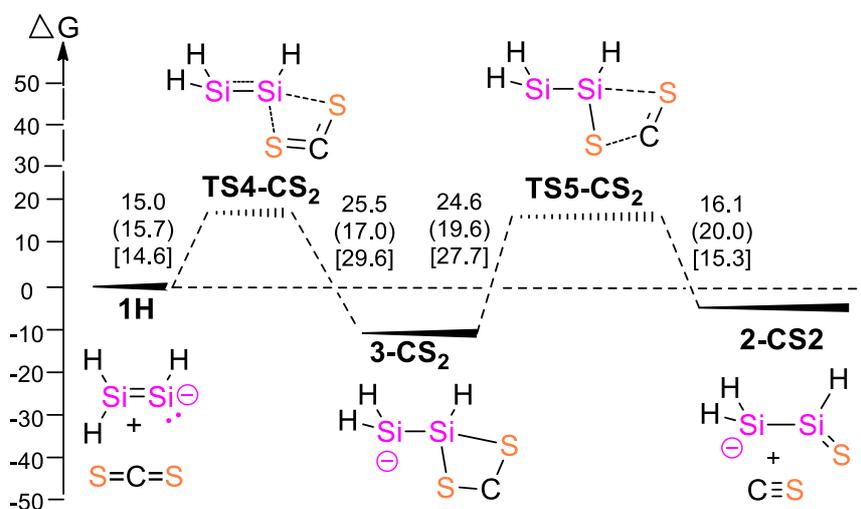
Figure S5. The proposed reaction path for activation of carbon disulfide at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.
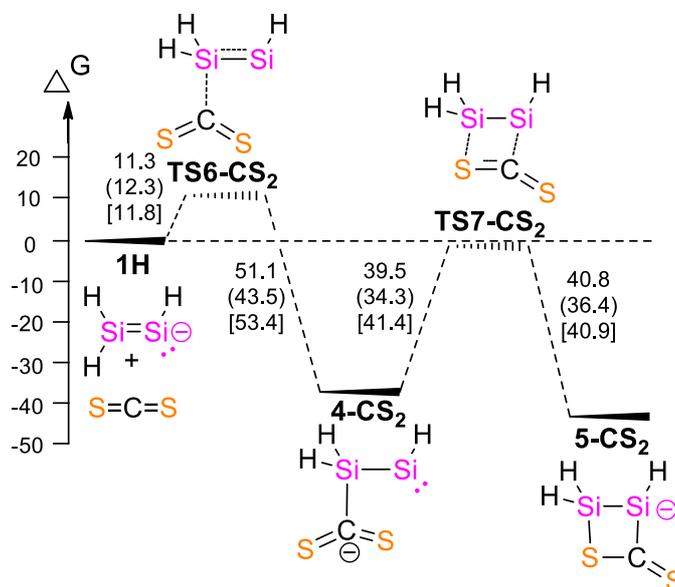

Figure S6. The IRC plot of **TS1-NH$_3$** at the wB97XD/6-31+G(d,p) level of theory.
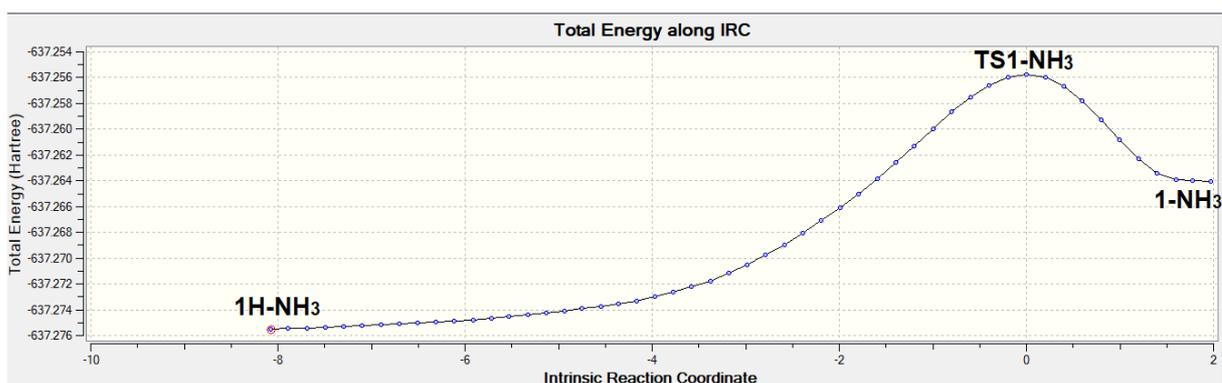
Figure S7. The IRC plot of **TS3-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.
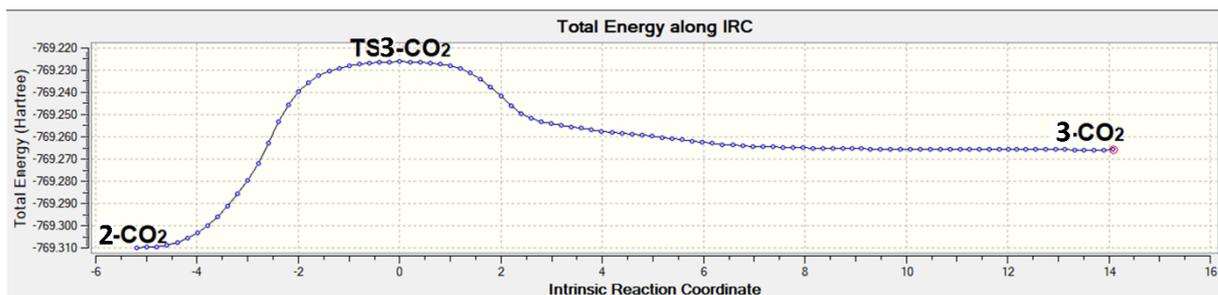
Figure S8. The IRC plot of **TS7-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.
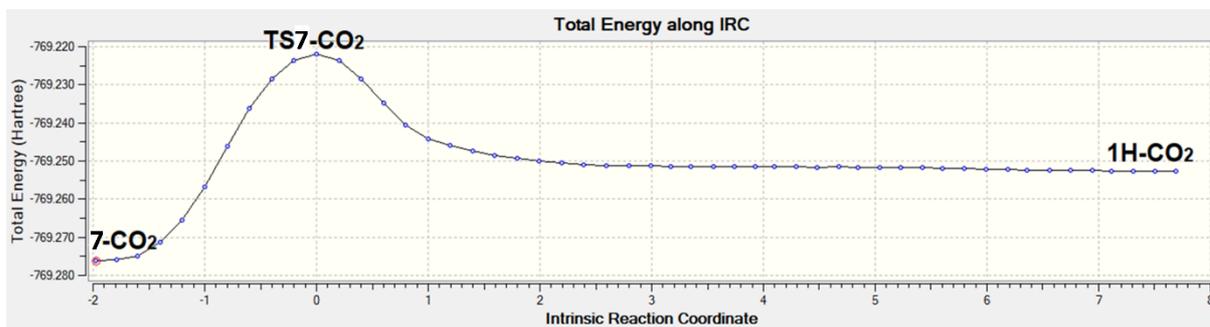
Figure S9. The IRC plot of **TS8-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.
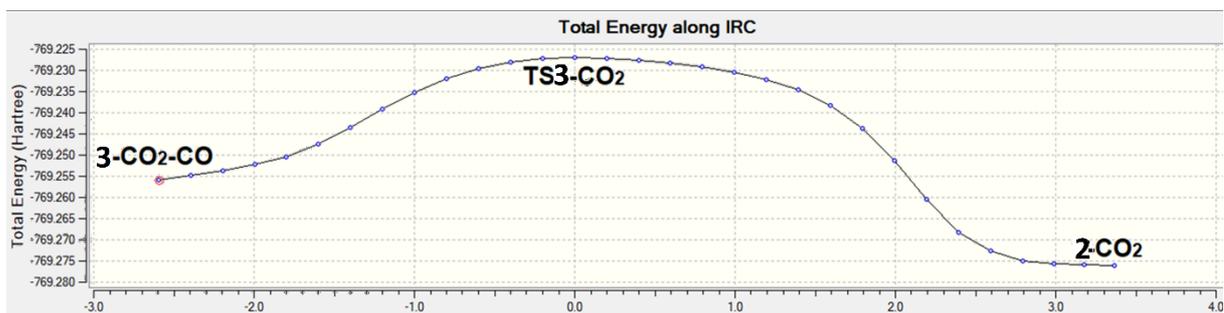
Figure S10. The IRC plot of **TS9-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.
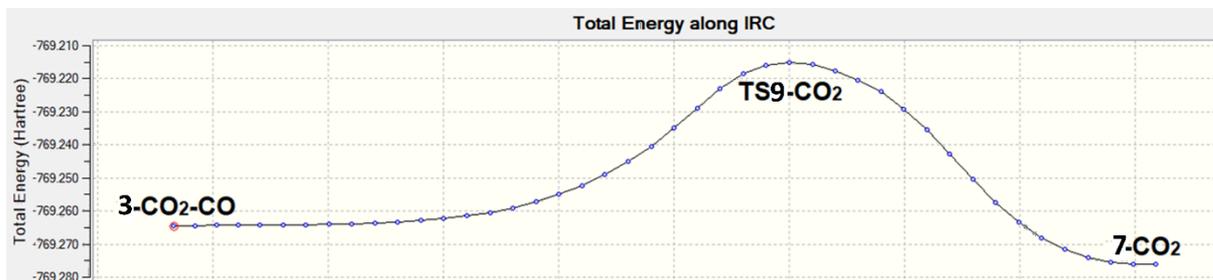
Figure S11. The IRC plot of **TS10-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.
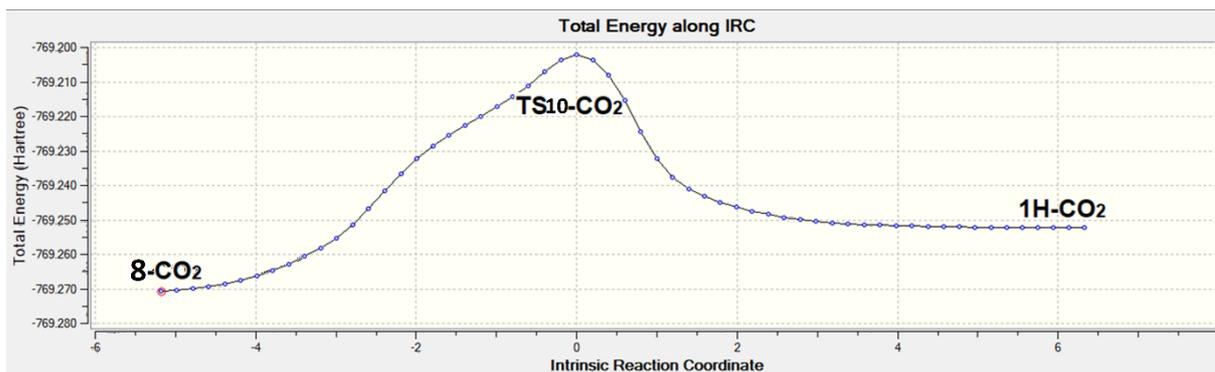
Figure S12. The IRC plot of **TS11-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.
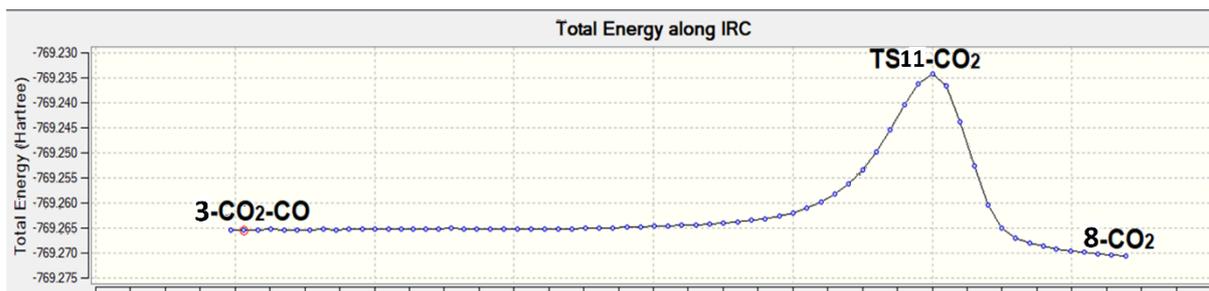
Figure S13. The IRC plot of **TS4-CS$_2$** at the wB97XD/6-31+G(d,p) level of theory.
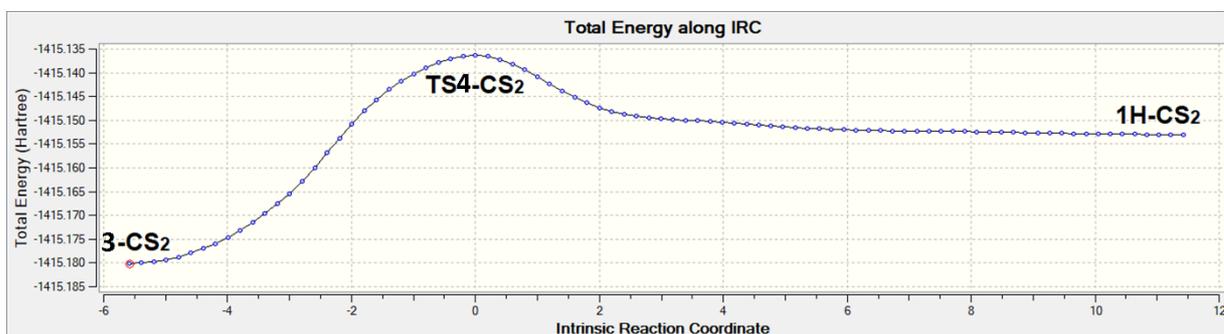
Figure S14. The IRC plot of **TS2-CS$_2$** at the wB97XD/6-31+G(d,p) level of theory.
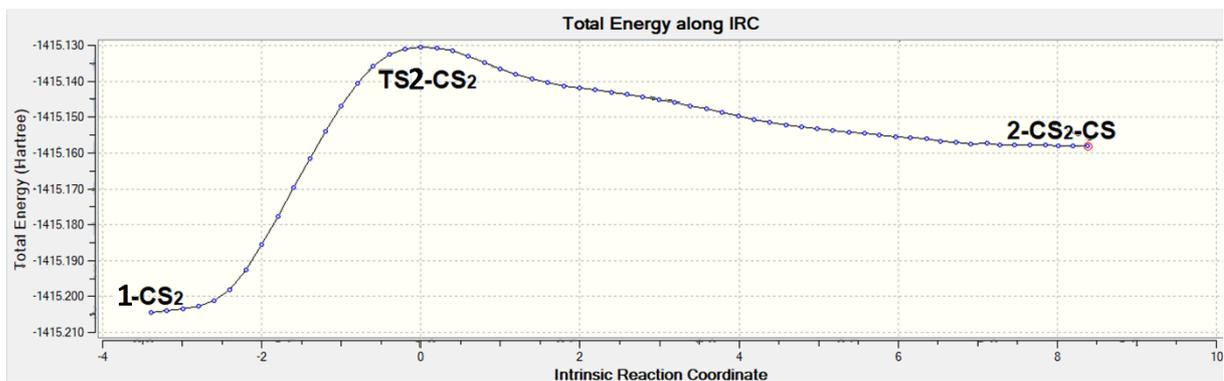
Figure S15. The IRC plot of **TS3-CS₂** at the wB97XD/6-31+G(d,p) level of theory.
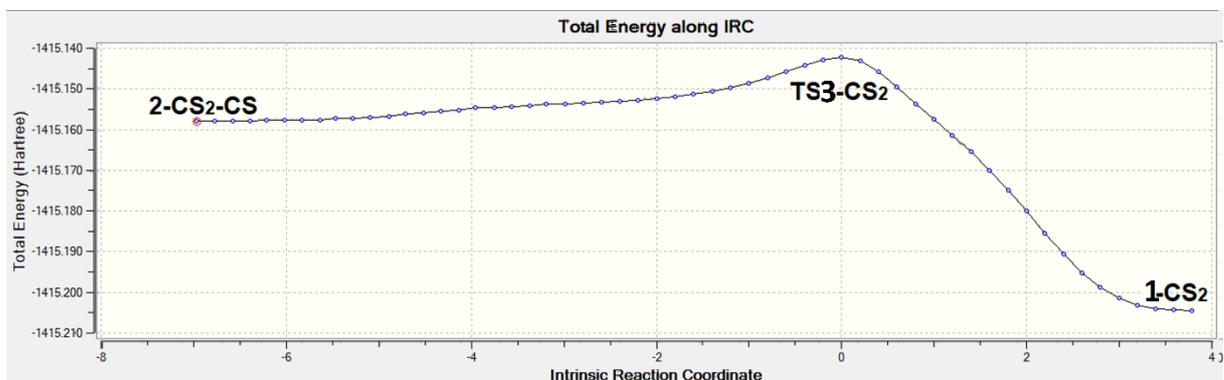
Figure S16. The IRC plot of **TS1-CS₂** at the wB97XD/6-31+G(d,p) level of theory.
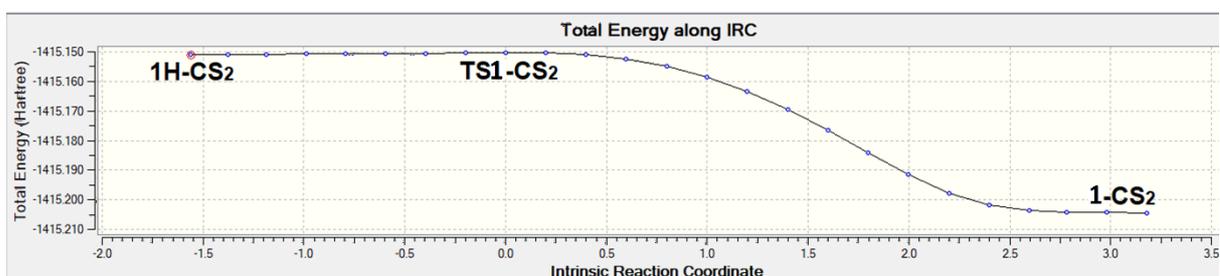
Figure S17. The IRC plot of **TS1-H₂** at the wB97XD/6-31+G(d,p) level of theory.
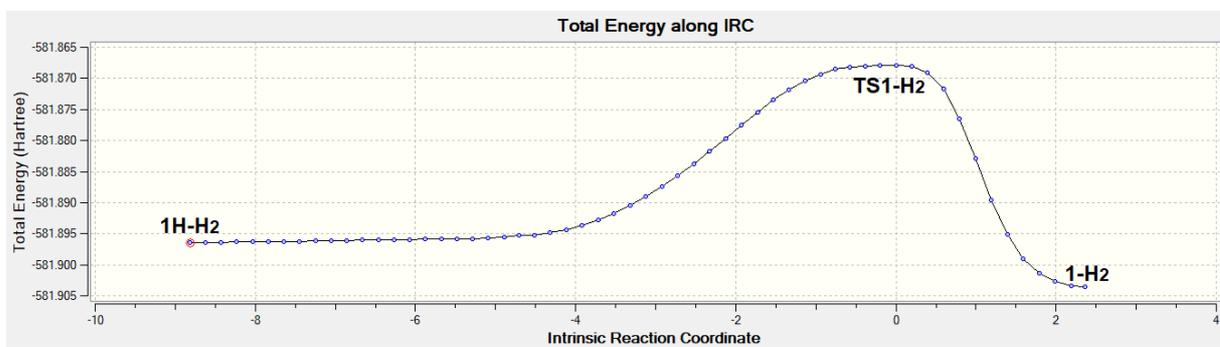

Figure S18. The IRC plot of **TS2-CH₄** at the wB97XD/6-31+G(d,p) level of theory.
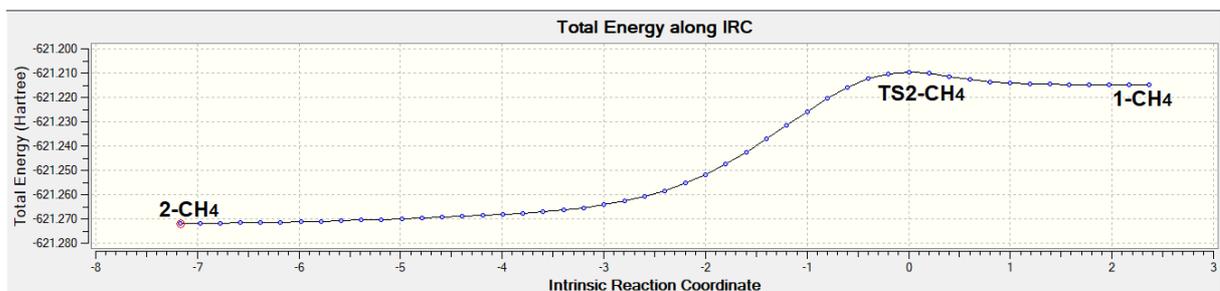
Figure S19. The IRC plot of **TS2'-CH₄** at the wB97XD/6-31+G(d,p) level of theory.
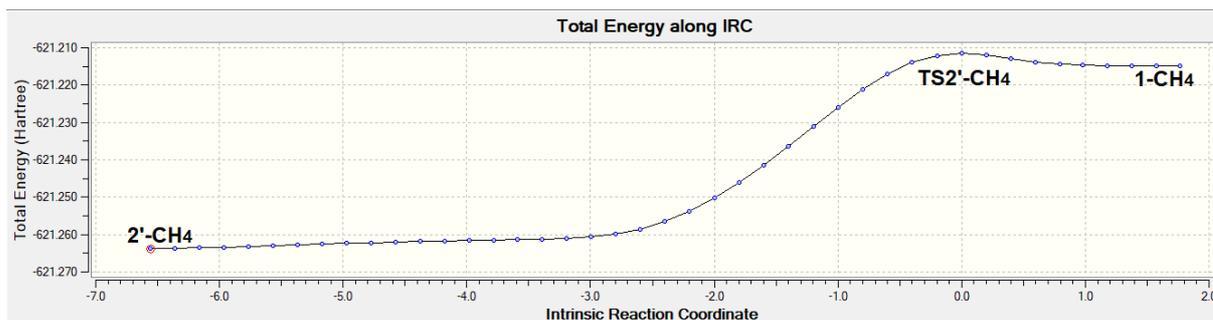
Figure S20. The IRC plot of **TS2-N₂O** at the wB97XD/6-31+G(d,p) level of theory.
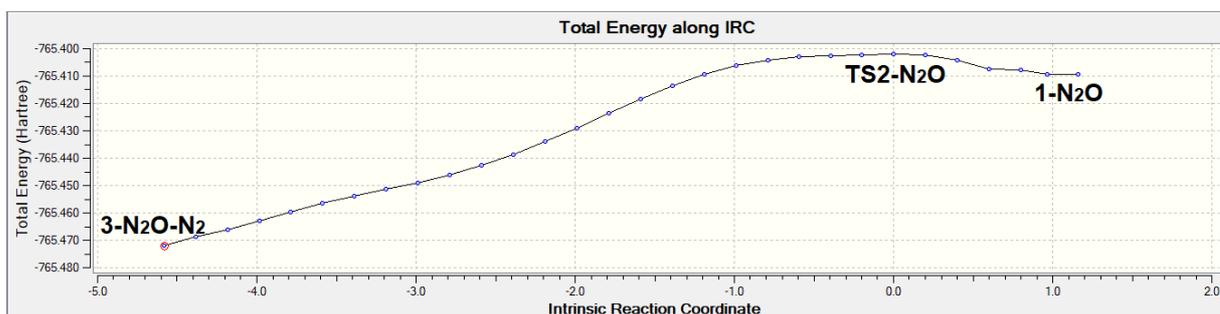

Figure S21. The proposed reaction path for activation of nitrous oxide at the wB97XD/6-31+G(d,p), CCSD(T)/6-31+G(d,p) (in parentheses), and wB97XD/cc-pVTZ (in square brackets) levels. The figure is prepared considering energies at the wB97XD/6-31+G(d,p) level. ΔG energies are given in kcal mol^{-1}. Energies given in the figure correspond to the activation energy barriers for the forward and reverse reactions.
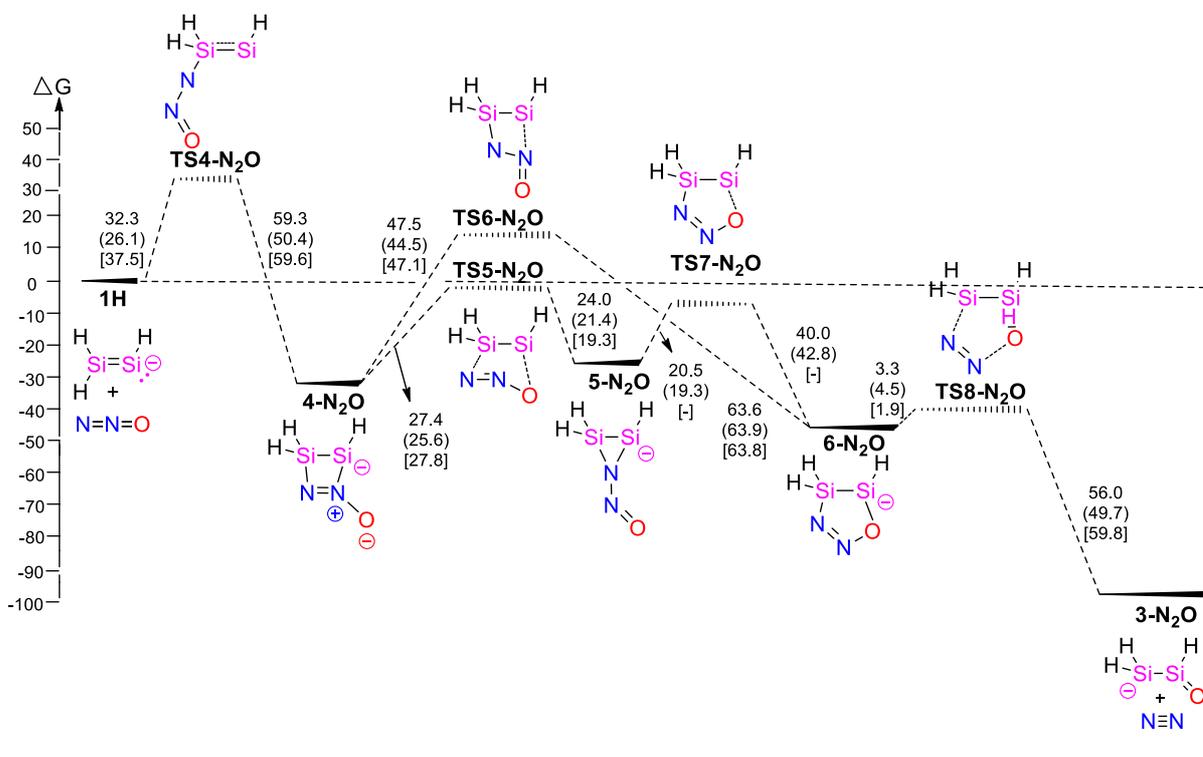
Table S1. Cartesian coordinates and energies of **1H** at the wB97XD/6-31+G(d,p) level of theory.

