

Exploration of the potential energy surface of C₄H₄ for rearrangement and decomposition reactions of vinylacetylene: A computational study. Part I†‡

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The potential energy surface (PES) of C₄H₄ was explored using quantum chemical methods (DFT, MP2, MP4, GVB-MP2, CCSD(T), G2M, CBSQ/APNO) and 43 different structures located at global and local minima were identified. The majority of these structures correspond to carbenes, a minority to closed shell systems and biradicals (carbyne structures were not investigated). Whereas the chemistry of the closed shell systems such as vinylacetylene (**1**), butatriene (**2**), methylenecyclopropene (**3**), cyclobutadiene (**5**) or tetrahedrane (**15**) is well known, the carbenes represent unusual structural entities. 2-Methyl-cycloprop-2-en-1-ylidene (**4**) ($\Delta\Delta H(298) = 36.2$ kcal mol⁻¹ relative to **1**) in its $\sigma^2\pi^0$ electron configuration at the carbene C of the ¹A ground state is of comparable stability to cyclobutadiene (**5**) ($\Delta\Delta H(298) = 33.4$ kcal mol⁻¹; exp. value: 32.1 kcal mol⁻¹) as a result of aromatic 2 π -delocalization; carbene 3-vinylidenecyclopropene (**13**) ($\Delta\Delta H(298) = 53.9$ kcal mol⁻¹) does not possess C_{2v} symmetry but has the vinylidene group bent toward the three-membered ring (C_s-symmetry) thus representing a frozen path point of the chelotropic addition of :C=C: to ethene. Allenyl carbene (**14**) has a triplet ground state and two low lying excited singlet states of closed shell (2.5 kcal mol⁻¹ higher) and open shell character (14.1 kcal mol⁻¹). Carbene **14** is a crossing point on the C₄H₄ PES connecting closed-shell systems with each other. Because of the stability of **1**, its rearrangement reactions are all connected with high activation enthalpies requiring 66 up to 92 kcal mol⁻¹ so that they energetically overlap with the activation enthalpies typical of decomposition reactions (from 90 kcal mol⁻¹ upward). The possible rearrangement reactions of **1** are investigated with a view to their relevance for the chemical behavior of the molecule under the conditions of Titan's atmosphere.

Introduction

The potential energy surface (PES) of neutral C₄H₄ contains a number of interesting organic species of closed shell, carbene, carbyne, and biradical type as well as their dissociation products (DP) (see Scheme 1 and structures **1–43**, **DP1–DP9** in Scheme 2). Therefore, the stationary points on the PES and the reaction paths connecting these points have been explored extensively using both experimental and theoretical means.^{1–72}

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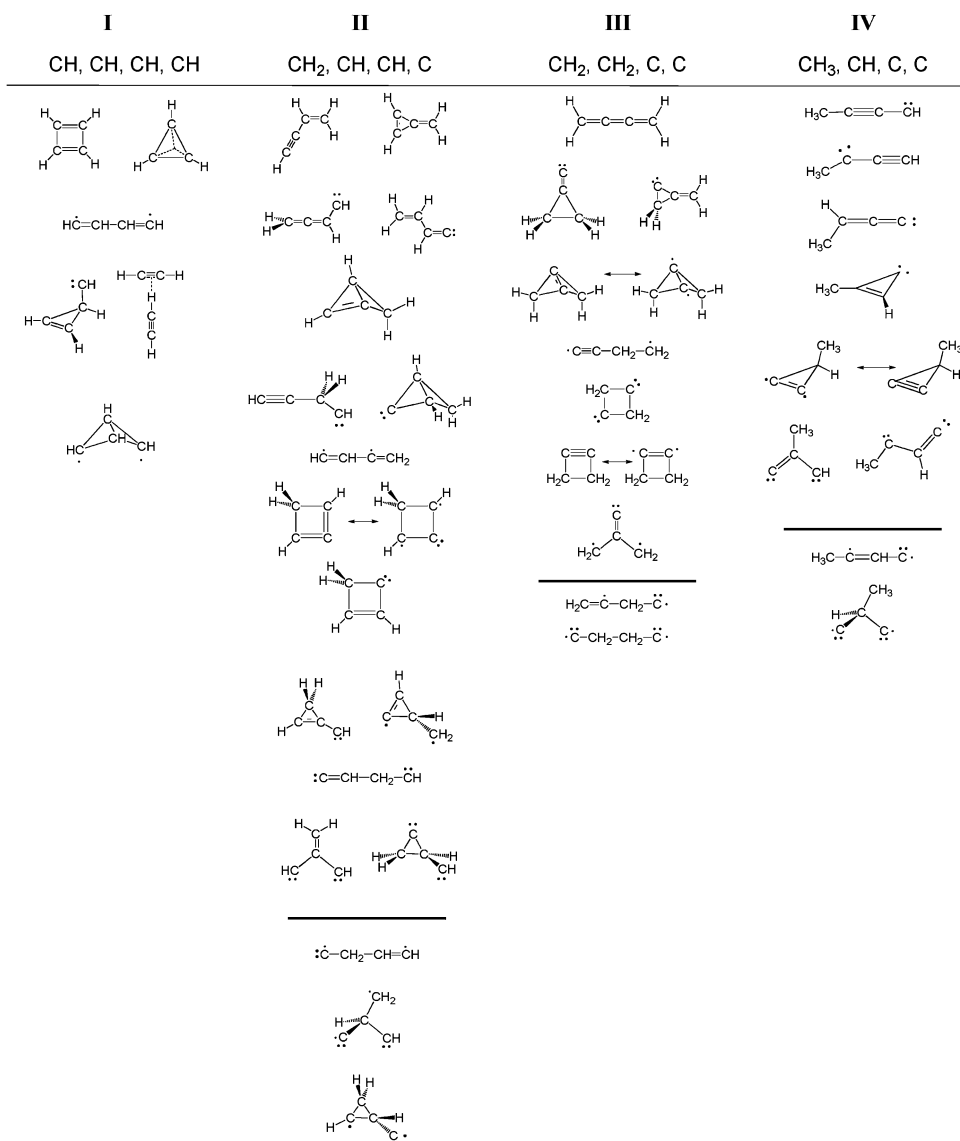
† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Computational details (Tables S1–S4, Fig. S1) including energies, geometries, frequencies, dipole moments, etc. of all structures investigated. See DOI: 10.1039/b609284e

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Most of PES investigations concerned the singlet ground state (S₀) surface,^{1–3,6,8–11} whereas some recent work also extended the investigations to the first excited triplet surface.^{4–7} Attention focused predominantly on the typical closed-shell organic species vinylacetylene (**1**), butatriene (**2**), methylenecyclopropene (**3**), cyclobutadiene (**5**) or tetrahedrane (**15**) in their singlet ground state.^{8–49} As a result, the regions close to the most stable minima of the S₀ PES are well-described whereas less is known about the reaction paths connecting these areas, while little is reported on the many carbenes and biradicals with unusual structures that are located on the C₄H₄ PES.

