Tricyclo[2.1.0.02,5]pent-3-ylidene: Stereoelectronic Control of Bridge-Flapping within a Nonclassical Nucleophilic Carbene

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ABSTRACT: Tricyclo[2.1.0.02,5]pent-3-ylidene is a carbene foreseen to rearrange to pyramidalene (c-C₃H₄), a highly strained molecule featuring an inverted C atom. Modeling of the carbene, using the (U)MPWB1K/cc-pVTZ/(U)MPWB1K/6-311G(d) theoretical model, indicated a large singlet–triplet energy gap (ΔEₛ–ₜ = -45 kcal/mol), a high gas-phase proton affinity (PA = 258 kcal/mol), and a preference for electron-poor alkenes. These properties are consistent with those of nucleophilic carbenes. Structural differences between the Cᵥ-symmetric singlet (ωₛcampo = ±44 deg) and Cᵥ₂-symmetric triplet (ωᵗcampo = 0 deg) stem from nonclassical electron delocalization in the former and the lack thereof in the latter. Degenerate bridge-flapping of the singlet's main bridge, which comprises the reactive divalent C₃ atom, is computed to be slow due to a high activation barrier of the Cᵥ₂-symmetric transition state (TS) (Eₜ = 17 kcal/mol). The position of the conformational equilibrium is subject to stereoelectronic control. 1-Substituted derivatives of the carbene (R-C=CH₂), are sensitive to inductive effects. A proximal conformation is preferred when R is electron-donating and a distal one is favored when R is electron-withdrawing. Finally, carbene rearrangements via 1,2-C atom shift or enyne fragmentation were computed. The Cᵥ₂-symmetric bridge-flapping TS has the proper geometry to initiate enyne fragmentation, however, because a cheletropic reaction within 1 between its C₃ atom and C₁–C₅ bond suffers from orbital misalignment. In contrast, the elementary step 1 → 2 via zwitterionic TS(1/2), (Scheme 1, path c), which stems from C=C bond heterolysis, is the likely mechanism because TS(1/2) is lower in energy than TS(1/2). The potential role of 1 in pyramidalene chemistry has been amply documented. In contrast, little is known about the carbene's innate character. Thus, key properties of 1 and pertinent structures are computed in this report. These include the following: (1) singlet–triplet energy gap (ΔEₛ–ₜ), (2) gas-phase proton affinity (PA), (3) hard–soft acid–base (HSAB) parameters, and (4) carbene–alkene cyclo-addition ΔΔE values. These data help classify the reactive nature of carbenes (e.g., (+)-electrophilic, (−)-nucleophilic, or (±)-ambiphilic).

INTRODUCTION

Tricyclo[2.1.0.02,5]pent-3-ylidene (1) is an enigmatic carbene, accessible only, as yet, via computational modeling. The reactive intermediate has garnered much interest as a possible precursor to pyramidalene (2), an elusive target featuring an inverted C atom. Direct reaction of 1 to 2 has been postulated to occur either by 1,3-C=H bond insertion via TS(1/2), (Scheme 1, path a) or by C=C bond insertion via TS(1/2)ₕ or TS(1/2)ₜ (Scheme 1, paths b and c). Pericyclic TS(1/2)ₕ is unlikely (Scheme 1, path b), however, because a cheletropic reaction within 1 between its C₃ atom and C₁–C₅ bond suffers from orbital misalignment. In contrast, the elementary step 1 → 2 via zwitterionic TS(1/2), (Scheme 1, path c), which stems from C=C bond heterolysis, is the likely mechanism because TS(1/2) is lower in energy than TS(1/2). The potential role of 1 in pyramidalene chemistry has been amply documented. In contrast, little is known about the carbene's innate character. Thus, key properties of 1 and pertinent structures are computed in this report. These include the following: (1) singlet–triplet energy gap (ΔEₛ–ₜ), (2) gas-phase proton affinity (PA), (3) hard–soft acid–base (HSAB) parameters, and (4) carbene–alkene cyclo-addition ΔΔE values. These data help classify the reactive nature of carbenes (e.g., (+)-electrophilic, (−)-nucleophilic, or (±)-ambiphilic).}