Si,1.1817593688,–0.1034233581,–0.0000217623
Si,–1.0061145393,–0.0016839959,–0.0001300314
H,–1.9166448894,–1.2010152858,0.0005130286
H,–1.9232598848,1.1948245723,–0.0001995603
H,1.2789469446,1.4333680675,0.0005613255

Zero-point correction=   0.022104 (Hartree/Particle)
 Thermal correction to energy=   0.026164
 Thermal correction to enthalpy=   0.027108
 Thermal correction to Gibbs free energy=   –0.003206
 Sum of electronic and zero-point energies=   –580.697055
 Sum of electronic and thermal energies=   –580.692996
 Sum of electronic and thermal enthalpies=   –580.692052
 Sum of electronic and thermal free energies=   –580.722366

Table S2. Cartesian coordinates and energies of **1-NH$_3$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.569424931,0.2758462159,–0.0341618174
Si,0.5278534613,–0.8591769966,–0.0940944537
H,0.7075090891,–0.9565601711,1.4322657402
H,–2.3644429778,–0.2697889562,–1.2177512433
H,–2.3586011688,–0.3975250865,1.086044598
H,0.6453932213,1.6560924899,0.2686386947
N,1.443372927,1.0455098701,0.0395237738
H,2.1720909946,1.1013543336,0.7456017914
H,1.8216343842,1.3268863009,–0.8588940838

Zero-point correction=   0.061573 (Hartree/Particle)
 Thermal correction to energy=   0.067955
 Thermal correction to enthalpy=   0.068899
 Thermal correction to Gibbs free energy=   0.032285
 Sum of electronic and zero-point energies=   –637.202528
 Sum of electronic and thermal energies=   –637.196146
 Sum of electronic and thermal enthalpies=   –637.195202
 Sum of electronic and thermal free energies=   –637.231816

Table S3. Cartesian coordinates and energies of **TS1-NH₃** at the wB97XD/6-31+G(d,p) level of theory.

Si,1.6049809268,0.1263221583,–0.0215020307
Si,–0.2271477663,1.4563715076,–0.2609555547
H,–0.5653502102,1.5382559307,1.23558574
H,2.6170311519,0.3200307387,–1.1260872739
 H,2.4128998014,0.2585130212,1.2508949505
H,–0.7882111375,–1.2266831021,0.08394336
N,–1.7346634482,–0.8477202111,0.0332518332
H,–2.2711898297,–1.1208557113,0.849872038
H,–2.1879451883,–1.177044882,–0.8115260624

Zero-point correction=   0.058777 (Hartree/Particle)
 Thermal correction to energy=   0.065667
 Thermal correction to enthalpy=   0.066611
 Thermal correction to Gibbs free energy=   0.028342
 Sum of electronic and zero-point energies=   –637.196990
 Sum of electronic and thermal energies=   –637.190101
 Sum of electronic and thermal enthalpies=   –637.189157
 Sum of electronic and thermal free energies=   –637.227426

Table S4. Cartesian coordinates and energies of **2-NH₃** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.4131081989,0.2368362222,0.1351619597
Si,0.7559424492,–0.7424622221,0.0148460406
H,0.8630287427,–0.7902694202,1.5619200538
H,–2.0693568266,0.5205431201,–1.1945303598
H,–2.4252731029,–0.6537373817,0.819699489
H,–1.5927848216,1.5558597543,0.8617030336
N,1.6999906092,0.7804521628,–0.3740588855
H,1.77072179,1.5063673582,0.3295356707
H,2.6162243588,0.6090484064,–0.7671040022

Zero-point correction=   0.057415 (Hartree/Particle)
 Thermal correction to energy=   0.063701
 Thermal correction to enthalpy=   0.064646
 Thermal correction to Gibbs free energy=   0.028398
 Sum of electronic and zero-point energies=   –637.258179
 Sum of electronic and thermal energies=   –637.251893
 Sum of electronic and thermal enthalpies=   –637.250949
 Sum of electronic and thermal free energies=   –637.287196

Table S5. Cartesian coordinates and energies of **TS2-NH₃** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.398235164,0.2116750493,0.007787681
Si,0.7348592852,–0.8848805898,–0.1194891667
H,0.8492725692,–1.0748466913,1.4029716161
H,–2.3098959912,0.0176602279,–1.1912747148
H,–2.3353803686,–0.155314,1.1469684641
H,0.0072029094,1.3658754474,0.0531991941
N,1.3202557345,1.0097809266,0.0113697447
H,1.8500566001,1.2392942386,0.8504445385
H,1.8458274254,1.3326113914,–0.7977293571

Zero-point correction=   0.055165 (Hartree/Particle)
 Thermal correction to energy=   0.060757
 Thermal correction to enthalpy=   0.061701
 Thermal correction to Gibbs free energy= 0.026974
 Sum of electronic and zero-point energies=   –637.190195
 Sum of electronic and thermal energies=   –637.184603
 Sum of electronic and thermal enthalpies=   –637.183659
 Sum of electronic and thermal free energies=   –637.218386

Table S6. Cartesian coordinates and energies of **1-CO₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.7027780164,–0.9897453951,–0.2397013349
Si,–0.5513078895,0.9642224583,0.1459239777
O,1.7897333849,0.1737129162,–1.1324556642
C,1.3153704916,0.0979203758,0.0056657706
O,1.7008102293,–0.3710745953,1.0820122609
H,–0.7086684963,2.0198892414,–0.9018443117
H,–0.7181604415,1.6360704678,1.4723413658
H,–1.6519532622,–1.3715934691,1.2389669358

Zero-point correction=   0.035167 (Hartree/Particle)
 Thermal correction to energy=   0.042350
 Thermal correction to enthalpy=   0.043294
 Thermal correction to Gibbs free energy= 0.002803
 Sum of electronic and zero-point energies=   –769.217044
 Sum of electronic and thermal energies=   –769.209861
 Sum of electronic and thermal enthalpies=   –769.208916
 Sum of electronic and thermal free energies=   –769.249407

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Table S7. Cartesian coordinates and energies of **TS1-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.5327832547,–0.9555458605,–0.2400601189
Si,–0.8582284824,1.115365699,0.1293670985
O,1.7973315818,0.0065690792,–1.1372930927
C,1.4589311292,–0.1781248985,–0.00696111
O,1.6923406206,–0.5260210183,1.1112798442
H,–0.6286075667,2.1319897271,–0.9463079593
H,–0.7647606662,1.849595713,1.4340561874
H,–1.6003933617,–1.1966254412,1.2727741507

Zero-point correction=   0.034145 (Hartree/Particle)
 Thermal correction to energy=   0.041155
 Thermal correction to enthalpy=   0.042100
 Thermal correction to Gibbs free energy=   0.002159
 Sum of electronic and zero-point energies=   –769.214063
 Sum of electronic and thermal energies=   –769.207053
 Sum of electronic and thermal enthalpies=   –769.206109
 Sum of electronic and thermal free energies=   –769.246049

Table S8. Cartesian coordinates and energies of **2-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.9212746059,–1.1051672883,–0.2656168123
Si,–0.7563706964,1.1873150182,0.2442610641
O,0.952707167,0.893007367,0.0953598222
C,0.9731418561,–0.4892318174,–0.0283302184
O,2.0341441427,–1.0762005627,–0.0159046423
H,–1.0814079971,2.2929825639,–0.7224848795
H,–0.9824626295,1.8339983367,1.5839833936
H,–1.0633592369,–1.5544916174,1.1895292725

Zero-point correction=   0.037843 (Hartree/Particle)
 Thermal correction to energy=   0.043658
 Thermal correction to enthalpy=   0.044602
 Thermal correction to Gibbs free energy=   0.008173
 Sum of electronic and zero-point energies=   –769.272115
 Sum of electronic and thermal energies=   –769.266300
 Sum of electronic and thermal enthalpies=   –769.265355
 Sum of electronic and thermal free energies=   –769.301785

Table S9. Cartesian coordinates and energies of **TS2-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.9168974574,1.2124843043,-0.3805609401
Si,0.9836422147,-0.9057157253,0.3022476857
O,−1.1893155937,-0.9040192462,-0.902935822
C,−1.0130648626,0.0032917533,-0.0539078535
O,−1.7494215045,0.5700518843,0.7446465257
H,1.12692713,−2.1758006892,-0.467656152
H,0.9086538798,−1.3384097134,1.7363136745
H,0.9862012791,1.6412644323,1.0839418816

Zero-point correction=   0.035180 (Hartree/Particle)
 Thermal correction to energy=   0.041447
 Thermal correction to enthalpy=   0.042391
 Thermal correction to Gibbs free energy=   0.004886
 Sum of electronic and zero-point energies=   −769.205511
 Sum of electronic and thermal energies=   −769.199244
 Sum of electronic and thermal enthalpies=   −769.198300
 Sum of electronic and thermal free energies=   −769.235805

Table S10. Cartesian coordinates and energies of **TS3-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,−1.6607574118,−1.1601326097,−0.1656391973
Si,−0.761024242,1.0383122613,0.0199449783
O,0.744765141,1.2328878586,−0.445159164
C,1.7177149477,−0.8029743309,0.3264563687
O,2.8342523712,−0.700820431,0.0924131797
H,−1.8732273755,1.6477155868,−0.8540632781
H,−1.1196716315,1.6060043693,1.3828799037
H,−2.607126799,−1.0330847044,1.0432782089

Zero-point correction=   0.032040 (Hartree/Particle)
 Thermal correction to energy=   0.039852
 Thermal correction to enthalpy=   0.040796
 Thermal correction to Gibbs free energy=   −0.001303
 Sum of electronic and zero-point energies=   −769.194115
 Sum of electronic and thermal energies=   −769.186303
 Sum of electronic and thermal enthalpies=   −769.185359
 Sum of electronic and thermal free energies=   −769.227458

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Table S11. Cartesian coordinates and energies of **TS4-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.8619603646,1.6215659084,–0.1415971628
Si,1.8045457066,–0.8170002889,–0.0409186088
O,–0.0193629312,–1.241496854,0.0462299206
C,–0.8059050187,–0.2351413125,0.0192750203
O,–2.05926095,–0.2601042094,0.1051480126
H,2.0997974241,–1.8560553011,–1.1253969196
H,2.1754703148,–1.7409342611,1.1207756517
H,–0.743273991,1.8269194786,1.3698235161

Zero-point correction=   0.035819 (Hartree/Particle)
 Thermal correction to energy=   0.041882
 Thermal correction to enthalpy=   0.042827
 Thermal correction to Gibbs free energy=   0.005382
 Sum of electronic and zero-point energies=   –769.214305
 Sum of electronic and thermal energies=   –769.208242
 Sum of electronic and thermal enthalpies=   –769.207298
 Sum of electronic and thermal free energies=   –769.244742

Table S12. Cartesian coordinates and energies of **4-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,2.2548339061,–0.8953470521,–0.2652504079
Si,–1.8089719168,–0.5265909318,–0.1911882987
O,–0.3651747818,0.7068116325,–0.1400409552
C,0.8296087851,0.303503033,–0.16421876
O,1.8576101818,1.0621914015,–0.1165849743
H,–2.5117694541,0.2619636222,–1.3028975586
H,–2.5452922789,0.2165007775,0.9292482731
H,2.2891565586,–1.1290314829,1.2509326817

Zero-point correction=   0.036049 (Hartree/Particle)
 Thermal correction to energy=   0.042827
 Thermal correction to enthalpy=   0.043771
 Thermal correction to Gibbs free energy=   0.004228
 Sum of electronic and zero-point energies=   –769.215969
 Sum of electronic and thermal energies=   –769.209191
 Sum of electronic and thermal enthalpies=   –769.208247
 Sum of electronic and thermal free energies=   –769.247789

Table S13. Cartesian coordinates and energies of **4'-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,2.5006676865,–0.099097424,–0.2512042282
Si,–2.2279697242,–0.3522449404,–0.2254775973
O,–0.4271422102,–1.0016687124,–0.3317642369
C,0.6508370285,–0.3554463051,–0.2436965757
O,0.8110674359,0.8993065304,–0.058488033
H,–1.9836713921,0.8274711622,–1.172632425
H,–1.9794885333,0.4817289221,1.0356464053
H,2.6556997089,–0.4000492328,1.2476156908

Zero-point correction=   0.035992 (Hartree/Particle)
 Thermal correction to energy=   0.042736
 Thermal correction to enthalpy=   0.043680
 Thermal correction to Gibbs free energy=   0.004724
 Sum of electronic and zero-point energies=   –769.212224
 Sum of electronic and thermal energies=   –769.205480
 Sum of electronic and thermal enthalpies=   –769.204536
 Sum of electronic and thermal free energies=   –769.243492

Table S14. Cartesian coordinates and energies of **TS5-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,2.2518442354,–0.5243419745,–0.0497859816
Si,–2.2509835715,–0.2104137803,–0.0848636855
O,–0.3785409594,–0.4531260535,–0.0910857111
C,0.5871857931,0.4269232676,–0.0770681281
O,0.5094675142,1.64835377,–0.091102139
H,–2.2781153152,0.8517602004,–1.1908529245
H,–2.2710171307,0.82144636,1.0499961824
H,2.2944005041,–0.5688578797,1.4758534674

Zero-point correction=   0.034688 (Hartree/Particle)
 Thermal correction to energy=   0.041222
 Thermal correction to enthalpy=   0.042166
 Thermal correction to Gibbs free energy=   0.003356
 Sum of electronic and zero-point energies=   –769.197052
 Sum of electronic and thermal energies=   –769.190517
 Sum of electronic and thermal enthalpies=   –769.189573
 Sum of electronic and thermal free energies=   –769.228383

Table S15. Cartesian coordinates and energies of **5-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,1.2684029059,–1.3419220824,–0.0033804785
Si,–2.0814610531,0.1498577289,0.0268401604
O,–0.2263423238,–0.1363866763,–0.3519804633
C,0.9539546543,0.5247781174,–0.0381419384
O,1.1129078899,1.7122591447,0.0429398234
H,–2.1106390633,1.5451220733,–0.5979507626
H,–1.802111261,0.6741429917,1.4401987884
H,1.0297412511,–1.4111802973,1.5090308705

Zero-point correction=   0.035234 (Hartree/Particle)
 Thermal correction to energy=   0.042183
 Thermal correction to enthalpy=   0.043127
 Thermal correction to Gibbs free energy=   0.003252
 Sum of electronic and zero-point energies=   –769.208513
 Sum of electronic and thermal energies=   –769.201564
 Sum of electronic and thermal enthalpies=   –769.200620
 Sum of electronic and thermal free energies=   –769.240495

Table S16. Cartesian coordinates and energies of **TS6-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.9028735706,–0.897099221,–0.6778972352
Si,–2.1538352913,–0.5253224332,0.363375956
O,–0.6516296803,–0.0330710498,–0.5627269164
C,0.7549996812,0.8666128615,0.0268647126
O,0.6228309987,1.9519617299,0.4281195658
H,–2.8446014535,0.8443656114,0.2960159132
H,–1.5682775469,–0.2854303467,1.7688731926
H,1.0102217214,–1.436135502,0.7557794612

Zero-point correction=   0.033731 (Hartree/Particle)
 Thermal correction to energy=   0.040381
 Thermal correction to enthalpy=   0.041325
 Thermal correction to Gibbs free energy=   0.002416
 Sum of electronic and zero-point energies=   –769.201692
 Sum of electronic and thermal energies=   –769.195042
 Sum of electronic and thermal enthalpies=   –769.194098
 Sum of electronic and thermal free energies=   –769.233008

Table S17. Cartesian coordinates and energies of **6-CO₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.9933059445,–1.5224668736,–0.4048617137
Si,–2.0817727181,–0.419842046,–0.5569328115
O,–0.4279097976,–1.0218983889,–0.979365145
H,–2.0085061251,0.8424587867,–1.4365820993
H,–1.6856961043,0.327789606,0.7357178761
H,0.8363704906,–1.2444094443,1.1260100433

Zero-point correction=   0.025116 (Hartree/Particle)
 Thermal correction to energy=   0.030403
 Thermal correction to enthalpy=   0.031347
 Thermal correction to Gibbs free energy=   –0.003135
 Sum of electronic and zero-point energies=   –655.943155
 Sum of electronic and thermal energies=   –655.937869
 Sum of electronic and thermal enthalpies=   –655.936924
 Sum of electronic and thermal free energies=   –655.971407

Table S18. Cartesian coordinates and energies of **7-CO₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.7392466133,0.6320452976,–0.2643039017
H,1.1351233754,1.3345665193,–1.5321580559
H,1.4860087901,1.3881344385,0.7969711499
Si,0.3359809006,–1.6880909781,–0.2328274479
H,0.5868698134,–1.7398391865,1.2814485714
C,–1.8959218603,0.111078842,0.0404631271
O,–1.442485378,–1.0980945564,–0.0483099978
O,–0.9448222545,1.0602006235,–0.0412834451

Zero-point correction=   0.036708 (Hartree/Particle)
 Thermal correction to energy=   0.042540
 Thermal correction to enthalpy=   0.043484
 Thermal correction to Gibbs free energy=   0.007174
 Sum of electronic and zero-point energies=   –769.239474
 Sum of electronic and thermal energies=   –769.233643
 Sum of electronic and thermal enthalpies=   –769.232699
 Sum of electronic and thermal free energies=   –769.269009

Table S19. Cartesian coordinates and energies of **TS7-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.9534913619,1.108104569,–0.0181413834
H,1.0212202945,1.9982793137,–1.2229203246
H,0.9712751899,2.022470228,1.1710263635
Si,1.3013546388,–1.1015851468,–0.097139991
H,1.2385063777,–1.1770660252,1.435269542
C,–1.8302303051,–0.1525404053,0.0199924921
O,–1.3812716603,–1.2617917525,–0.0138025321
O,–1.5638088973,1.0213772191,0.0168798334

Zero-point correction=   0.034012 (Hartree/Particle)
 Thermal correction to energy=   0.040883
 Thermal correction to enthalpy=   0.041828
 Thermal correction to Gibbs free energy=   0.002735
 Sum of electronic and zero-point energies=   –769.187909
 Sum of electronic and thermal energies=   –769.181038
 Sum of electronic and thermal enthalpies=   –769.180093
 Sum of electronic and thermal free energies=   –769.219186

Table S20. Cartesian coordinates and energies of **3-CO$_2$-CO** at the wB97XD/6-31+G(d,p) level of theory.

Si,–2.4766167084,–0.5895573291,–0.1329081295
Si,–0.2818942136,0.0115561482,0.1798756835
O,1.0273031194,–0.192232871,–0.6458652738
C,3.3864747814,0.0788849288,0.4564383413
O,4.0441379514,–0.2290568174,–0.4223303653
H,–2.6620027869,–0.2002285525,–1.5894209262
H,–0.0222742491,0.4497340039,1.6169343571
H,–3.0151278941,0.6708994892,0.5372763129

Zero-point correction=   0.032190 (Hartree/Particle)
 Thermal correction to energy=   0.041140
 Thermal correction to enthalpy=   0.042085
 Thermal correction to Gibbs free energy=   –0.005017
 Sum of electronic and zero-point energies=   –769.233763
 Sum of electronic and thermal energies=   –769.224813
 Sum of electronic and thermal enthalpies=   –769.223869
 Sum of electronic and thermal free energies=   –769.270970

Table S21. Cartesian coordinates and energies of **3-CO₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.5814797345,0.3227593597,0.1125105502
Si,2.8087003657,–0.1513565222,–0.2275906726
H,3.2777903798,0.9369178124,0.7352944774
H,2.9657494268,–1.3636118873,0.6769938164
H,0.3219794846,1.8239275449,–0.0128940326
O,–0.7201873914,–0.5295303075,0.1755688611

Zero-point correction=   0.026160 (Hartree/Particle)
 Thermal correction to energy=   0.031210
 Thermal correction to enthalpy=   0.032154
 Thermal correction to Gibbs free energy=   –0.001485
 Sum of electronic and zero-point energies=   –655.956316
 Sum of electronic and thermal energies=   –655.951266
 Sum of electronic and thermal enthalpies=   –655.950322
 Sum of electronic and thermal free energies=   –655.983961

Table S22. Cartesian coordinates and energies of **TS8-CO₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.7083125031,1.0522017044,–0.1580151992
H,1.1883006176,1.5846147313,–1.4964345235
H,1.9440134321,1.351874653,0.7309476722
Si,1.3713604983,–1.2042137745,0.0151519884
H,0.7940337268,–1.3215279731,1.4240817115
C,–2.3169623432,–0.3100622106,0.0907663599
O,–1.6667716401,–1.206758176,–0.2148521646
O,–0.7301327946,1.5278640454,0.3092901552

Zero-point correction=   0.032222 (Hartree/Particle)
 Thermal correction to energy=   0.039868
 Thermal correction to enthalpy=   0.040812
 Thermal correction to Gibbs free energy=   –0.000590
 Sum of electronic and zero-point energies=   –769.194795
 Sum of electronic and thermal energies=   –769.187149
 Sum of electronic and thermal enthalpies=   –769.186205
 Sum of electronic and thermal free energies=   –769.227607

Table S23. Cartesian coordinates and energies of **TS9-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.515611795,–0.560608187,0.0176046259
H,–1.6136893539,–1.4353820819,–1.1857037968
H,–2.9613421586,–0.4503827252,0.4772243013
Si,–0.2465124351,1.2521041323,–0.0461777616
H,–0.4522953199,2.0314695689,1.2296647589
C,1.8044392908,–0.6300883837,0.0758408452
O,1.3819193262,0.7489901183,–0.1144020699
O,0.9228684455,–1.4783214418,0.0452040971

Zero-point correction=   0.033277 (Hartree/Particle)
 Thermal correction to energy=   0.039709
 Thermal correction to enthalpy=   0.040653
 Thermal correction to Gibbs free energy=   0.002889
 Sum of electronic and zero-point energies=   –769.181747
 Sum of electronic and thermal energies=   –769.175315
 Sum of electronic and thermal enthalpies=   –769.174371
 Sum of electronic and thermal free energies=   –769.212135

Table S24. Cartesian coordinates and energies of **8-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.24218311,–0.0627257495,0.4256646272
Si,1.928463958,0.5129563106,–0.0698686416
H,2.3559441323,–0.9507911314,0.0619108374
H,1.75521945,0.5433639863,–1.5831186742
H,–0.3923935393,–0.7785901002,1.7363930004
O,–1.5508952736,1.1319241927,0.3939542128
C,–2.3090690809,0.3412976382,–0.3798600914
O,–1.5450875364,–0.7374361467,–0.5850752707

Zero-point correction=   0.035550 (Hartree/Particle)
 Thermal correction to energy=   0.042002
 Thermal correction to enthalpy=   0.042946
 Thermal correction to Gibbs free energy=   0.005149
 Sum of electronic and zero-point energies=   –769.235021
 Sum of electronic and thermal energies=   –769.228569
 Sum of electronic and thermal enthalpies=   –769.227625
 Sum of electronic and thermal free energies=   –769.265423

Table S25. Cartesian coordinates and energies of **TS10-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.3195618049,–0.6017524476,0.1405985117
Si,2.3804937235,0.1825979474,–0.0696580123
H,3.5148782971,–0.4820454512,0.6605378935
H,2.8964719181,0.4833889284,–1.4470583526
H,0.3874897302,–1.0750594673,1.5820406316
O,–1.1567696168,0.9708080822,0.3295446663
C,–2.2628800938,0.536510833,0.0082126576
O,–2.6892327632,–0.4885334248,–0.4511489958

Zero-point correction=   0.033068 (Hartree/Particle)
 Thermal correction to energy=   0.040459
 Thermal correction to enthalpy=   0.041403
 Thermal correction to Gibbs free energy=   0.000229
 Sum of electronic and zero-point energies=   –769.169105
 Sum of electronic and thermal energies=   –769.161714
 Sum of electronic and thermal enthalpies=   –769.160770
 Sum of electronic and thermal free energies=   –769.201944

Table S26. Cartesian coordinates and energies of **TS11-CO$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.0897820158,–0.3529008413,0.4212889094
Si,2.1596762285,0.3196200428,–0.2291313441
H,2.8491322016,–0.3261070669,0.9644186897
H,2.4286773154,–0.7171264712,–1.3016529082
H,–0.2039220957,–0.1376931532,1.8813998163
O,–1.6799779987,1.1539796583,0.066999418
C,–2.3070369793,0.1978911468,–0.3177417238
O,–1.1262926876,–1.0621573153,–0.3786298572

