

Supporting Information

Metal-Catalyzed C-C Bond Cleavage in Alkanes: Effects of Methyl Substitution on Transition State Structures and Stability

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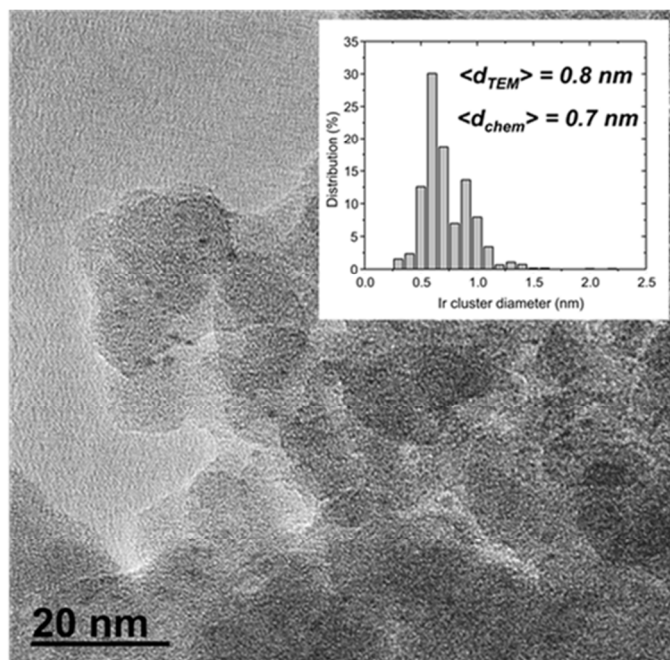


Figure S1. Representative image and particle size distribution of 0.7 nm Ir-SiO₂ as obtained by transmission electron microscopy, 1,234 clusters were counted to determine $\langle d_{TEM} \rangle$, the surface-averaged diameter.

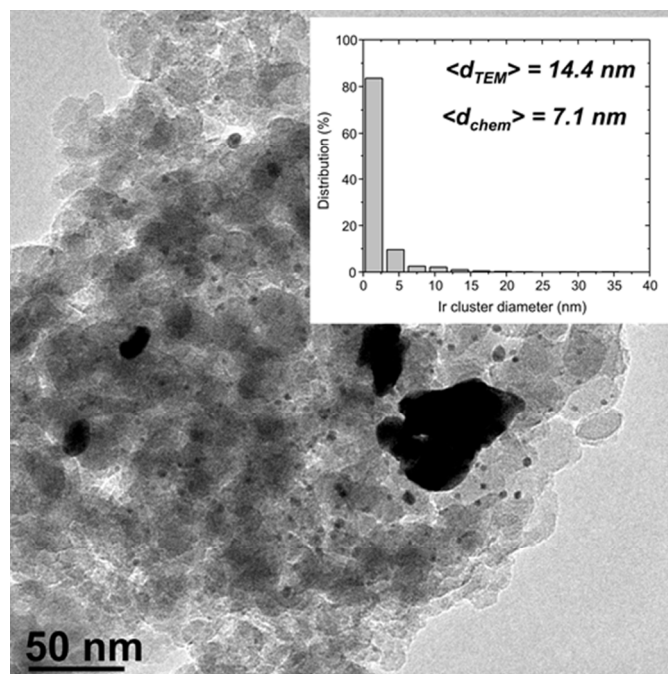


Figure S2. Representative image and particle size distribution of 7 nm Ir-SiO₂ as obtained by transmission electron microscopy, 1,029 clusters were counted to determine $\langle d_{TEM} \rangle$, the surface-averaged diameter.