Scheme 1. Posited Rearrangements of Carbene 1 to Pyramidalene (2)
Scheme 2. [1,2]-Sigmatropic Rearrangements of Polycyclic Carbenes 1 and 4 Give Bridgehead Alkenes

(a)

(b)

1,2-H atom shift (Scheme 2a), while orbital alignment (Figure 1b) should foster 1 → 3 via a 1,2-C atom shift reaction (Scheme 2a). Indeed, this may be so efficient that 1 and 3 may actually be mesomers (i.e., 1 ↔ 3) and not isomers (i.e., 1 ≡ 3). The possibility is explored in this report.

Singlet adamantylidene (1\4) has a C\4-symmetric equilibrium geometry and undergoes degenerate bridge-flapping via C\2-symmetric TS(4/4)\eq (Scheme 3a).\50,62-65 An analogous conformer equilibrium has been computed for 1 (Scheme 2a), but its \Es is considerably higher.\4-7 Another possible similarity between carbenes 1 and 4 has to do with the conduction of stereoelectronic effects through their polycyclic C-atoms frameworks.\64 An example of this is shown for prox-4-R, where R is an EDG (Figure 2). The potential for 1 to do this is investigated by comparing 1-substituted tricyclo[2.2.1.0\2,5\]pent-3-ylienes (1-R; Scheme 3b) with \gamma-substituted adamantylidenes (4-R; Scheme 3a).\54,65

(4)\60-65 (Scheme 2b). Carbone 4 does not yield 5, however, because the bridgehead C=C double bond violates Bredt’s rule.\66-69 Strain within 5, caused by the severely distorted \pi bond, impedes 4 → 5. Orbital alignment is also unfavorable. The divalent C2 atom’s empty \alpha orbital is orthogonal to the \alpha-C=H bonds within 4. These factors contribute to a high \DeltaG°\12,96 computed to be 52.7 kcal/mol.\60 Instead of a 1,2-H atom shift, 4 reacts via a 1,3-C=H bond insertion reaction (cf. Scheme 1, path a), requiring only 11.8 kcal/mol.\60 Thus, orbital misalignment (Figure 1a) should preclude 1 → 3 via a 1,2-C atom shift should proceed (cf. Scheme 2).

Figure 1. [1,2]-Sigmatropic rearrangements within carbene 1 depend on orbital alignment; (a) 1,2-H atom shifts should not be possible, but (b) 1,2-C atom shift should proceed (cf. Scheme 2).

Results and Discussion

The (U)MPWB1K/cc-pVTZ/(U)MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model was used to compute equilibrium geometries, transition state (TS) geometries, single-point energies, zero-point vibrational energy (ZPVE) values, and intrinsic reaction coordinates (IRCs). The MPWB1K method was chosen because it gives accurate activation energy (\Es) values for carbone reactions.\70-72

The theoretical model’s suitability was tested by comparing relevant TS and \Es results against the reported ones:\2,3,5,7 (1) 1 → [TS(1/2)],\32 → 2 (Scheme 1, path a) and (2) 1 → [TS(1/2)],\34 → 2 (Scheme 1, path c). The 1,3-C=H bond insertion reaction (Scheme 1, path a) was modeled using MPWB1K and MP2 since MP2 was used in an earlier report:\5 E = 32.7 and 33.5 kcal/mol. The transition state TS(1/2) was confirmed herein by an IRC (see the Supporting Information) and leaves no doubt that the earlier \Es is erroneous.\7,73 The conversion of 1 to 2 via zwitterionic TS(1/2) (Scheme 1, path c) requires much less energy: \Es = 2.2,\4,5,7,3.5,2,3 and 5.2 kcal/mol. The transition state TS(1/2) was confirmed by a plateau-type IRC (see the Supporting Information), which can indicate ring opening within strained hydrocarbons.\75

The computed structures for 1,\4,7 TS(1/2)\eq and TS(1/2)\eq are presented in Figure 3a–d. Fundamental properties of carbone 1, such as \DeltaES,TS were computed (Table 1). The difference between the computed and experimental \DeltaES,T values for CH3 was used to obtain corrected \DeltaES,T values (eq