Zero-point correction=   0.032698 (Hartree/Particle)
 Thermal correction to energy=   0.039781
 Thermal correction to enthalpy=   0.040725
 Thermal correction to Gibbs free energy=   0.001209
 Sum of electronic and zero-point energies=   –769.201479
 Sum of electronic and thermal energies=   –769.194396
 Sum of electronic and thermal enthalpies=   –769.193452
 Sum of electronic and thermal free energies=   –769.232968

Table S27. Cartesian coordinates and energies of **1-CS$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.8164224078,0.675033626,0.2889791631
H,–1.182106128,1.3099702752,1.5997630508
H,–1.701049023,1.3793954878,–0.6975476341
Si,–0.6774130487,–1.6663999618,0.1698844473
H,–0.7916104621,–1.6077639862,–1.356203445
C,2.2721101549,0.0273264132,–0.0523018312
S,1.2602894326,1.4077143717,–0.0983818438
S,1.6362024821,–1.5252772259,0.1458090929

Zero-point correction=   0.032415 (Hartree/Particle)
 Thermal correction to energy=   0.039147
 Thermal correction to enthalpy=   0.040091
 Thermal correction to Gibbs free energy=   0.000917
 Sum of electronic and zero-point energies=   –1415.172029
 Sum of electronic and thermal energies=   –1415.165297
 Sum of electronic and thermal enthalpies=   –1415.164353
 Sum of electronic and thermal free energies=   –1415.203526

Table S28. Cartesian coordinates and energies of **TS1-CS$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,1.3418301084,1.160782752,–0.0362483392
H,1.4595030869,2.0354397903,–1.2521470137
H,1.2857558061,2.0946680665,1.1409474525
Si,1.6038378489,–1.0312259727,–0.0614519908
H,1.4455685236,–1.0933351998,1.4662418708
C,–2.2104322672,–0.2698833332,0.0170465485
S,–2.3234286606,1.2871244915,0.1368346465
S,–1.6643802161,–1.7209419946,–0.1282820646

Zero-point correction=   0.029795 (Hartree/Particle)
 Thermal correction to energy=   0.037707
 Thermal correction to enthalpy=   0.038651
 Thermal correction to Gibbs free energy=   –0.005027
 Sum of electronic and zero-point energies=   –1415.120394
 Sum of electronic and thermal energies=   –1415.112482
 Sum of electronic and thermal enthalpies=   –1415.111538
 Sum of electronic and thermal free energies=   –1415.155216

Table S29. Cartesian coordinates and energies of **2-CS$_2$-CS** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.4778112169,0.2758184533,–0.0924500168
Si,–2.6313054749,–0.2897835986,–0.5582085652
H,–2.9262353613,–1.00390244,0.7506006327
H,–3.3660479239,1.0171323597,–0.3559750812
H,0.2971350292,–0.9190549599,0.4315112555
C,4.9386926512,–0.5308265465,0.3295560945
S,0.7315828602,1.7857332717,–0.6445626894
S,3.4339884364,–0.3351165397,0.1395283699

Zero-point correction=   0.029084 (Hartree/Particle)
 Thermal correction to energy=   0.038284
 Thermal correction to enthalpy=   0.039229
 Thermal correction to Gibbs free energy=   –0.008331
 Sum of electronic and zero-point energies=   –1415.128200
 Sum of electronic and thermal energies=   –1415.118999
 Sum of electronic and thermal enthalpies=   –1415.118055
 Sum of electronic and thermal free energies=   –1415.165614

Table S30. Cartesian coordinates and energies of **2-CS$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.1310912771,–0.1171029468,0.1906619931
Si,–3.2947897409,–0.699543873,–0.2310566269
H,–3.4221316966,–1.7400602794,0.8709891046
H,–4.0690490843,0.4550072924,0.371110148
H,–0.263488877,–1.3506981858,0.3286572667
S,–0.0720143242,1.5783559926,–0.0132988856

Zero-point correction=   0.025032 (Hartree/Particle)
 Thermal correction to energy=   0.030319
 Thermal correction to enthalpy=   0.031263
 Thermal correction to Gibbs free energy=   –0.003713
 Sum of electronic and zero-point energies=   –978.947598
 Sum of electronic and thermal energies=   –978.942311
 Sum of electronic and thermal enthalpies=   –978.941367
 Sum of electronic and thermal free energies=   –978.976342

Table S31. Cartesian coordinates and energies of **TS2-CS₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.1214458922,0.8065663964,0.4027564898
H,–1.7432094381,1.6233011606,1.4891128787
H,–2.3853899245,0.6797681982,–0.6332743569
Si,–2.0921403482,–1.1145213149,–0.1767106584
H,–1.2362369818,–1.1081427076,–1.4292945604
C,2.0681334,0.1061292432,–0.1629165007
S,0.7120390443,1.5559217258,–0.2767045169
S,1.5866341405,–1.4188267016,0.1769232249

Zero-point correction=   0.028978 (Hartree/Particle)
 Thermal correction to energy=   0.036378
 Thermal correction to enthalpy=   0.037322
 Thermal correction to Gibbs free energy=   –0.004138
 Sum of electronic and zero-point energies=   –1415.101446
 Sum of electronic and thermal energies=   –1415.094046
 Sum of electronic and thermal enthalpies=   –1415.093102
 Sum of electronic and thermal free energies=   –1415.134562

Table S32. Cartesian coordinates and energies of **TS3-CS₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.5160026675,–1.3868092578,–0.1680342329
H,–1.3439772268,–1.7532106049,–1.6083672454
H,–2.7998852179,–2.0484896041,0.2607421674
Si,–1.4239721128,0.7858537769,0.268960853
H,–1.898803269,1.0769464856,1.6692306872
C,2.0844547594,0.366249529,0.0316197334
S,1.7720212269,–1.1916898892,0.1308886311
S,0.3127495077,1.7523915645,–0.2705945938

Zero-point correction=   0.029383 (Hartree/Particle)
 Thermal correction to energy=   0.037044
 Thermal correction to enthalpy=   0.037988
 Thermal correction to Gibbs free energy=   –0.003919
 Sum of electronic and zero-point energies=   –1415.112911
 Sum of electronic and thermal energies=   –1415.105250
 Sum of electronic and thermal enthalpies=   –1415.104306
 Sum of electronic and thermal free energies=   –1415.146213

Table S33. Cartesian coordinates and energies of **3-CS₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.0908551801,–0.0314293509,0.4782869451
Si,2.1130024265,0.3195281836,–0.1404609869
H,2.4438175874,–1.1652590031,0.0300580896
H,1.8630386305,0.2948868081,–1.6431960802
H,–0.2362313819,–0.5607296405,1.8753228719
C,–2.6775587016,0.5136614537,–0.401933253
S,–1.833187344,–0.9917853828,–0.5743807142
S,–1.5820260369,1.621125932,0.3763041277

Zero-point correction=   0.030930 (Hartree/Particle)
 Thermal correction to energy=   0.038352
 Thermal correction to enthalpy=   0.039296
 Thermal correction to Gibbs free energy=   –0.001738
 Sum of electronic and zero-point energies=   –1415.149280
 Sum of electronic and thermal energies=   –1415.141858
 Sum of electronic and thermal enthalpies=   –1415.140914
 Sum of electronic and thermal free energies=   –1415.181948

Table S34. Cartesian coordinates and energies of **TS4-CS₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.9639037426,–0.6710498649,0.2008349143
Si,3.0680741242,–0.1489797615,–0.1178694543
H,4.2195477394,–0.7098831998,0.6607671604
H,3.5914967415,0.2329563918,–1.4666988065
H,1.0270692409,–1.0878839041,1.6560299618
C,–2.1072602749,0.6793168001,–0.0391006352
S,–2.8278552844,–0.7503387711,–0.2145703096
S,–0.6320910294,1.2914423094,0.0860951691

Zero-point correction=   0.029631 (Hartree/Particle)
 Thermal correction to energy=   0.037438
 Thermal correction to enthalpy=   0.038382
 Thermal correction to Gibbs free energy=   –0.004885
 Sum of electronic and zero-point energies=   –1415.106747
 Sum of electronic and thermal energies=   –1415.098941
 Sum of electronic and thermal enthalpies=   –1415.097997
 Sum of electronic and thermal free energies=   –1415.141264

Table S35. Cartesian coordinates and energies of **4-CS$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,1.9495269977,0.7730719783,–1.0147728744
Si,1.15735308,–0.3251448551,0.9466629944
C,–0.6216121246,–0.2317543374,0.228831552
H,1.4835149167,–1.7711096133,1.1807794243
H,1.1928815909,0.2887623845,2.3154041277
H,1.8237575016,2.1506722229,–0.3512884142
S,–0.3646361223,0.5184986471,–1.3166168514
S,–2.0670468399,–0.748066427,0.8439560416

Zero-point correction=   0.033126 (Hartree/Particle)
 Thermal correction to energy=   0.039077
 Thermal correction to enthalpy=   0.040021
 Thermal correction to Gibbs free energy=   0.002467
 Sum of electronic and zero-point energies=   –1415.198054
 Sum of electronic and thermal energies=   –1415.192103
 Sum of electronic and thermal enthalpies=   –1415.191159
 Sum of electronic and thermal free energies=   –1415.228713

Table S36. Cartesian coordinates and energies of **TS5-CS$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.0613642318,–0.2608246026,0.2439788484
Si,2.0209707483,0.0227988454,–0.4056240847
H,2.9498141738,–0.7751135976,0.4604286644
H,2.2250456312,–0.4111609201,–1.8217339731
H,–0.3181646784,–0.2496320813,1.7061532597
C,–3.0586325526,0.8548932804,–0.1059363656
S,–1.8347112598,–0.2808859841,–0.9180431697
S,–2.3938989308,1.9399649599,0.9596380606

Zero-point correction=   0.029247 (Hartree/Particle)
 Thermal correction to energy=   0.036953
 Thermal correction to enthalpy=   0.037897
 Thermal correction to Gibbs free energy=   –0.004241
 Sum of electronic and zero-point energies=   –1415.109184
 Sum of electronic and thermal energies=   –1415.101478
 Sum of electronic and thermal enthalpies=   –1415.100534
 Sum of electronic and thermal free energies=   –1415.142672

Table S37. Cartesian coordinates and energies of **TS6-CS₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.3372987264,–0.5790322383,–1.125785504
Si,–1.3391334257,0.2051869582,0.9822420913
C,0.4730858049,0.002056508,–0.109444068
H,–1.5410328201,1.5790583612,1.5155430288
H,–1.1596308832,–0.6567370547,2.188652414
H,–1.3528725001,–1.9919791816,–0.5485169319
S,0.8644141558,1.6480928359,–0.3189885491
S,1.5307263948,–1.2500171886,0.289973519

Zero-point correction=   0.031440 (Hartree/Particle)
 Thermal correction to energy=   0.038186
 Thermal correction to enthalpy=   0.039130
 Thermal correction to Gibbs free energy=   –0.000333
 Sum of electronic and zero-point energies=   –1415.133954
 Sum of electronic and thermal energies=   –1415.127208
 Sum of electronic and thermal enthalpies=   –1415.126264
 Sum of electronic and thermal free energies=   –1415.165727

Table S38. Cartesian coordinates and energies of **5-CS₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.1837652096,–0.6776193974,–0.872253735
Si,–1.2767380596,0.6197501103,1.0969618113
C,0.67810116,–0.4333396556,–0.4337933393
H,–2.0091947136,1.9260296816,1.2040319815
H,–1.3502705395,0.0597841718,2.4873679301
H,–1.3914830777,–2.093675581,–0.3598881026
S,0.8302969702,0.9965776958,0.6464723149
S,2.0059954698,–1.2571860255,–0.980676861

Zero-point correction=   0.033144 (Hartree/Particle)
 Thermal correction to energy=   0.039785
 Thermal correction to enthalpy=   0.040729
 Thermal correction to Gibbs free energy=   0.001539
 Sum of electronic and zero-point energies=   –1415.199224
 Sum of electronic and thermal energies=   –1415.192583
 Sum of electronic and thermal enthalpies=   –1415.191639
 Sum of electronic and thermal free energies=   –1415.230829

Table S39. Cartesian coordinates and energies of **TS7-CS$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,2.3205287348,–0.0101767973,–0.9289417595
Si,1.5170446542,–0.204066167,1.1174057025
C,–1.2051095674,0.0558534053,–0.1316918315
H,1.2860140633,–1.5176417835,1.8031055306
H,1.246267079,0.8556293119,2.1444412053
H,2.2748627183,1.5197537559,–0.8083114072
S,–1.4093822194,1.6297722863,–0.1442793294
S,–1.6431794629,–1.4637440117,–0.2773871108

Zero-point correction=   0.029150 (Hartree/Particle)
 Thermal correction to energy=   0.037177
 Thermal correction to enthalpy=   0.038121
 Thermal correction to Gibbs free energy=   –0.006118
 Sum of electronic and zero-point energies=   –1415.111924
 Sum of electronic and thermal energies=   –1415.103897
 Sum of electronic and thermal enthalpies=   –1415.102953
 Sum of electronic and thermal free energies=   –1415.147192

Table S40. Cartesian coordinates and energies of **1-H$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.317120832,–0.0328596317,0.0821048819
Si,1.3546787072,–0.0746791542,–0.1157702288
H,1.6213672579,0.044210816,1.3850747623
H,–1.5736718876,0.3093718095,–1.3858458799
H,–1.9050034541,1.2861313885,0.6215760775
H,1.9983075513,1.2822251158,–0.4639405398
H,0.0393266574,0.931842656,0.0538909268

Zero-point correction=   0.037777 (Hartree/Particle)
 Thermal correction to energy=   0.042774
 Thermal correction to enthalpy=   0.043718
 Thermal correction to Gibbs free energy=   0.010898
 Sum of electronic and zero-point energies=   –581.865847
 Sum of electronic and thermal energies=   –581.860850
 Sum of electronic and thermal enthalpies=   –581.859906
 Sum of electronic and thermal free energies=   –581.892727

Table S41. Cartesian coordinates and energies of **TS1-H$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.2542563414,–0.1365118785,0.0678003403
Si,1.1837360725,–0.1924583074,–0.0830817362
H,1.5137875824,0.0549562256,1.3900199426
H,–1.4892098894,0.2506272627,–1.3993063329
H,–1.5106079673,1.2727266205,0.6314152312
H,1.5307884004,1.4587992002,–0.3465125455
H,0.6738761427,1.424466877,–0.0737298995

Zero-point correction=   0.036027 (Hartree/Particle)
 Thermal correction to energy=   0.040629
 Thermal correction to enthalpy=   0.041573
 Thermal correction to Gibbs free energy=   0.009731
 Sum of electronic and zero-point energies=   –581.831918
 Sum of electronic and thermal energies=   –581.827316
 Sum of electronic and thermal enthalpies=   –581.826372
 Sum of electronic and thermal free energies=   –581.858213

Table S42. Cartesian coordinates and energies of **2-H$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.3747631391,–0.1433557367,0.0362234009
Si,0.9565660557,–0.1711590061,0.4662713145
H,1.7716577772,–0.7313817964,–0.6760860957
H,–1.2788773938,1.0457049367,–0.9342578282
H,–1.6902564341,0.7141633164,1.2731671769
H,1.7168847968,1.0949657486,0.7988615395
H,1.3458173372,–1.0766544625,1.6115904922

Zero-point correction=   0.038696 (Hartree/Particle)
 Thermal correction to energy=   0.043461
 Thermal correction to enthalpy=   0.044405
 Thermal correction to Gibbs free energy=   0.012276
 Sum of electronic and zero-point energies=   –581.916702
 Sum of electronic and thermal energies=   –581.911937
 Sum of electronic and thermal enthalpies=   –581.910993
 Sum of electronic and thermal free energies=   –581.943122

Table S43. Cartesian coordinates and energies of **TS2-H$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.2954622917,–0.0972692917,–0.0958766352
Si,1.2192877257,0.0475721653,–0.1033247178
H,1.8807268331,–1.3060080012,0.0612932623
H,–1.4326213204,1.4195372946,–0.2437721668
H,–1.7924482325,–0.0930350228,1.3675616942
H,2.0770512082,0.9109104647,0.8129306005
H,0.2547350777,–0.2189796089,1.1097439629

Zero-point correction=   0.036808 (Hartree/Particle)
 Thermal correction to energy=   0.041309
 Thermal correction to enthalpy=   0.042254
 Thermal correction to Gibbs free energy=   0.010571
 Sum of electronic and zero-point energies=   –581.862139
 Sum of electronic and thermal energies=   –581.857638
 Sum of electronic and thermal enthalpies=   –581.856693
 Sum of electronic and thermal free energies=   –581.888376

Table S44. Cartesian coordinates and energies of **1-CH$_4$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.8595510126,0.1774135511,–0.0118516799
Si,0.7168419274,–0.6572023927,–0.00252015
H,0.765369482,–0.948892067,1.5016788077
H,–1.7636277634,0.8648025252,–1.3751996404
H,–2.1447413449,1.4815253419,0.7637960242
H,–0.3169547525,0.6190835018,0.3267849895
H,3.0838781909,0.2335080072,–0.0174206654
H,2.0443362743,1.3100114019,–0.9566312017
C,2.103859104,0.7328771746,–0.0255703283
H,2.0724158948,1.4336619559,0.8170088443

Zero-point correction=   0.067198 (Hartree/Particle)
 Thermal correction to energy=   0.073974
 Thermal correction to enthalpy=   0.074918
 Thermal correction to Gibbs free energy=   0.036977
 Sum of electronic and zero-point energies=   –621.147800
 Sum of electronic and thermal energies=   –621.141024
 Sum of electronic and thermal enthalpies=   –621.140080
 Sum of electronic and thermal free energies=   –621.178021

Table S45. Cartesian coordinates and energies of **TS1-CH$_4$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.6086606378,0.2400494829,0.0351264255
Si,0.5119962442,–0.9567000106,–0.1161418567
H,0.6811719109,–1.1496029563,1.3959587701
H,–1.50367552,1.0118193408,–1.2872311018
H,–1.2865273564,1.4462936607,0.9391708872
H,0.4337164189,0.6438882394,0.128240996
H,2.6903876631,0.3397640939,0.4373380282
H,2.0389328162,1.1080714851,–1.0511887184
C,1.8297088658,0.8401154118,–0.0137680501
H,1.638194595,1.7584342522,0.5592186201

Zero-point correction=   0.066099 (Hartree/Particle)
 Thermal correction to energy=   0.072125
 Thermal correction to enthalpy=   0.073069
 Thermal correction to Gibbs free energy=   0.037314
 Sum of electronic and zero-point energies=   –621.100019
 Sum of electronic and thermal energies=   –621.093994
 Sum of electronic and thermal enthalpies=   –621.093049
 Sum of electronic and thermal free energies=   –621.128804

Table S46. Cartesian coordinates and energies of **2-CH$_4$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.7551158808,0.185125065,–0.08951233
Si,0.4184236948,–0.4064363714,0.6168266234
H,0.8345156948,–1.7905087761,0.1668286855
H,–1.3016761176,0.4178907603,–1.5428729538
H,–1.5797514994,1.6518212445,0.3464611755
H,0.5473379168,–0.5118848414,2.1213450591
H,1.9680880192,0.7602237517,–0.9808540873
H,1.7531648426,1.7186527374,0.4872271118
C,1.9047370414,0.6999335405,0.1118650294
H,2.8616772882,0.3246658895,0.4968846864

Zero-point correction=   0.067863 (Hartree/Particle)
 Thermal correction to energy=   0.074327
 Thermal correction to enthalpy=   0.075271
 Thermal correction to Gibbs free energy=   0.038316
 Sum of electronic and zero-point energies=   –621.203964
 Sum of electronic and thermal energies=   –621.197500
 Sum of electronic and thermal enthalpies=   –621.196556
 Sum of electronic and thermal free energies=   –621.233512

Table S47. Cartesian coordinates and energies of **2'-CH$_4$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.2740537674,0.5750666685,–0.2278455232
Si,0.7135501287,–0.7094335924,–0.4378224348
H,0.4602408288,–1.451685856,0.8897072878
H,–2.5472373838,–0.2268931544,–0.3529026187
H,–1.5156217692,1.3840518896,1.0331807421
H,–1.4473503072,1.624893934,–1.3014171352
H,2.9443655662,0.1787935295,0.4339659863
H,2.1246966886,1.4278274549,–0.503064809
C,1.966596693,0.6453982831,0.2515402785
H,1.6499173222,1.1348208431,1.1821862263

Zero-point correction=   0.068205 (Hartree/Particle)
 Thermal correction to energy=   0.074533
 Thermal correction to enthalpy=   0.075477
 Thermal correction to Gibbs free energy=   0.038959
 Sum of electronic and zero-point energies=   –621.195773
 Sum of electronic and thermal energies=   –621.189445
 Sum of electronic and thermal enthalpies=   –621.188501
 Sum of electronic and thermal free energies=   –621.225019

Table S48. Cartesian coordinates and energies of **TS2-CH$_4$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.8142425232,0.1069835878,–0.0154036734
Si,0.5956713923,–0.5967918573,–0.1213689631
H,0.9247657919,–1.731941611,0.8311761069
H,–1.578970007,1.1962640161,–1.0655200179
H,–2.0018568389,1.1316116321,1.13138626
H,–0.1867742395,0.1524632985,1.0227993545
H,2.9461426247,0.2432973514,–0.609735071
H,1.8373634432,1.5872944615,–0.320498449
C,2.1294009824,0.5917793081,0.0354231671
H,2.5161383741,0.6932928129,1.056380286

Zero-point correction=   0.066585 (Hartree/Particle)
 Thermal correction to energy=   0.072698
 Thermal correction to enthalpy=   0.073642
 Thermal correction to Gibbs free energy=   0.037296
 Sum of electronic and zero-point energies=   –621.143052
 Sum of electronic and thermal energies=   –621.136939
 Sum of electronic and thermal enthalpies=   –621.135995
 Sum of electronic and thermal free energies=   –621.172340

Table S49. Cartesian coordinates and energies of **TS2'-CH₄** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.715669093,0.109781409,0.0393664393
Si,0.675845656,–0.7316279869,–0.1267872256
H,0.6490597835,–1.0573707996,1.3705647647
H,–2.239970842,0.6870163693,–1.263134977
H,–2.2248443068,1.1491971486,1.0347194398
H,–0.3791067213,0.9157177699,–0.0899788244
H,2.9909243989,0.2138876046,0.1658178864
H,2.0742075027,1.2804405597,–0.9094756759
C,2.015156601,0.7038048431,0.0225889492
H,1.862462021,1.4043950825,0.8530522234

Zero-point correction=   0.066370 (Hartree/Particle)
 Thermal correction to energy=   0.072458
 Thermal correction to enthalpy=   0.073403
 Thermal correction to Gibbs free energy=   0.037448
 Sum of electronic and zero-point energies=   –621.145218
 Sum of electronic and thermal energies=   –621.139129
 Sum of electronic and thermal enthalpies=   –621.138185
 Sum of electronic and thermal free energies= –621.174140

Table S50. Cartesian coordinates and energies of **1-N₂** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.6574607107,–0.6792850016,–0.0906920118
Si,0.020958052,1.0413875351,–0.1594304244
H,0.3197334689,1.5571207719,1.2437796113
H,–2.2679792028,–0.2757494518,1.2573823763
N,1.5187479824,–0.0886668783,0.0853182726
N,2.4474054267,–0.7163997957,0.0502185447
H,–2.6294260164,0.1464688204,–0.9432033688

Zero-point correction=   0.030530 (Hartree/Particle)
 Thermal correction to energy=   0.037005
 Thermal correction to enthalpy=   0.037949
 Thermal correction to Gibbs free energy=   0.000089
 Sum of electronic and zero-point energies=   –690.157573
 Sum of electronic and thermal energies=   –690.151098
 Sum of electronic and thermal enthalpies=   –690.150154
 Sum of electronic and thermal free energies= –690.188014

Table S51. Cartesian coordinates and energies of **TS1-N$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.6935011214,–0.6763192181,–0.0267542255
Si,–0.1404538767,1.0805955334,–0.1825655963
H,0.1441954162,1.4428494976,1.2794071707
H,–2.531251998,–0.1923721032,1.1560715638
N,1.6889682319,–0.2004285019,0.1491394219
N,2.6506901705,–0.7265811408,–0.0190528485
H,–2.5967858225,–0.188443067,–1.1576284862

Zero-point correction=   0.029445 (Hartree/Particle)
 Thermal correction to energy=   0.035820
 Thermal correction to enthalpy=   0.036765
 Thermal correction to Gibbs free energy=   –0.001215
 Sum of electronic and zero-point energies=   –690.156176
 Sum of electronic and thermal energies=   –690.149801
 Sum of electronic and thermal enthalpies=   –690.148857
 Sum of electronic and thermal free energies=   –690.186836

Table S52. Cartesian coordinates and energies of **2-N$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,1.2224540621,–0.1530245968,0.1554962329
Si,–0.9623739217,–1.1012783485,–0.1077416318
H,–1.292681475,–1.2990070023,1.3807461986
H,1.8488936442,0.089024632,1.5069780461
N,–1.0104756138,0.8134932616,–0.089345141
N,0.1446558737,1.3186635735,–0.1646055135
H,2.4463414306,–0.2207985195,–0.7395761912

Zero-point correction=   0.032025 (Hartree/Particle)
 Thermal correction to energy=   0.037243
 Thermal correction to enthalpy=   0.038188
 Thermal correction to Gibbs free energy=   0.003781
 Sum of electronic and zero-point energies=   –690.142611
 Sum of electronic and thermal energies=   –690.137393
 Sum of electronic and thermal enthalpies=   –690.136449
 Sum of electronic and thermal free energies=   –690.170856