Remote areas of the PES can be reached by exciting a stable organic species such as **1** photochemically. If internal conversion to the ground state follows immediately and the excess energy cannot be dissipated within the medium, it will be possible that *via* repeated rearrangement processes energetically high-lying local minima of the PES could be populated. Knowledge of these structures is desirable to understand the chemistry of compounds such as **1** under the conditions of combustion chemistry, the chemistry of oxygen-deficit flames, or astrochemical processes taking place in hydrocarbon-rich planetary atmospheres of planets such as Jupiter, Saturn,



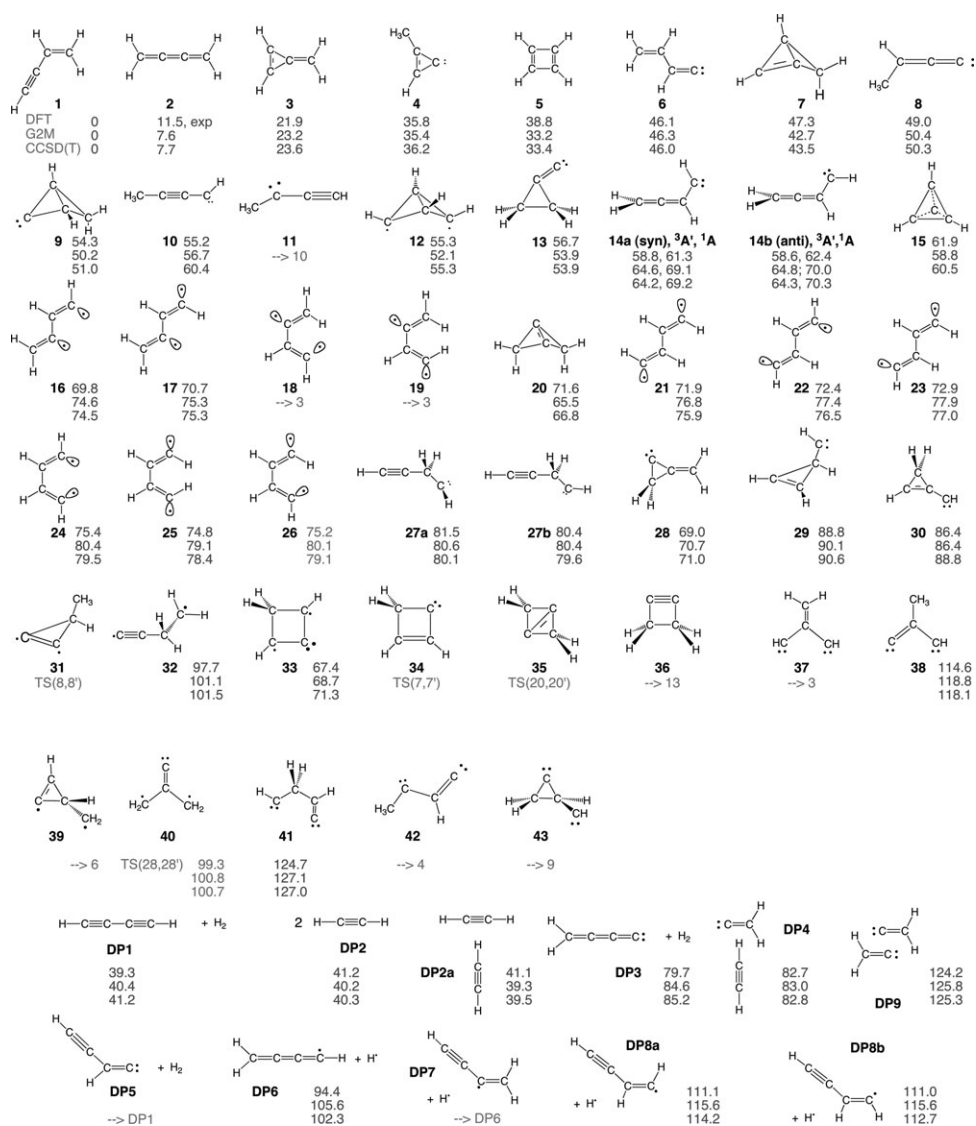
Scheme 1 Grouping of C₄H₄ structures to be expected on the C₄H₄ PES. The horizontal bars separate highly unstable carbyne structures from more stable structures.

Uranus, and Neptune or the moons Titan and Triton.⁴ The present investigation was triggered by the fact that C₄ hydrocarbons such as **1**, diacetylene (**DP1**) or butadiene are candidates for the formation of aromatic compounds, which have been recently found in the atmosphere of Saturn's moon Titan.^{73–75} In the adjacent paper (henceforth called part II)⁷⁶ we will explicitly discuss the role **1** may play in the chemistry of Titan's atmosphere, whereas in this paper we will establish the basis for this discussion by exploring the PES and the rearrangement/decomposition possibilities of **1**.

For the purpose of giving a detailed account on the structural manifold of C₄H₄ we have systematically scanned the PES for possible structures by ordering them in four classes **I**, **II**, **III**, **IV** according to their composition into CH_{*n*} (*n* = 0, 1, 2, 3) units (Scheme 1). A total of 43 reasonable C₄H₄ structures (containing just tetravalent C; by including pentavalent C the number of possible structures does not increase significantly) can be identified, of which 7 contain a carbyne carbon. In view

of the fact that the experiments carried out in part II⁷⁶ use 220 nm laser pulses corresponding to an excitation energy of 130 kcal einstein⁻¹ we have limited our search on the C₄H₄ PES to maximally 115 kcal mol⁻¹ (above **1**) thus excluding the highly unstable carbyne structures (separated by a horizontal bar from the other structures in Scheme 1). The remaining 36 structures have been investigated in this work where, if relevant, the conformational space has been searched for the most stable conformers. For example, there are 10 different potential conformers of the 1,3- and 1,4-butadienediyl biradicals (**16–19** and **21–26**, Scheme 2), which were all investigated in this work.

This work has the following objectives: (1) Identification of all local minima on the C₄H₄ PES in the 0 to 115 kcal mol⁻¹ range. (2) Determination of the geometry of these structures and rationalization of their relative stability. (3) Exploring the rearrangement possibilities of **1**, describing the transition states (TSs) involved, and calculating relevant activation



Scheme 2 Minimum C_4H_4 structures 1–43 and dissociation products DP1–DP9 located at the C_4H_4 PES. For each structure the relative enthalpy value $\Delta\Delta H(298)$ (reference is 1) calculated at the DFT (top entry), G2M (middle entry), and CCSD(T) level of theory (bottom entry) is given. Some structures were identified as TSs and moved to Scheme 3. Others rearranged to more stable structures, which is also indicated. For **2**, the DFT level ($2.9 \text{ kcal mol}^{-1}$) is far below the experimental value of $11.5 \text{ kcal mol}^{-1}$ so that the latter is given. For carbene **14**, values for both the T ground state and the S excited state are listed.