Figure 2. \gamma-Substituted adamantylidenes (4-R) exhibit stereoelectronic effects based on proper orbital alignment and the \sigma inductive effect of R (e.g., R\EDG).
The singlet ground state $^1\text{I}$ is 45 kcal/mol below the triplet state $^3\text{I}$. The remarkably large $\Delta E_{S-T}$ is due to two factors. First, $^3\text{I}$ is destabilized because the bond angle $\theta_{\text{carbene}}$, centered on the divalent C3 atom, is exceedingly small at

Figure 3. (a–l) Structures of 1, 2, 3, 6, 11, 12, and related molecules computed using the (U)MPWB1K/cc-pVTZ//(U)MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model. (ORTEP structures are 50% ellipsoids.)
Table 1. Singlet vs Triplet Carbene $1^a$

| Carbene Aspect/Property | $1^a$ | $1^b$ |
|-------------------------|-------|-------|
| spin multiplicity (2S + 1) | 1    | 3    |
| electron configuration  | $1^a$(σ²p²) | $1^b$(σ²p¹) |
| symmetry point group    | C₁    | Cᵥ   |
| θ$_{carbene}$           | 84.9  | 82.6  |
| ΔE$^a_b$                | 0 deg | 44.9 kcal/mol$^c$ |
| $\omega_{flap}$         | ±43.5 deg | 0 deg |

$^a$Computed using the (U)MPWB1K/cc-pVTZ//(U)MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model. $^b$Bond angle of C2-C3-C4. $^c$ΔE$_{S^b-T}$ = 44.9 kcal/mol strongly suggests that $1^a$ is a hypervalent carbene. This classification is somewhat paradoxical since the reactive C3 atom of $1^a$ is formally hypervalent.78

$\Delta E_{S^b-T} = \Delta E_{S^b-T(comp)} - 4.6$ kcal/mol

The main bridge of $C_s$-symmetric $1^a$, which comprises the reactive divalent C3 atom, is torsionally bent by $\omega_{flap} = ±43.5$ deg from the $\sigma$ mirror plane within $C_s$-symmetric $1^a$, which also exists within TS($1/1$)$_{flap}$. The degenerate conformerism $1^a \rightleftharpoons [TS(1/1)]_{flap}$ entails a b$_1$-symmetric vibration $\nu/c = 502$ cm$^{-1}$) wherein the C3 atom flaps toward and away from C1 (Scheme 3b). Bridge-flapping within $1^a$ is well established (Scheme 3a).50,63,66 Its main bridge is bent to a lesser extent: $\omega_{flap} = ±15.1,64,65 ±18.5,53$ and ±19.77 deg.

Table 2 lists important aspects for carbenes 1 and 4. They share many similar properties, such as symmetry, ground-state multiplicity, polarity, prox = dist flapping equilibria, and gas-phase PA values that are comparable to those of other nucleophilic carbens. Given these similarities, carbenes $1^a$-$R$ should exhibit π-facial selectivity, as with carbenes $4^a$-$R$, because tilting of the main bridge exposes one side while shielding the other.

However, there are some distinct differences between carbenes 1 and 4 (cf. Table 2). The bond angle θ$_{carbene}$ centered on the divalent C atom of 1 is much lower than that of 4. This leads to ΔE$_{S^b-T}$ values for 1 and 4 that are vastly different, as mentioned (Table 1). The prox = dist flapping rate for 1 will be much slower than that for 4, especially at low temperatures. This is inferred from their disparate $E_a$ values (Table 2). Thus, product selectivities based on reaction kinetics will differ greatly for 1 and 4.64 Carbene 1 is not anticipated to undergo diastereoselective C–H bond insertion reactions despite its π-facial selectivity. In contrast to 4, 1 lacks the axial β C–H bonds that sterically orient the intermolecular transition states computed for 4.64,65