Table S53. Cartesian coordinates and energies of **TS2-N$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,1.3460700303,–0.2007748807,–0.0656067514
Si,–0.9542798036,–0.9313828588,–0.1503043378
H,–1.2786774597,–1.3653835793,1.288944509
H,1.6707037286,0.166279815,1.3703400586
N,–1.0293214718,0.986185113,0.1683184141
N,–0.1269526497,1.6673725855,–0.1307709493
H,2.5109466258,–1.1745211947,–0.3168379433

Zero-point correction=   0.029994 (Hartree/Particle)
 Thermal correction to energy=   0.035262
 Thermal correction to enthalpy=   0.036206
 Thermal correction to Gibbs free energy=   0.001613
 Sum of electronic and zero-point energies=   –690.127172
 Sum of electronic and thermal energies=   –690.121904
 Sum of electronic and thermal enthalpies=   –690.120960
 Sum of electronic and thermal free energies=   –690.155553

Table S54. Cartesian coordinates and energies of **1-N$_2$O** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.6218614411,0.7780676695,–0.1579903405
O,1.0894745671,–1.4375047459,–0.3691915176
H,–1.1134749816,1.6328245217,0.9750294631
H,–0.8770694105,1.6374419356,–1.3671225823
N,1.8143606448,–0.2683914222,–0.1498033979
N,1.2117336819,0.7962663133,–0.0210157666
Si,–0.7336416092,–1.5693601001,–0.2264261195
H,–0.7695224514,–1.5693441719,1.3165202613

Zero-point correction=   0.036894 (Hartree/Particle)
 Thermal correction to energy=   0.042682
 Thermal correction to enthalpy=   0.043626
 Thermal correction to Gibbs free energy=   0.007463
 Sum of electronic and zero-point energies=   –765.372684
 Sum of electronic and thermal energies=   –765.366896
 Sum of electronic and thermal enthalpies=   –765.365952
 Sum of electronic and thermal free energies=   –765.402115

Table S55. Cartesian coordinates and energies of **TS1-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.2038066189,1.0324615326,–0.010185869
O,1.7847884635,–1.1395368889,0.0332441863
H,–1.1587147872,1.9337318429,1.1921027113
H,–1.3094531699,1.9421640922,–1.2010694212
N,1.9412935346,0.0535337925,0.0184966807
N,1.6699705744,1.1638631403,–0.0128328695
Si,–1.3896842734,–1.1679854213,–0.1170358057
H,–1.271575723,–1.2705040903,1.413387387

Zero-point correction=	0.033590 (Hartree/Particle)
Thermal correction to energy=	0.040930
Thermal correction to enthalpy=	0.041875
Thermal correction to Gibbs free energy=	0.001145
Sum of electronic and zero-point energies=	−765.285299
Sum of electronic and thermal energies=	−765.277959
Sum of electronic and thermal enthalpies=	−765.277015
Sum of electronic and thermal free energies=	−765.317744

Table S56. Cartesian coordinates and energies of **TS1'-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.2086605043,1.037000329,–0.0124255908
H,–1.1611180949,1.9539377785,1.1777898645
H,–1.2713454608,1.9356125,–1.2148353359
N,1.9030059327,–0.1198574212,0.0193301785
Si,–1.3412391882,–1.1655155404,–0.1050286847
H,–1.2492120625,–1.2553364142,1.4278684509
O,1.7815541539,1.0818350004,0.0071698724
N,1.577367224,–1.216076232,0.0008022452

Zero-point correction=	0.033526 (Hartree/Particle)
Thermal correction to energy=	0.040856
Thermal correction to enthalpy=	0.041800
Thermal correction to Gibbs free energy=	0.001076
Sum of electronic and zero-point energies=	−765.285066
Sum of electronic and thermal energies=	−765.277736
Sum of electronic and thermal enthalpies=	−765.276792
Sum of electronic and thermal free energies=	−765.317517

Table S57. Cartesian coordinates and energies of **2-N$_2$O** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.3800724777,1.1940958033,–0.1003178008
H,–1.6511086794,1.6370158843,0.6166462548
H,–0.7346021233,1.4312810231,–1.5607503509
N,2.0432315603,–1.7744645003,–0.6409856839
Si,–0.8079127837,–1.2097709041,0.0636667217
H,–0.4743471208,–1.4496604195,1.5273763517
O,1.007253727,1.7420031542,0.3987589918
N,0.9975578978,–1.5704990409,–0.3043944842

Zero-point correction=   0.035599 (Hartree/Particle)
 Thermal correction to energy=   0.042827
 Thermal correction to enthalpy=   0.043771
 Thermal correction to Gibbs free energy=   0.002949
 Sum of electronic and zero-point energies=   –765.412360
 Sum of electronic and thermal energies=   –765.405133
 Sum of electronic and thermal enthalpies=   –765.404188
 Sum of electronic and thermal free energies=   –765.445011

Table S58. Cartesian coordinates and energies of **TS2-N$_2$O** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.5889581977,0.8161786113,–0.1146712111
O,1.0526874327,–1.5317466741,–0.5959645075
H,–1.1424763546,1.782323347,0.9064698441
H,–0.6327838189,1.6547645737,–1.3653418018
N,2.0247680443,0.0201106299,–0.066181723
N,1.316060558,0.9146211364,0.1379655845
Si,–0.5588115145,–1.5632128412,–0.1651624987
H,–0.5691272694,–1.5548866631,1.3939878535

Zero-point correction=   0.034922 (Hartree/Particle)
 Thermal correction to energy=   0.040915
 Thermal correction to enthalpy=   0.041860
 Thermal correction to Gibbs free energy=   0.005259
 Sum of electronic and zero-point energies=   –765.367122
 Sum of electronic and thermal energies=   –765.361128
 Sum of electronic and thermal enthalpies=   –765.360184
 Sum of electronic and thermal free energies=   –765.396784

Table S59. Cartesian coordinates and energies of **3-N$_2$O-N$_2$** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.0473313661,0.8775004464,–0.0087384435
H,–2.5654946459,–1.4062755337,0.7151736964
H,–2.3606722403,1.5818792229,–0.344491444
N,2.5119399388,–0.407286751,–0.5686378995
Si,–1.2796674118,–1.4106392813,–0.1086360474
H,–0.2960759259,–1.8246739943,0.974214232
O,0.1768753856,1.8377540934,0.0578933247
N,2.6788472656,–0.4008282024,0.5197645813

Zero-point correction=   0.032758 (Hartree/Particle)
 Thermal correction to energy=   0.041843
 Thermal correction to enthalpy=   0.042788
 Thermal correction to Gibbs free energy=   –0.004028
 Sum of electronic and zero-point energies=   –765.442577
 Sum of electronic and thermal energies=   –765.433491
 Sum of electronic and thermal enthalpies=   –765.432547
 Sum of electronic and thermal free energies=   –765.479363

Table S60. Cartesian coordinates and energies of **3-N$_2$O** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.5814797345,0.3227593597,0.1125105502
Si,2.8087003657,–0.1513565222,–0.2275906726
H,3.2777903798,0.9369178124,0.7352944774
H,2.9657494268,–1.3636118873,0.6769938164
H,0.3219794846,1.8239275449,–0.0128940326
O,–0.7201873914,–0.5295303075,0.1755688611

 Zero-point correction=   0.026160 (Hartree/Particle)
 Thermal correction to energy=   0.031210
 Thermal correction to enthalpy=   0.032154
 Thermal correction to Gibbs free energy=   –0.001485
 Sum of electronic and zero-point energies=   –655.956316
 Sum of electronic and thermal energies=   –655.951266
 Sum of electronic and thermal enthalpies=   –655.950322
 Sum of electronic and thermal free energies=   –655.983961

Table S61. Cartesian coordinates and energies of **TS3-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.4324618025,0.0614898683,0.3020167591
H,–1.859606632,1.4840374687,–0.2304361569
H,–1.7552091693,0.2280269985,1.7751983896
N,2.7088904051,–1.2277548685,0.1257686825
Si,0.4940565409,1.3228426553,–0.0666012679
H,0.5456459834,1.0558946615,–1.5654161694
O,–1.9527777564,–1.2438865531,–0.3986148453
N,2.0686904309,–0.3475692307,–0.0716333918

Zero-point correction=	0.033624 (Hartree/Particle)
Thermal correction to energy=	0.040960
Thermal correction to enthalpy=	0.041904
Thermal correction to Gibbs free energy=	0.000626
Sum of electronic and zero-point energies=	–765.405362
Sum of electronic and thermal energies=	–765.398026
Sum of electronic and thermal enthalpies=	–765.397082
Sum of electronic and thermal free energies=	–765.438360

Table S62. Cartesian coordinates and energies of **4-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,–1.011775642,–1.0541722596,–0.1498239435
Si,–0.662327695,1.2838933953,–0.3586275743
O,1.785156045,–1.2165263601,0.5724555738
H,–0.7187612093,2.0105210504,–1.6739490871
H,–1.0983324333,2.3213696564,0.6380837356
H,–1.3795619787,–0.982480844,1.3342534022
N,0.8587889141,–0.4620839056,0.2172304155
N,1.0387899992,0.7929872671,–0.0065075222

Zero-point correction=	0.037910 (Hartree/Particle)
Thermal correction to energy=	0.043640
Thermal correction to enthalpy=	0.044584
Thermal correction to Gibbs free energy=	0.008464
Sum of electronic and zero-point energies=	–765.347038
Sum of electronic and thermal energies=	–765.341308
Sum of electronic and thermal enthalpies=	–765.340364
Sum of electronic and thermal free energies=	–765.376484

Table S63. Cartesian coordinates and energies of **TS4-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,–2.2497628055,–0.8204262652,–0.0379786478
Si,–0.8038011183,0.8917627942,–0.1847730299
O,3.1391583611,–0.66161675,–0.1345138281
H,–0.245476189,1.3092972887,–1.5089805907
H,–0.8303133674,2.1270310567,0.6587835671
H,–2.665299023,–0.3668859341,1.3706717196
N,1.9519677634,–0.2878480033,–0.0544685156
N,1.2349273788,0.368175813,0.6091413254

Zero-point correction=   0.033117 (Hartree/Particle)
 Thermal correction to energy=   0.040205
 Thermal correction to enthalpy=   0.041149
 Thermal correction to Gibbs free energy=   0.000957
 Sum of electronic and zero-point energies=   −765.249844
 Sum of electronic and thermal energies=   −765.242756
 Sum of electronic and thermal enthalpies=   −765.241812
 Sum of electronic and thermal free energies=   −765.282004

Table S64. Cartesian coordinates and energies of **5-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.6918252769,1.4278786161,–0.0928223866
Si,1.4196702939,–0.8243090328,–0.2030408621
O,–2.3170700141,0.1716848072,0.3142899688
H,1.6440313432,–1.6134948431,–1.4608321222
H,1.7515349706,–1.7624940163,0.9195193852
H,0.9016700677,1.5172231125,1.4293877354
N,–1.4465864278,–0.6794055204,0.0767357937
N,–0.2314375103,–0.2161841231,–0.0597965121

Zero-point correction=   0.036426 (Hartree/Particle)
 Thermal correction to energy=   0.042848
 Thermal correction to enthalpy=   0.043792
 Thermal correction to Gibbs free energy=   0.005544
 Sum of electronic and zero-point energies=   −765.340211
 Sum of electronic and thermal energies=   −765.333790
 Sum of electronic and thermal enthalpies=   −765.332845
 Sum of electronic and thermal free energies=   −765.371093

Table S65. Cartesian coordinates and energies of **TS5-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,1.3551275047,0.7431382813,–0.1056551677
Si,0.0307899015,–1.3038533514,–0.0032464424
O,–0.6206095856,1.7127385317,0.0894650724
H,–0.0867619239,–2.1538622367,–1.2418506695
H,0.1510014483,–2.2473867191,1.1589797206
H,1.3027270498,0.7969522676,1.4255140837
N,–1.460389212,–0.335103335,0.3819649916
N,–0.9481561828,0.5417355616,–0.4036295887

Zero-point correction=   0.034516 (Hartree/Particle)
 Thermal correction to energy=   0.040570
 Thermal correction to enthalpy=   0.041514
 Thermal correction to Gibbs free energy=   0.004630
 Sum of electronic and zero-point energies=   –765.270853
 Sum of electronic and thermal energies=   –765.264799
 Sum of electronic and thermal enthalpies=   –765.263855
 Sum of electronic and thermal free energies=   –765.300739

Table S66. Cartesian coordinates and energies of **6-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,1.0578081453,–1.1332130807,–0.0054275007
Si,–1.2266292495,–0.5777820618,–0.0060566013
O,1.2773068156,0.6749511838,–0.2139655671
H,–2.0936875033,–0.7120383531,–1.2291386855
H,–2.1825174078,–0.8553567145,1.1187989978
H,1.0184856085,–1.1087634477,1.5372568287
N,–0.8996030088,1.2302477642,0.0685992692
N,0.2623165998,1.6157357099,–0.051047741

Zero-point correction=   0.036892 (Hartree/Particle)
 Thermal correction to energy=   0.042679
 Thermal correction to enthalpy=   0.043624
 Thermal correction to Gibbs free energy=   0.007462
 Sum of electronic and zero-point energies=   –765.372686
 Sum of electronic and thermal energies=   –765.366899
 Sum of electronic and thermal enthalpies=   –765.365955
 Sum of electronic and thermal free energies=   –765.402117

Table S67. Cartesian coordinates and energies of **TS6-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,0.6697676423,1.3909316227,–0.0823658902
Si,1.2119365001,–0.8445560834,–0.1123212254
O,–2.4182994694,–0.0126067258,–0.0083594568
H,1.3030648178,–1.6709778605,–1.3594983385
H,2.0716552114,–1.5309257972,0.8974620816
H,1.0525114337,1.4057295813,1.4081494999
N,–1.2193465419,–0.1244173684,–0.3177395952
N,–0.4317405939,–0.7011383687,0.5791939246

Zero-point correction=   0.035721 (Hartree/Particle)
 Thermal correction to energy=   0.041529
 Thermal correction to enthalpy=   0.042473
 Thermal correction to Gibbs free energy=   0.005968
 Sum of electronic and zero-point energies=   –765.303096
 Sum of electronic and thermal energies=   –765.297288
 Sum of electronic and thermal enthalpies=   –765.296344
 Sum of electronic and thermal free energies=   –765.332849

Table S68. Cartesian coordinates and energies of **TS7-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,–0.1401967912,1.230505548,–0.1624053639
Si,1.5795861014,–0.3603236773,0.1566885002
O,–1.8787543962,0.148049441,0.1645296008
H,2.4128466382,–0.9097756966,–0.9758330978
H,2.0452836061,–1.2383096357,1.3061508017
H,–0.2695034842,1.6161544717,1.309069647
N,–1.3375137149,–1.0184444545,–0.0459788627
N,–0.1002119592,–0.9203519966,–0.2552382253

Zero-point correction=   0.035027 (Hartree/Particle)
 Thermal correction to energy=   0.041176
 Thermal correction to enthalpy=   0.042120
 Thermal correction to Gibbs free energy=   0.004755
 Sum of electronic and zero-point energies=   –765.308150
 Sum of electronic and thermal energies=   –765.302000
 Sum of electronic and thermal enthalpies=   –765.301056
 Sum of electronic and thermal free energies=   –765.338422

Table S69. Cartesian coordinates and energies of **TS8-N₂O** at the wB97XD/6-31+G(d,p) level of theory.

Si,1.3588051883,–0.7184500746,0.0311279486
Si,–1.0098492686,–0.9389221896,–0.0577645458
O,1.2215292147,0.8971921362,–0.3616028136
H,–1.7706671973,–1.0122054421,–1.3559273294
H,–1.9844242265,–1.5961776891,0.8913026284
H,1.2631123376,–0.7740565777,1.586485527
N,–0.4321136451,1.7273925079,0.1006624076
N,–1.2758414033,0.9438623289,0.2353761773

Zero-point correction=   0.034920 (Hartree/Particle)
 Thermal correction to energy=   0.040915
 Thermal correction to enthalpy=   0.041859
 Thermal correction to Gibbs free energy=   0.005256
 Sum of electronic and zero-point energies=   –765.367123
 Sum of electronic and thermal energies=   –765.361128
 Sum of electronic and thermal enthalpies=   –765.360184
 Sum of electronic and thermal free energies=   –765.396787

Table S70. Cartesian coordinates and energies of **CH₄** at the wB97XD/6-31+G(d,p) level of theory.

C,–0.466101679,1.228813476,0.
H,–0.1021554461,0.1993784016,–0.0000008954
H,–0.1021360109,1.7435238834,0.8915131081
H,–0.1021374731,1.7435249173,–0.8915131081
H,–1.5579777859,1.2288267017,0.0000008954

Zero-point correction=   0.045177 (Hartree/Particle)
 Thermal correction to energy=   0.048043
 Thermal correction to enthalpy=   0.048987
 Thermal correction to Gibbs free energy=   0.027858
 Sum of electronic and zero-point energies=   –40.463270
 Sum of electronic and thermal energies=   –40.460404
 Sum of electronic and thermal enthalpies=   –40.459460
 Sum of electronic and thermal free energies=   –40.480589

Table S71. Cartesian coordinates and energies of CO_2 at the wB97XD/6-31+G(d,p) level of theory.

C,–2.89632792,1.01694912,–0.18983508
O,–1.7316107302,1.01694912,–0.18983508
O,–4.0610451098,1.01694912,–0.18983508

Zero-point correction=   0.011788 (Hartree/Particle)
 Thermal correction to energy=   0.014413
 Thermal correction to enthalpy=   0.015358
 Thermal correction to Gibbs free energy=   –0.008915
 Sum of electronic and zero-point energies=   –188.515157
 Sum of electronic and thermal energies=   –188.512531
 Sum of electronic and thermal enthalpies=   –188.511587
 Sum of electronic and thermal free energies=   –188.535859

Table S72. Cartesian coordinates and energies of CS_2 at the wB97XD/6-31+G(d,p) level of theory.

C,–2.89632792,1.01694912,–0.18983508
S,–1.3402588527,1.01694912,–0.18983508
S,–4.4523969873,1.01694912,–0.18983508

Zero-point correction=   0.007000 (Hartree/Particle)
 Thermal correction to energy=   0.010084
 Thermal correction to enthalpy=   0.011028
 Thermal correction to Gibbs free energy=   –0.015916
 Sum of electronic and zero-point energies=   –834.419915
 Sum of electronic and thermal energies=   –834.416831
 Sum of electronic and thermal enthalpies=   –834.415887
 Sum of electronic and thermal free energies=   –834.442831

Table S73. Cartesian coordinates and energies of H_2 at the wB97XD/6-31+G(d,p) level of theory.

H,0.8210977054,0.94396278,–0.00078691
H,0.0786417546,0.94396278,–0.00078691

Zero-point correction=   0.010174 (Hartree/Particle)
 Thermal correction to energy=   0.012534
 Thermal correction to enthalpy=   0.013478
 Thermal correction to Gibbs free energy=   –0.001313
 Sum of electronic and zero-point energies=   –1.164882
 Sum of electronic and thermal energies=   –1.162521
 Sum of electronic and thermal enthalpies=   –1.161577
 Sum of electronic and thermal free energies=   –1.176368

Table S74. Cartesian coordinates and energies of N_2 at the wB97XD/6-31+G(d,p) level of theory.

N,−1.6778037367,1.11765359,−0.1469878
N,−2.7791146233,1.11765359,−0.1469878

Zero-point correction=   0.005705 (Hartree/Particle)
 Thermal correction to energy=   0.008066
 Thermal correction to enthalpy=   0.009010
 Thermal correction to Gibbs free energy=   −0.012738
 Sum of electronic and zero-point energies=   −109.483665
 Sum of electronic and thermal energies=   −109.481304
 Sum of electronic and thermal enthalpies=   −109.480360
 Sum of electronic and thermal free energies=   −109.502108

Table S75. Cartesian coordinates and energies of N_2O at the wB97XD/6-31+G(d,p) level of theory.

N,−2.7403422355,1.11765359,−0.1469878
N,−1.6136149554,1.11765359,−0.1469878
O,−0.4254203491,1.11765359,−0.1469878

Zero-point correction=   0.011310 (Hartree/Particle)
 Thermal correction to energy=   0.014002
 Thermal correction to enthalpy=   0.014946
 Thermal correction to Gibbs free energy=   −0.010004
 Sum of electronic and zero-point energies=   −184.589687
 Sum of electronic and thermal energies=   −184.586995
 Sum of electronic and thermal enthalpies=   −184.586050
 Sum of electronic and thermal free energies=   −184.611001

Table S76. Cartesian coordinates and energies of NH_3 at the wB97XD/6-31+G(d,p) level of theory.

N,−0.6641077547,0.3979977364,−0.0561138388
H,−0.3081971901,−0.550737759,−0.0561139515
H,−0.3081800395,0.8723589536,0.7655115427
H,−0.308180043,0.8723591476,−0.8777391097

Zero-point correction=   0.034765 (Hartree/Particle)
 Thermal correction to energy=   0.037640
 Thermal correction to enthalpy=   0.038584
 Thermal correction to Gibbs free energy=   0.016736
 Sum of electronic and zero-point energies=   −56.511552
 Sum of electronic and thermal energies=   −56.508676
 Sum of electronic and thermal enthalpies=   −56.507732
 Sum of electronic and thermal free energies=   −56.529581

Table S77. Cartesian coordinates and energies of **CO** at the wB97XD/6-31+G(d,p) level of theory.

C,–0.3697585089,0.57198486,–0.00748768
O,0.7648195289,0.57198486,–0.00748768

Zero-point correction=   0.005105 (Hartree/Particle)
 Thermal correction to energy=   0.007466
 Thermal correction to enthalpy=   0.008410
 Thermal correction to Gibbs free energy=   –0.014028
 Sum of electronic and zero-point energies=   –113.272180
 Sum of electronic and thermal energies=   –113.269819
 Sum of electronic and thermal enthalpies=   –113.268875
 Sum of electronic and thermal free energies=   –113.291313

Table S78. Cartesian coordinates and energies of **CS** at the wB97XD/6-31+G(d,p) level of theory.