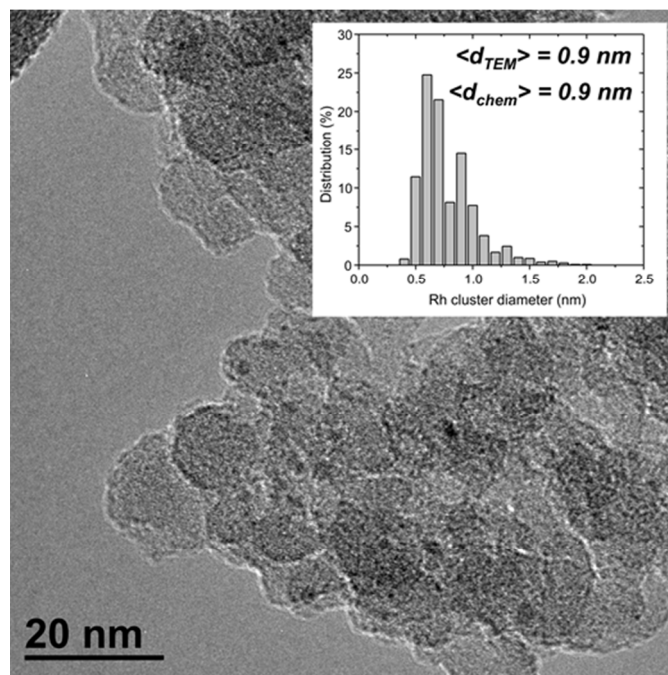


Figure S3. Representative image and cluster size distribution of 0.9 nm Rh-SiO₂ as obtained by transmission electron microscopy, 1,024 clusters were counted to determine $\langle d_{TEM} \rangle$, the surface-averaged diameter.

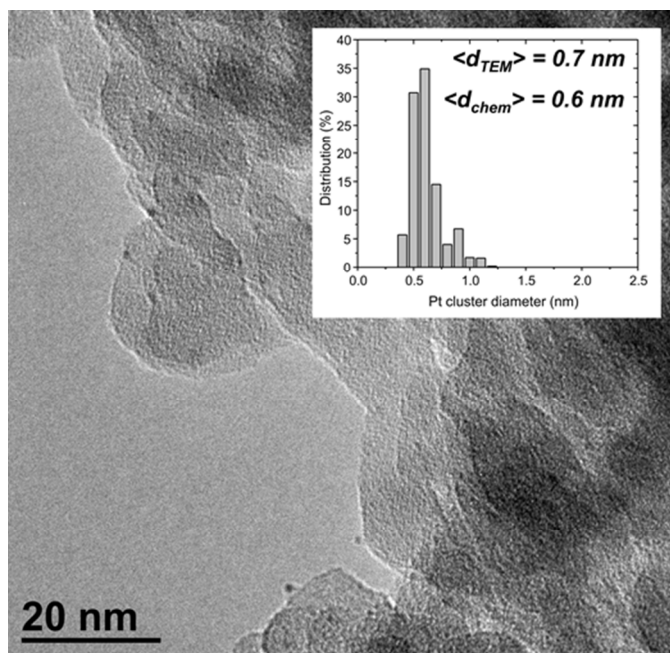


Figure S4. Representative image and cluster size distribution of 0.6 nm Pt-SiO₂ as obtained by transmission electron microscopy, 1,055 clusters were counted to determine $\langle d_{TEM} \rangle$, the surface-averaged diameter.