Carbene 1 has a gas-phase PA of 258 kcal/mol (Table 2 and eq 2). This is in the range of N-heterocyclic carbene (NHC) ylides.40,78–83 Its PA is unusually high for a hydrocarbon and exceeds that of other nucleophilic carbens. Given these similarities, carbenes $1^a$-$R$ share many similar properties, such as symmetry, ground-state multiplicity, polarity, prox = dist flapping equilibria, and gas-phase PA values that are comparable to those of other nucleophilic carbens. However, there are some distinct differences between carbenes 1 and 4 (cf. Table 2). The bond angle θ$_{carbene}$ centered on the divalent C atom of 1 is much lower than that of 4. This leads to ΔE$_{S^b-T}$ values for 1 and 4 that are vastly different, as mentioned (Table 1). The prox = dist flapping rate for 1 will be much slower than that for 4, especially at low temperatures. This is inferred from their disparate $E_a$ values (Table 2). Thus, product selectivities based on reaction kinetics will differ greatly for 1 and 4.64 Carbene 1 is not anticipated to undergo diastereoselective C–H bond insertion reactions despite its π-facial selectivity. In contrast to 4, 1 lacks the axial β C–H bonds that sterically orient the intermolecular transition states computed for 4.64,65

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Scheme 4. Protonation of 1 or 2 Gives Carbocation 6\textsuperscript{a}

![Diagram of carbocation 6](image)

“Note that carbocation 6 represents both Brønsted–Lowry conjugate acids 1H\textsuperscript{+} and 2H\textsuperscript{+}, which are identical to each other (i.e., 1H\textsuperscript{+} \equiv 2H\textsuperscript{+}), according to quantum chemical computations.

Indeed, one may view 1 as “iso-pyramidane” (i.e., 1 \equiv iso-2)\textsuperscript{1d} because protonation of either 1 or 2 gives 6 (i.e., 1H\textsuperscript{+} \equiv 2H\textsuperscript{+} \equiv 6; cf. Scheme 4)\textsuperscript{2,9,10} This notion is also supported by comparing their frontier MOs.

\[ PA = H^0_\text{B} - H^0_{\text{BH}^+} \text{ for B: } +H^+ \rightarrow [B - H]^+ \] (2)

An MO correlation diagram between 1 and 2 has been reported at the MINDO/3 level of theory\textsuperscript{11,12} However, 1 was treated as having Cs symmetry\textsuperscript{11} instead of the C\textsubscript{2v} symmetry found using ab initio methods. Thus, a new comparison was warranted. Frontier MO details for 1 and 2 are shown in Figure 4c,d and Table 3 and are found in Figure 4c,d and Table 3 of the text.

![Diagram of MOs for carbene 1 and 2](image)

Table 3. Frontier MOs of Carbene 1 (“iso-Pyramidane”)\textsuperscript{a}

| Orbital | E | Occupancy |
|---------|---|-----------|
| HOMO(-2) | -9.31 eV | ↓ |
| HOMO(-1) | -9.18 eV | ↓ |
| HOMO | -6.74 eV |   |
| LUMO(+1) | 2.17 eV |   |

\textsuperscript{a}Computed using the MPWB1K/cc-pVTZ//MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model.
4-R\text{-}\text{dist}\text{-}4-R ratio (cf. Scheme 3a). This, in turn, influences both intramolecular and intermolecular product selectivities (Table 6). The nature of R is the determining factor: (1) $\sigma < 0$ (−) if R = R\text{EDG} and (2) $\sigma > 0$ (+) if R = R\text{EWG}. A similar situation for carbenes 1-R was researched. Its bridge-flapping may be subject to $\sigma$ inductive effects too. Note that carbenes 1-R would not be diastereoselective, however, since they lack

Table 4. Frontier MOs of Pyramidane (2)$^a$

| Orbital | HOMO$^{−1}$ | HOMO$^{−1}$ | HOMO | LUMO |
|---------|-------------|-------------|-------|------|
| $E$     | −8.82 eV    | −8.82 eV    | −7.85 eV | 2.07 eV |

$^a$Computed using the MPWB1K/cc-pVTZ//MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model.

