

Carbene Routes to Cyclopropatetrahedrane

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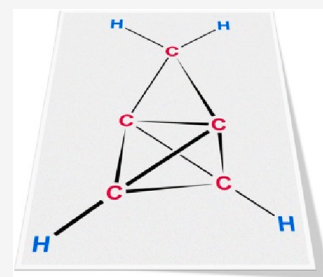
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ABSTRACT: The formation of cyclopropatetrahedrane (tetracyclo[2.1.0.0^{1,3}.0^{2,4}]pentane) via four different carbene reactions is computed using the (U)CCSD(T)(full)/cc-pVTZ// (U) ω B97X-D/cc-pVTZ + 1.3686(E_{ZPVE}) theoretical model. Intrinsic reaction coordinate plots confirm that each carbene is directly linked to cyclopropatetrahedrane via a unique cyclopropanation step. Each elementary step is assessed according to the structure and energy of its transition state.



This report assesses four carbene reactions that ostensibly could form cyclopropatetrahedrane (**1**; ¹ Figure 1a),^{2,3} a cyclopropane-fused derivative of tetrahedrane (**2**; ¹ Figure 1b).^{4–7} To date, **1** and **2** remain hypothetical constructs,

($\Delta_{\text{strain}}H^\circ = 157 \text{ kcal/mol}$)^{2a} is phenomenal and (**2**) the bridging CH_2 -group of **1** establishes a bond that connects two inverted C atoms (i.e., each C atom has four bonds pointing in the same direction;^{10–12} ¹ Figure 1a; cf. ¹ Figures S2 and S3 in Supporting Information). Also, the long C1–C4 bond ($r = 1.664 \text{ \AA}$)^{2a} of **1** is electron-depleted, weak, and prone to breakage when compared with typical aliphatic C–C bonds. Routes to **1** have been proposed, such as via a 2,4-dihalotricyclo[1.1.1.0^{1,3}]pentane synthon (**5**; ¹ Scheme 1).^{4,5} However, carbene routes to **1** have never been investigated.

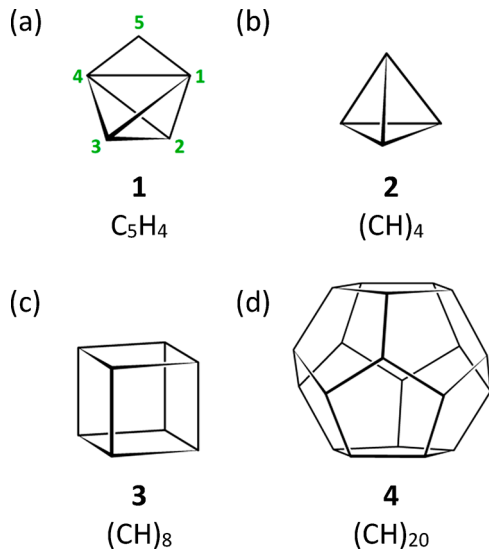
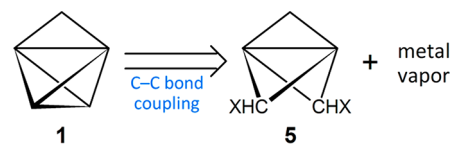


Figure 1. Cyclopropatetrahedrane (**1**) is a cyclopropane-fused derivative of tetrahedrane (**2**), which itself is one of the Platonic-solid-like hydrocarbons that also include cubane (**3**) and dodecahedrane (**4**).

although derivatives of **2**⁴ as well as pristine **3** and **4** (¹ Figure 1c,d)^{8,9} have been prepared (cf. ¹ Table S1 in Supporting Information). Nevertheless, earlier computations suggest that **1** will be kinetically stable because (1) it occupies a deep energy minimum on the C_5H_4 hypersurface and (2) none of its 21 vibrational normal modes falls below $\bar{\nu} = 443 \text{ cm}^{-1}$.^{2,3} Forming **1** will be challenging because (1) its computed strain energy