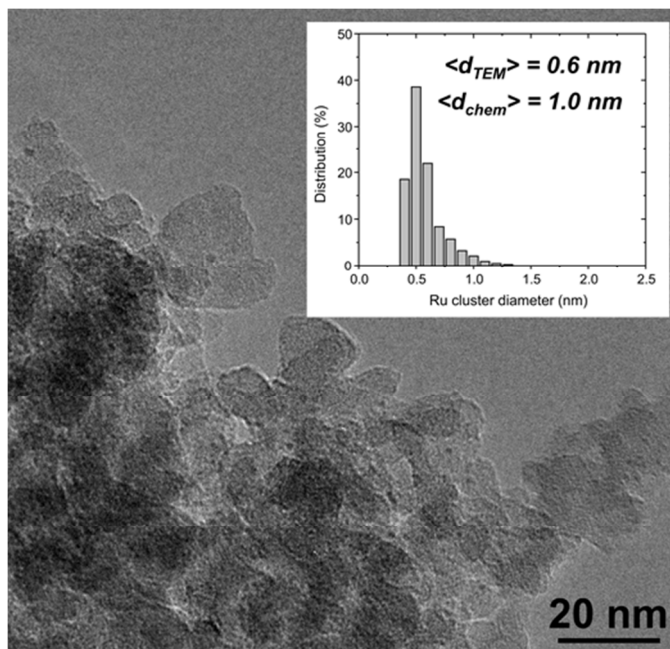


Figure S5. Representative image and cluster size distribution of 1.0 nm Ru-SiO₂ as obtained by transmission electron microscopy, 1,048 clusters were counted to determine $\langle d_{TEM} \rangle$, the surface-averaged diameter.

Statistical Mechanics Entropy Estimates for $^3\text{C}-^x\text{C}$ Bond Cleavage Transition States

The total entropy of C-C bond cleavage transition states (S^\ddagger) is given by:

$$S^\ddagger = S^\ddagger_{2D,trans} + S^\ddagger_{vib} + S^\ddagger_{1D,rot} + S^\ddagger_{config} \quad (\text{S1})$$

Where $S^\ddagger_{2D,trans}$ is the entropy of frustrated two-dimensional translations, S^\ddagger_{vib} is the entropy of intramolecular vibrations (assumed to be identical to those in the gas-phase analog), S^\ddagger_{config} is the entropy of trans-gauche configurations about each C-C bond, and $S^\ddagger_{1D,rot}$ is the entropy of rigid rotations of the alkyl-chains attached to the C-atoms in the C-C bond being cleaved.¹ Transition state structures contain free alkyl chains which are assumed to possess the bond lengths and angles of the gaseous analogs (0.109 nm C-H and 0.154 nm C-C bonds; 109.5° H-C-H and C-C-C bond angles),^{2,3} based on spectroscopic studies of chemisorbed hydrocarbon fragments.^{4,5} Each form of entropy (e.g., $S^\ddagger_{2D,trans}$ or S^\ddagger_{vib}) can be calculated from the partition function describing the energy of that form of motion using the Sackur-Tetrode equation:⁶

$$S_x = k_B \ln(q_x) + k_B T \left[\frac{\partial \ln(q_x)}{\partial T} \right] \quad (\text{S2})$$

where x denotes the specific degree of freedom.

The partition function for translational motion of strongly-bound hydrocarbons reflects their frustrated movement parallel to the surface, treated as harmonic oscillations, which is described by two degenerate vibrational modes:⁶

$$q_{2D,trans} = \left(\frac{1}{1 - e^{-h\nu_i/k_B T}} \right)^2 \quad (\text{S3})$$

where the frequency (ν_i) is the same for each of these two modes if we consider that the potential energy surface is isotropic. The frequency of this vibration is given by:

$$\nu_i = \left(\frac{E_d}{2md_M^2} \right)^{1/2} \quad (\text{S4})$$

where m is the mass of the transition state complex; d_M is the M-M distance at the surface (e.g., $d_{Ir} = 0.25$ nm), and E_d is the energy barrier for surface diffusion. E_d is assumed to be 46 kJ mol^{-1} based on calculations for methyl groups chemisorbed on Ir(111).⁷

The vibrational partition function (q_{vib}) consists of the product of all independent intramolecular vibrations (q_{ν_i}) of the transition state:

$$q_{vib} = \prod_i \frac{e^{-h\nu_i/2k_B T}}{1 - e^{-h\nu_i/k_B T}} \quad (\text{S6})$$

where ν_i is the frequency of the i -th vibrational mode. We assume that these modes are identical to those of the gas-phase alkane reactant, which have been calculated using the coupled-cluster doubles (CCD) level of theory with a 6-31G* basis set.⁸ The sole exceptions are that the transition state excludes the $\nu(\text{C-C})$ mode corresponding to the reaction coordinate⁹ and γ $\nu(\text{C-H})$ modes, present in the gas-phase alkane, are absent in

the transition state because y H-atoms have been removed in the process of forming the C-M bonds that coordinate the transition state to the surface. Vibrational modes include stretching, bending and deformation, as well as hindered rotations of methylene and methyl units within chains. Vibrations normal to the surface correspond to $\nu(\text{M-C})$ modes with frequencies assumed to be $400 - 500 \text{ cm}^{-1}$, by analogy with those reported for methyl groups at on-top sites on close-packed metal surfaces.^{7,10-12}