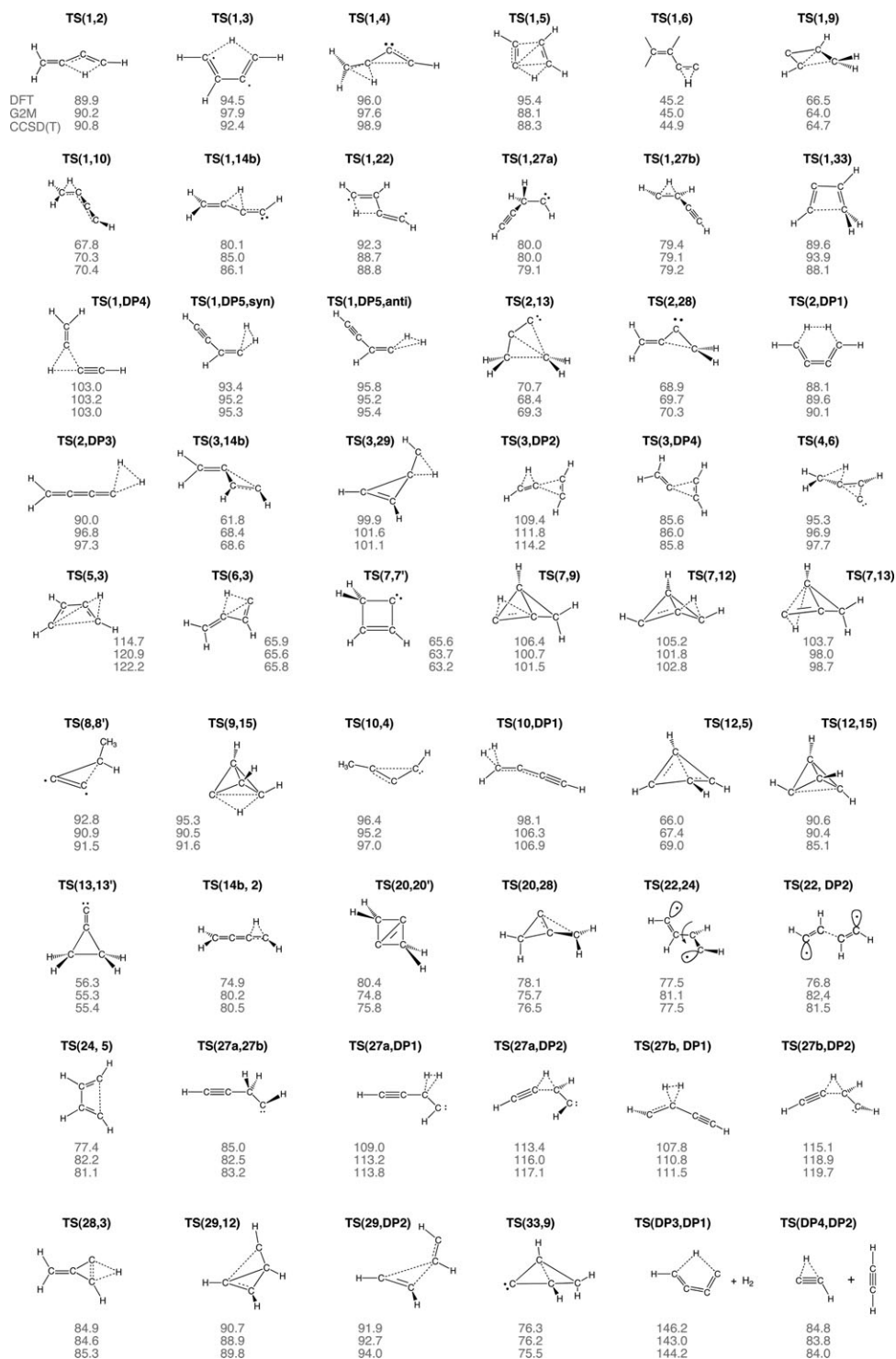
enthalpies. (4) The latter objective implied to investigate also dissociation reactions of **1** that can lead to the potential dissociation products DP1 to DP9 (where the acetylene dimer DP2a^{51–56} of Scheme 1 is added to this group, see Scheme 2). In total, $43 + 9 = 52$ C_4H_4 structures (Scheme 2) and a multitude of TSs (Scheme 3) were calculated to describe reactions R1–R32 shown in Scheme 4. These reactions, the reactants, TSs, and products associated with them provide a near-exhaustive description of the topology of the C_4H_4 PES, the energetics along the reaction paths, and the chemistry taking place on this surface.

2. Computational methods

Four levels of theory were employed in this work, namely density functional theory (DFT),⁷⁷ second order Møller–

Plesset (MP2) perturbation theory,⁷⁸ coupled cluster theory including all single and double excitations with a perturbative treatment of the triple excitations (CCSD(T)),⁷⁹ and GVB-MP2 (general valence bond-MP2).^{80–83} In selected cases, either CASSCF,⁸⁴ G2M⁸⁵ or CBS-APNO⁸⁶ model calculations were carried out. In the case of RDFT (restricted DFT) calculations, the internal and external stability of the R solution were investigated with the help of appropriate stability tests.⁸⁷

For an external instability, the corresponding unrestricted (U) solution was determined. Singlet open-shell biradicals were treated both with the broken-symmetry (BS) UDFT approach and with the restricted open shell theory for low-spin cases (ROSS-DFT) of Gräfenstein, Kraka, and Cremer.⁸⁸ At the ROSS-DFT level,⁸⁸ the two-configurational problem is reformulated in a way that one can essentially remain within the realm of single-configuration theory at the cost of building

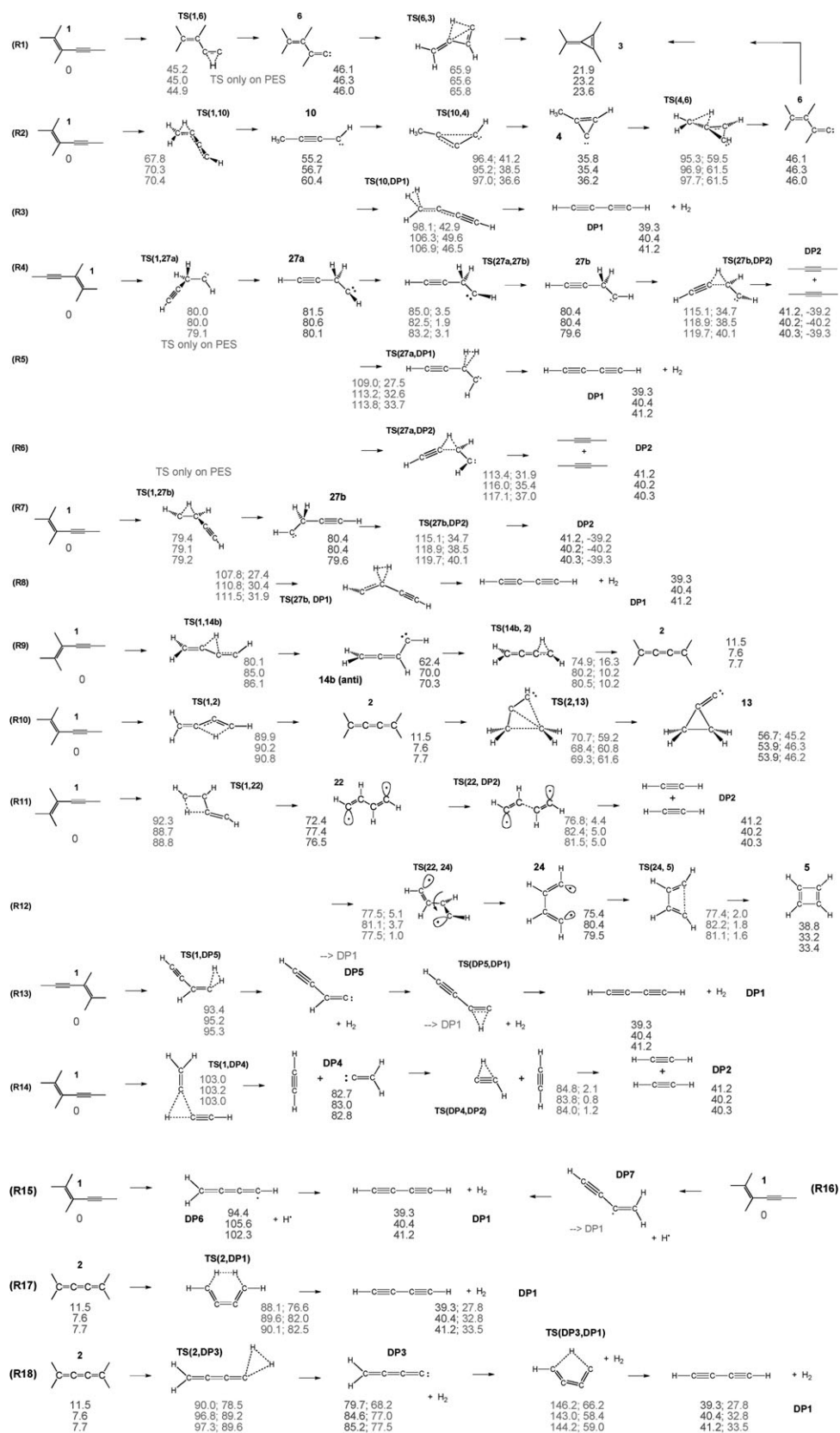


Scheme 3 TS structures of reactions **R1–R32** taking place on the C_4H_4 PES. For each structure the relative enthalpy value $\Delta\Delta H(298)$ (reference is **1**) calculated at the DFT (top entry), G2M (middle entry), and CCSD(T) level of theory (bottom entry) is given.