C,–0.433475068,0.57198486,–0.00748768
S,1.101536088,0.57198486,–0.00748768

Zero-point correction=   0.003046 (Hartree/Particle)
 Thermal correction to energy=   0.005416
 Thermal correction to enthalpy=   0.006360
 Thermal correction to Gibbs free energy=   –0.017526
 Sum of electronic and zero-point energies=   –436.171381
 Sum of electronic and thermal energies=   –436.169011
 Sum of electronic and thermal enthalpies=   –436.168067
 Sum of electronic and thermal free energies=   –436.191953

Table S79. energies of **1-H** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.022377 (Hartree/Particle)
 Thermal correction to energy=   0.026362
 Thermal correction to enthalpy=   0.027306
 Thermal correction to Gibbs free energy=   –0.002876
 Sum of electronic and zero-point energies=   –579.738866
 Sum of electronic and thermal energies=   –579.734882
 Sum of electronic and thermal enthalpies=   –579.733938
 Sum of electronic and thermal free energies=   –579.764119

Table S80. energies of **1-NH₃** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.061612 (Hartree/Particle)
 Thermal correction to energy=   0.067926
 Thermal correction to enthalpy=   0.068871
 Thermal correction to Gibbs free energy=   0.032249
 Sum of electronic and zero-point energies=   −636.102495
 Sum of electronic and thermal energies=   −636.096180
 Sum of electronic and thermal enthalpies=   −636.095236
 Sum of electronic and thermal free energies=   −636.131858

Table S81. energies of **TS1-NH₃** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.058884 (Hartree/Particle)
 Thermal correction to energy=   0.065712
 Thermal correction to enthalpy=   0.066657
 Thermal correction to Gibbs free energy=   0.028729
 Sum of electronic and zero-point energies=   −636.099812
 Sum of electronic and thermal energies=   −636.092983
 Sum of electronic and thermal enthalpies=   −636.092039
 Sum of electronic and thermal free energies=   −636.129967

Table S82. energies of **2-NH₃** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.057729 (Hartree/Particle)
 Thermal correction to energy=   0.063931
 Thermal correction to enthalpy=   0.064876
 Thermal correction to Gibbs free energy=   0.028805
 Sum of electronic and zero-point energies=   −636.157464
 Sum of electronic and thermal energies=   −636.151262
 Sum of electronic and thermal enthalpies=   −636.150318
 Sum of electronic and thermal free energies=   −636.186388

Table S83. energies of **TS2-NH₃** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.054813 (Hartree/Particle)
 Thermal correction to energy=   0.060453
 Thermal correction to enthalpy=   0.061397
 Thermal correction to Gibbs free energy=   0.026555
 Sum of electronic and zero-point energies=   −636.087713
 Sum of electronic and thermal energies=   −636.082074
 Sum of electronic and thermal enthalpies=   −636.081129
 Sum of electronic and thermal free energies=   −636.115971

Table S84. energies of **1-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.035008 (Hartree/Particle)
 Thermal correction to energy=   0.041420
 Thermal correction to enthalpy=   0.042364
 Thermal correction to Gibbs free energy=   0.003867
 Sum of electronic and zero-point energies=   −767.860994
 Sum of electronic and thermal energies=   −767.854582
 Sum of electronic and thermal enthalpies=   −767.853638
 Sum of electronic and thermal free energies=   −767.892135

Table S85. energies of **TS1-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.034063 (Hartree/Particle)
 Thermal correction to energy=   0.040358
 Thermal correction to enthalpy=   0.041302
 Thermal correction to Gibbs free energy=   0.003002
 Sum of electronic and zero-point energies=   −767.861204
 Sum of electronic and thermal energies=   −767.854909
 Sum of electronic and thermal enthalpies=   −767.853965
 Sum of electronic and thermal free energies=   −767.892265

Table S86. energies of **2-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.037637 (Hartree/Particle)
 Thermal correction to energy=   0.043648
 Thermal correction to enthalpy=   0.044593
 Thermal correction to Gibbs free energy=   0.006867
 Sum of electronic and zero-point energies=   −767.916177
 Sum of electronic and thermal energies=   −767.910166
 Sum of electronic and thermal enthalpies=   −767.909222
 Sum of electronic and thermal free energies=   −767.946948

Table S87. energies of **TS2-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.035278 (Hartree/Particle)
 Thermal correction to energy=   0.041607
 Thermal correction to enthalpy=   0.042551
 Thermal correction to Gibbs free energy=   0.004728
 Sum of electronic and zero-point energies=   −767.851863
 Sum of electronic and thermal energies=   −767.845534
 Sum of electronic and thermal enthalpies=   −767.844590
 Sum of electronic and thermal free energies=   −767.882413

Table S88. energies of **TS3-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.031566 (Hartree/Particle)
 Thermal correction to energy=   0.038708
 Thermal correction to enthalpy=   0.039652
 Thermal correction to Gibbs free energy=   −0.001016
 Sum of electronic and zero-point energies=   −767.852163
 Sum of electronic and thermal energies=   −767.845021
 Sum of electronic and thermal enthalpies=   −767.844077
 Sum of electronic and thermal free energies=   −767.884745

Table S89. energies of **3-CO₂-CO** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.031845 (Hartree/Particle)
 Thermal correction to energy=   0.038247
 Thermal correction to enthalpy=   0.039191
 Thermal correction to Gibbs free energy=   0.000614
 Sum of electronic and zero-point energies=   −767.892529
 Sum of electronic and thermal energies=   −767.886127
 Sum of electronic and thermal enthalpies=   −767.885183
 Sum of electronic and thermal free energies=   −767.923760

Table S90. energies of **3-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.026268 (Hartree/Particle)
 Thermal correction to energy=   0.031240
 Thermal correction to enthalpy=   0.032185
 Thermal correction to Gibbs free energy=   −0.001320
 Sum of electronic and zero-point energies=   −654.846192
 Sum of electronic and thermal energies=   −654.841220
 Sum of electronic and thermal enthalpies=   −654.840276
 Sum of electronic and thermal free energies=   −654.873781

Table S91. energies of **TS4-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Si,1.593431,–0.970822,–0.107786
Si,–1.982978,–0.456518,0.000753
O,–0.716262,0.925461,0.000859
C,0.500728,0.537219,–0.017248
O,1.522014,1.268348,0.019153
H,–2.823921,0.175479,–1.111137
H,–2.799155,0.159018,1.13906
H,1.626349,–1.125517,1.413935

Zero-point correction=   0.035684 (Hartree/Particle)
 Thermal correction to energy=   0.041784
 Thermal correction to enthalpy=   0.042728
 Thermal correction to Gibbs free energy=   0.005180
 Sum of electronic and zero-point energies=   –767.861135
 Sum of electronic and thermal energies=   –767.855036
 Sum of electronic and thermal enthalpies=   –767.854092
 Sum of electronic and thermal free energies=   –767.891640

Table S92. energies of **4-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Si,1.879622,–0.785789,–0.108758
Si,–2.187883,–0.469155,–0.003246
O,–0.760119,0.783667,0.016198
C,0.439629,0.395705,–0.012791
O,1.457895,1.168413,0.014065
H,–2.910918,0.293197,–1.120242
H,–2.923952,0.281136,1.112548
H,1.930536,–0.995997,1.410392

Zero-point correction=   0.036012 (Hartree/Particle)
 Thermal correction to energy=   0.042768
 Thermal correction to enthalpy=   0.043712
 Thermal correction to Gibbs free energy=   0.004608
 Sum of electronic and zero-point energies=   –767.862065
 Sum of electronic and thermal energies=   –767.855309
 Sum of electronic and thermal enthalpies=   –767.854364
 Sum of electronic and thermal free energies=   –767.893469

Table S93. energies of **4'-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Si,2.317142,–0.14093,–0.090357
Si,–2.415002,0.00223,0.014847
O,–0.67498,–0.801754,–0.029429
C,0.453194,–0.240849,–0.032429
O,0.717876,1.009564,–0.004286
H,–2.095587,1.033913,–1.072405
H,–2.074486,0.959848,1.161453
H,2.477781,–0.269335,1.432395

Zero-point correction=   0.035881 (Hartree/Particle)
 Thermal correction to energy=   0.042632
 Thermal correction to enthalpy=   0.043577
 Thermal correction to Gibbs free energy=   0.004610
 Sum of electronic and zero-point energies=   –767.858430
 Sum of electronic and thermal energies=   –767.851678
 Sum of electronic and thermal enthalpies=   –767.850734
 Sum of electronic and thermal free energies=   –767.889701

Table S94. energies of **TS5-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Si,2.229322,–0.483001,–0.089296
Si,–2.281832,–0.363106,0.012433
O,–0.401817,–0.524014,–0.055669
C,0.526045,0.395579,–0.028605
O,0.396655,1.61195,0.014159
H,–2.385822,0.744051,–1.043763
H,–2.312165,0.616519,1.192458
H,2.318149,–0.592027,1.431096

Zero-point correction=   0.034380 (Hartree/Particle)
 Thermal correction to energy=   0.040104
 Thermal correction to enthalpy=   0.041048
 Thermal correction to Gibbs free energy=   0.004344
 Sum of electronic and zero-point energies=   –767.845144
 Sum of electronic and thermal energies=   –767.839420
 Sum of electronic and thermal enthalpies=   –767.838476
 Sum of electronic and thermal free energies=   –767.875181

Table S95. energies of **5-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Si,1.606534,–0.944181,–0.031255
Si,–2.019962,–0.402865,0.027137
O,–0.157498,–0.174405,–0.354884
C,0.804607,0.770903,–0.024006
O,0.640856,1.955549,0.084397
H,–2.423637,0.947513,–0.565738
H,–1.884612,0.145166,1.452562
H,1.401736,–1.108599,1.478767

Zero-point correction=   0.034273 (Hartree/Particle)
 Thermal correction to energy=   0.040552
 Thermal correction to enthalpy=   0.041496
 Thermal correction to Gibbs free energy=   0.003242
 Sum of electronic and zero-point energies=   –767.858747
 Sum of electronic and thermal energies=   –767.852468
 Sum of electronic and thermal enthalpies=   –767.851524
 Sum of electronic and thermal free energies=   –767.889778

Table S96. energies of **TS6-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Si,1.030732,–1.269539,–0.001463
Si,–1.954305,0.014302,0.083622
O,–0.242225,–0.148302,–0.547995
C,1.230003,0.624012,0.061703
O,1.318936,1.785282,0.060621
H,–2.243837,1.371348,–0.573902
H,–1.571493,0.62946,1.444094
H,0.751642,–1.267392,1.508376

Zero-point correction=   0.033591 (Hartree/Particle)
 Thermal correction to energy=   0.040358
 Thermal correction to enthalpy=   0.041302
 Thermal correction to Gibbs free energy=   0.001971
 Sum of electronic and zero-point energies=   –767.855256
 Sum of electronic and thermal energies=   –767.848490
 Sum of electronic and thermal enthalpies=   –767.847545
 Sum of electronic and thermal free energies=   –767.886876

Table S97. energies of **6-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Si,–1.667486,0.018684,0.009346
Si,1.599398,0.072084,–0.13077
O,–0.126848,–0.457456,–0.004892
H,2.064207,–0.632221,1.157819
H,1.425706,1.445504,0.555031
H,–1.521902,1.575615,0.026225

Zero-point correction=   0.025482 (Hartree/Particle)
Thermal correction to energy=   0.030670
Thermal correction to enthalpy=   0.031615
Thermal correction to Gibbs free energy=   –0.002589
Sum of electronic and zero-point energies=   –654.837428
Sum of electronic and thermal energies=   –654.832240
Sum of electronic and thermal enthalpies=   –654.831295
Sum of electronic and thermal free energies=   –654.865499

Table S98. energies of **7-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.036695 (Hartree/Particle)
Thermal correction to energy=   0.042710
Thermal correction to enthalpy=   0.043654
Thermal correction to Gibbs free energy=   0.006310
Sum of electronic and zero-point energies=   –767.888361
Sum of electronic and thermal energies=   –767.882347
Sum of electronic and thermal enthalpies=   –767.881403
Sum of electronic and thermal free energies=   –767.918746

Table S99. energies of **TS7-CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.033392 (Hartree/Particle)
Thermal correction to energy=   0.038977
Thermal correction to enthalpy=   0.039922
Thermal correction to Gibbs free energy=   0.003695
Sum of electronic and zero-point energies=   –767.841449
Sum of electronic and thermal energies=   –767.835864
Sum of electronic and thermal enthalpies=   –767.834920
Sum of electronic and thermal free energies=   –767.871147

Table S100. energies of **TS8-CO$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.031998 (Hartree/Particle)
 Thermal correction to energy=   0.038894
 Thermal correction to enthalpy=   0.039838
 Thermal correction to Gibbs free energy=   0.000180
 Sum of electronic and zero-point energies=   −767.854092
 Sum of electronic and thermal energies=   −767.847197
 Sum of electronic and thermal enthalpies=   −767.846252
 Sum of electronic and thermal free energies=   −767.885911

Table S101. energies of **TS9-CO$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.033083 (Hartree/Particle)
 Thermal correction to energy=   0.038855
 Thermal correction to enthalpy=   0.039800
 Thermal correction to Gibbs free energy=   0.003469
 Sum of electronic and zero-point energies=   −767.840441
 Sum of electronic and thermal energies=   −767.834668
 Sum of electronic and thermal enthalpies=   −767.833724
 Sum of electronic and thermal free energies=   −767.870054

Table S102. energies of **8-CO$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.035252 (Hartree/Particle)
 Thermal correction to energy=   0.041132
 Thermal correction to enthalpy=   0.042076
 Thermal correction to Gibbs free energy=   0.005098
 Sum of electronic and zero-point energies=   −767.882046
 Sum of electronic and thermal energies=   −767.876166
 Sum of electronic and thermal enthalpies=   −767.875222
 Sum of electronic and thermal free energies=   −767.912200

Table S103. energies of **TS10-CO$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.033052 (Hartree/Particle)
 Thermal correction to energy=   0.038815
 Thermal correction to enthalpy=   0.039759
 Thermal correction to Gibbs free energy=   0.003004
 Sum of electronic and zero-point energies=   −767.828429
 Sum of electronic and thermal energies=   −767.822666
 Sum of electronic and thermal enthalpies=   −767.821722
 Sum of electronic and thermal free energies=   −767.858477

Table S104. energies of **TS11-CO$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.032645 (Hartree/Particle)
 Thermal correction to energy=   0.039011
 Thermal correction to enthalpy=   0.039956
 Thermal correction to Gibbs free energy=   0.001674
 Sum of electronic and zero-point energies=   −767.854316
 Sum of electronic and thermal energies=   −767.847950
 Sum of electronic and thermal enthalpies=   −767.847005
 Sum of electronic and thermal free energies=   −767.885287

Table S105. energies of **1-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.032439 (Hartree/Particle)
 Thermal correction to energy=   0.039228
 Thermal correction to enthalpy=   0.040172
 Thermal correction to Gibbs free energy=   0.000837
 Sum of electronic and zero-point energies=   −1413.078245
 Sum of electronic and thermal energies=   −1413.071456
 Sum of electronic and thermal enthalpies=   −1413.070511
 Sum of electronic and thermal free energies=   −1413.109847

Table S106. energies of **TS1-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.029537 (Hartree/Particle)
 Thermal correction to energy=   0.036766
 Thermal correction to enthalpy=   0.037710
 Thermal correction to Gibbs free energy=   −0.004463
 Sum of electronic and zero-point energies=   −1413.041671
 Sum of electronic and thermal energies=   −1413.034442
 Sum of electronic and thermal enthalpies=   −1413.033498
 Sum of electronic and thermal free energies=   −1413.075671

Table S107. energies of **2-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.025270 (Hartree/Particle)
 Thermal correction to energy=   0.030414
 Thermal correction to enthalpy=   0.031358
 Thermal correction to Gibbs free energy=   −0.003317
 Sum of electronic and zero-point energies=   −977.461200
 Sum of electronic and thermal energies=   −977.456056
 Sum of electronic and thermal enthalpies=   −977.455112
 Sum of electronic and thermal free energies=   −977.489787

Table S108. energies of **TS2-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.028961 (Hartree/Particle)
 Thermal correction to energy=   0.036437
 Thermal correction to enthalpy=   0.037381
 Thermal correction to Gibbs free energy=   −0.004885
 Sum of electronic and zero-point energies=   −1413.013063
 Sum of electronic and thermal energies=   −1413.005587
 Sum of electronic and thermal enthalpies=   −1413.004643
 Sum of electronic and thermal free energies=   −1413.046909

Table S109. energies of **TS3-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.029668 (Hartree/Particle)
 Thermal correction to energy=   0.037311
 Thermal correction to enthalpy=   0.038255
 Thermal correction to Gibbs free energy=   −0.003739
 Sum of electronic and zero-point energies=   −1413.032963
 Sum of electronic and thermal energies=   −1413.025319
 Sum of electronic and thermal enthalpies=   −1413.024375
 Sum of electronic and thermal free energies=   −1413.066370

Table S110. energies of **3-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.031091 (Hartree/Particle)
 Thermal correction to energy=   0.038456
 Thermal correction to enthalpy=   0.039400
 Thermal correction to Gibbs free energy=   −0.001563
 Sum of electronic and zero-point energies=   −1413.054532
 Sum of electronic and thermal energies=   −1413.047167
 Sum of electronic and thermal enthalpies=   −1413.046223
 Sum of electronic and thermal free energies=   −1413.087186

Table S111. energies of **TS4-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.029734 (Hartree/Particle)
 Thermal correction to energy=   0.035789
 Thermal correction to enthalpy=   0.036733
 Thermal correction to Gibbs free energy=   −0.001633
 Sum of electronic and zero-point energies=   −1413.028805
 Sum of electronic and thermal energies=   −1413.022749
 Sum of electronic and thermal enthalpies=   −1413.021805
 Sum of electronic and thermal free energies=   −1413.060172

Table S112. energies of **TS5-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.029830 (Hartree/Particle)
 Thermal correction to energy=   0.037395
 Thermal correction to enthalpy=   0.038339
 Thermal correction to Gibbs free energy=   −0.003836
 Sum of electronic and zero-point energies=   −1413.022313
 Sum of electronic and thermal energies=   −1413.014748
 Sum of electronic and thermal enthalpies=   −1413.013804
 Sum of electronic and thermal free energies=   −1413.055979

Table S113. energies of **4-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.033102 (Hartree/Particle)
 Thermal correction to energy=   0.039101
 Thermal correction to enthalpy=   0.040045
 Thermal correction to Gibbs free energy=   0.002379
 Sum of electronic and zero-point energies=   −1413.104255
 Sum of electronic and thermal energies=   −1413.098255
 Sum of electronic and thermal enthalpies=   −1413.097311
 Sum of electronic and thermal free energies=   −1413.134977

Table S114. energies of **TS6-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.029414 (Hartree/Particle)
 Thermal correction to energy=   0.036562
 Thermal correction to enthalpy=   0.037506
 Thermal correction to Gibbs free energy=   −0.004651
 Sum of electronic and zero-point energies=   −1413.031605
 Sum of electronic and thermal energies=   −1413.024458
 Sum of electronic and thermal enthalpies=   −1413.023514
 Sum of electronic and thermal free energies=   −1413.065671

Table S115. energies of **5-CS$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.033446 (Hartree/Particle)
 Thermal correction to energy=   0.040052
 Thermal correction to enthalpy=   0.040996
 Thermal correction to Gibbs free energy=   0.001893
 Sum of electronic and zero-point energies=   −1413.106750
 Sum of electronic and thermal energies=   −1413.100143
 Sum of electronic and thermal enthalpies=   −1413.099199
 Sum of electronic and thermal free energies=   −1413.138302

Table S116. energies of **TS7-CS₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.031858 (Hartree/Particle)
 Thermal correction to energy=   0.038499
 Thermal correction to enthalpy=   0.039443
 Thermal correction to Gibbs free energy=   0.000230
 Sum of electronic and zero-point energies=   −1413.048619
 Sum of electronic and thermal energies=   −1413.041979
 Sum of electronic and thermal enthalpies=   −1413.041034
 Sum of electronic and thermal free energies=   −1413.080247

Table S117. energies of **1-H₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.037645 (Hartree/Particle)
 Thermal correction to energy=   0.042477
 Thermal correction to enthalpy=   0.043421
 Thermal correction to Gibbs free energy=   0.010983
 Sum of electronic and zero-point energies=   −580.885311
 Sum of electronic and thermal energies=   −580.880478
 Sum of electronic and thermal enthalpies=   −580.879534
 Sum of electronic and thermal free energies=   −580.911972

Table S118. energies of **TS1-H₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.035548 (Hartree/Particle)
 Thermal correction to energy=   0.040110
 Thermal correction to enthalpy=   0.041054
 Thermal correction to Gibbs free energy=   0.009306
 Sum of electronic and zero-point energies=   −580.849170
 Sum of electronic and thermal energies=   −580.844608
 Sum of electronic and thermal enthalpies=   −580.843664
 Sum of electronic and thermal free energies=   −580.875411

Table S119. energies of **2-H₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.038715 (Hartree/Particle)
 Thermal correction to energy=   0.043353
 Thermal correction to enthalpy=   0.044297
 Thermal correction to Gibbs free energy=   0.012482
 Sum of electronic and zero-point energies=   −580.935984
 Sum of electronic and thermal energies=   −580.931346
 Sum of electronic and thermal enthalpies=   −580.930402
 Sum of electronic and thermal free energies=   −580.962217

Table S120. energies of **TS2-H$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.036778 (Hartree/Particle)
 Thermal correction to energy=   0.041185
 Thermal correction to enthalpy=   0.042130
 Thermal correction to Gibbs free energy=   0.010629
 Sum of electronic and zero-point energies=   −580.880423
 Sum of electronic and thermal energies=   −580.876016
 Sum of electronic and thermal enthalpies=   −580.875071
 Sum of electronic and thermal free energies=   −580.906572

Table S121. energies of **1-CH$_4$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.067535 (Hartree/Particle)
 Thermal correction to energy=   0.073998
 Thermal correction to enthalpy=   0.074942
 Thermal correction to Gibbs free energy=   0.038011
 Sum of electronic and zero-point energies=   −620.063043
 Sum of electronic and thermal energies=   −620.056580
 Sum of electronic and thermal enthalpies=   −620.055636
 Sum of electronic and thermal free energies=   −620.092567

Table S122. energies of **TS1-CH$_4$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.065837 (Hartree/Particle)
 Thermal correction to energy=   0.071844
 Thermal correction to enthalpy=   0.072788
 Thermal correction to Gibbs free energy=   0.037093
 Sum of electronic and zero-point energies=   −620.012127
 Sum of electronic and thermal energies=   −620.006120
 Sum of electronic and thermal enthalpies=   −620.005175
 Sum of electronic and thermal free energies=   −620.040870

Table S123. energies of **2-CH$_4$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.068463 (Hartree/Particle)
 Thermal correction to energy=   0.074592
 Thermal correction to enthalpy=   0.075536
 Thermal correction to Gibbs free energy=   0.039613
 Sum of electronic and zero-point energies=   −620.117924
 Sum of electronic and thermal energies=   −620.111795
 Sum of electronic and thermal enthalpies=   −620.110851
 Sum of electronic and thermal free energies=   −620.146773

Table S124. energies of **2'-CH₄** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.068404 (Hartree/Particle)
 Thermal correction to energy=   0.074625
 Thermal correction to enthalpy=   0.075569
 Thermal correction to Gibbs free energy=   0.039371
 Sum of electronic and zero-point energies=   −620.110802
 Sum of electronic and thermal energies=   −620.104581
 Sum of electronic and thermal enthalpies=   −620.103637
 Sum of electronic and thermal free energies=   −620.139835

Table S125. energies of **TS2-CH₄** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.066812 (Hartree/Particle)
 Thermal correction to energy=   0.072685
 Thermal correction to enthalpy=   0.073629
 Thermal correction to Gibbs free energy=   0.037992
 Sum of electronic and zero-point energies=   −620.057093
 Sum of electronic and thermal energies=   −620.051219
 Sum of electronic and thermal enthalpies=   −620.050275
 Sum of electronic and thermal free energies=   −620.085912

Table S126. energies of **TS2'-CH₄** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.066400 (Hartree/Particle)
 Thermal correction to energy=   0.072414
 Thermal correction to enthalpy=   0.073358
 Thermal correction to Gibbs free energy=   0.037586
 Sum of electronic and zero-point energies=   −620.059669
 Sum of electronic and thermal energies=   −620.053655
 Sum of electronic and thermal enthalpies=   −620.052711
 Sum of electronic and thermal free energies=   −620.088483

Table S127. energies of **1-N₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.029720 (Hartree/Particle)
 Thermal correction to energy=   0.035610
 Thermal correction to enthalpy=   0.036554
 Thermal correction to Gibbs free energy=   0.000169
 Sum of electronic and zero-point energies=   −688.975045
 Sum of electronic and thermal energies=   −688.969155
 Sum of electronic and thermal enthalpies=   −688.968210
 Sum of electronic and thermal free energies=   −689.004595

Table S128. energies of **TS1-N₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.028756 (Hartree/Particle)
 Thermal correction to energy=   0.033680
 Thermal correction to enthalpy=   0.034624
 Thermal correction to Gibbs free energy=   −0.000080
 Sum of electronic and zero-point energies=   −688.977420
 Sum of electronic and thermal energies=   −688.972496
 Sum of electronic and thermal enthalpies=   −688.971552
 Sum of electronic and thermal free energies=   −689.006256

Table S129. energies of **2-N₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.031582 (Hartree/Particle)
 Thermal correction to energy=   0.037029
 Thermal correction to enthalpy=   0.037973
 Thermal correction to Gibbs free energy=   0.002654
 Sum of electronic and zero-point energies=   −688.957284
 Sum of electronic and thermal energies=   −688.951837
 Sum of electronic and thermal enthalpies=   −688.950893
 Sum of electronic and thermal free energies=   −688.986212

Table S130. energies of **TS2-N₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.029753 (Hartree/Particle)
 Thermal correction to energy=   0.035137
 Thermal correction to enthalpy=   0.036081
 Thermal correction to Gibbs free energy=   0.001193
 Sum of electronic and zero-point energies=   −688.948782
 Sum of electronic and thermal energies=   −688.943398
 Sum of electronic and thermal enthalpies=   −688.942454
 Sum of electronic and thermal free energies=   −688.977342

Table S131. energies of **1-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.036683 (Hartree/Particle)
 Thermal correction to energy=   0.042682
 Thermal correction to enthalpy=   0.043626
 Thermal correction to Gibbs free energy=   0.006357
 Sum of electronic and zero-point energies=   −764.034963
 Sum of electronic and thermal energies=   −764.028963
 Sum of electronic and thermal enthalpies=   −764.028019
 Sum of electronic and thermal free energies=   −764.065289

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Table S132. energies of **TS1-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.032903 (Hartree/Particle)
 Thermal correction to energy=   0.038970
 Thermal correction to enthalpy=   0.039914
 Thermal correction to Gibbs free energy=   0.002151
 Sum of electronic and zero-point energies=   −763.949556
 Sum of electronic and thermal energies=   −763.943489
 Sum of electronic and thermal enthalpies=   −763.942545
 Sum of electronic and thermal free energies=   −763.980308

Table S133. energies of **TS1'-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.032812 (Hartree/Particle)
 Thermal correction to energy=   0.038886
 Thermal correction to enthalpy=   0.039831
 Thermal correction to Gibbs free energy=   0.002111
 Sum of electronic and zero-point energies=   −763.949799
 Sum of electronic and thermal energies=   −763.943725
 Sum of electronic and thermal enthalpies=   −763.942781
 Sum of electronic and thermal free energies=   −763.980500

Table S134. energies of **2-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.034559 (Hartree/Particle)
 Thermal correction to energy=   0.040622
 Thermal correction to enthalpy=   0.041566
 Thermal correction to Gibbs free energy=   0.004076
 Sum of electronic and zero-point energies=   −764.082021
 Sum of electronic and thermal energies=   −764.075959
 Sum of electronic and thermal enthalpies=   −764.075014
 Sum of electronic and thermal free energies=   −764.112504

Table S135. energies of **TS2-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.034610 (Hartree/Particle)
 Thermal correction to energy=   0.041562
 Thermal correction to enthalpy=   0.042506
 Thermal correction to Gibbs free energy=   0.003724
 Sum of electronic and zero-point energies=   −764.041543
 Sum of electronic and thermal energies=   −764.034591
 Sum of electronic and thermal enthalpies=   −764.033646
 Sum of electronic and thermal free energies=   −764.072429

Table S136. energies of **TS3-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.032988 (Hartree/Particle)
 Thermal correction to energy=   0.038941
 Thermal correction to enthalpy=   0.039885
 Thermal correction to Gibbs free energy= 0.002132
 Sum of electronic and zero-point energies=   −764.078612
 Sum of electronic and thermal energies=   −764.072659
 Sum of electronic and thermal enthalpies=   −764.071715
 Sum of electronic and thermal free energies=   −764.109469

Table S137. energies of **3-N₂O-N₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.032323 (Hartree/Particle)
 Thermal correction to energy=   0.038910
 Thermal correction to enthalpy=   0.039854
 Thermal correction to Gibbs free energy= −0.000459
 Sum of electronic and zero-point energies=   −764.119485
 Sum of electronic and thermal energies=   −764.112898
 Sum of electronic and thermal enthalpies=   −764.111954
 Sum of electronic and thermal free energies=   −764.152267