The one-dimensional rotational partition function, $q_{1D,rot}$ describes rotation about the surface normal by alkyl chains which are bonded to the catalyst cluster surface by a C-atom at one end. The number of alkyl chains (n) and their length depends on the exact points of attachment that coordinate the transition state to the catalyst surface. For example, $^2\text{C}-^2\text{C}$ bond cleavage at the central bond in n-hexane involved the two propyl chains (i.e., three C-atoms long) that form from the α and β C-atoms bound to the surface (Fig. 4a). In contrast, transition states that cleave the $^3\text{C}-^3\text{C}$ bond in 2,3-dimethylbutane (Fig. 4b) and the $^3\text{C}-^2\text{C}$ bond in methylcyclohexane (Fig. 4c) have one methyl chain and zero free alkyl chains, respectively. The motion of these free alkyl chains are described as a rigid rotor:⁶

$$q_{1D,rot} = \prod_i^n \left(\frac{8\pi^3 k_B T \cdot I_{z,i}}{h^2} \right)^{1/2} \quad (\text{S7})$$

in which $I_{z,i}$ is the moment of inertia about the normal axis of rotation for the i -th alkyl rigid rotor. Each alkyl chain is assumed to rotate freely, but steric and electronic interactions with surfaces or vicinal adsorbates could hinder rotation and decrease $q_{1D,rot}$.⁶ The moment of inertia ($I_{z,i}$) for each alkyl chain:⁶

$$I_{z,i} = \sum_j^l m_j \cdot r_j^2 \quad (\text{S8})$$

reflects the mass (m_j) and distance from the rotational axis (r_j) for each C- and H-atom in the alkyl chain (total number, l). Alkyl chains have C-C and C-H bond lengths and angles equal to those in gaseous alkanes,^{2,3} and are assumed to exist as pure trans-conformers because these configurations are most stable¹³ and are most frequently observed in adsorbed hydrocarbons.^{4,5} The values of $I_{z,i}$ as a function of the number of carbon atoms in the alkyl chain are shown in Figure S6.

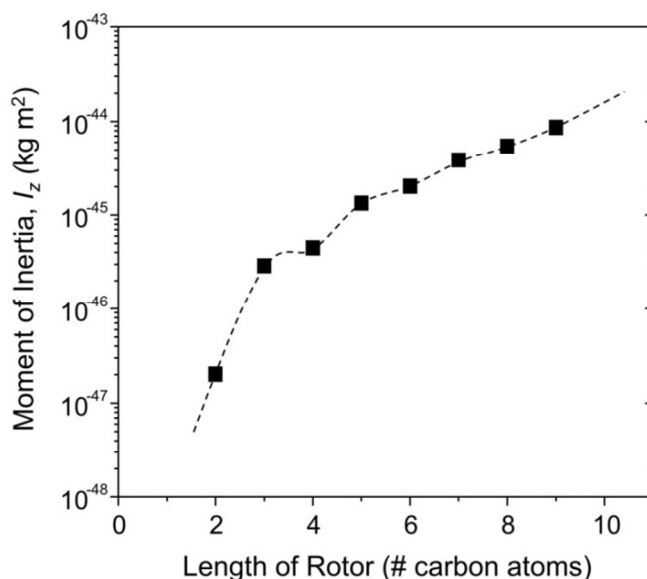


Figure S6. Moment of inertia for calculated for the one-dimension rigid rotation of alkyl chains about the surface normal. The structure of the alkyl chain is determined using equilibrium gas-phase alkane geometries where C-H and C-C bond lengths are 0.109 nm and 0.154 nm, respectively, and H-C-H and C-C-C bond angles are 109.5°.^{2,3} The alkyl chains are assumed to exist as all-trans conformers.^{4,5}