Scheme 1. A Proposed Retrosynthesis of Cyclopropatetrahedrane (**1**)



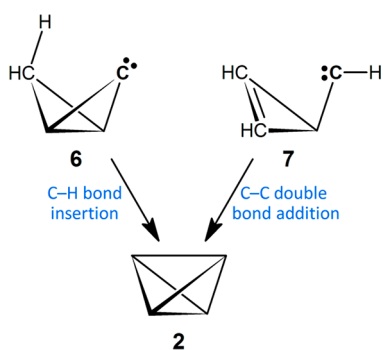
Carbene reaction intermediates are uncharged, electron-deficient, and highly energetic.^{13–27} They are prized for their ability to form a wide variety of cyclopropanes, which can be done in two ways. The divalent C atom ($:\text{C}<$) can (1) insert into a homocyclical C–H bond (e.g., carbene **6** \rightarrow **2**) or (2) add to a C=C double bond (e.g., carbene **7** \rightarrow **2**) (¹ Scheme 2).²⁸ These two signature reactions are useful when building polycycloalkanes. Thus, an examination of carbene routes to highly strained **1** is warranted.

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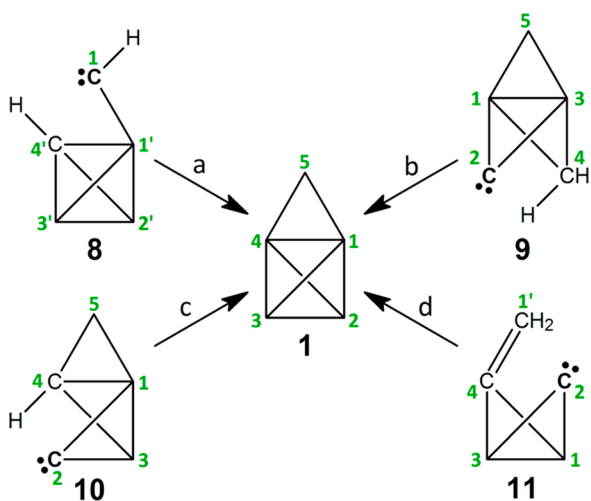
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Scheme 2. Types of Intramolecular Carbene Cyclopropanations



Four routes to **1** via four different hypothetical carbene reaction intermediates (Scheme 3) were evaluated using the

Scheme 3. Four Carbene Routes to Cyclopropatetrahedrane (**1**)

(U)CCSD(T)(full)/cc-pVTZ//((U)ωB97X-D/cc-pVTZ + 1.3686(E_{ZPVE})) theoretical model (see Computational Methods). Paths a–c depict homocyclopropanation reactions within carbenes **8**–**10**, respectively, and path d depicts a C–C double bond addition reaction within carbene **11**. The structures in Scheme 3 are drawn in a uniform manner to emphasize the new bonds being formed (cf. Figure 2): (1) path a, C_{α} – C_{β} ; (2) path b, C_{γ} – C_{γ} ; (3) path c, C_{β} – C_{γ} ; and (4) path d, C_{α} – C_{β} and C_{β} – C_{γ} . Each elementary step is characterized in terms of its transition state (TS) structure, activation energy (E_a), and net energy change (ΔE) (Table 1). Intrinsic reaction coordinate (IRC) plots (Figure 3a–d) and videos (see Supporting Information) are also provided to demonstrate that each carbene is directly linked to **1**.

Path a involves the hypothetical carbene (tetrahedryl)-carbene (**8**).²⁹ A homocyclopropanation reaction via **TSa** was confirmed by its one, and only one, imaginary frequency (Table 1, path a), by animating the corresponding vibration, and by plotting the IRC, which links **8** directly to **1** (i.e., **8** → **TSa** → **1**; Figure 3a (blue)).