Table 5. Differences in Frontier MO Energy Gaps ($\Delta\Delta E$) between Carbenes and Alkenes$^{a,b}$

| Reactants | [D$_2$] | [C$_2$] | [D$_{2z}$] | [C$_z$] | [G$_2$] | [G$_{2z}$] |
|-----------|--------|--------|--------|-------|-------|-------|
| C=\text{C} | 5.55 | 4.12 | 3.33 | 3.19 | 0.87 | −1.13 |
| C=\text{N} | 5.31 | 3.88 | 3.09 | 2.95 | 0.63 | −1.37 |

Table 6. Selective C–H Bond Insertions of $\gamma$-Substituted Adamantylidienes$^{a,b}$

| carbone 4-R | R\text{EDG} | R\text{EWG} |
|-------------|-------------|-------------|
| favored conformer | prox | dist |
| intramolecular$^b$ | as | s |
| intermolecular$^c$ | anti | syn |

$^a$ cf. Ref 64. $^b$Monosubstituted 2,4-didehydroadamantane product: asymmetric (as) or symmetric (s). $^c$$\gamma$-Disubstituted adamantane solvolysis product: anti or syn.

$^a$Computed using the MPWB1K/cc-pVTZ//MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model and eqs 3−5. $^b$Units in eV.
sterically directing CH₂ groups. Moreover, their flipping equilibria are much slower. The bridge-flapping \( E_\text{flap} \) for 1 (\( E_\text{flap} = 12.8,2.9 \) \( E_\text{flap} = 13.5,2.9 \) \( E_\text{flap} = 14.6,5.7 \) \( E_\text{flap} = 16.2,3 \) and \( E_\text{flap} = 17.0,4 \) kcal/mol) is significantly higher than that for 4 (\( E_\text{flap} = 1.15 \) kcal/mol).

Bridge-flapping transition states \( \text{TS}(1/1)_\text{flap} \) and \( \text{TS}(\text{prox}-1-R/\text{dist}-1-R)_\text{flap} \) were computed for 1 and a set of 1-substituted derivatives 1-R, respectively, and verified by IRC analyses (Figure 6). Conformational effects caused by the following R-group substituents were explored: SiMe₃, PMe₂, H, Me, OMe, and Br. When R = H, the degenerate step 1 → \([\text{TS}(1/1)_\text{flap}]\) → 1 gives a symmetric curve since \( \Delta E_\text{flap} = 0 \) (Figure 6). However, when R ≠ H, then \( \Delta E_\text{flap} \neq 0 \) (eq 6) because the distinct conformers \( \text{prox}-1-R \) and \( \text{dist}-1-R \) have different energies (i.e., \( E_\text{prox} \neq E_\text{dist} \)). For example, \( \Delta E_\text{flap} \) increases by 4.3 kcal/mol with 1-SiMe₂ but decreases by 6.7 kcal/mol with 1-Br (cf. eq 6, Table 7, and Figure 6). The preference for a proximal or distal conformation is influenced by the σ inductive effect of substituent R, which can be quantified by a σ₁ value.⁹² Hence, a conformational bias based on the proximity of C3 to substituted C1 or unsubstituted C5 is observed. A proximal (\( \text{prox} \)) conformation is established when the divalent C atom (\( \geq C_2 \)) leans toward substituted C1, while a distal (\( \text{dist} \)) conformation exists when \( \geq C_3 \) is tilted toward unsubstituted C5. It is evident from the energy profiles that \( \text{prox}-1-R \) is energetically preferred when R is an EDG, while \( \text{dist}-1-R \) is favored when R is an EWG. Hence, \( \Delta E_\text{flap} \) decreases as R becomes more electron-withdrawing. These trends accord well with those of carbenes 4-R.

\[
\Delta E_\text{flap} = E_\text{dist} - E_\text{prox}
\]