Table S138. energies of **3-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.026268 (Hartree/Particle)
 Thermal correction to energy=   0.031240
 Thermal correction to enthalpy=   0.032185
 Thermal correction to Gibbs free energy= −0.001320
 Sum of electronic and zero-point energies=   −654.846192
 Sum of electronic and thermal energies=   −654.841220
 Sum of electronic and thermal enthalpies=   −654.840276
 Sum of electronic and thermal free energies=   −654.873781

Table S139. energies of **4-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.037867 (Hartree/Particle)
 Thermal correction to energy=   0.043777
 Thermal correction to enthalpy=   0.044721
 Thermal correction to Gibbs free energy= 0.007957
 Sum of electronic and zero-point energies=   −764.004526
 Sum of electronic and thermal energies=   −763.998616
 Sum of electronic and thermal enthalpies=   −763.997672
 Sum of electronic and thermal free energies=   −764.034436

Table S140. energies of **TS4-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.032912 (Hartree/Particle)
 Thermal correction to energy=   0.038662
 Thermal correction to enthalpy=   0.039606
 Thermal correction to Gibbs free energy=   0.002477
 Sum of electronic and zero-point energies=   −763.923715
 Sum of electronic and thermal energies=   −763.917965
 Sum of electronic and thermal enthalpies=   −763.917021
 Sum of electronic and thermal free energies=   −763.954150

Table S141. energies of **5-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.036185 (Hartree/Particle)
 Thermal correction to energy=   0.042009
 Thermal correction to enthalpy=   0.042954
 Thermal correction to Gibbs free energy=   0.006181
 Sum of electronic and zero-point energies=   −763.997826
 Sum of electronic and thermal energies=   −763.992002
 Sum of electronic and thermal enthalpies=   −763.991058
 Sum of electronic and thermal free energies=   −764.027831

Table S142. energies of **TS5-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.034317 (Hartree/Particle)
 Thermal correction to energy=   0.040684
 Thermal correction to enthalpy=   0.041629
 Thermal correction to Gibbs free energy=   0.003055
 Sum of electronic and zero-point energies=   −763.932220
 Sum of electronic and thermal energies=   −763.925852
 Sum of electronic and thermal enthalpies=   −763.924908
 Sum of electronic and thermal free energies=   −763.963481

Table S143. energies of **6-N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.036681 (Hartree/Particle)
 Thermal correction to energy=   0.042678
 Thermal correction to enthalpy=   0.043623
 Thermal correction to Gibbs free energy=   0.006373
 Sum of electronic and zero-point energies=   −764.034982
 Sum of electronic and thermal energies=   −764.028984
 Sum of electronic and thermal enthalpies=   −764.028040
 Sum of electronic and thermal free energies=   −764.065289

Table S144. energies of **TS7-N$_2$O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.034915 (Hartree/Particle)
 Thermal correction to energy=   0.040272
 Thermal correction to enthalpy=   0.041216
 Thermal correction to Gibbs free energy=   0.005732
 Sum of electronic and zero-point energies=   −763.967873
 Sum of electronic and thermal energies=   −763.962516
 Sum of electronic and thermal enthalpies=   −763.961572
 Sum of electronic and thermal free energies=   −763.997056

Table S145. energies of **TS8-N$_2$O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.034601 (Hartree/Particle)
 Thermal correction to energy=   0.041563
 Thermal correction to enthalpy=   0.042507
 Thermal correction to Gibbs free energy=   0.003703
 Sum of electronic and zero-point energies=   −764.041560
 Sum of electronic and thermal energies=   −764.034599
 Sum of electronic and thermal enthalpies=   −764.033654
 Sum of electronic and thermal free energies=   −764.072458

Table S146. energies of **NH$_3$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.034981 (Hartree/Particle)
 Thermal correction to energy=   0.037850
 Thermal correction to enthalpy=   0.038794
 Thermal correction to Gibbs free energy=   0.016954
 Sum of electronic and zero-point energies=   −56.375586
 Sum of electronic and thermal energies=   −56.372717
 Sum of electronic and thermal enthalpies=   −56.371773
 Sum of electronic and thermal free energies=   −56.393614

Table S147. energies of **CH$_4$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.045499 (Hartree/Particle)
 Thermal correction to energy=   0.048361
 Thermal correction to enthalpy=   0.049305
 Thermal correction to Gibbs free energy=   0.028180
 Sum of electronic and zero-point energies=   −40.345451
 Sum of electronic and thermal energies=   −40.342589
 Sum of electronic and thermal enthalpies=   −40.341645
 Sum of electronic and thermal free energies=   −40.362770

Table S148. energies of **N₂O** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.010930 (Hartree/Particle)
 Thermal correction to energy=   0.013769
 Thermal correction to enthalpy=   0.014713
 Thermal correction to Gibbs free energy=   −0.010465
 Sum of electronic and zero-point energies=   −184.210217
 Sum of electronic and thermal energies=   −184.207378
 Sum of electronic and thermal enthalpies=   −184.206434
 Sum of electronic and thermal free energies=   −184.231612

Table S149. energies of **CS₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.006870 (Hartree/Particle)
 Thermal correction to energy=   0.010054
 Thermal correction to enthalpy=   0.010998
 Thermal correction to Gibbs free energy=   −0.016130
 Sum of electronic and zero-point energies=   −833.298139
 Sum of electronic and thermal energies=   −833.294955
 Sum of electronic and thermal enthalpies=   −833.294011
 Sum of electronic and thermal free energies=   −833.321139

Table S150. energies of **CO₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.011586 (Hartree/Particle)
 Thermal correction to energy=   0.014276
 Thermal correction to enthalpy=   0.015220
 Thermal correction to Gibbs free energy=   −0.009145
 Sum of electronic and zero-point energies=   −188.119387
 Sum of electronic and thermal energies=   −188.116697
 Sum of electronic and thermal enthalpies=   −188.115753
 Sum of electronic and thermal free energies=   −188.140119

Table S151. energies of **N₂** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.005696 (Hartree/Particle)
 Thermal correction to energy=   0.008057
 Thermal correction to enthalpy=   0.009001
 Thermal correction to Gibbs free energy=   −0.012746
 Sum of electronic and zero-point energies=   −109.268502
 Sum of electronic and thermal energies=   −109.266142
 Sum of electronic and thermal enthalpies=   −109.265197
 Sum of electronic and thermal free energies=   −109.286945

Table S152. energies of **H$_2$** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.010128 (Hartree/Particle)
 Thermal correction to energy=   0.012489
 Thermal correction to enthalpy=   0.013433
 Thermal correction to Gibbs free energy=   −0.001358
 Sum of electronic and zero-point energies=   −1.155018
 Sum of electronic and thermal energies=   −1.152658
 Sum of electronic and thermal enthalpies=   −1.151713
 Sum of electronic and thermal free energies=   −1.166504

Table S153. energies of **CO** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.005125 (Hartree/Particle)
 Thermal correction to energy=   0.007485
 Thermal correction to enthalpy=   0.008430
 Thermal correction to Gibbs free energy=   −0.014008
 Sum of electronic and zero-point energies=   −113.040522
 Sum of electronic and thermal energies=   −113.038162
 Sum of electronic and thermal enthalpies=   −113.037217
 Sum of electronic and thermal free energies=   −113.059655

Table S154. energies of **CS** at the CCSD(T)/6-31+G(d,p) level of theory.

Zero-point correction=   0.003047 (Hartree/Particle)
 Thermal correction to energy=   0.005417
 Thermal correction to enthalpy=   0.006361
 Thermal correction to Gibbs free energy=   −0.017525
 Sum of electronic and zero-point energies=   −435.577509
 Sum of electronic and thermal energies=   −435.575139
 Sum of electronic and thermal enthalpies=   −435.574195
 Sum of electronic and thermal free energies=   −435.598081

Table S155. Cartesian coordinates and energies of **1-H** at the wB97XD/cc-pVTZ level of theory.

Si,1.1864561646,–0.1108401295,0.0000975842
Si,–0.991895252,0.0061101979,–0.0000302669
H,–1.9184676722,–1.1822811913,0.0004719066
H,–1.9134357706,1.1981729202,–0.0001240249
H,1.2737705303,1.4274582028,0.000509801

Zero-point correction=   0.022264 (Hartree/Particle)
 Thermal correction to energy=   0.026281
 Thermal correction to enthalpy=   0.027226
 Thermal correction to Gibbs free energy=   –0.003000
 Sum of electronic and zero-point energies=   –580.745693
 Sum of electronic and thermal energies=   –580.741675
 Sum of electronic and thermal enthalpies=   –580.740731
 Sum of electronic and thermal free energies=   –580.770956

Table S156. Cartesian coordinates and energies of **1-NH₃** at the wB97XD/cc-pVTZ level of theory.

Si,1.4325562882,–0.4191322764,0.0402611306
Si,–0.5194781761,0.9531897951,–0.1654150974
H,–0.7590301832,1.1297036743,1.3453023012
H,2.3378446561,0.0417125698,–1.1029393982
H,2.2261126538,0.2008762546,1.1891858171
H,–0.8595586738,–1.5046571627,0.1274382469
N,–1.6314284923,–0.8362792984,–0.0086816903
H,–2.2642569829,–0.8459056669,0.7804739271
H,–2.1370790897,–1.0557228892,–0.8556012369

Zero-point correction=   0.060881 (Hartree/Particle)
 Thermal correction to energy=   0.067273
 Thermal correction to enthalpy=   0.068217
 Thermal correction to Gibbs free energy=   0.031650
 Sum of electronic and zero-point energies=   –637.266143
 Sum of electronic and thermal energies=   –637.259751
 Sum of electronic and thermal enthalpies=   –637.258807
 Sum of electronic and thermal free energies=   –637.295374

Table S157. Cartesian coordinates and energies of **TS1-NH$_3$** at the wB97XD/cc-pVTZ level of theory.

Si,1.305495181,–0.6697551492,–0.0037426493
Si,–0.0821348354,1.1485082895,–0.091131064
H,–0.4358232092,1.1498096338,1.4037426611
H,2.3831936707,–0.5518447606,–1.061366226
H,2.099806773,–0.8053259664,1.2790629025
H,–1.3061700198,–1.2546751294,–0.105848671
N,–2.1210360167,–0.6439169296,–0.0518785832
H,–2.6199585225,–0.8303280829,0.8080464137
H,–2.7285250212,–0.8204099052,–0.8407627839

Zero-point correction=   0.058536 (Hartree/Particle)
 Thermal correction to energy=   0.065348
 Thermal correction to enthalpy=   0.066292
 Thermal correction to Gibbs free energy=   0.028437
 Sum of electronic and zero-point energies=   –637.261411
 Sum of electronic and thermal energies=   –637.254599
 Sum of electronic and thermal enthalpies=   –637.253655
 Sum of electronic and thermal free energies=   –637.291509

Table S158. Cartesian coordinates and energies of **2-NH$_3$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.4567815617,0.1835206982,–0.0042464976
Si,0.739085914,–0.7408321623,–0.1152823755
H,0.6680833513,–1.121027226,1.3895410198
H,–1.9918314773,0.7545913588,–1.2957957034
H,–2.5129191866,–0.8342373202,0.3578159251
H,–1.7555143235,1.3121852711,0.9631380899
N,1.6667654435,0.8337297732,–0.0811198908
H,1.6110019853,1.3697095918,0.7741014487
H,2.6439238551,0.7015990155,–0.2985700161

Zero-point correction=   0.057251 (Hartree/Particle)
 Thermal correction to energy=   0.063498
 Thermal correction to enthalpy=   0.064442
 Thermal correction to Gibbs free energy=   0.028242
 Sum of electronic and zero-point energies=   –637.324168
 Sum of electronic and thermal energies=   –637.317921
 Sum of electronic and thermal enthalpies=   –637.316977
 Sum of electronic and thermal free energies=   –637.353176

Table S159. Cartesian coordinates and energies of **TS2-NH₃** at the wB97XD/cc-pVTZ level of theory.

Si,–1.3942424533,0.2140296666,0.0130926197
Si,0.7414842237,–0.8887731429,–0.1270940836
H,0.8368188255,–1.0778015266,1.3958598557
H,–2.3156900956,0.0233322882,–1.1803290678
H,–2.3325184123,–0.1609866749,1.1474610267
H,0.0297303916,1.3539960379,0.0573870152
N,1.3303337495,0.9918092304,0.0117365974
H,1.8595819184,1.2052920153,0.8499093807
H,1.8598848525,1.311742106,–0.7908503439

Zero-point correction=   0.054748 (Hartree/Particle)
 Thermal correction to energy=   0.060389
 Thermal correction to enthalpy=   0.061333
 Thermal correction to Gibbs free energy=   0.026505
 Sum of electronic and zero-point energies=   –637.255255
 Sum of electronic and thermal energies=   –637.249613
 Sum of electronic and thermal enthalpies=   –637.248669
 Sum of electronic and thermal free energies=   –637.283497

Table S160. Cartesian coordinates and energies of **2-CO₂** at the wB97XD/cc-pVTZ level of theory.

Si,–0.0291583364,1.4966521127,–0.1306971547
Si,1.4074234008,–0.3562029785,0.0413117738
O,–0.0489255525,–1.2652282448,–0.093426165
C,–1.0000149165,–0.2546263168,–0.0145227681
O,–2.1652395973,–0.54272283,0.061320369
H,2.3108797482,–0.8354524053,–1.0639178151
H,2.1314948302,–0.8350121628,1.2715839125
H,–0.0953275764,1.7432508255,1.3768898476

Zero-point correction=   0.037796 (Hartree/Particle)
 Thermal correction to energy=   0.043627
 Thermal correction to enthalpy=   0.044571
 Thermal correction to Gibbs free energy=   0.008127
 Sum of electronic and zero-point energies=   –769.384562
 Sum of electronic and thermal energies=   –769.378731
 Sum of electronic and thermal enthalpies=   –769.377786
 Sum of electronic and thermal free energies=   –769.414230

Table S161. Cartesian coordinates and energies of **TS2'-CO₂** at the wB97XD/cc-pVTZ level of theory.

Si,–1.6599823747,–0.6235415071,–0.4691606527
Si,–0.353909472,1.0467399587,0.3984894929
O,1.990372112,0.2180612045,–0.8877182733
C,1.2277817994,–0.2137548727,–0.0336307135
O,1.1660476129,–1.2534322789,0.6301111743
H,–0.2643350036,2.3413688227,–0.3437319846
H,–0.4016234059,1.3843555473,1.8557399509
H,–1.8276012681,–1.2942058743,0.888103006

Zero-point correction=   0.034897 (Hartree/Particle)
 Thermal correction to energy=   0.041340
 Thermal correction to enthalpy=   0.042284
 Thermal correction to Gibbs free energy=   0.003945
 Sum of electronic and zero-point energies=   −769.325123
 Sum of electronic and thermal energies=   −769.318680
 Sum of electronic and thermal enthalpies=   −769.317736
 Sum of electronic and thermal free energies=   −769.356075

Table S162. Cartesian coordinates and energies of **3-CO₂** at the wB97XD/cc-pVTZ level of theory.

Si,–0.649358989,0.3217909184,0.0200461147
Si,1.6006769177,–0.1340719271,–0.1503805702
H,1.9284081219,0.9498799001,0.8757597281
H,1.6620347846,–1.3438349199,0.7702990766
H,–0.8888991801,1.8268073111,–0.1164519048
O,–1.9505216551,–0.5121372825,0.0160125555

Zero-point correction=   0.026133 (Hartree/Particle)
 Thermal correction to energy=   0.031185
 Thermal correction to enthalpy=   0.032129
 Thermal correction to Gibbs free energy=   −0.001499
 Sum of electronic and zero-point energies=   −656.034363
 Sum of electronic and thermal energies=   −656.029312
 Sum of electronic and thermal enthalpies=   −656.028367
 Sum of electronic and thermal free energies=   −656.061995

Table S163. Cartesian coordinates and energies of **TS3-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.5643823792,–1.2029054239,–0.1612529513
Si,–0.7811425488,1.0239115275,0.1615468347
O,0.7038735057,1.3208631649,–0.2728059259
C,1.7567912739,–0.7804921276,0.2417721278
O,2.8380029308,–0.6333007499,–0.0672449875
H,–1.9207260659,1.5941838855,–0.7099893011
H,–1.1986833482,1.5292127974,1.5313790611
H,–2.4947003683,–1.2337190739,1.0652691422

Zero-point correction=   0.031728 (Hartree/Particle)
 Thermal correction to energy=   0.039561
 Thermal correction to enthalpy=   0.040505
 Thermal correction to Gibbs free energy=   –0.001653
 Sum of electronic and zero-point energies=   –769.310262
 Sum of electronic and thermal energies=   –769.302430
 Sum of electronic and thermal enthalpies=   –769.301486
 Sum of electronic and thermal free energies=   –769.343644

Table S164. Cartesian coordinates and energies of **4-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,1.8936620954,–0.7690120042,–0.1017125479
Si,–2.1864295287,–0.4680214775,–0.0148390079
O,–0.7614673041,0.7623158239,0.0085871888
C,0.4311652766,0.3765784018,–0.0153186267
O,1.4437684277,1.1502475763,0.0103472755
H,–2.918195058,0.322093078,–1.1092689583
H,–2.9146141156,0.2785126579,1.1113676415
H,1.9369202068,–0.9815370562,1.419003035

Zero-point correction=   0.035976 (Hartree/Particle)
 Thermal correction to energy=   0.042710
 Thermal correction to enthalpy=   0.043654
 Thermal correction to Gibbs free energy=   0.004320
 Sum of electronic and zero-point energies=   –769.329791
 Sum of electronic and thermal energies=   –769.323057
 Sum of electronic and thermal enthalpies=   –769.322113
 Sum of electronic and thermal free energies=   –769.361447

Table S165. Cartesian coordinates and energies of **4'-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,2.3017708879,–0.1174453248,–0.0927675658
Si,–2.4000644394,–0.0024305739,0.0172967257
O,–0.6800461264,–0.8041262509,–0.0303709274
C,0.443214226,–0.2494081189,–0.0325336226
O,0.7075381565,0.9952754568,0.0035919214
H,–2.079791428,1.0333057235,–1.0680813823
H,–2.0533591781,0.9673433401,1.1535468721
H,2.4666759015,–0.2698272518,1.4291069788

Zero-point correction=   0.035971 (Hartree/Particle)
 Thermal correction to energy=   0.042653
 Thermal correction to enthalpy=   0.043597
 Thermal correction to Gibbs free energy=   0.004838
 Sum of electronic and zero-point energies=   –769.326868
 Sum of electronic and thermal energies=   –769.320187
 Sum of electronic and thermal enthalpies=   –769.319242
 Sum of electronic and thermal free energies=   –769.358002

Table S166. Cartesian coordinates and energies of **TS4-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,1.571354309,–0.971427308,–0.1061042721
Si,–1.9519463582,–0.4521858069,–0.003384588
O,–0.7147462473,0.9278987813,–0.0051619504
C,0.4983979579,0.5429835933,–0.020513352
O,1.5142573499,1.2676279662,0.0164513026
H,–2.8179840371,0.1752316892,–1.1011514211
H,–2.7766557301,0.1451726135,1.1408503569
H,1.5975287559,–1.1226335286,1.4166029243

Zero-point correction=   0.035750 (Hartree/Particle)
 Thermal correction to energy=   0.041766
 Thermal correction to enthalpy=   0.042710
 Thermal correction to Gibbs free energy=   0.005417
 Sum of electronic and zero-point energies=   –769.327291
 Sum of electronic and thermal energies=   –769.321275
 Sum of electronic and thermal enthalpies=   –769.320331
 Sum of electronic and thermal free energies=   –769.357623

Table S167. Cartesian coordinates and energies of **5-CO₂** at the wB97XD/cc-pVTZ level of theory.

Si,1.5739325336,–0.9435155088,–0.0484549478
Si,–1.9950431422,–0.4112959009,0.0356415502
O,–0.1574759915,–0.1786170374,–0.3433942712
C,0.8061715602,0.7804020176,–0.011999048
O,0.6241295526,1.9497625639,0.1006746724
H,–2.4065523679,0.9284023513,–0.5800362209
H,–1.8790761599,0.1759274604,1.4480742041
H,1.4019380153,–1.1119849461,1.4664740613

Zero-point correction=   0.035078 (Hartree/Particle)
 Thermal correction to energy=   0.042027
 Thermal correction to enthalpy=   0.042971
 Thermal correction to Gibbs free energy=   0.002986
 Sum of electronic and zero-point energies=   –769.321928
 Sum of electronic and thermal energies=   –769.314979
 Sum of electronic and thermal enthalpies=   –769.314035
 Sum of electronic and thermal free energies=   –769.354021

Table S168. Cartesian coordinates and energies of **TS5-CO₂** at the wB97XD/cc-pVTZ level of theory.

Si,2.2156048101,–0.4764220965,–0.0971345095
Si,–2.267594869,–0.3679036373,0.0126721763
O,–0.4062972772,–0.5272252462,–0.0458457326
C,0.513781405,0.3952464657,–0.0194287961
O,0.38338378,1.6013896197,0.0251511453
H,–2.3674761305,0.7427227132,–1.0439115643
H,–2.3066149169,0.6307823161,1.1792092259
H,2.3237481987,–0.5926391346,1.422101055

Zero-point correction=   0.034515 (Hartree/Particle)
 Thermal correction to energy=   0.041039
 Thermal correction to enthalpy=   0.041983
 Thermal correction to Gibbs free energy=   0.003263
 Sum of electronic and zero-point energies=   –769.307425
 Sum of electronic and thermal energies=   –769.300901
 Sum of electronic and thermal enthalpies=   –769.299957
 Sum of electronic and thermal free energies=   –769.338677

Table S169. Cartesian coordinates and energies of **6-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.6542434462,0.0169030557,0.0119269192
Si,1.5810532926,0.0740663625,–0.1389379563
O,–0.126253959,–0.4580919423,0.0081870558
H,2.0658545689,–0.6277334675,1.1478412274
H,1.4180600858,1.4392478728,0.5700429611
H,–1.5113955421,1.5778181188,0.0136987929

Zero-point correction=   0.025048 (Hartree/Particle)
 Thermal correction to energy=   0.030292
 Thermal correction to enthalpy=   0.031236
 Thermal correction to Gibbs free energy=   –0.003072
 Sum of electronic and zero-point energies=   –656.023017
 Sum of electronic and thermal energies=   –656.017773
 Sum of electronic and thermal enthalpies=   –656.016829
 Sum of electronic and thermal free energies=   –656.051137

Table S170. Cartesian coordinates and energies of **TS6-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,1.0433128359,–1.2721178236,0.001341136
Si,–1.9489387761,0.0239400165,0.074350098
O,–0.2358906723,–0.1500307618,–0.5262457716
C,1.1884636141,0.6116787046,0.0400552982
O,1.2698992036,1.7671586501,0.045776612
H,–2.1955427511,1.4022742399,–0.5604973832
H,–1.5800587043,0.623843049,1.4455879875
H,0.7782082502,–1.2675750746,1.5146880232

Zero-point correction=   0.033820 (Hartree/Particle)
 Thermal correction to energy=   0.040401
 Thermal correction to enthalpy=   0.041345
 Thermal correction to Gibbs free energy=   0.002627
 Sum of electronic and zero-point energies=   –769.318345
 Sum of electronic and thermal energies=   –769.311764
 Sum of electronic and thermal enthalpies=   –769.310820
 Sum of electronic and thermal free energies=   –769.349538

Table S171. Cartesian coordinates and energies of **7-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,1.0055433957,–0.8417716531,–0.0205355512
H,1.8118140786,–1.2543194006,–1.2212404782
H,1.8197238712,–1.3870145484,1.1191228465
Si,–1.3461947759,–0.7462243583,–0.0853587284
H,–1.4031257876,–0.8797759455,1.4436175682
C,0.1311251716,1.6964875371,0.0193368971
O,–1.0003202298,1.0822998791,–0.0504615781
O,1.1975482761,0.8800964898,0.052264024

Zero-point correction=   0.036748 (Hartree/Particle)
 Thermal correction to energy=   0.042583
 Thermal correction to enthalpy=   0.043527
 Thermal correction to Gibbs free energy=   0.007234
 Sum of electronic and zero-point energies=   –769.352535
 Sum of electronic and thermal energies=   –769.346700
 Sum of electronic and thermal enthalpies=   –769.345756
 Sum of electronic and thermal free energies=   –769.382049

Table S172. Cartesian coordinates and energies of **TS7-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,0.9262104853,1.0884457118,–0.0032866949
H,1.0048126125,1.9962699309,–1.1946757939
H,0.954539942,2.0036704283,1.1840769052
Si,1.2809961009,–1.1159123056,–0.0928519983
H,1.212801205,–1.1780154451,1.4390010473
C,–1.8159844895,–0.1382611321,0.0057537233
O,–1.3787146739,–1.2450762565,–0.0280423477
O,–1.5129311823,1.0227660682,0.010554159

Zero-point correction=   0.034404 (Hartree/Particle)
 Thermal correction to energy=   0.041120
 Thermal correction to enthalpy=   0.042064
 Thermal correction to Gibbs free energy=   0.003401
 Sum of electronic and zero-point energies=   –769.300513
 Sum of electronic and thermal energies=   –769.293797
 Sum of electronic and thermal enthalpies=   –769.292853
 Sum of electronic and thermal free energies=   –769.331515