An intriguing aspect of the carbene itself was found. Its computed singlet–triplet energy gap (ΔE_{S-T})³⁰ of -6.7 kcal/mol, corrected for the experimental ΔE_{S-T} of CH_2 (eq 1; see Supporting Information),³¹ indicates that alkylcarbene **8** has a

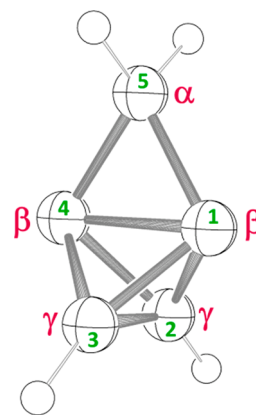


Figure 2. C_{2v} -symmetric cyclopropatetrahedrane (**1**) comprises (a) one 2° -C atom (α), (b) two 4° -C atoms (β), and (c) two 3° -C atoms (γ). (ORTEP structure shows 50% ellipsoids.)

Table 1. Computed Data for Carbene Isomerizations to **1**^{a,b}

Carbene	IRC path	$\bar{\nu}_{TS}$ (cm^{-1})	E_a (kcal/mol)	ΔE (kcal/mol)
8	a	1164i	15.8	−50.2
9	b	915i	14.2	−24.5
10	c	961i	3.5	−29.2
11	d	329i	27.8	10.0

^aCf. Scheme 3. ^bCCSD(T)(full)/cc-pVTZ//ωB97X-D/cc-pVTZ + 1.3686(E_{ZPVE}) theoretical model.

singlet ground state, and decidedly so. Hyperconjugation^{32–35} between the $\text{C1}'$ – $\text{C4}'$ “banana” bond and the vacant p orbital of the carbene’s divalent C atom is a contributing factor (cf. Figure S1 in Supporting Information). The $:\text{CH}$ -group of the lowest energy conformation of **8** is bent 41 deg toward the $\text{C1}'$ – $\text{C4}'$ bond in comparison to the $:\text{C}\cdot\text{H}$ -group of triplet (tetrahedryl)carbene (i.e., **38**) (Scheme 3, path a) even though this deformation causes the $\text{C1}'$ atom’s four bonds to point in one direction (i.e., $\text{C1}'$ is an inverted C atom; cf. Figure S2 in Supporting Information). The distorted geometry of **8** may assist the formation of **TSa** since a triangular array comprising the C1 , $\text{C1}'$, and $\text{C4}'$ atoms is already established (Figure 3a (blue)). Thus, the high ΔH^\ddagger may be more prohibitive than ΔS^\ddagger for the homocyclopropanation reaction **8** → **1**.

$$\Delta E_{S-T} = \Delta E_{S-T(\text{comp})} - 1.25 \text{ kcal/mol} \quad (1)$$

Path b involves the hypothetical carbene tricyclo[1.1.1.0]^{1,3}-pent-2-ylidene (**9**). A homocyclopropanation reaction via **TSb** was confirmed by its one, and only one, imaginary frequency (Table 1, path b), by animating the corresponding vibration, and by plotting the IRC, which links **9** directly to **1** (i.e., **9** → **TSb** → **1**; Figure 3b (green)).

Path c involves the hypothetical carbene *trans*-tricyclo[2.1.0.0]^{1,3}pent-2-ylidene (**10**). A homocyclopropanation reaction via **TSc** was confirmed by its one, and only one, imaginary frequency (Table 1, path c), by animating the corresponding vibration, and by plotting the IRC, which links **10** directly to **1** (i.e., **10** → **TSc** → **1**; Figure 3c (yellow)).

Path d involves the hypothetical carbene 4-methylenebicyclo[1.1.0]but-2-ylidene (**11**). A cycloaddition reaction via **TSd** was confirmed by its one, and only one, imaginary frequency (Table 1, path d), by animating the corresponding vibration, and by plotting the IRC, which links **11** directly to **1** (i.e., **11** → **TSd** → **1**; Figure 3d (red)). However, in contrast