The dipole moment of \( 1^1 \) (\( \mu = 4.2 \) D) is high for a hydrocarbon. It is readily understood when one considers the intramolecular MO interaction between the carbene’s empty p orbital and its high-lying HOMO (−1) (Table 3), which features bent C–C bonds having mixed σ/π-character (Figure 1b). Such donor–acceptor interactions are common within classical singlet carbenes (e.g., CC1₃) and nonclassical ones (e.g., bicyclo[2.2.1]hept-2-en-7-ylidene) 51,87,89 when the relevant orbitals are nearby, close in energy, and properly aligned. However, NHCs are such extreme examples of singlet carbenes that they are better described as ylides. The large \( \Delta E_\text{S–T} \) value of −44.9 kcal/mol for 1 (Table 2) and the polycyclic carbene’s reluctance to form the strained bridgehead alkene 5, as depicted in Scheme 2a and Figure 1a, mean that the nonclassical carbene \( 1^1 \) has considerable ylidic character. Indeed, \( 1^1 \) is better described (and presented)⁹ by the two equivalent resonance forms shown in Scheme 5. The singlet carbene is a “gem-zwitterion”⁹³ and its ylidic forms are 1,2-zwitterions. It is easy to see from Scheme 5 how TS(1/2)ₜ, which is a 1,3-zwitterion with \( \mu = 4.1 \) D, is readily attained from \( 1^1 \) (Scheme 1, path c: \( E_\text{flap} = 2.2,3.5^7 \) and \( 5.2^7 \) kcal/mol). In contrast, the ylidic nature of \( 1^1 \) might be responsible for the high relative energy of TS(1/2)ₜ⁺ (Scheme 1, path a: \( E_\text{flap} = 32.7^3 \) and \( 33.5^2 \) kcal/mol), which is less polar with \( \mu = 2.8 \) D.

Carbene 1 and alkene 3 are functional isomers (i.e., 1 \( \equiv 3 \)) according to classical force-field modeling (Figure 7a). However, they are identical molecules (i.e., 1 \( \equiv 3 \)) according to quantum chemical computations. They are not two species separated by a 1,2-C atom shift TS (i.e., no 1 \( \rightarrow [\text{TS}(1/3)] \) \( \rightarrow 3 \)), which explains why none could be found. Structures 1 and 3 are resonance forms of the same entity (i.e., 1 \( \equiv 3 \)). They share the same set of Cartesian coordinates and ylide resonance forms (Scheme 5). The equivalence of 1 and 3 points toward a key relationship between TS(1/1)ₜ (Figure 3g) and TS(3/3)ₜₕ (Figures 3h and 7c). The IRC for bridge-flapping within so-called 3 reveals that it is actually a reaction path for degenerate transverse bridge-flapping within 1 (Figure 8b). Drawing in ylide form recasts the motion represented by the IRC as straightforward bridge-flapping.

Carbene 1 comprises (cyclopentadienyl)carbene (7)⁹⁴–102 and cyclobutylidene (8)⁹⁰–109 units and should react according to their known rearrangement types. Examples of these include

![Figure 6](https://dx.doi.org/10.1021/jacs.0c02414)

**Figure 6.** The \( \text{prox} \equiv \text{dist} \) flapping equilibrium for carbenes 1-R reverses if \( R_{\text{ENC}} \) is replaced by \( R_{\text{SP3}} \) (computed using the MPWB1K/6-311G(d)//MPWB1K/6-311G(d) theoretical model).

| R    | \( \omega_{\text{flap prox-1-R}} \) (deg) | \( \omega_{\text{flap TS(\text{prox}-1-R/dist-1-R)}} \) (deg) | \( \omega_{\text{flap dist-1-R}} \) (deg) | \( \Delta E_\text{flap} \) (kcal/mol) | \( E_\text{prox-1-R} \) (kcal/mol) | \( E_\text{dist-1-R} \) (kcal/mol) |
|------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|-------------------|-------------------|
| SiMe₃ | −42.5 | 0.8 | 41.4 | 4.3 | 15.8 | 11.4 |
| PMe₂ | −43.0 | 0.1 | 42.2 | 1.6 | 15.8 | 14.1 |
| H   | ±43.5 | 0.0 | 44.9 | −1.5 | 16.8 | 18.3 |
| Me  | −43.3 | 0.0 | 44.9 | −5.6 | 18.7 | 24.3 |
| OMe | −45.6 | 0.0 | 44.9 | −6.7 | 16.7 | 23.5 |
| Br  | −44.5 | 0.0 | 44.9 | 18.7 | 24.3 | 38.9 |

*Computed using the MPWB1K/cc-pVTZ//MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model. †See eq 6. ‡The prox and dist stereodecriptors do not apply when R = H.*
Scheme 5. Nonclassically Delocalized Carbene 1 Is Polar and Gives Pyramidane (2) via Low-Barrier 1,3-Zwitterionic Transition State TS(1/2). 