The conformational partition function, q_{config} , accounts for the probability that the alkyl chains can adopt one of three distinct rotational conformations (trans-, gauche+, and gauche-).¹⁴ These trans and gauche conformations introduce degrees of freedom (and entropy gains) not included in partition functions describing the translational, vibrational, and rotational motions of the activated complex. The value of q_{config} depends on the number of C-C bonds ($n - 1$, where n is the number of C-atoms) in the n-alkane. The conformational partition function for a linear, α,β – bound hydrocarbon is equal to:^{14,15}

$$q_{config} = (n - 1) \cdot \left(1 + 2 \exp\left(\frac{-\Delta H_{gt}}{RT}\right) \right)^{(n-1)} \quad (S9)$$

in which ΔH_{gt} is the difference in enthalpy (zero point vibrational energy) between trans and gauche conformations at each C-C bond (2.5 kJ mol⁻¹ per C-C unit).¹³ We assume that similar energy differences exist between eclipsed- and staggered- conformations of C-C bonds in isoalkanes and cycloalkanes.

The entropies of translation, vibrations, and conformations depend only on the mass and on the total number of C-C and C-H bonds of the transition state (and thus on the chain length of the n-alkane reactant). Rotational entropies, however, differ depending on the location of the α,β C-atoms (i.e., the points of attachment to the surface for ²C-²C and ²C-¹C bond cleavage) and the α,β , and γ and δ C-atoms (i.e., the points of attachment to the surface for ³C-^xC bond cleavage) within the alkane. Their location determines the length and number of the pendant alkyl chains and consequently their respective moments of inertia (I_z , Fig. S6).

The rotational entropy increases monotonically with the length of the alkyl chains as shown in Figure S7. The amount of rotational entropy also increases in proportion to the number of alkyl rotors. Thus, deeply dehydrogenated surface species with multiple points of attachment will have much less rotational entropy compared to species that contain long alkyl chains with only two C-atoms bonded to the surface.

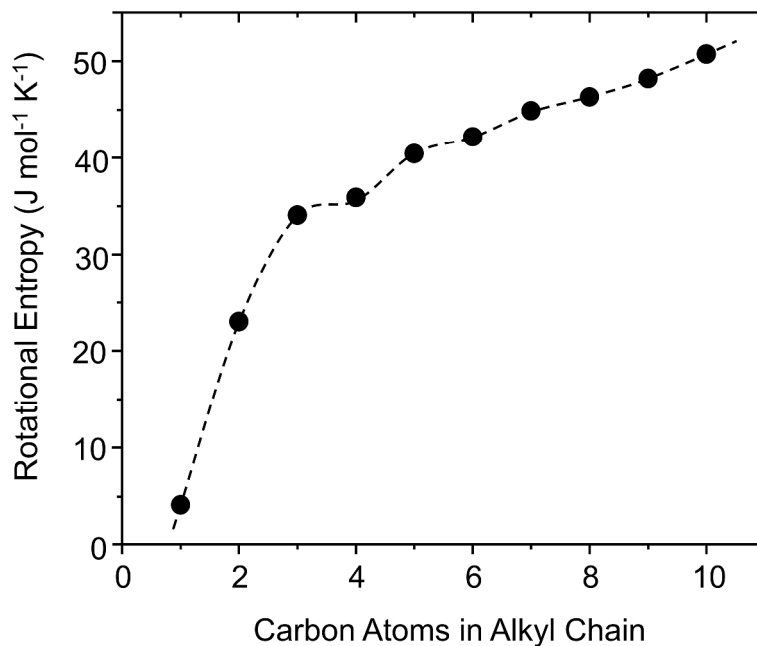


Figure S7. One-dimensional rotational entropy (●) as a function of the number of carbon atoms, i.e., the length, of the alkyl chain assuming an all-trans conformer on metal cluster surfaces at 593 K.