Table S173. Cartesian coordinates and energies of **TS8-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,0.8049368465,0.9891034545,–0.1395650698
H,1.3486337787,1.4619205578,–1.4771424087
H,2.0463723022,1.2113494594,0.756838671
Si,1.2010247744,–1.3497363747,–0.0024546989
H,0.6540988397,–1.3926306701,1.4227505414
C,–2.3168212721,–0.1263271939,0.0828768429
O,–1.7396936465,–1.0586391086,–0.2212465219
O,–0.5835246229,1.5874998757,0.298193644

Zero-point correction=   0.032339 (Hartree/Particle)
 Thermal correction to energy=   0.039862
 Thermal correction to enthalpy=   0.040806
 Thermal correction to Gibbs free energy=   –0.000098
 Sum of electronic and zero-point energies=   –769.310420
 Sum of electronic and thermal energies=   –769.302897
 Sum of electronic and thermal enthalpies=   –769.301953
 Sum of electronic and thermal free energies=   –769.342857

Table S174. Cartesian coordinates and energies of **TS9-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.5026915738,–0.4996834203,0.0169647975
H,–1.6145365282,–1.4045909426,–1.1647380961
H,–2.9475866983,–0.3943529162,0.4775458999
Si,–0.192512468,1.2830925449,–0.0943455769
H,–0.3784936308,2.0508601995,1.1960651355
C,1.7629903564,–0.7001221874,0.1018766218
O,1.3854968641,0.7027262094,–0.1896223832
O,0.8553916786,–1.5019604873,0.1549446016

Zero-point correction=   0.033236 (Hartree/Particle)
 Thermal correction to energy=   0.039715
 Thermal correction to enthalpy=   0.040659
 Thermal correction to Gibbs free energy=   0.002872
 Sum of electronic and zero-point energies=   –769.292631
 Sum of electronic and thermal energies=   –769.286152
 Sum of electronic and thermal enthalpies=   –769.285208
 Sum of electronic and thermal free energies=   –769.322995

Table S175. Cartesian coordinates and energies of **8-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,0.0384087725,0.0769063758,0.4632323593
Si,–2.1536807205,–0.1571736701,–0.1922702747
H,–2.4712672414,1.1789232325,0.4856103334
H,–1.93384735,0.3931878503,–1.596837917
H,0.2039238813,0.2444734384,1.9478914819
O,1.2783039853,–1.0710337141,–0.0155240114
C,2.0647466609,–0.0823867262,–0.4541526746
O,1.3525040118,1.0243712134,–0.229017297

Zero-point correction=   0.035665 (Hartree/Particle)
 Thermal correction to energy=   0.042084
 Thermal correction to enthalpy=   0.043028
 Thermal correction to Gibbs free energy=   0.005305
 Sum of electronic and zero-point energies=   –769.350714
 Sum of electronic and thermal energies=   –769.344296
 Sum of electronic and thermal enthalpies=   –769.343352
 Sum of electronic and thermal free energies=   –769.381075

Table S176. Cartesian coordinates and energies of **TS10-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,0.3011655939,–0.5676283279,0.1073958934
Si,2.3569796909,0.2085287122,–0.1350308299
H,3.5050196478,–0.4282440241,0.5972228062
H,2.8676464277,0.4894198307,–1.5191504169
H,0.4012423728,–1.0127356119,1.5552316931
O,–1.1734812745,0.9895847338,0.2857624995
C,–2.2593221123,0.4842560137,0.0335769138
O,–2.6288113462,–0.5837093267,–0.3516595592

Zero-point correction=   0.033310 (Hartree/Particle)
 Thermal correction to energy=   0.040660
 Thermal correction to enthalpy=   0.041605
 Thermal correction to Gibbs free energy=   0.000686
 Sum of electronic and zero-point energies=   –769.280093
 Sum of electronic and thermal energies=   –769.272743
 Sum of electronic and thermal enthalpies=   –769.271799
 Sum of electronic and thermal free energies=   –769.312718

Table S177. Cartesian coordinates and energies of **TS11-CO$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,0.0780756298,–0.3244356569,0.4399050981
Si,2.1336477197,0.3842309431,–0.2452856785
H,2.7776406871,–0.2531727813,0.9826363246
H,2.3828671825,–0.7267121368,–1.2508246048
H,–0.1940657112,–0.0477576668,1.896620142
O,–1.6371285322,1.1100310223,–0.0108153629
C,–2.2708844853,0.1573636795,–0.3526392709
O,–1.0874604904,–1.1621254032,–0.2724296476

Zero-point correction=   0.033015 (Hartree/Particle)
 Thermal correction to energy=   0.039993
 Thermal correction to enthalpy=   0.040938
 Thermal correction to Gibbs free energy=   0.001753
 Sum of electronic and zero-point energies=   –769.317050
 Sum of electronic and thermal energies=   –769.310071
 Sum of electronic and thermal enthalpies=   –769.309127
 Sum of electronic and thermal free energies=   –769.348311

Table S178. Cartesian coordinates and energies of **1-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–0.7087395782,1.4282724261,–0.1182530731
H,–1.261435146,1.9609846924,–1.4100197334
H,–1.3282596239,2.3305561371,0.9092402078
Si,1.5933132712,1.0075599596,0.0317452824
H,1.5000975327,1.0236353375,1.5601153489
C,–0.4520222641,–1.7119025326,0.0160232545
S,–1.6984969074,–0.5587713053,0.1015240811
S,1.1595167158,–1.2610567147,–0.0970373682

Zero-point correction=   0.032489 (Hartree/Particle)
 Thermal correction to energy=   0.039264
 Thermal correction to enthalpy=   0.040208
 Thermal correction to Gibbs free energy=   0.000916
 Sum of electronic and zero-point energies=   –1415.304989
 Sum of electronic and thermal energies=   –1415.298214
 Sum of electronic and thermal enthalpies=   –1415.297270
 Sum of electronic and thermal free energies=   –1415.336562

Table S179. Cartesian coordinates and energies of **TS1-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.8225957207,–1.1549942369,–0.0702331034
H,–1.9783384202,–1.9883189399,–1.3111041883
H,–1.8068034206,–2.1400770266,1.0643582763
Si,–2.0163798842,1.0368387253,–0.0106665164
H,–1.8515441269,1.0188844338,1.5166933504
C,1.7440859519,0.1680931306,0.004901465
S,1.8413532356,–1.388632446,0.0319635714
S,1.2201853851,1.6254073597,–0.047625855

Zero-point correction=   0.029994 (Hartree/Particle)
 Thermal correction to energy=   0.037852
 Thermal correction to enthalpy=   0.038796
 Thermal correction to Gibbs free energy=   –0.004796
 Sum of electronic and zero-point energies=   –1415.250546
 Sum of electronic and thermal energies=   –1415.242688
 Sum of electronic and thermal enthalpies=   –1415.241744
 Sum of electronic and thermal free energies=   –1415.285336

Table S180. Cartesian coordinates and energies of **2-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–0.1063602861,0.5167914966,0.0330827327
Si,2.028450277,–0.2695729181,–0.1528019631
H,2.6295038021,0.7676779761,0.7852244423
H,1.974765395,–1.4725704705,0.7675486164
H,–0.1241832101,2.0174190483,–0.1711136483
S,–1.9334679779,–0.3001311323,0.0132508199

Zero-point correction=   0.024992 (Hartree/Particle)
 Thermal correction to energy=   0.030296
 Thermal correction to enthalpy=   0.031240
 Thermal correction to Gibbs free energy=   –0.003747
 Sum of electronic and zero-point energies=   –979.033271
 Sum of electronic and thermal energies=   –979.027968
 Sum of electronic and thermal enthalpies=   –979.027024
 Sum of electronic and thermal free energies=   –979.062011

Table S181. Cartesian coordinates and energies of **TS2-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.0808891848,0.8063899215,0.3925008254
H,–1.7242775759,1.6323227576,1.4604028526
H,–2.3788596992,0.6379339264,–0.6314802298
Si,–2.0455599856,–1.1124636877,–0.189764602
H,–1.1989520754,–1.0826682676,–1.4477959729
C,2.0613756528,0.1119104237,–0.1175450005
S,0.7386071844,1.5724992269,–0.2737312514
S,1.5554686837,–1.4069243008,0.1665993785

Zero-point correction=   0.028826 (Hartree/Particle)
 Thermal correction to energy=   0.036213
 Thermal correction to enthalpy=   0.037157
 Thermal correction to Gibbs free energy=   –0.004165
 Sum of electronic and zero-point energies=   –1415.233349
 Sum of electronic and thermal energies=   –1415.225962
 Sum of electronic and thermal enthalpies=   –1415.225017
 Sum of electronic and thermal free energies=   –1415.266339

Table S182. Cartesian coordinates and energies of **TS3-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.4718995239,–1.417316832,–0.161600621
H,–1.2683777906,–1.7773391427,–1.5989023978
H,–2.7535809686,–2.0962124232,0.2431074546
Si,–1.4036085815,0.7511303193,0.2767120835
H,–1.9111600597,1.055485203,1.6617225084
C,2.0902376063,0.4007485148,0.0396187248
S,1.8034094293,–1.1520713862,0.1441823701
S,0.2985538888,1.751428747,–0.2734701225

Zero-point correction=   0.029432 (Hartree/Particle)
 Thermal correction to energy=   0.037143
 Thermal correction to enthalpy=   0.038087
 Thermal correction to Gibbs free energy=   –0.003918
 Sum of electronic and zero-point energies=   –1415.242840
 Sum of electronic and thermal energies=   –1415.235129
 Sum of electronic and thermal enthalpies=   –1415.234185
 Sum of electronic and thermal free energies=   –1415.276190

Table S183. Cartesian coordinates and energies of **3-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,0.4917626612,–0.0690524304,0.52728895
Si,2.6678307564,0.0988382308,–0.2527307417
H,2.9955248633,–1.2607358789,0.3722890858
H,2.3439521594,–0.4210200395,–1.6488480756
H,0.404119673,–0.1368908168,2.0255539407
C,–2.1144517421,0.0956711959,–0.3993247548
S,–1.2304307895,–1.3555068021,–0.1081790666
S,–1.0640045817,1.4199155411,–0.0294063377

Zero-point correction=   0.030969 (Hartree/Particle)
 Thermal correction to energy=   0.038389
 Thermal correction to enthalpy=   0.039333
 Thermal correction to Gibbs free energy=   –0.001695
 Sum of electronic and zero-point energies=   –1415.285547
 Sum of electronic and thermal energies=   –1415.278128
 Sum of electronic and thermal enthalpies=   –1415.277184
 Sum of electronic and thermal free energies=   –1415.318212

Table S184. Cartesian coordinates and energies of **TS4-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,1.0025128004,–0.6680412401,0.1476746612
Si,3.0887464091,–0.0925754694,–0.1706399948
H,4.2738305439,–0.5762211379,0.6097093261
H,3.6065758332,0.3250695239,–1.5113797835
H,1.096045913,–1.0747043369,1.6042337598
C,–2.05838878,0.6395099393,0.0163144185
S,–2.7470834954,–0.801871246,–0.1012602263
S,–0.6076372241,1.2908549671,0.0619058391

Zero-point correction=   0.029829 (Hartree/Particle)
 Thermal correction to energy=   0.037619
 Thermal correction to enthalpy=   0.038563
 Thermal correction to Gibbs free energy=   –0.004633
 Sum of electronic and zero-point energies=   –1415.236523
 Sum of electronic and thermal energies=   –1415.228732
 Sum of electronic and thermal enthalpies=   –1415.227788
 Sum of electronic and thermal free energies=   –1415.270985

Table S185. Cartesian coordinates and energies of **TS5-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–0.8458414807,–0.0172441489,0.4597384343
Si,–2.8462126635,–0.4703862533,–0.3775485094
H,–3.7482921336,–0.7574368287,0.790308835
H,–3.383864763,0.7634933783,–1.0380788487
H,–0.3335253683,–0.9300838871,1.5127836325
C,2.2756647044,0.5256152375,–0.0049451411
S,0.6051686199,1.3562064631,–0.1741531585
S,2.2149000848,–1.121205961,–0.0345762441

Zero-point correction=   0.029134 (Hartree/Particle)
 Thermal correction to energy=   0.036921
 Thermal correction to enthalpy=   0.037866
 Thermal correction to Gibbs free energy=   –0.004403
 Sum of electronic and zero-point energies=   –1415.240468
 Sum of electronic and thermal energies=   –1415.232681
 Sum of electronic and thermal enthalpies=   –1415.231736
 Sum of electronic and thermal free energies=   –1415.274005

Table S186. Cartesian coordinates and energies of **4-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–2.204400343,–0.1881035378,–0.0810192729
Si,–0.4505983517,1.4239240629,–0.0501784224
C,0.820629227,–0.0033256384,–0.0052117057
H,–0.1599223493,2.3116670749,–1.2258760751
H,–0.2223320195,2.3157579719,1.1346240277
H,–2.4197285583,–0.0640716351,1.4323921394
S,–0.2035940973,–1.3910612532,0.1155236548
S,2.4652484921,–0.0026800451,–0.0940083458

Zero-point correction=   0.033123 (Hartree/Particle)
 Thermal correction to energy=   0.040012
 Thermal correction to enthalpy=   0.040956
 Thermal correction to Gibbs free energy=   –0.000072
 Sum of electronic and zero-point energies=   –1415.327293
 Sum of electronic and thermal energies=   –1415.320404
 Sum of electronic and thermal enthalpies=   –1415.319460
 Sum of electronic and thermal free energies=   –1415.360488

Table S187. Cartesian coordinates and energies of **TS6-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,2.171128786,0.0430941857,–1.0303549002
Si,1.5322704647,–0.2557827877,1.0537153515
C,–1.2172308715,0.0344879691,–0.0533769651
H,1.3213228582,–1.5963242364,1.6922494705
H,1.3639382305,0.7397359202,2.1630694097
H,2.1727503306,1.5606023975,–0.7978599186
S,–1.4626601235,1.5942489102,0.0566597391
S,–1.637780675,–1.4751323584,–0.2811461869

Zero-point correction=   0.029528 (Hartree/Particle)
 Thermal correction to energy=   0.037469
 Thermal correction to enthalpy=   0.038414
 Thermal correction to Gibbs free energy=   –0.005461
 Sum of electronic and zero-point energies=   –1415.240338
 Sum of electronic and thermal energies=   –1415.232397
 Sum of electronic and thermal enthalpies=   –1415.231452
 Sum of electronic and thermal free energies=   –1415.275327

Table S188. Cartesian coordinates and energies of **TS7-CS$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.358986562,–0.562973551,–1.1168130791
Si,–1.3041312743,0.2030823935,0.9899072977
C,0.4833914198,0.0096735592,–0.0961537656
H,–1.4712685213,1.5702103256,1.5508612818
H,–1.1481486714,–0.679529429,2.1848691818
H,–1.3750979998,–1.9724765715,–0.5278771408
S,0.8630986312,1.6419166565,–0.3442712469
S,1.5240849778,–1.2495823835,0.277699471

Zero-point correction=   0.031576 (Hartree/Particle)
 Thermal correction to energy=   0.038369
 Thermal correction to enthalpy=   0.039313
 Thermal correction to Gibbs free energy=   –0.000369
 Sum of electronic and zero-point energies=   –1415.262585
 Sum of electronic and thermal energies=   –1415.255792
 Sum of electronic and thermal enthalpies=   –1415.254848
 Sum of electronic and thermal free energies=   –1415.294530

Table S189. Cartesian coordinates and energies of **1-H$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,−1.3367452769,−0.0761486867,−0.1242398983
Si,1.3367731678,0.0761410906,−0.1241683216
H,1.5641159123,−1.4179975804,0.0990251403
H,−1.5638530946,1.4180901759,0.0984910492
H,−1.9618207196,−0.4849377466,1.2234488909
H,1.9616108057,0.4854024106,1.2234836393
H,−0.0000327947,0.0000193366,0.8611035

Zero-point correction=   0.037287 (Hartree/Particle)
 Thermal correction to energy=   0.042308
 Thermal correction to enthalpy=   0.043252
 Thermal correction to Gibbs free energy= 0.010396
 Sum of electronic and zero-point energies=   −581.919782
 Sum of electronic and thermal energies=   −581.914761
 Sum of electronic and thermal enthalpies=   −581.913817
 Sum of electronic and thermal free energies=   −581.946673

Table S190. Cartesian coordinates and energies of **TS1-H$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,−1.2619330784,−0.1452219181,0.0750576129
Si,1.1593555652,−0.2015705165,−0.086592138
H,1.5030061393,0.0701545433,1.3789873612
H,−1.4870658776,0.2442281846,−1.3927505457
H,−1.5117548048,1.263999645,0.6345384138
H,1.5758674856,1.4598696835,−0.3630316267
H,0.7454085706,1.4697833782,−0.0841190775

Zero-point correction=   0.035929 (Hartree/Particle)
 Thermal correction to energy=   0.040534
 Thermal correction to enthalpy=   0.041478
 Thermal correction to Gibbs free energy= 0.009641
 Sum of electronic and zero-point energies=   −581.885270
 Sum of electronic and thermal energies=   −581.880665
 Sum of electronic and thermal enthalpies=   −581.879721
 Sum of electronic and thermal free energies=   −581.911558

Table S191. Cartesian coordinates and energies of **2-H$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.2787763626,0.0000817563,–0.1421997177
Si,1.085005269,0.0002849907,0.0084117413
H,1.7985331695,0.000356851,1.342031975
H,–1.4106052459,–1.1290201307,0.8936127054
H,–1.4107322876,1.1292643678,0.8935095962
H,1.7396492822,–1.172023636,–0.6836635644
H,1.7393691755,1.1727518008,–0.6836597359

Zero-point correction=   0.038385 (Hartree/Particle)
 Thermal correction to energy=   0.043195
 Thermal correction to enthalpy=   0.044139
 Thermal correction to Gibbs free energy=   0.011934
 Sum of electronic and zero-point energies=   –581.968061
 Sum of electronic and thermal energies=   –581.963251
 Sum of electronic and thermal enthalpies=   –581.962307
 Sum of electronic and thermal free energies=   –581.994512

Table S192. Cartesian coordinates and energies of **TS2-H$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.301094118,–0.1033074811,–0.100633359
Si,1.2156271712,0.0519356228,–0.1050681833
H,1.8913167532,–1.2949105081,0.04372444
H,–1.4303790236,1.4083153195,–0.287133653
H,–1.7887656194,–0.0458049232,1.3644843101
H,2.0786059236,0.9070348354,0.811212537
H,0.261717913,–0.2409798654,1.1091839083

Zero-point correction=   0.036468 (Hartree/Particle)
 Thermal correction to energy=   0.040989
 Thermal correction to enthalpy=   0.041933
 Thermal correction to Gibbs free energy=   0.010217
 Sum of electronic and zero-point energies=   –581.915481
 Sum of electronic and thermal energies=   –581.910960
 Sum of electronic and thermal enthalpies=   –581.910016
 Sum of electronic and thermal free energies=   –581.941733

Table S193. Cartesian coordinates and energies of **1-CH₄** at the wB97XD/cc-pVTZ level of theory.

Si,–1.8758011327,0.0883287824,0.0030346772
Si,0.7136957361,–0.7010856504,–0.1215613462
H,0.8095973395,–1.1975604247,1.3242397917
H,–1.7530154542,0.9608145865,–1.2459078387
H,–2.1622247388,1.2837564965,0.9378880839
H,–0.3377569207,0.4729300414,0.4304508528
H,3.0589769568,0.2280093213,–0.0536435119
H,1.989847147,1.3884464492,–0.8336802999
C,2.0736083371,0.7027683217,0.013140997
H,2.0432317299,1.2885560762,0.9336865941

Zero-point correction=   0.066719 (Hartree/Particle)
 Thermal correction to energy=   0.073489
 Thermal correction to enthalpy=   0.074433
 Thermal correction to Gibbs free energy=   0.036577
 Sum of electronic and zero-point energies=   –621.211578
 Sum of electronic and thermal energies=   –621.204808
 Sum of electronic and thermal enthalpies=   –621.203864
 Sum of electronic and thermal free energies=   –621.241721

Table S194. Cartesian coordinates and energies of **TS1-CH₄** at the wB97XD/cc-pVTZ level of theory.

Si,–1.6263906362,0.2035772833,0.0369949393
Si,0.5190038199,–0.9551588121,–0.1081388383
H,0.6880123444,–1.1278985121,1.4050094572
H,–1.5073758157,0.9724672709,–1.2862672054
H,–1.3173929787,1.4238215887,0.9269783098
H,0.4186120809,0.6498055094,0.1267378106
H,2.6687115379,0.3797872953,0.4313255786
H,2.0040364382,1.1383585406,–1.0482514653
C,1.8049706096,0.869923805,–0.0135186873
H,1.6046385997,1.7821040311,0.5592051007

Zero-point correction=   0.065433 (Hartree/Particle)
 Thermal correction to energy=   0.071569
 Thermal correction to enthalpy=   0.072513
 Thermal correction to Gibbs free energy=   0.036486
 Sum of electronic and zero-point energies=   –621.162591
 Sum of electronic and thermal energies=   –621.156455
 Sum of electronic and thermal enthalpies=   –621.155510
 Sum of electronic and thermal free energies=   –621.191538

Table S195. Cartesian coordinates and energies of **2-CH₄** at the wB97XD/cc-pVTZ level of theory.

Si,–1.7320541431,0.1431897168,0.0003132854
Si,0.5080939799,–0.5996915652,–0.000000724
H,0.8488705815,–1.4932240847,–1.1728152139
H,–1.4397089125,1.1502287593,–1.1285043517
H,–1.4395402543,1.1498120574,1.1294573371
H,0.8490715114,–1.4936406218,1.1724379127
H,1.8319301318,1.3360839851,–0.8794720281
H,1.8322374785,1.3356275617,0.8800428798
C,1.9198692251,0.6948010422,0.000103847
H,2.9138194016,0.2392361494,–0.0001869443

Zero-point correction=   0.067609 (Hartree/Particle)
 Thermal correction to energy=   0.073986
 Thermal correction to enthalpy=   0.074930
 Thermal correction to Gibbs free energy=   0.038356
 Sum of electronic and zero-point energies=   –621.265428
 Sum of electronic and thermal energies=   –621.259051
 Sum of electronic and thermal enthalpies=   –621.258107
 Sum of electronic and thermal free energies=   –621.294680

Table S196. Cartesian coordinates and energies of **2'-CH₄** at the wB97XD/cc-pVTZ level of theory.

Si,–1.4523829289,0.2057675012,0.0054030202
Si,0.6832052108,–0.8260746164,–0.1246942022
H,0.6491109156,–1.1792655106,1.374695627
H,–2.5890139532,–0.753902762,0.259663429
H,–1.7138639269,1.2925957458,1.0288670215
H,–1.8970863766,0.8895087045,–1.2672700418
H,2.8087959037,0.5532089808,0.1762640207
H,1.7077785394,1.3848084793,–0.9102938806
C,1.7573692878,0.817974678,0.024649426
H,1.4616133283,1.4873167995,0.8368225802

Zero-point correction=   0.067750 (Hartree/Particle)
 Thermal correction to energy=   0.074172
 Thermal correction to enthalpy=   0.075116
 Thermal correction to Gibbs free energy=   0.038343
 Sum of electronic and zero-point energies=   –621.256753
 Sum of electronic and thermal energies=   –621.250331
 Sum of electronic and thermal enthalpies=   –621.249386
 Sum of electronic and thermal free energies=   –621.286159

Table S197. Cartesian coordinates and energies of **TS2-CH$_4$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.8289666042,0.0958504775,–0.011666335
Si,0.5918952601,–0.5795080682,–0.1372059676
H,0.9443422872,–1.7326337897,0.7832468137
H,–1.6018522427,1.1797801982,–1.066999474
H,–1.9995411967,1.1341815632,1.1252384991
H,–0.1929645512,0.1251793918,1.0335232023
H,2.9395065156,0.2627360918,–0.6055141997
H,1.8336411918,1.6016070306,–0.3200925015
C,2.1207874252,0.6081077391,0.0320833884
H,2.4995529148,0.7041823655,1.0515855743

Zero-point correction=   0.065840 (Hartree/Particle)
 Thermal correction to energy=   0.071947
 Thermal correction to enthalpy=   0.072891
 Thermal correction to Gibbs free energy=   0.036644
 Sum of electronic and zero-point energies=   –621.207029
 Sum of electronic and thermal energies=   –621.200921
 Sum of electronic and thermal enthalpies=   –621.199977
 Sum of electronic and thermal free energies=   –621.236224

Table S198. Cartesian coordinates and energies of **TS2'-CH$_4$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.7139364021,0.1097045582,0.0443004171
Si,0.6798599218,–0.7394462099,–0.1124771365
H,0.6525452957,–1.0350119646,1.3896424004
H,–2.2622499874,0.6150556147,–1.2763303669
H,–2.2307453366,1.1950547359,0.9829569679
H,–0.3929259528,0.9244643586,–0.1474270813
H,2.9830232218,0.2312723466,0.1623559596
H,2.058806115,1.2691963226,–0.9231228571
C,2.0051238815,0.7056279684,0.0124911725
H,1.845603243,1.4119212695,0.8301385242

Zero-point correction=   0.065814 (Hartree/Particle)
 Thermal correction to energy=   0.071982
 Thermal correction to enthalpy=   0.072926
 Thermal correction to Gibbs free energy=   0.036795
 Sum of electronic and zero-point energies=   –621.208338
 Sum of electronic and thermal energies=   –621.202170
 Sum of electronic and thermal enthalpies=   –621.201226
 Sum of electronic and thermal free energies=   –621.237357

Table S199. Cartesian coordinates and energies of **1-N$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.6896438076,–0.6327793643,–0.05254428
Si,0.0529854445,1.0239301742,–0.1478969571
H,0.4172954493,1.5168281355,1.2488434231
H,–2.1843466666,–0.2746149257,1.3540272802
N,1.4987438875,–0.1749457318,0.056478838
N,2.3777210468,–0.8490672235,0.014669564
H,–2.663594354,0.3075609356,–0.7751148683

Zero-point correction=   0.030431 (Hartree/Particle)
 Thermal correction to energy=   0.036859
 Thermal correction to enthalpy=   0.037803
 Thermal correction to Gibbs free energy=   0.000150
 Sum of electronic and zero-point energies=   –690.244708
 Sum of electronic and thermal energies=   –690.238280
 Sum of electronic and thermal enthalpies=   –690.237336
 Sum of electronic and thermal free energies=   –690.274989

Table S200. Cartesian coordinates and energies of **TS1-N$_2$** at the wB97XD/cc-pVTZ level of theory.