Note that tricyclo[2.1.0.0\textsuperscript{2,5}]pent-3-ylidene (1) is identical to tricyclo[2.1.0.0\textsuperscript{2,5}]pent-2-ene (3), according to quantum chemical computations.

Figure 7. The bridgehead alkene tricyclo[2.1.0.0\textsuperscript{2,5}]pent-2-ene (3) was optimized with the (a) MMFF94 method and used as the starting geometry for (b–d) quantum chemical models, which were bridge-flapping transition states TS(3/3)\textsuperscript{flap}. (ORTEP structures are 50\% ellipsoids.)
ring enlargement or ring contraction via a 1,2-C atom shift reaction and cyclopropanation via a 1,3-C−H bond insertion reaction (Scheme 6). (Cyclopropyl)carbenes can also react via enyne fragmentation reactions when structural circumstances are favorable. The most important of these is orbital alignment. The rigid \( C_2 \)-symmetric carbene nortricyclylidene (9) is a perfect example of this and yields the \( C_2 \)-symmetric enyne (cyclopent-3-en-1-yl)ethyne (10) almost exclusively (Scheme 7).\(^{94−96} \) Presently, IRC calculations show that (cycloprop-2-en-1-yl)ethyne (11) is formed from the \( C_2 \)-symmetric carbene 1 via a shared TS,\(^{75,110} \) namely, \( C_{2v} \)-symmetric TS(1/1)\(_{\text{trap}} \). At this bifurcation point, either bridge-flapping will continue or enyne fragmentation will commence toward TS(1/11)\(_{\text{frag}} \) (Scheme 8a and Figure 8a). Depictions of

Scheme 6. Rearrangements of (Cyclopropyl)carbene (7) and Cyclobutylidene (8)

Scheme 7. Enyne Fragmentation within Nortricyclylidene (9)
the properly aligned orbitals of the combined bridge-flapping/enyne fragmentation transition states are found in Figure 9. Since it did not lead to a 1,2-H atom shift TS or a 1,2-C atom shift TS that would ultimately give enyne 11.

**CONCLUSIONS**

Inherent characteristics of tricyclo[2.1.0.0²,5]pent-3-ylidene (1) were computed using DFT. The divalent C atom of singlet 1 is stabilized by nonclassical electron delocalization from flanking bent bonds comprising well-aligned $\sigma$/π-type orbitals. This interaction is responsible for the singlet carbene’s bent C₂-symmetric structure. Its main bridge is tilted ±43.5 deg from a C₂v-symmetric geometry, which triplet 1 and the bridge-flapping TS do have. The energy barrier for flapping ($E_a = 17.0$ kcal/mol) is much higher than that computed for adamantylidene ($E_a = 1.1$ kcal/mol), whose main bridge is tilted only ±19.7 deg from a C₂v-symmetric geometry. Thus, bridge-flapping conformerism within singlet 1 is relatively slow.

The sizeable $\Delta E_s-T$ ($−44.9$ kcal/mol) and gas-phase PA ($258$ kcal/mol) values computed for 1 suggest that the singlet is nucleophilic. This is further supported by a 2-D philicity chart of tabulated $\Delta\Delta E$ values obtained from the frontier MO energies of singlet 1 and representative sets of carbenes and alkenes. Computations reveal that singlet 1 will react more quickly and completely with electron-poor alkenes than with electron-rich alkenes.

When singlet 1 is substituted at C1, the corresponding carbene 1-R adopts a proximal conformation as the divalent C atom leans toward C1 and a distal one as it bends toward C5. The thermodynamic preference for a prox or dist conformation depends on the $\sigma$ inductive effect of the R-group. A proximal conformation is preferred when R is an EDG, while a distal one is favored when R is an EWG. This controllable stereo-electronic behavior parallels that for γ-adamantylidenes, which consequently undergo intramolecular and intermolecular reactions with high diastereoselectivity.