The translational, vibrational, and conformational entropies of these transition states are much greater than their rotational entropies and account for hydrogenolysis turnover rates. Yet, rotational entropies, the smallest contributor to total entropy, represent the sole entropic determinant of the position of C-C bond cleavage in a given n-alkane, because such entropies reflect partition functions that are sensitive to the length of the two alkyl chains pendant to the α,β C-atoms bound to the surface. Estimates for the

entropy of transition states that cleave the $^3\text{C}-^1\text{C}$ bond in isobutane are calculated using equations S1-S9. The composition of the transition state ($\text{C}_n\text{H}_{2n+2-y}$) and the number of C-atoms bound to the surface (γ) were determined from the experimental value of λ ($\lambda=4.0$, Table 2) using Eq. 4. Additionally, bond-order conservation suggests that y and γ values should be similar. These arguments lead to at least three possible transition state structures for isobutane.

The transition state structure with the greatest S^\ddagger is a α,β,γ -coordinated structure in which two H-atoms are removed from the α ^1C -atom, one H-atom is removed from the β ^3C -atom, and two H-atoms are removed from the γ ^1C -atom (i.e., $y=5$, $\gamma=3$; and therefore, $\lambda=4$). This structure has the greatest entropy of the possibilities for isobutane, because it has a free ethyl alkyl chain (i.e., the $^3\text{C}-^1\text{CH}_3$ group) which has $S^\ddagger_{1D,rot}$ equal to $22 \text{ J mol}^{-1} \text{ K}^{-1}$. Alternatively, a different α,β,γ -coordinated structure may form in which three H-atoms are removed from the α ^1C -atom, one H-atom is removed from the β ^3C -atom, and one H-atom is removed from the γ ^1C -atom (i.e., $y=5$, $\gamma=3$; and $\lambda=4$). This structure would have slightly less entropy, because the completely dehydrogenated ^1C -atom would be incapable of rotational degrees of freedom while the two H-atoms remaining on the methylenelike γ ^1C -atom would possess a small amount of rotational entropy ($\sim R/2$). The transition state structure with the least S^\ddagger is a $\alpha,\beta,\gamma,\delta$ -coordinated structure in which one H-atom is removed from each of the four C-atoms ($y=4$) and every C-atom is bonded to the surface ($\gamma=4$). This structure has the least entropy of the possibilities for isobutane, because all C-atoms are bound to the surface and only H-atoms are free to rotate. Thus, depending on the exact number and position from which H-atoms are removed from isobutane to form the transition state, the statistical mechanics estimates

for the value of S^\ddagger for isobutane fall in the range of 196-225 J mol⁻¹ K⁻¹. The average value from these calculations leads an average estimate for S^\ddagger of isobutane of 210 ± 14 J mol⁻¹ K⁻¹. In comparison, estimates for S^\ddagger for structures that cleave the ²C-²C or the ²C-¹C bond in n-butane (y=4, γ=2) are 248 and 240 J mol⁻¹ K⁻¹, respectively. Differences in S^\ddagger between all these transition states arise only from changes among values of $S^\ddagger_{ID,rot}$ that result from changing the intramolecular position and number of the C-M bonds.

Measured values for S^\ddagger for transition states that cleave C-C bonds in branched alkanes have greater uncertainty than those for n-alkanes, because the values of y and γ, which appears in the equation used to find S^\ddagger , are unknown for isoalkanes (e.g., for isobutane y=4, γ=4 or y=5, γ=3 are both possibilities). The absolute uncertainty in S^\ddagger is proportional to uncertainty in γ:

$$S^\ddagger = \Delta S^\ddagger - \lambda \cdot S_{H_2} + \gamma \cdot S_{H^*} + S_{C_n H_{2n+2}} \quad (\text{S10})$$

where we assume, whenever possible that the values of y and γ are equal, however, for reasons described above the value of γ could decrease by a value of 1. Estimates for S_{H^*} show that it is 35 J mol⁻¹ K⁻¹, and therefore, we assume that the uncertainty of measured S^\ddagger is -35 J mol⁻¹ K⁻¹, which results in an asymmetric uncertainty.