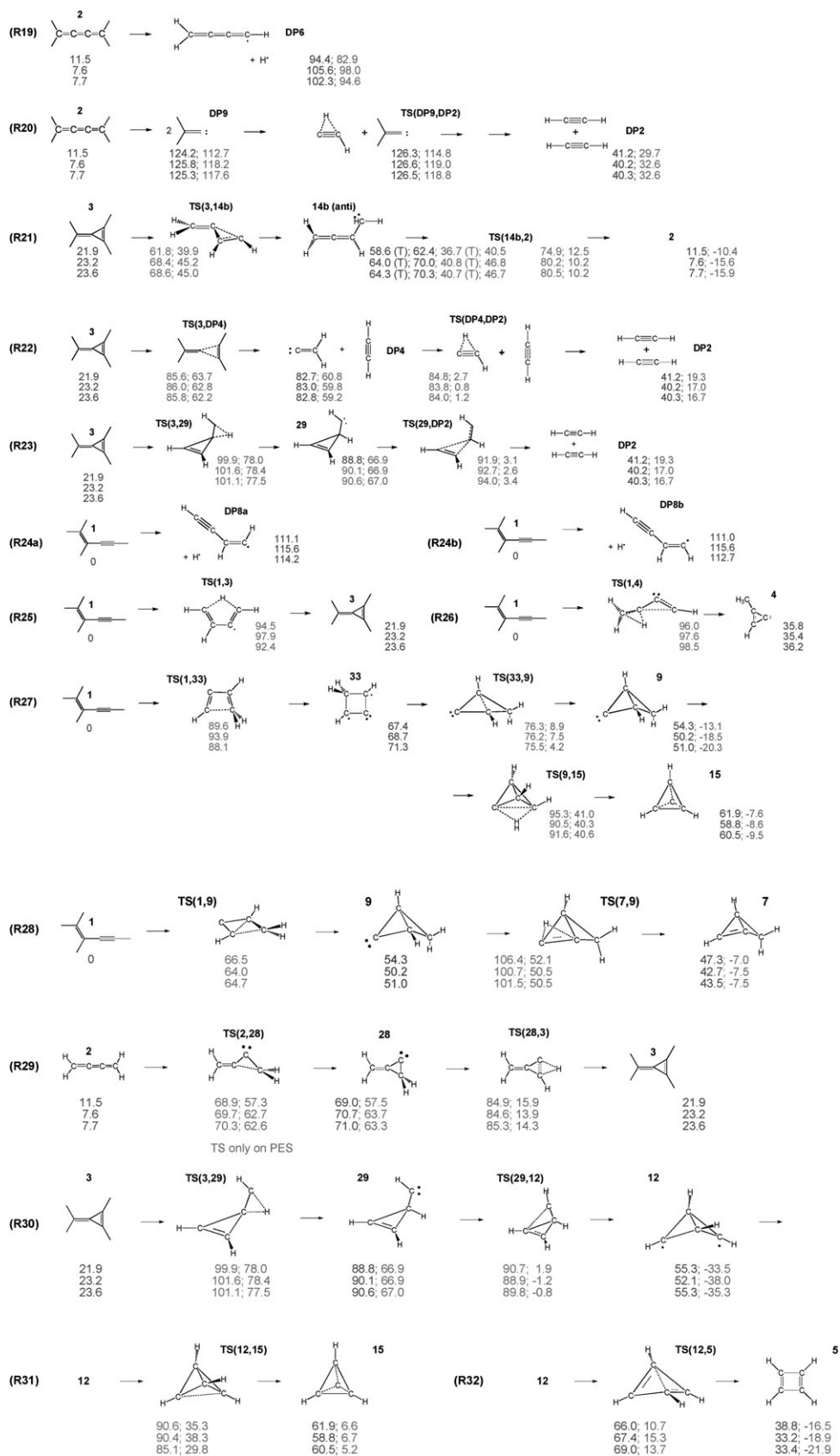
up a more complicated Fock matrix. For the purpose of employing a consistent description of S and T biradicals in the case of carbene **14**, the latter were also calculated at the restricted open-shell DFT (RODFT) level of theory. Hence, DFT calculations were performed at five different levels, namely at the RDFT, UDFT, BS-UDFT, RODFT, and ROSS-DFT levels of theory to adequately describe closed-

shell molecules, T excited states, and S-biradicals. The triplet excited states were investigated principally in order to assess whether the carbenes investigated possess an S or T ground state.

In all calculations the B3LYP hybrid functional^{89–92} was applied. DFT calculations of biradicals were checked by CASSCF and GVB-MP2 calculations, where in the former



Scheme 4 Reactions **R1**–**R32** taking place on the C_4H_4 PES. For each structure the relative enthalpy value $\Delta\Delta H(298)$ (reference is **1**) calculated at the DFT (top entry), G2M (middle entry), and CCSD(T) level of theory (bottom entry) is given. Numbers in a second column give the same values with regard to a new reference (previous reactant in a multistep reaction) to simplify the comparison of reaction and activation enthalpies.



Scheme 4 Continued.

case a (6,6) active space (including 4 π MOs and the 2 singly-occupied σ MOs for biradicals) and in the latter case a (2,2) active space (the two single electrons) were chosen. The GVB-MP2 calculations were carried out at GVB(1) according to a method developed by Konkoli and Cremer⁸³ using just the diagonal Fock operator.

Exploratory calculations were performed with the 6-31G(d,p) basis set (basis A) or variations of this basis set including diffuse functions.⁹³ For the purpose of obtaining more reliable results, all geometry optimizations and frequency calculations were carried out with the 6-311++G(3df,3pd) basis set (basis B).⁹⁴ In the case of the CCSD(T) calculations, Dunning's correlation consistent polarized basis set cc-pVTZP (basis C),⁹⁵ which corresponds to a (10s5p2d1f/5s2p1d) [4s3p2d1f/3s2p1d] basis, was employed. All DFT calculations were carried out with the standard pruned (50,194) fine grid,⁹⁶ which is a reasonable compromise between calculational cost and accuracy.

For each molecule investigated, geometry and vibrational frequencies were determined where the latter were used to verify local/global minimum character of the stationary points found in the geometry optimization, to calculate zero-point energies (ZPE), and to determine absolute enthalpies $H(298)$. Reaction enthalpies $\Delta\Delta H(298)$, activation enthalpies $\Delta H^\ddagger(298)$, and heats of formation $\Delta H_f^0(298)$ were derived from absolute enthalpies. In the case of the heats of formation, the experimental value of **1**⁹⁷ was used as a reference. Other $\Delta H_f^0(298)$ values of C_4H_4 isomers available in the literature⁹⁷⁻⁹⁹ were used to determine the accuracy of calculated heats of formation and, if necessary, to define an improved reference value.

G2M(CC2) calculations were carried out as described in the original literature.⁸⁵ We note in this connection that in the case of biradicaloid structures the Hartree-Fock reference functions were also tested for stability and BS descriptions were applied at the CCSD(T), G2M, *etc.* level of theory. The BS solutions provided a consistent description although this may not always be the case. One has to consider that in this case the frontier orbitals are mixed, which results in an increase of the HOMO-LUMO gap and thereby in a reduction of dynamical electron correlation at lower levels such as MP2 or MP4 where this effect may even perpetuate to the CCSD(T) level of theory. The implicit inclusion of non-dynamical correlation effects by the BS description may partially compensate for the loss of dynamical electron correlation, balance it or even overcompensate where predictions are difficult to make. Since these implications have a stronger relevance for MP4 (the starting point of the G2M incremental scheme) than CCSD(T), we prefer to discuss the latter results and consider the G2M results as additional confirmation, which may not always be reliable. We note that the problem of correctly describing biradical structure is inherent in all G or G-similar methods and needs some more investigation.