The Walsh orbitals of TS(1/1)flap (Figure 9a) and TS(3/3)flap (Figure 9b) combine with the π orbital of the divalent C atom and trivalent C atom, respectively, to give extended π-systems that stabilize the shared transition states. Stabilization is achieved also with TS(1/1)frag (Figure 9c) and TS(3/3)frag (Figure 9d). Nonclassical three-center two-electron (3C2E) bonding arises from intramolecular π → π electron donation. Finally, the ostensible H atom-bridged TS 12 does not involve a hydride migration. Instead, TS animation of the ν/c = 201 cm⁻¹ vibrational normal mode (Figure 3l) shows H atom wagging. The IRC for this motion was limited and inconclusive

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Rearrangements of polar carbene 1 were investigated. The formation of pyramidane (2) via a 1,3-C–H bond insertion TS or via a 1,3-swittnerionic TS was conclusively proven by their IRCs. That for \( 1 \rightarrow 2 \) is very flat and requires a supplemental geometry optimization to reach 2. Formation of tricyclo[2.1.0.0^2,5]pent-2-ene (3) via [1,2]-sigmatropic transformations of 1, for example, is unlikely since bridgehead alkenes have high strain energies. The IRC computed for bridge-flipping within 3 was found to be identical to that for \( \text{transverse} \) bridge-flipping within 1. Hence, 1 and 3 are the same molecule. This is seen from their shared ylodic resonance form, which increases in importance as carbene nucleophilicity increases, as with NHCs. Although TS(3\( /3 \))\_sup{lep} violates Bredt’s rule, strain is mitigated during \( \text{transverse} \) bridge-flipping within 1 by a lengthening of the cyclopropane unit’s C–C bonds to 1.678 Å.

The enyne fragmentation of singlet 1 was also modeled. An IRC analysis of the enyne TS showed that the elementary step begins from a TS—that for singlet 1 bridge-flipping. Thus, the \( C_3 \)-symmetric TS is a shared TS and bifurcation point. Such stringent orbital alignment will preclude enyne formation in the case of 1.

Overall, the results anticipate that 1 is a nonclassically delocalized carbene. Its electron lone pair is a source of substantial Lewis basicity, making the carbene as nucleophilic as most NHCs. The carbene will react faster and more completely with electron-poor alkenes than with electron-rich ones. Also, its 1-substituted derivatives are subject to stereoelectronic control in a similar way as for \( \gamma \)-substituted adamantylidenes. Finally, carbene 1 and bridgehead alkene 3 are the same entity. They have the same set of Cartesian coordinates despite having different Lewis structures.

**Computational Methods**

Quantum chemical calculations were performed using the Spartan’14 Parallel Suite (v. 1.1.8) computer program. The restricted or unrestricted SCF wave functions of molecular equilibrium geometries and transition states were computed using the DFT method (U)MPWB1K with a 6-311G(d) basis set. Frozen-core second-order Möller–Plesset perturbation theory (MP2(fc)) with a 6-31G(d) basis set was used to check earlier works. 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 (\( E_{\text{ZPVE}} \)) and temperature-dependent thermal vibrational energy (\( \Delta \omega \)) values. Each reaction transition state (TS) had one, and only one, imaginary frequency 1/2 c whose normal mode was animated to verify the motions expected for the elementary step. Intrinsic reaction coordinates (IRCs) were subsequently generated to follow conformational bridge-flipping, enyne fragmentation, etc. Single-point energy (E) values were computed using the (U)MPWB1K/cc-pVTZ theoretical model. All \( E_{\text{ZPVE}} \) values were scaled by \( z = 0.9513 \) before being added to E (\( T = 0 \) K; \( p = 0 \) atm). Relative energy values (\( \Delta \epsilon \)) are specified with regard to tricyclo[2.1.0.0^2,5]-pent-3-yldiene, the 1-substituted carbene’s proximal conformer, etc., which were set equal to \( [0] \). Conversion of \( E \) values to enthalpy (\( H_e \)) values was done according to eq S1 (see the Supporting Information; computational standard state: \( T = 298.15 \) K; \( p = 1 \) atm; cf. Table S1). All \( \Delta \epsilon \) values were scaled by \( \nu = 0.9462 \) 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 \( H_e \) (eq S1).

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