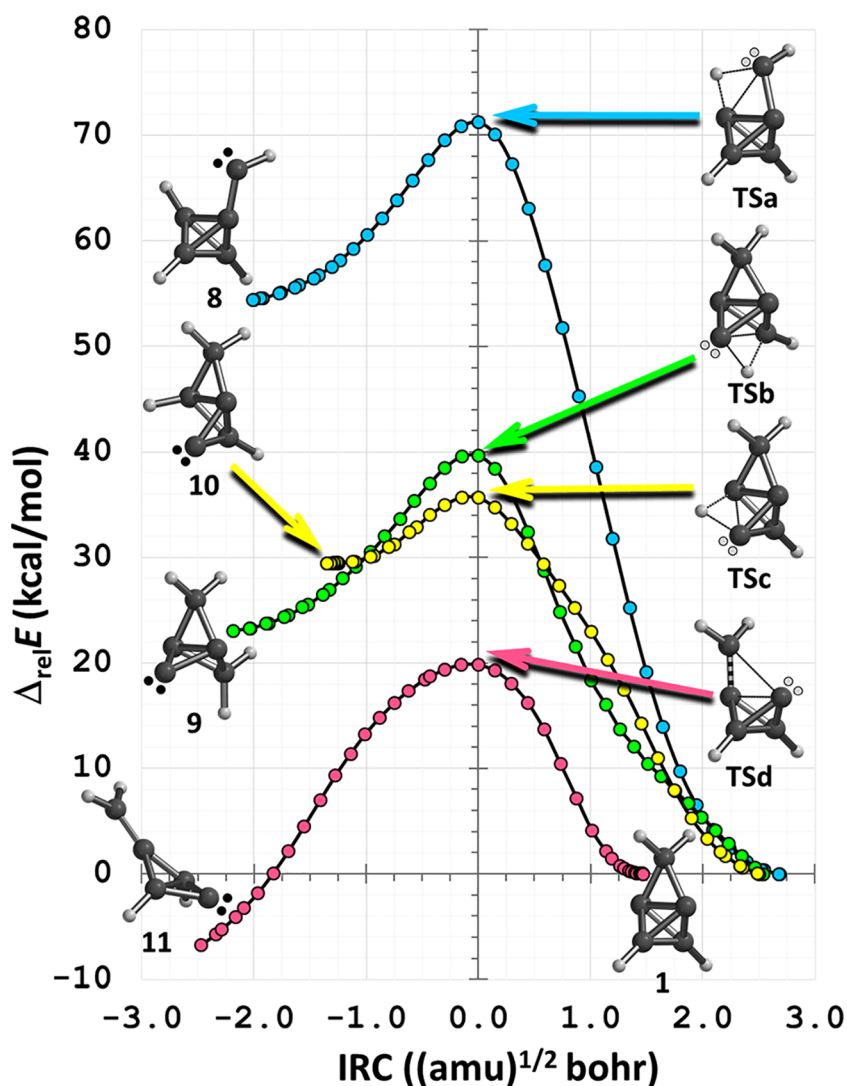


Figure 3. Four IRCs were computed using the CCSD(T)/cc-pVTZ// ω B97X-D/cc-pVTZ theoretical model. Routes (a)–(c) depict homocyclopropanation reactions within carbenes 8–10, respectively, while route (d) depicts a C–C double bond addition reaction within carbene 11.

to those of the homocyclopropanation reactions (Table 1, paths a–c), the net ΔE computed for this elementary step is positive. This indicates a thermodynamic preference for a *cycloreversion* of **1** (i.e., **1** \rightarrow **11**). However, **1** \rightarrow **11** is computed to have a high ΔH^\ddagger (18.1 kcal/mol; see Supporting Information). Of course, this enthalpy barrier is not insurmountable even in a frozen Ar matrix ($T = \text{ca. } 10 \text{ K}$) under photolytic conditions.³⁶