Some of the molecules investigated turned out to be conformationally flexible and, therefore, it was verified by analysis of the low frequency vibrational modes that the most stable conformation had been found. In addition, the intrinsic reaction coordinate (IRC) was followed from a TS into the entrance or exit channel of a reaction in those cases, in which

the topology of the PES (connection paths between reactant, TS, and product) was not clear. Calculations were performed with the *ab initio* packages COLOGNE2006,¹⁰⁰ Gaussian 03,¹⁰¹ and GAMESS.¹⁰²

3. Stationary points on the PES of C_4H_4

Calculated relative energies ΔE , zero-point energies (ZPE), relative enthalpies $\Delta\Delta H(298)$, and entropies S of C_4H_4 structures **1-43**, **DP1-DP9** and the TSs of reactions **R1-R32** are listed in Tables S1, S2, and S3 of the ESI together with details describing the calculational procedure in each case.† Also, in Table S1, dipole moments μ and the value of the imaginary frequency of a TS or the lowest frequency of a C_4H_4 minimum structure are given. Heats of formations $\Delta H_f^0(298)$ (last column of Table S1‡ are determined for the best calculational result obtained (as indicated) and compared when possible with experimental values.⁹⁷⁻⁹⁹ Also, the calculated equilibrium geometries are summarized in the ESI.‡ In Schemes 2, 3 and 4, the most reasonable enthalpy differences $\Delta\Delta H(298)$ obtained with regard to ref. **1** are summarized for minimum structures (Scheme 2), TSs (Scheme 3; TSs are identified by reactant and product number), and reactions **R1-R32** (Scheme 4). In the schemes, the DFT, G2M, and CCSD(T) value are given as the upper, middle, and lower numbers, respectively. At times these values are listed in a second column with regard to a new reference as, *e.g.*, the enthalpy of the reactant rather than that of **1** always providing the DFT value first, below the G2M value, and finally the CCSD(T) value (sometimes these values are listed in a second column with regard to a new reference as, *e.g.*, the reactant enthalpy in the step before or at the beginning of the reaction). In the following discussion, we will focus exclusively on calculated enthalpy differences $\Delta\Delta H(298)$, activation enthalpies $\Delta H^\ddagger(298)$ (all given relative to **1**), and heats of formation at 298 K $\Delta H_f^0(298)$.

Stationary points on the C_4H_4 PES

Because of the low H/C ratio all C_4H_4 structures located at stationary points on the PES possess double or triple bonds, alternatively carbene or carbyne carbons, two radical centers, and/or highly strained ring units. Hence there is just one structure, namely **1** with an optimal arrangement of CC connectivities whereas all other structures suffer from (highly) unstable CC bond arrangements, which leads to a rapid increase in energy. There is a clustering of structures at 50 ± 10 kcal mol⁻¹ (**6-15**) where most of them possess carbene functionality or belong to the tetrahedrane-bicyclobutene group.

The C_4H_4 minimum structures calculated in this work can be arranged in four groups: (a) The relatively stable closed-shell systems **1**, **2**, and **3** with $\Delta H_f^0(298)$ values of 70.4 (**1**, reference value^{27,97}), 83.0 (**2**, exp. value;²⁷ RMP2 value 81.9 kcal mol⁻¹; DFT values are too low by 9-10 kcal mol⁻¹), and 92.3 kcal mol⁻¹ (**3**, RDFT/B), *i.e.* within 22 kcal mol⁻¹ of the $\Delta H_f^0(298)$ value of **1** as the most stable form. (b) The vinylidenes and conjugated carbenes **6**, **8**, **9**, **10**, **13**, **14**, and **28** with $\Delta\Delta H(298)$ values between 35 and 70 kcal mol⁻¹ above that of **1**. Scattered between these structures are members of the cyclobutadiene-tetrahedrane group, namely besides **5**

and **15** also **7** and **12**. (c) The butadienediyl biradicals **16–19** and **21–26**, which are 70–80 kcal mol⁻¹ less stable than **1**. (d) The non-conjugated carbenes **27** to **29** being 80 to 90 kcal mol⁻¹ less stable than **1**. (e) The remaining structures **30–43** all possess two or more reactive centers and therefore rearrange with the exception of **32**, **33**, **38**, and **41** to more stable structures. In the following we will discuss some interesting C₄H₄ isomers with unexpectedly low energy.

(a) Carbenes **4** and **28**

The ground state of 2-methyl-cycloprop-2-en-1-ylidene **4** (¹A') possesses a $\sigma^2\pi^0$ electron configuration at the carbene carbon and is just 36 kcal mol⁻¹ above **1**, a stability similar to the antiaromatic system **5** (33.4 kcal mol⁻¹). This is the result of an aromatic 2 π electron delocalization (of the double bond electrons) in the three-membered ring (reflected by CC single bond lengths of $r(\text{HC}-\text{C}) = 1.406$ and $r(\text{MeC}-\text{C}) = 1.416$ Å) which largely compensates for ring strain and the carbene functionality. The parent carbene, cyclopropenylidene, was previously described in connection with the C₃H₃ PES.^{103,104} Carbene **28**, despite its structural similarity to **4**, does not benefit from aromatic π -electron delocalization and therefore it is 35 kcal mol⁻¹ (71 kcal mol⁻¹ relative to **1**) less stable than **4** with the exocyclic double bond strongly influencing the stability by virtue of its increased ring strain. Calculations reveal that **28**, although located at a minimum of the PES, does cease to be a minimum structure as soon as vibrational and thermal corrections are added to its energy.

(b) Carbenes **6** and **8**

On the PES, a minimum of 46 kcal mol⁻¹ above **1** and corresponding to vinylvinylidene **6** (¹ $\sigma^2\pi_{\text{ip}}^0$) (ip: in plane π -orbital) could be located both at the DFT and CCSD(T) level of theory using augmented basis sets of VDZ and VTZ quality. However the PES in the direction of a H-shift yielding **1** is so flat that after adding vibrational and thermal corrections to the calculated energy, **6** ceases to exist as a stable minimum structure. (We found however stable triplet and singlet excited states of **6**.) Gunion and co-workers⁵⁹ estimated the lifetime of **6** in the 20–200 fs range basing their estimate on CISD calculations and a RHF reaction path. We note that these calculations could not provide the accuracy needed in this case (as mentioned already by Worthington and co-workers¹⁰⁵) and that **6** behaves similarly as ethynylvinylidene, for which Collins and co-workers¹⁰⁶ found an energy barrier of just 0.6 kcal mol⁻¹ at the CCSD(T)/TZ2P level of theory (2.7 kcal mol⁻¹ at CISD/DZP!), which after ZPE corrections vanishes. According to our calculations, there is little chance that **6** can be observed under other than matrix conditions. Vinylidene, which has been investigated at the highest levels of theory,^{107–111} is located at a rather flat part of the PES as reflected by a 2 kcal mol⁻¹ barrier for isomerization to acetylene. Carbene **8** is 50 kcal mol⁻¹ less stable than **1** and can, despite the unstable allene functionality, obtain stabilization from a 2 π allyl delocalization involving the empty $\pi\pi$ -orbital of the $\sigma^2\pi^0$ configuration of **8** ($r(\text{C}=\text{C}) = 1.328$; $r(\text{C}=\text{C}:) = 1.274$ Å).