Similar reasoning was used to estimate $S^\ddagger_{ID,rot}$, and thus S^\ddagger , for structures that lead to ³C-³C and ³C-¹C bond cleavage in 2,3-dimethylbutane and for C-C bond cleavage in 2-methylpentane. The number of possible ways to remove y H-atoms from these reactants is greater than for isobutane (because there are more C-atoms), and therefore the uncertainties in these estimates are larger (±25-35 J mol⁻¹ K⁻¹). The comparisons between

predictions for S^\ddagger (from statistical mechanics) and measured values of S^\ddagger (found using Eq. S10 and estimates for γ , S_{H_2} , S_{H^*} , and $S_{C_nH_{2n+2}}$) are shown in the main text (Figure 5).

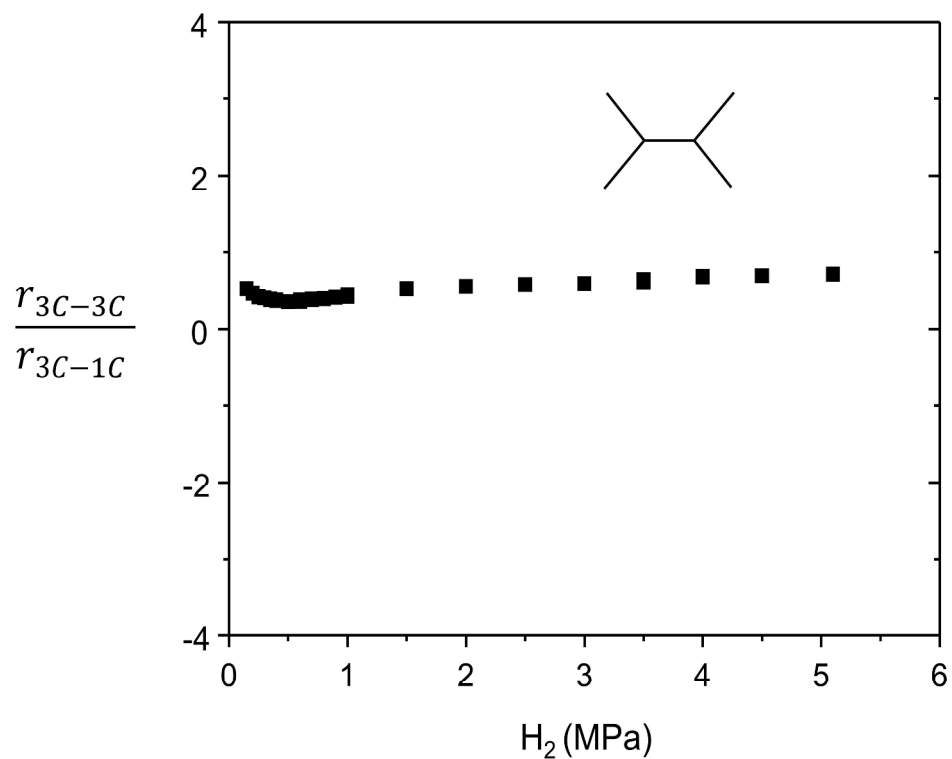


Figure S8. Values of the ratio of the rate of C-C bond cleavage at ³C-³C bond to that at ³C-¹C bonds, where each bond cleavage rate has been normalized by the number of the indicated bonds in the reactant, for 2,3-dimethylbutane (2,3-DMB) as a function of H₂ pressure on 0.7 nm Ir clusters at 10 kPa 2,3-DMB, 593 K.