Computational chemistry was used to assess the viability of forming cyclopropanetetrahedrane (**1**) via four different carbene reactions. The hypothesis appears to be valid because a TS was found for each of the elementary steps (i.e., Scheme 3, paths a–d). Furthermore, the respective IRC plots (Figure 3a–d) reveal a direct link between each carbene and **1**. The IRCs and ZPVE-corrected single-point energies show that the homocyclopropanation C–H bond insertion reactions via H atom transfer are exothermic but the C–C double bond addition reaction is endothermic. The formation of **1** via a homocyclopropanation C–H bond insertion within *trans*-tricyclo[2.1.0.0^{1,3}]pent-2-ylidene (**10**) requires an E_a of just 3.5 kcal/mol. The bent posture adopted by the electron-seeking :CH-group of (tetrahedral)carbene (**8**) is akin to a house plant that is bent toward a sunlit window;

each “stalk” bends to obtain what it needs. In contrast, stabilizing hyperconjugation is precluded in triplet (tetrahedral)carbene (**38**) because of its half-occupied p orbital. Thus, the triplet carbene is strictly C_s -symmetric.

COMPUTATIONAL METHODS

Quantum chemical calculations were performed on **1**, carbenes 8–11, transition states TSa–TSd, and intrinsic reaction coordinate (IRC) paths a–d using the Spartan’20 (v.1.1.4) computer program.³⁷ Restricted SCF wave functions of molecular equilibrium geometries and transition states were computed using a (100,434) DFT integration grid, the RSH-GGA functional ω B97X-D,³⁸ and Dunning’s cc-pVTZ basis set. Unrestricted SCF wave functions were computed for triplet-state carbenes. Normal-mode vibrational analyses were performed at the level of geometry optimization. The harmonic frequencies were used to obtain temperature-independent zero-point vibrational energy (E_{ZPVE})³⁹ and temperature-dependent thermal vibrational energy ($\Delta_{\text{vib}}H$) values. Each reaction TS had one, and only one, imaginary frequency, $\bar{\nu}_{\text{TS}}$. Its vibration was animated to verify that the motions conformed to the elementary step. An IRC was computed to ensure that the carbene followed a direct route to **1**. Single-point energy (E) values were computed using the CCSD(T)-(full) coupled-cluster theory method and Dunning’s cc-pVTZ basis

set. All E_{ZPVE} values were scaled by $z = 1.3686^{40}$ before being added to E ($T = 0$ K; $p = 0$ atm). Relative energy values ($\Delta_{rel}E$) are specified with regard to **1** ($\Delta_{rel}E = [0]$). Conversion of E values to enthalpy (H_T) values was done according to eq S1 (see Supporting Information; computational standard state: $T = 298.15$ K; $p = 1$ atm; cf. Table S2). All $\Delta_{vib}H$ values were scaled by $H = 0.956^{40}$ before being added to the ZPVE-corrected E values. The increase in kinetic energy, due to translations ($3(1/2)RT$) and rotations ($3(1/2)RT$), for each nonlinear molecule was then added. Finally, RT (i.e., “ pV work” needed to expand 1 mol of ideal gas to $V = 24.465$ L at $T = 298.15$ K and $p = 1$ atm) was added to obtain H_T (eq S1).

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online [Supporting Information](#).

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.2c02217>.

Computational methods, Cartesian coordinates, ORTEP structures, energies/enthalpies, and geometric proof of inverted C atoms (PDF)

Energy results (XLSX)

IRC data (XLSX)

Inverted carbon atom data (XLSX)

IRC data and video (wB97X-D_cc-pVTZ.IRC_path a__{(Tricyclo[1_1_0_0(2,4)]but-1-yl)carbene_(8)}) (MOV)

IRC data and video (wB97X-D_cc-pVTZ.IRC_path b__{Tricyclo[1_1_1_0(1,3)]pent-2-ylidene_(9)}) (MOV)

IRC data and video (wB97X-D_cc-pVTZ.IRC_path c__{Tricyclo[2_1_0_0(1,3)]pent-2-ylidene_(10)}) (MOV)

IRC data and video (wB97X-D_cc-pVTZ.IRC_path d__{4-Methylenebicyclo[1_1_0]but-2-ylidene_(11)}) (MOV)

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Notes

The authors declare no competing financial interest.

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