(c) Carbenes **10** and **11**

Molecules **10** and **11** can be considered as resonance forms of the same structure where the interaction of the methyl group with the triple bond as stabilizing factor gives **10** the larger weight. This is supported by the fact that geometry optimization of **11** leads to **10**. Carbene **10** (electron configuration ¹ $\sigma^2\pi^0$) is stabilized by the same type of allyl-type 2 π delocalization as is possessed by **8**, reflected by a bond length of 1.338 Å for the formal CC: single bond and 1.235 Å for the triple bond. The parent carbene, propargylene, HCCCH, was found by Mebel and co-workers¹⁰³ to possess a triplet (T) ground state, which is also the case for **10** (³A' state is 11 kcal mol⁻¹ below the ¹A' state; see the ESI.†)

(d) Carbene **13**

In the C_{2v}-symmetrical geometry, this structure turns out to be a TS (**TS(13,13')**) for the bending motion of the C=C: unit. The minimum structure was obtained by either optimizing a C_s form of **13** or by a geometry optimization of the cyclobutene **36**, which opens to give the stable C_s-symmetrical form **13**, which is 54 kcal mol⁻¹ less stable than **1**. (Actually the bending surface is so flat that after vibrational corrections **TS(13,13')** possesses a 0.4 kcal mol⁻¹ lower enthalpy than the minimum structures **13**.) The unusual stability of **13** is a direct result of its $\sigma^2\pi_{\text{ip}}^0$ electron configuration and the fact that the in-plane $\pi\pi$ -orbital at the carbene C is the ideal acceptor for the density of the CC Walsh orbitals of the three-membered ring, thereby strengthening the H₂C–CH₂ bond whereby weakening the two H₂C–C: bonds. This leads to substantial stabilization as known from acceptor (CN, COOH, etc.) substituted cyclopropane rings.¹¹² In the case of **13** the stabilization effect is so strong (in-plane overlap combined with a short C=C bond length of 1.273 Å) that the C=C: unit tends to dissociate during optimization. However the C_{2v} reaction path for the decomposition into ethene and :C=C: is symmetry-forbidden¹¹³ and therefore the C=C: unit must bend sideways as it does in carbene-double bond additions.¹¹⁴ Structure **13** is the precursor of the decomposition reaction reflecting the preferred reaction mode. It can be considered as a frozen transient point of carbene decomposition revealing the symmetry requirements of the reaction. Previous investigations of **13**⁶⁴ do not mention this point.

(d) Allenylcarbene **14**

This carbene has previously been discussed by several authors^{60,61} and in view of the important role **14** plays for the rearrangements of **1**, **2**, and **3** (see reaction Scheme 4), we investigated the lowest states of **14** where the conformational interconversion between *syn* form **14a** and *anti* form **14b** was explicitly considered. Carbene **14** possesses a T ground state ³A'' with C_s symmetry. *Syn* form **14a** and *anti* form **14b** have comparable stabilities (CCSD(T): 64.2 and 64.3 kcal mol⁻¹, Scheme 2), so that one can consider the two conformations to have essentially the same heat of formation, $\Delta H_{\text{f}}^0(298) = 70.4 + 64.2 = 134.6$ kcal mol⁻¹ where the experimental heat of formation of **1** is taken as reference (Table S1, ESI).† The two minima are separated by a rotational barrier of 4.6 ($\Delta H^{\ddagger}(298) = 3.4$) kcal mol⁻¹. The stability of **14**-T is a direct consequence

of the $^3\sigma^1\pi^1$ electron configuration (for the σ , π notation, see Fig. S1 in the ESI.†)

The first excited state of **14** corresponds to a closed-shell $^1\sigma^2\pi^0$ configuration ($^1A'$ state) provided the C_s -symmetry of **14-T** is retained. At RB3LYP and UB3LYP, the C_s -symmetrical $^1A'$ state is found to be a TS for both the *syn* and the *anti* form. There exist two C_1 -symmetrical, enantiomeric *syn*-forms (**14a-S**₀, 1A and **14a'-S**₀, 1A) and two C_1 -symmetrical, enantiomeric *anti*-forms (**14b-S**₀, 1A and **14b'-S**₀, 1A), for which the C framework is no longer planar and for which the HCCH unit is rotated by 12–15° from a planar *syn* or *anti* arrangement (see ESI)† Also, in Table S1, dipole moments μ and the value of the imaginary freq to reduce eclipsing interactions. The *syn* forms possess a somewhat larger stability (–1.1 kcal mol^{–1}; $\Delta H_f^0(298) = 139.2$ and 140.7 kcal mol^{–1}, respectively, Table S1) than the *anti* forms, which is a result of a more favorable arrangement of the vicinal CH bonds and differences in an anomeric delocalization of the σ^2 lone pair at the carbene C (*syn*: into a CC bond, *anti*: into a CH bond).

The calculated geometries for both **14-T** and **14-S**₀ (ESI)† suggest that these structures have to be considered as carbenes rather than biradicals. Enforcing the biradical character by lengthening the C=C(H) bond in **14-T** and **14-S**₀ and reoptimizing the molecular geometry as a function of the C=C(H) bond length leads to an increase in energy and finally to a rearrangement of **14** to **3**. The enthalpies of the S₀ forms are 2.5 (*syn*) and 3.6 kcal mol^{–1} (*anti*) higher than the corresponding T forms of **14**. Results of ESR experiments as well as *ab initio* calculations carried out for vinylmethylene^{115–117} suggest that this carbene possesses a T ground state and a S–T splitting of less than 1 kcal mol^{–1}. Allenylcarbene **14** should not differ so strongly from vinylmethylene and, therefore, our results can be considered to be in line with experiment and other theoretical investigations.

Carbene **14** was postulated⁶¹ as an intermediate in the photolysis of 3,4-pentadienoyl chloride yielding after HCl elimination and subsequent decarbonylation first allenyl ketene and then the corresponding carbene, which immediately decomposes to **1** and acetylene. Wrobel and co-workers⁶⁰ were able to trap **14** in an argon matrix at 10 K after photochemical rearrangement of **2**. Measured and calculated infrared spectra indicated that two forms of **14** (either *syn* and *anti* form of S-**14** or a mixture of S-**14** and T-**14**) were present in the matrix.

Carbene 27

Although the enthalpy of this carbene is quite high (80 kcal mol^{–1} above **1**) and thereby experimentally less relevant, there are some interesting electronic features that determine the geometry of the two stable conformers **27a** and **27b** (Scheme 2). There is the possibility of a 1,3-through-space interaction involving the triple bond and the empty $p\pi$ -orbital of the carbene atom. This is only possible for a C–CH₂–C–H dihedral angle close to 90° which is realized for **27a** ($r(C:C_3) = 1.986$ Å; for **27b**, $r(C:C_3) = 2.517$ Å) and obtained when optimizing the formal *syn* form (the *syn* form itself turns out to be the TS(**1,27a**)). The *anti*-form **27b** is stabilized by (a) reduced bond eclipsing and (b) hyperconjugative interactions involving the CH₂ group and the carbene C with its empty $p\pi$ -orbital thus being 1 kcal mol^{–1} more stable than **27a**. It is

separated from **27a** by a rotational barrier (TS(**27a**, **27b**), Scheme 3) of 3.1 kcal mol^{–1}.

Bicyclobutane structures 7 and 9

Both structures are surprisingly stable (43.5 and 51.0 kcal mol^{–1}, respectively, Scheme 2) possessing enthalpies up to 16 kcal mol^{–1} below that of tetrahydrene (**15**). In the case of **7**, the (non-planar) geometry resembles more that of a cyclobutenyl biradical rather than that of a bicyclobutene. The central HC···C through-space interaction is 1.803 Å and by this does no longer qualify as a normal CC single bond. An allyl 3π -system is established ($r(C=CH) = 1.364$; $r(HC-CH) = 1.411$ Å), which leads to the stabilization of **7**. As in the case of **13**, it is useful to consider **7** as the (frozen) precursor of a decomposition reaction, which would be the [2 + 2]-cycloreversion reaction yielding vinyl radical HC•=CH₂ and ethynyl radical HC=C• ↔ HC•=C:, which can only dissociate with $\pi^2s + \pi^2$ a stereochemistry¹¹³ thus enforcing a puckering of structure **7**. In addition, the HC• centers can interact more strongly *via* their additional single electrons than centers C: and CH₂, which therefore will dissociate first as reflected by calculated bond lengths of $r(HC,CH) = 1.411$ and $r(C,CH_2) = 1.568$ Å. Carbene **9** has a ground state with $^1\sigma^2\pi^0$ electron configuration and therefore benefits from the delocalization of the central HC–CH bent bond into the empty $p\pi$ -orbital at the carbene C atom. This leads to a weakening of the central bond (1.599 Å), but a stabilization of the HC–C: bonds (1.421 Å) and accordingly to an overall stabilization of the molecule.