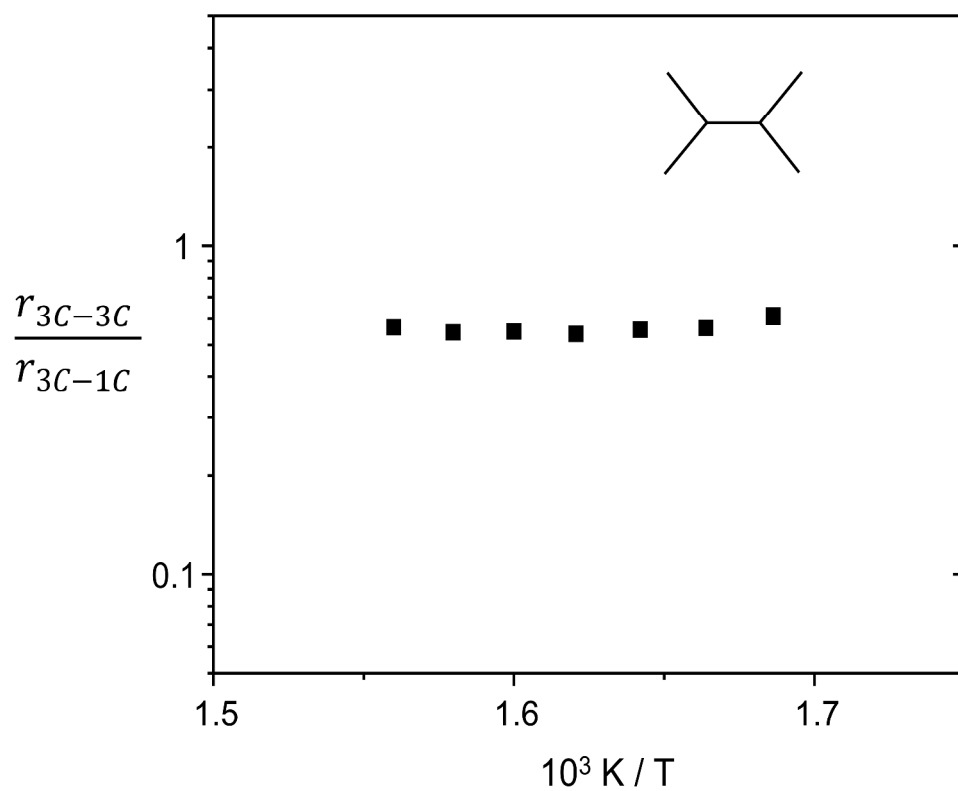


Figure S9. Values of the ratio of the rate of C-C bond cleavage at $^3C-^3C$ bond to that at $^3C-^1C$ bonds, where each bond cleavage rate has been normalized by the number of the indicated bonds in the reactant, for 2,3-dimethylbutane (2,3-DMB) as a function of inverse temperature on H*-saturated 0.7 nm Ir clusters, 10 kPa 2,3-DMB, 3.5 MPa H₂.

Citations

- (1) Flaherty, D. W.; Iglesia, E. *J. Am. Chem. Soc.* **2013**, *135*, 18586.
- (2) *CRC Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 2011; Vol. 92.
- (3) Tait, S. L.; Dohnalek, Z.; Campbell, C. T.; Kay, B. D. *J. Chem. Phys.* **2005**, *122*, 164708.
- (4) Ilharco, L. M.; Garcia, A. R.; Lopes da Silva, J. *Surf. Sci.* **1997**, *371*, 289.
- (5) Yang, M.; Somorjai, G. A. *J. Am. Chem. Soc.* **2004**, *126*, 7698.
- (6) McQuarrie, D. A. *Statistical Mechanics*; University Science Books: Sausalito, CA, 2000.
- (7) Krekelberg, W. P.; Greeley, J.; Mavrikakis, M. *J. Phys. Chem. B* **2004**, *108*, 987.
- (8) <http://cccbdb.nist.gov/>.
- (9) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: Sausalito, CA, 2006.
- (10) Ford, D. C.; Xu, Y.; Mavrikakis, M. *Surf. Sci.* **2005**, *587*, 159.
- (11) Herron, J. A.; Tonelli, S.; Mavrikakis, M. *Surf. Sci.* **2013**, *614*, 64.
- (12) Mavrikakis, M.; Rempel, J.; Greeley, J.; Hansen, L. B.; Norskov, J. K. *J. Chem. Phys.* **2002**, *117*, 6737.
- (13) Smith, G. D.; Jaffe, R. L. *J. Phys. Chem.* **1996**, *100*, 18718.
- (14) Gellman, A. J.; Paserba, K. R. *J. Phys. Chem. B* **2002**, *106*, 13231
- (15) Paserba, K. R.; Gellman, A. J. *J. Chem. Phys.* **2001**, *115*, 6737.