Si,–1.6657614404,–0.7110923239,0.005847601
Si,–0.1664854369,1.0947378936,–0.1311449124
H,0.1547583484,1.3918383435,1.3373720339
H,–2.4730314624,–0.249982489,1.2177181406
N,1.7028891492,–0.1854638467,0.1085629505
N,2.6379286639,–0.7254221175,–0.0744048801
H,–2.5983188219,–0.17473946,–1.0805779335

Zero-point correction=   0.029138 (Hartree/Particle)
 Thermal correction to energy=   0.035556
 Thermal correction to enthalpy=   0.036501
 Thermal correction to Gibbs free energy=   –0.001585
 Sum of electronic and zero-point energies=   –690.243231
 Sum of electronic and thermal energies=   –690.236813
 Sum of electronic and thermal enthalpies=   –690.235868
 Sum of electronic and thermal free energies=   –690.273954

Table S201. Cartesian coordinates and energies of **2-N₂** at the wB97XD/cc-pVTZ level of theory.

Si,1.0842490701,–0.5321014476,–0.008326986
Si,–1.2987775658,–0.5115354851,–0.1252996074
H,–1.6148094078,–0.7956218122,1.3523444608
H,1.813623876,–0.7155937511,1.2997048866
N,–0.5723680239,1.2292146027,0.1037433971
N,0.6736463833,1.2602113949,–0.082383139
H,2.151447668,–0.9822165016,–0.9930620121

Zero-point correction=   0.031813 (Hartree/Particle)
 Thermal correction to energy=   0.037041
 Thermal correction to enthalpy=   0.037985
 Thermal correction to Gibbs free energy=   0.003589
 Sum of electronic and zero-point energies=   –690.224641
 Sum of electronic and thermal energies=   –690.219413
 Sum of electronic and thermal enthalpies=   –690.218469
 Sum of electronic and thermal free energies=   –690.252864

Table S202. Cartesian coordinates and energies of **TS2-N₂** at the wB97XD/cc-pVTZ level of theory.

Si,1.3299706921,–0.1315827926,–0.0362218543
Si,–0.9207934572,–0.9919297027,–0.1255916378
H,–1.2283530951,–1.4275850647,1.3159894162
H,1.6217523377,0.2748371742,1.3931651814
N,–1.0712363231,0.909190378,0.1531056467
N,–0.1958091705,1.6113113912,–0.157508369
H,2.586283016,–0.9871713833,–0.2809863831

Zero-point correction=   0.030049 (Hartree/Particle)
 Thermal correction to energy=   0.035220
 Thermal correction to enthalpy=   0.036164
 Thermal correction to Gibbs free energy=   0.001778
 Sum of electronic and zero-point energies=   –690.211049
 Sum of electronic and thermal energies=   –690.205878
 Sum of electronic and thermal enthalpies=   –690.204934
 Sum of electronic and thermal free energies=   –690.239320

Table S203. Cartesian coordinates and energies of **1-N₂O** at the wB97XD/cc-pVTZ level of theory.

Si,–1.0319396105,–0.8553150787,–0.0529317985
O,1.0522637188,1.0068387872,–0.1576304027
H,–1.8910522041,–1.4445267111,1.0304079021
H,–1.8509795141,–1.1287333052,–1.2881894841
N,–0.1797566122,1.6398297347,0.0493125056
N,–1.1888386788,0.9603885763,0.1326967866
Si,1.319596492,–0.7736612327,–0.0391464545
H,1.2333734089,–0.8565327704,1.5028199455

Zero-point correction=   0.036654 (Hartree/Particle)
 Thermal correction to energy=   0.042477
 Thermal correction to enthalpy=   0.043422
 Thermal correction to Gibbs free energy=   0.007214
 Sum of electronic and zero-point energies=   −765.481222
 Sum of electronic and thermal energies=   −765.475399
 Sum of electronic and thermal enthalpies=   −765.474454
 Sum of electronic and thermal free energies=   −765.510662

Table S204. Cartesian coordinates and energies of **TS1-N₂O** at the wB97XD/cc-pVTZ level of theory.

Si,–1.1440615298,1.0317003646,0.0124657093
O,1.7095917908,–1.1412981672,–0.0045227202
H,–1.1451631202,1.9300942813,1.2163854058
H,–1.2842172356,1.9563915558,–1.1632325101
N,1.9122686367,0.0380897129,–0.0003011852
N,1.632559226,1.1400697614,–0.0109043366
Si,–1.3191580901,–1.1686721982,–0.1108278338
H,–1.1999426777,–1.2634943106,1.4180554708

Zero-point correction=   0.033911 (Hartree/Particle)
 Thermal correction to energy=   0.041057
 Thermal correction to enthalpy=   0.042001
 Thermal correction to Gibbs free energy=   0.001920
 Sum of electronic and zero-point energies=   −765.397745
 Sum of electronic and thermal energies=   −765.390599
 Sum of electronic and thermal enthalpies=   −765.389654
 Sum of electronic and thermal free energies=   −765.429736

Table S205. Cartesian coordinates and energies of **TS2-N$_2$O** at the wB97XD/cc-pVTZ level of theory.

Si,–0.9243784289,–1.0008226395,–0.1038447944
O,1.1284440316,1.0133702195,–0.3124557888
H,–1.8773568037,–1.7404248364,0.8063044298
H,–1.6678463262,–1.1071992307,–1.4128286532
N,–0.5518377958,1.6742562776,0.1054497004
N,–1.3321918849,0.8348627278,0.2094980556
Si,1.4204433564,–0.5827444001,0.049254864
H,1.2329578517,–0.6767381182,1.6020141867

Zero-point correction=   0.034570 (Hartree/Particle)
 Thermal correction to energy=   0.040582
 Thermal correction to enthalpy=   0.041526
 Thermal correction to Gibbs free energy=   0.004872
 Sum of electronic and zero-point energies=   –765.477892
 Sum of electronic and thermal energies=   –765.471880
 Sum of electronic and thermal enthalpies=   –765.470936
 Sum of electronic and thermal free energies=   –765.507590

Table S206. Cartesian coordinates and energies of **2-N$_2$O** at the wB97XD/cc-pVTZ level of theory.

Si,1.4103681281,–0.1188004786,0.2368145988
H,2.2672408718,–1.2192130276,–0.3806110482
H,1.6699857181,–0.3250834032,1.7218458062
N,–2.0372815424,1.3895522091,0.0698521602
Si,–0.7446495268,–1.2909356742,0.0038778053
H,–0.8603436791,–1.2674871294,–1.5133266058
O,1.516384031,1.3375083778,–0.3130746642
N,–1.5802740007,0.3893321262,–0.0250250523

Zero-point correction=   0.035664 (Hartree/Particle)
 Thermal correction to energy=   0.042892
 Thermal correction to enthalpy=   0.043836
 Thermal correction to Gibbs free energy=   0.002907
 Sum of electronic and zero-point energies=   –765.527309
 Sum of electronic and thermal energies=   –765.520080
 Sum of electronic and thermal enthalpies=   –765.519136
 Sum of electronic and thermal free energies=   –765.560065

Table S207. Cartesian coordinates and energies of **TS1'-N₂O** at the wB97XD/cc-pVTZ level of theory.

Si,–1.116431387,1.0541417967,0.0039673095
H,–1.0697015948,1.9723990579,1.1921142998
H,–1.1690490478,1.9704904763,–1.1854611258
N,1.8743079898,–0.169320707,0.0033307987
Si,–1.3211506685,–1.1407401858,–0.0996810868
H,–1.2317704573,–1.2208599736,1.4321639317
O,1.7468662322,1.0259535102,0.0002681333
N,1.5072759333,–1.2447399748,–0.0196822604

Zero-point correction=   0.033979 (Hartree/Particle)
 Thermal correction to energy=   0.041036
 Thermal correction to enthalpy=   0.041980
 Thermal correction to Gibbs free energy=   0.002263
 Sum of electronic and zero-point energies=   –765.397269
 Sum of electronic and thermal energies=   –765.390213
 Sum of electronic and thermal enthalpies=   –765.389269
 Sum of electronic and thermal free energies=   –765.428986

Table S208. Cartesian coordinates and energies of **TS3-N₂O** at the wB97XD/cc-pVTZ level of theory.

Si,–1.486951227,–0.033958287,0.2596791517
H,–1.8902270753,1.4070080674,–0.2702329467
H,–1.8313582454,0.15540753,1.7258022703
N,2.7819708915,–1.0667424516,0.1774740987
Si,0.4341828415,1.2476642203,–0.0690154895
H,0.5080429558,0.9967265037,–1.5685853699
O,–2.0256477372,–1.3151562064,–0.441287008
N,2.0464485961,–0.2889813764,–0.0497237065

Zero-point correction=   0.033660 (Hartree/Particle)
 Thermal correction to energy=   0.040839
 Thermal correction to enthalpy=   0.041783
 Thermal correction to Gibbs free energy=   0.001208
 Sum of electronic and zero-point energies=   –765.521252
 Sum of electronic and thermal energies=   –765.514073
 Sum of electronic and thermal enthalpies=   –765.513129
 Sum of electronic and thermal free energies=   –765.553703

Table S209. Cartesian coordinates and energies of **4-N₂O** at the wB97XD/cc-pVTZ level of theory.

Si,–0.0803990185,1.454573972,–0.1195079132
Si,1.4586419165,–0.3429572271,0.0198943952
O,–2.1327798327,–0.5374051668,0.0297119367
H,2.3649794959,–0.7495933684,–1.1107784847
H,2.2501628012,–0.7320704974,1.2382398668
H,–0.1586763525,1.6488643266,1.3960790002
N,–0.9143044257,–0.3375371393,–0.0077969436
N,–0.0597395842,–1.2953528996,–0.0437788574

Zero-point correction=   0.038135 (Hartree/Particle)
 Thermal correction to energy=   0.043835
 Thermal correction to enthalpy=   0.044779
 Thermal correction to Gibbs free energy=   0.008738
 Sum of electronic and zero-point energies=   −765.454662
 Sum of electronic and thermal energies=   −765.448962
 Sum of electronic and thermal enthalpies=   −765.448018
 Sum of electronic and thermal free energies=   −765.484059

Table S210. Cartesian coordinates and energies of **TS4-N₂O** at the wB97XD/cc-pVTZ level of theory.

Si,–2.228884237,–0.8521113688,–0.0545398074
Si,–0.8044623407,0.8799658386,–0.1569177267
O,3.0949010146,–0.5976015782,–0.1326219879
H,–0.2923199257,1.3725142588,–1.4759861045
H,–0.8649449074,2.0994871452,0.7089405573
H,–2.6453322315,–0.4245764109,1.3623870266
N,1.9070042832,–0.2621926133,–0.0643328416
N,1.1860143446,0.4180227286,0.5611858842

Zero-point correction=   0.033416 (Hartree/Particle)
 Thermal correction to energy=   0.040393
 Thermal correction to enthalpy=   0.041337
 Thermal correction to Gibbs free energy=   0.001532
 Sum of electronic and zero-point energies=   −765.357220
 Sum of electronic and thermal energies=   −765.350243
 Sum of electronic and thermal enthalpies=   −765.349299
 Sum of electronic and thermal free energies=   −765.389104

Table S211. Cartesian coordinates and energies of **5-N₂O** at the wB97XD/cc-pVTZ level of theory.

Si,0.5142537558,1.422229269,–0.1062380648
Si,1.4103648048,–0.7588985925,0.0251967213
O,–2.3996499902,–0.015675503,0.024604337
H,1.8254823036,–1.6166254999,–1.1364611005
H,1.6995305524,–1.5945132082,1.2381425527
H,0.5744716317,1.6277036294,1.4190858326
N,–1.4654857821,–0.8104193105,–0.0419853762
N,–0.272848276,–0.2744797843,–0.0435219021

Zero-point correction=   0.036545 (Hartree/Particle)
 Thermal correction to energy=   0.042910
 Thermal correction to enthalpy=   0.043854
 Thermal correction to Gibbs free energy=   0.005889
 Sum of electronic and zero-point energies=   –765.448359
 Sum of electronic and thermal energies=   –765.441994
 Sum of electronic and thermal enthalpies=   –765.441050
 Sum of electronic and thermal free energies=   –765.479015

Table S212. Cartesian coordinates and energies of **TS5-N₂O** at the wB97XD/cc-pVTZ level of theory.

Si,1.0784457478,–1.0690783313,–0.0721049396
Si,–1.2866943328,–0.4736278769,–0.0311448594
O,1.3761511552,1.0720258483,0.1063125118
H,–2.122772795,–0.6566681265,–1.2745671886
H,–2.1715648801,–0.8395851497,1.1262051228
H,1.0496455056,–0.9877209781,1.4602206569
N,–0.8383940173,1.2499455325,0.303477915
N,0.1836656166,0.9834930816,–0.419380219

Zero-point correction=   0.034512 (Hartree/Particle)
 Thermal correction to energy=   0.040538
 Thermal correction to enthalpy=   0.041482
 Thermal correction to Gibbs free energy=   0.004688
 Sum of electronic and zero-point energies=   –765.379140
 Sum of electronic and thermal energies=   –765.373114
 Sum of electronic and thermal enthalpies=   –765.372170
 Sum of electronic and thermal free energies=   –765.408964

Table S213. Cartesian coordinates and energies of **6-N$_2$O** at the wB97XD/cc-pVTZ level of theory.

Si,1.3196242309,–0.7734367738,–0.0390896808
Si,–1.0318999366,–0.8554089986,–0.0530075077
O,1.0520518098,1.0070353905,–0.1575232843
H,–1.8508274926,–1.1289070267,–1.2883217477
H,–1.8909909618,–1.4447737005,1.0302657659
H,1.2333352701,–0.8563709943,1.5028687151
N,–1.1890609908,0.9602678996,0.1326685027
N,–0.1800609291,1.6398472038,0.0493672367

Zero-point correction=   0.036654 (Hartree/Particle)
 Thermal correction to energy=   0.042477
 Thermal correction to enthalpy=   0.043422
 Thermal correction to Gibbs free energy=   0.007214
 Sum of electronic and zero-point energies=   –765.481222
 Sum of electronic and thermal energies=   –765.475399
 Sum of electronic and thermal enthalpies=   –765.474454
 Sum of electronic and thermal free energies=   –765.510661

Table S214. Cartesian coordinates and energies of **TS6-N$_2$O** at the wB97XD/cc-pVTZ level of theory.

Si,0.6024842932,1.4169776847,–0.0770924659
Si,1.2328695943,–0.7882395657,–0.1085405756
O,–2.3991423025,–0.1126657953,–0.0265097408
H,1.354503425,–1.6286005017,–1.346236912
H,2.1388157542,–1.4327840488,0.8901782069
H,1.0149290269,1.4276240446,1.4068987683
N,–1.2055186731,–0.1644942406,–0.3172212982
N,–0.400301118,–0.7119165772,0.5869650173

Zero-point correction=   0.035538 (Hartree/Particle)
 Thermal correction to energy=   0.041382
 Thermal correction to enthalpy=   0.042326
 Thermal correction to Gibbs free energy=   0.005712
 Sum of electronic and zero-point energies=   –765.409884
 Sum of electronic and thermal energies=   –765.404040
 Sum of electronic and thermal enthalpies=   –765.403096
 Sum of electronic and thermal free energies=   –765.439710

Table S215. Cartesian coordinates and energies of **TS8-N₂O** at the wB97XD/cc-pVTZ level of theory.

Si,1.4199539771,–0.5832317707,0.0494951925
Si,–0.9249372031,–1.0002549029,–0.1040598922
O,1.1288038901,1.0130274593,–0.3122624458
H,–1.6683409144,–1.1063360382,–1.4131016267
H,–1.8782523856,–1.7394923659,0.8060312716
H,1.23215689,–0.677198558,1.6022108183
N,–0.5513052092,1.6746821874,0.1053418907
N,–1.3320610448,0.8356429891,0.2092387917

Zero-point correction=   0.034570 (Hartree/Particle)
 Thermal correction to energy=   0.040582
 Thermal correction to enthalpy=   0.041526
 Thermal correction to Gibbs free energy=   0.004872
 Sum of electronic and zero-point energies=   –765.477892
 Sum of electronic and thermal energies=   –765.471880
 Sum of electronic and thermal enthalpies=   –765.470936
 Sum of electronic and thermal free energies=   –765.507590

Table S216. Cartesian coordinates and energies of **NH₃** at the wB97XD/cc-pVTZ level of theory.

H,0.0003025273,0.9369366262,–0.2555428974
H,–0.8115622703,–0.4682064667,–0.2555428974
H,0.8112597429,–0.4687304594,–0.2555428974

Zero-point correction=   0.034607 (Hartree/Particle)
 Thermal correction to energy=   0.037473
 Thermal correction to enthalpy=   0.038417
 Thermal correction to Gibbs free energy=   0.016584
 Sum of electronic and zero-point energies=   –56.528728
 Sum of electronic and thermal energies=   –56.525862
 Sum of electronic and thermal enthalpies=   –56.524917
 Sum of electronic and thermal free energies=   –56.546750

Table S217. Cartesian coordinates and energies of CO_2 at the wB97XD/cc-pVTZ level of theory.

C,0.,0.,0.
O,0.,0.,1.156428551
O,0.,0.,−1.156428551

Zero-point correction=   0.011910 (Hartree/Particle)
 Thermal correction to energy=   0.014516
 Thermal correction to enthalpy=   0.015460
 Thermal correction to Gibbs free energy=   −0.008770
 Sum of electronic and zero-point energies=   −188.584127
 Sum of electronic and thermal energies=   −188.581521
 Sum of electronic and thermal enthalpies=   −188.580577
 Sum of electronic and thermal free energies=   −188.604807

Table S218. Cartesian coordinates and energies of CS_2 at the wB97XD/cc-pVTZ level of theory.

C,0.,0.,0.
S,0.,0.,1.5514908801
S,0.,0.,−1.5514908801

Zero-point correction=   0.007078 (Hartree/Particle)
 Thermal correction to energy=   0.010149
 Thermal correction to enthalpy=   0.011093
 Thermal correction to Gibbs free energy=   −0.015822
 Sum of electronic and zero-point energies=   −834.500352
 Sum of electronic and thermal energies=   −834.497281
 Sum of electronic and thermal enthalpies=   −834.496337
 Sum of electronic and thermal free energies=   −834.523252

Table S219. Cartesian coordinates and energies of H_2 at the wB97XD/cc-pVTZ level of theory.

H,0.,0.,0.3715520474
H,0.,0.,−0.3715520474

Zero-point correction=   0.010106 (Hartree/Particle)
 Thermal correction to energy=   0.012466
 Thermal correction to enthalpy=   0.013410
 Thermal correction to Gibbs free energy=   −0.001383
 Sum of electronic and zero-point energies=   −1.166498
 Sum of electronic and thermal energies=   −1.164137
 Sum of electronic and thermal enthalpies=   −1.163193
 Sum of electronic and thermal free energies=   −1.177986

Table S220. Cartesian coordinates and energies of **CH₄** at the wB97XD/cc-pVTZ level of theory.

C,0.,0.,0.
H,0.6280284278,0.6280284278,0.6280284278
H,−0.6280284278,−0.6280284278,0.6280284278
H,−0.6280284278,0.6280284278,−0.6280284278
H,0.6280284278,−0.6280284278,−0.6280284278

Zero-point correction=   0.044883 (Hartree/Particle)
 Thermal correction to energy=   0.047751
 Thermal correction to enthalpy=   0.048695
 Thermal correction to Gibbs free energy=   0.027574
 Sum of electronic and zero-point energies=   −40.474937
 Sum of electronic and thermal energies=   −40.472069
 Sum of electronic and thermal enthalpies=   −40.471124
 Sum of electronic and thermal free energies=   −40.492246

Table S221. Cartesian coordinates and energies of **N₂** at the wB97XD/cc-pVTZ level of theory.

N,0.,0.,0.5441701524
N,0.,0.,−0.5441701524

Zero-point correction=   0.005680 (Hartree/Particle)
 Thermal correction to energy=   0.008040
 Thermal correction to enthalpy=   0.008984
 Thermal correction to Gibbs free energy=   −0.012741
 Sum of electronic and zero-point energies=   −109.522293
 Sum of electronic and thermal energies=   −109.519932
 Sum of electronic and thermal enthalpies=   −109.518988
 Sum of electronic and thermal free energies=   −109.540713

Table S222. Cartesian coordinates and energies of **N₂O** at the wB97XD/cc-pVTZ level of theory.

N,0.,0.,−1.1892100423
N,0.,0.,−0.0736630968
O,0.,0.,1.1036401391

Zero-point correction=   0.011475 (Hartree/Particle)
 Thermal correction to energy=   0.014127
 Thermal correction to enthalpy=   0.015072
 Thermal correction to Gibbs free energy=   −0.009801
 Sum of electronic and zero-point energies=   −184.656615
 Sum of electronic and thermal energies=   −184.653963
 Sum of electronic and thermal enthalpies=   −184.653019
 Sum of electronic and thermal free energies=   −184.677892

Table S223. Cartesian coordinates and energies of **CO** at the wB97XD/cc-pVTZ level of theory.

C,0.,0.,–0.6430796996
O,0.,0.,0.4809976996

Zero-point correction=   0.005113 (Hartree/Particle)
 Thermal correction to energy=   0.007474
 Thermal correction to enthalpy=   0.008418
 Thermal correction to Gibbs free energy=   –0.014002
 Sum of electronic and zero-point energies=   –113.311403
 Sum of electronic and thermal energies=   –113.309042
 Sum of electronic and thermal enthalpies=   –113.308098
 Sum of electronic and thermal free energies=   –113.330518

Table S224. Cartesian coordinates and energies of **CS** at the wB97XD/cc-pVTZ level of theory.

C,0.,0.,–1.1140072915
S,0.,0.,0.4162742915

Zero-point correction=   0.003067 (Hartree/Particle)
 Thermal correction to energy=   0.005437
 Thermal correction to enthalpy=   0.006381
 Thermal correction to Gibbs free energy=   –0.017499
 Sum of electronic and zero-point energies=   –436.215878
 Sum of electronic and thermal energies=   –436.213508
 Sum of electronic and thermal enthalpies=   –436.212564
 Sum of electronic and thermal free energies=   –436.236444

Table S225. Imaginary frequencies and vibrational frequencies (cm^{-1}) of optimized structures at the wB97XD/6-31+G(d,p) level of theory.

	1H	1-NH_3	TS1-NH_3	2-NH_3	TS2-NH_3	1-CO_2	TS1-CO_2
Freq.	315.39	102.70	−2220.63	137.63	−1553.11	43.59	−133.78
I.F.	0	0	1	0	1	0	1
	2-CO_2	TS2-CO_2	3-CO_2	TS3-CO_2	TS4-CO_2	4-CO_2	4'-CO_2
Freq.	107.98	−331.83	192.12	−149.16	−159.83	48.9	85.92
I.F.	0	1	0	1	1		
	TS5-CO_2	5-CO_2	TS6-CO_2	6-CO_2	TS9-CO_2	7-CO_2	TS10-CO_2
Freq.	−137.85	55.38	339.24	95.78	−370.93	118.09	−359.62
I.F.					1	0	1
	TS11-CO_2	TS8-CO_2	TS7-CO_2	8-CO_2	1-CS_2	TS1-CS_2	2CS_2-CS
Freq.	−445.12	−203.84	−340.91	137.21	87.16	−69.57	38.08
I.F.	1	1	1	0	0	1	0
	2-CS_2	TS2-CS_2	TS3-CS_2	3-CS_2	TS4-CS_2	4-CS_2	TS5-CS_2
Freq.	151.50	−242.08	−248.23	96.13	−136.49	−5.69	−138.15
I.F.	0	1	1	0	1	1	1
	5-CS_2	TS6-CS_2	TS7-CS_2	1-H_2	TS1-H_2	2-H_2	TS2-H_2
Freq.	−79.11	−252.74	−240.22	188.70	−302.40	166.56	−581.86
I.F.	1	1	1	0	1	0	1
	1-CH_4	TS1-CH_4	2-CH_4	2'-CH_4	TS2-CH_4	TS2'-CH_4	1-N_2
Freq.	82.17	−1242.59	95.76	120.80	−502.68	−486.82	49.25
I.F.	0	1	0	0	1	1	0
	TS1-N_2	2-N_2	TS2-N_2	1-N_2O	TS1-N_2O	TS1'-N_2O	2-N_2O
Freq.	−206.61	186.32	−254.12	131.08	−241.86	−245.24	28.70
I.F.	1	0	1	0	1	1	0
	TS2-N_2O	3-N_2O-N_2	3-N_2O	TS3-N_2O	4-N_2O	TS4-N_2O	5-N_2O
Freq.	−183.04	28.51	192.12	−319.63	150.97	−447.91	57.64
I.F.	1	0	0	1	0	1	0
	TS5-N_2O	6-N_2O	TS6-N_2O	TS7-N_2O	TS8-N_2O		
Freq.	304.53	131.37	−329.0	439.54	−181.14		
I.F.	1	0	1	1	1		