Tetrahydrene (15), cyclobutadiene (5), biradical 12, and bicyclobutene 20

The $\Delta H_f^0(298)$ value of **15** is 130.3 kcal mol^{–1} (CCSD(T)/C; G2M: 129.2 kcal mol^{–1}) whereas G2 predicts 128 kcal mol^{–1}.^{39,48} The most likely rearrangement mechanism leading to cyclobutadiene (**5**) involves the intermediate **12**, which is separated by relatively high barrier from **15** ($\Delta H^\ddagger(298) = 25$ kcal mol^{–1}; TS(**12,15**): $\Delta\Delta H(298) = 85.1$ kcal mol^{–1}) and a smaller one ($\Delta H^\ddagger(298) = 13.7$ kcal mol^{–1}; TS(**12,5**): 69.0 kcal mol^{–1}, Schemes 2, 3) from **5**. The isomerization of **15** to **5** is symmetry-forbidden^{1,113} where the orbital crossing accompanying the breaking of a CC bond in **15** takes place in the first step leading to **12**, which is reflected by the relatively large barrier. TS(**12,15**) has the H atoms on the breaking CC bond at both *endo* and *exo* position where the IRC calculations reveal that in the exit channel CH flipping occurs. Intermediate **12** corresponds to a 1,3-singlet-biradical (55.3 kcal mol^{–1} above **1**), which is 5 kcal mol^{–1} more stable than **15** because of a partial release of the high strain energy of **15** (estimated to be 136 kcal mol^{–139}) and the possibility of the single electrons delocalizing into the central $\sigma^*(CC)$ orbital and the $\sigma^*(CH)$ bonds at the bridge thus lengthening the bridge bond to 1.649 Å. The various states of **5**, its structure deformation by a pseudo Jahn–Teller effect and its antiaromaticity have been extensively discussed in the literature.^{31–45} The CCSD(T) value for $\Delta H_f^0(298)$ obtained in this work is 103.8 kcal mol^{–1} in reasonable agreement with $\Delta H_f^0(298) = 102.5$ kcal mol^{–1} measured recently by Kass and co-workers.⁴⁶

Bicyclo[1.1.0] but-1(3)-ene (**20**)^{3,57,58} with a double bond forming the bridge suffers from ring strain and possesses therefore a much higher enthalpy ($\Delta\Delta H(298) = 66.8$ kcal mol⁻¹; $\Delta H_f^0(298) = 137.2$ kcal mol⁻¹). An experimentally based estimate of $\Delta H_f^0(298)$ is 130 ± 10 kcal mol⁻¹.⁵⁸

Biradicals 16–19 and 21–26

Only 1,3-butadienediyl biradicals **16** and **17** are stable in their S-state ($\Delta\Delta H(298) = 74.5$ and 75.3 kcal mol⁻¹) and do not close to **3** when calculated with BS-UDFT, GVB-MP2 or CASSCF(6,6). More interesting are the singlet 1,4-butadienediyl biradical forms **21–26**, which apart from **26** (imaginary frequency of 77i at DFT, Table S1† are all minimum structures. Their relative enthalpies are between 75 and 80 kcal mol⁻¹. Rotation at the central CC bond or inversion at the terminal C atom requires only a few kcal mol⁻¹ and leads to their mutual interconversion.

Cyclobutene (**36**), methyl-cyclopropyne (**31**), and other elusive structures

Molecule **36** has been investigated by various authors^{62–64} and found to be highly unstable (78 kcal mol⁻¹ above **1**). The most likely rearrangement of **36** is that to **13** (see above), which was previously investigated to require an enthalpic barrier of 0–4.6 kcal mol⁻¹ depending on the level of theory used (MP4 or TCSCF).⁶⁴ In this work, no barrier was found, *i.e.* **36** rearranges immediately to **13**, (Scheme 2) which suggests that **36** does not exist as a true minimum. A similar observation was made for methyl-cyclopropyne (**31**), which dissociates to C₂ (¹Σ_g⁺) and methyl carbene (¹A') and has been found to be as elusive as cyclopropyne itself.¹¹⁸ Structure **33** is also interesting, which can be reached by ring closure of **1** *via* an activation enthalpy of 95.4 kcal mol⁻¹, which is just 71 kcal mol⁻¹ above **1**. This carbene connects **1** with the cyclobutadiene-tetrahydro part of the C₄H₄ PES. For other highly unstable structures (**32**, **34**, **35**, **37–43**) $\Delta\Delta H(298)$ values or rearrangement mode are given in Scheme 2.

Dissociation products DP2 and DP6–DP7

Two acetylene molecules (**DP2**) can form a van der Waals complex (**DP2a**) with a T-structure.^{51–56} Although **DP2a** was found on the PES (binding energy: 0.8 kcal mol⁻¹) there is little difference in the $\Delta H_f^0(298)$ values of **DP2** and **DP2a** (110.7 and 109.9 kcal mol⁻¹; $\Delta\Delta H(298) = 40.3$ kcal mol⁻¹), which are calculated 2 kcal mol⁻¹ higher than the experimental value for **DP2** (108.7 kcal mol⁻¹).¹⁹⁷ Other reasonable dissociation products are found above 80 kcal mol⁻¹ (**DP3**: 85.2; **DP4**: 82.8; **DP6**: 102.3 kcal mol⁻¹, Scheme 2). Structures **DP5** and **DP7** were not found to occupy a stationary point since they rearrange to **DP1** and **DP6**, respectively. **DP6** was previously found at the CISD level of theory to have a C_s-symmetrical ²A' ground state,⁷² whereas both DFT and CCSD(T) suggest a C_{2v}-symmetrical ²B₂ state.

4. Reaction channels leading to rearrangement or decomposition of **1**

The majority of all reactions taking place on the C₄H₄ PES involve a carbene, which is a direct result of the low H/C ratio

(see Scheme 4). A minority of reactions involves 1,3- or 1,4-biradicals. There are just a few reaction paths leading directly from one of the five closed-shell systems **1**, **2**, **3**, **5**, and **15** to another. In this work we focus on the reactions of **1** and report its direct rearrangement to **3** requiring an activation enthalpy $\Delta H^\ddagger(298)$ of 65.8 kcal mol⁻¹ (**R1**; carbene **6**, although located at an energy minimum, does not exist since it does not correspond to an enthalpy minimum, see Scheme 4). All other direct rearrangements of **1** to a closed shell C₄H₄ system involve $\Delta H^\ddagger(298)$ values close to 90 kcal mol⁻¹ and more (to **2** *via* 1,3-H shift, **R10**: 90.8; again to **3**, however by 1,4-H shift, **R25**; **TS(1,3)**: 92.4 kcal mol⁻¹) and therefore, they are of less importance. **TS(1,5)** and **TS(1,15)** were not considered because they are unimportant according to experimental results of Hofmann and co-workers.⁷¹ All other rearrangement between **1** and a closed-shell molecule involve one or more intermediates and will be discussed in the following.

Rearrangement paths starting from **1**

In view of the fact that **1** is the most stable structure on the C₄H₄ PES (a result of the conjugated multiple bonds) and just a small set of closed shell systems with comparable stability (just **2** and **3**) exists, it is understandable that all possible rearrangements of **1** involve the breaking of rather stable CH or CC bonds and therefore require a $\Delta H^\ddagger(298)$ value larger than 65 kcal mol⁻¹ (Scheme 4). The second lowest enthalpic barrier is calculated for **R2** (**TS(1,10)**: $\Delta H^\ddagger(298) = 70.4$ kcal mol⁻¹), which leads to carbene **10** ($\Delta\Delta H(298) = 60.4$ kcal mol⁻¹). Carbene **10** can either rearrange to carbene **4** (**TS(10,4)**: $\Delta H^\ddagger(298) = 36.6$; $\Delta\Delta H(298) = 97.0$ kcal mol⁻¹), from where **3** can be reached (**TS(4,6)**: $\Delta H^\ddagger(298) = 61.5$ kcal mol⁻¹; $\Delta\Delta H(298) = 97.7$ kcal mol⁻¹) *via* **6** and **TS(6,3)**, or **10** can decompose to **DP1** (**R3**, **TS(10,DP1)**: $\Delta H^\ddagger(298) = 46.5$; $\Delta\Delta H(298) = 106.9$ kcal mol⁻¹; see Schemes 2 and 3).

Beside carbene **10**, also carbenes **27** (*e.g.*, **R7**, $\Delta\Delta H(298)$ of **TS(1,27b)**: 79.2 kcal mol⁻¹) and **14** (**R9**, $\Delta\Delta H(298)$ of **TS(1,14b)**: 86.1 kcal mol⁻¹) are directly accessible from **1** by appropriate 1,2-H-shifts so that reactions **R1**, **R2**, **R4**, **R7**, and **R9** exhaust the five possible 1,2-shifts of the four H atoms in **1**. Considering a laser excitation wavelength of 220 nm, as used in part II, all these reactions are energetically accessible.

The most likely follow up reactions of **27** (either **a** or **b**) are H₂-loss (**R5** or **R8**; **TS(27a,DP1)** and **TS(27b,DP1)**, $\Delta H^\ddagger(298) = 33.7$ kcal mol⁻¹) or H-shift combined with CC bond cleavage yielding two acetylene molecules (**R6** and **R7**, **TS(27a,DP2)** and **TS(27b,DP2)**, $\Delta H^\ddagger(298) = 37.0$ and 40.1 kcal mol⁻¹). With a total activation enthalpy of maximally 120 kcal mol⁻¹ the formation of both **DP1** and **DP2** are possible under experimental conditions, however not preferred *via* these paths.

Carbene **14** is an interesting cross-point on the C₄H₄ PES because **2** (**R9**, **TS(14b,2)**: $\Delta\Delta H(298) = 80.5$; $\Delta H^\ddagger(298) = 10.2$ kcal mol⁻¹) and **3** can be formed *via* 1,2-H shift or a rotation of the CH₂ group combined with 1,3-CC bond formation. In the latter case, it matters whether **14** is formed in its excited singlet or its triplet ground state because only in the latter case does a barrier to the conversion **14** → **3** exist (**R21** reverse, **TS(14b,3)**: $\Delta\Delta H(298) = 64.3$; $\Delta H^\ddagger(298) = 4.3$ kcal mol⁻¹;

starting from **3**: $\Delta H^\ddagger(298) = 45.0 \text{ kcal mol}^{-1}$). A S–T inter-system crossing cannot be excluded for **14** according to an estimate of spin–orbit coupling close to the crossing point of S_0 and T-PES made in this work. The rearrangement **14** \rightarrow **3** can also pass through one of the 1,3-biradical structures **18** or **19**, which close to **3**. The TS for forming the stable 1,3-biradical **16** from **14** is larger than 10 kcal mol^{-1} ($\Delta\Delta H(298) = 74.5 \text{ kcal mol}^{-1}$), which was not further explored in this work. Also, the 1,2-H-shifts connecting **16** with the 1,4-biradicals **24**–**26** and by this the cyclobutadiene(5)-tetrahedrane(**15**) part of the PES were outside the scope of the present investigation.

Both **5** and **15** are directly accessible from **1** *via* ring formation where either the C1,C4 bond is formed (**R27**, **TS(1,33)**, $\Delta H^\ddagger(298) = 88.1 \text{ kcal mol}^{-1}$) and the relative stable carbene **33** ($\Delta\Delta H(298) = 71.3 \text{ kcal mol}^{-1}$) with a 2π -allyl system results or C1,C3 and C1,C4 bond formation occurs simultaneously (**R28**: **TS(1,9)**, $\Delta H^\ddagger(298) = 64.7 \text{ kcal mol}^{-1}$) thus yielding carbene **9** ($\Delta\Delta H(298) = 51.0 \text{ kcal mol}^{-1}$), which is the bond stretching isomer of **33** (**TS(33,9)**: $\Delta H^\ddagger(298) = 77.2 \text{ kcal mol}^{-1}$). Carbene **9** can rearrange with an activation enthalpy of $40.6 \text{ kcal mol}^{-1}$ ($91.6 \text{ kcal mol}^{-1}$ relative to **1**) to **15**, by which the cyclobutadiene-tetrahedrane part of the PES is accessible.

Decomposition paths starting from **1**

There are two reasonable 1,3-H shifts for **1** (**R10** and **R11**), which lead to **2** (see above) and to the biradical part of the PES (**TS(1,22)**: $\Delta H^\ddagger(298) = 88.8 \text{ kcal mol}^{-1}$). Once biradical **22** is reached, rapid dissociation to **DP2** (**TS(22,DP2)**: $\Delta H^\ddagger(298) = 5.0 \text{ kcal mol}^{-1}$) or rotation (**R12**, **TS(22,24)**: $\Delta H^\ddagger(298) = 1.0 \text{ kcal mol}^{-1}$) and ring closure to **5** (**TS(24,5)**: $\Delta H^\ddagger(298) = 1.6 \text{ kcal mol}^{-1}$) follows immediately. Considering the amount of excess energy under the experimental conditions, even formation of **12** and **5** cannot be excluded although energy excess would revert the process and lead in the end preferentially to decomposition product **DP2**. Hence, **R11** must be considered as a decomposition reaction in the same way as **R13**, **R14**, **R15**, and **R24**. Dissociation of the H at the triple bond requires the highest enthalpy and therefore it was not considered in this work. This is followed by the dissociation of the terminal vinyl H atoms (**R24a** and **R24b**: 114 and $113 \text{ kcal mol}^{-1}$, respectively) and, finally, the central H atom (**R16** leading to **DP7**). **DP7** does not exist because the 2-vinyl radical immediately rearranges to the resonance-stabilized butatrienyl radical **DP6** (**R15**: $\Delta\Delta H(298) = 102.3 \text{ kcal mol}^{-1}$) where the much lower dissociation enthalpy reflects the stabilization of **DP6** relative to **DP7**. **R13** (H_2 loss) and **R14** (C2,C3 bond cleavage accompanied by a 1,2-H shift) have $\Delta H^\ddagger(298)$ values of 95.3 and $103.0 \text{ kcal mol}^{-1}$ and lead to **DP1** and **DP2**, respectively. Again these reactions should be accessible under experimental conditions thus increasing the amount of acetylene and diacetylene.

Rearrangement/decomposition paths not starting from **1**

Molecules **2** and **3** are connected by reactions **R21** (*via* carbene **14**; already discussed) and **R27** (*via* carbene **28**) where in the latter case the investigation of **TS(2,28)** reveals that **28** does no

longer exist when increasing the basis set to VTZ quality. Hence, the activation enthalpy of **R27** is determined by **TS(28,3)** ($\Delta H^\ddagger(298) = 85.3 \text{ kcal mol}^{-1}$) where the reverse reaction requires $\Delta H^\ddagger(298) = 61.7 \text{ kcal mol}^{-1}$.

There are five decomposition reactions, which we have investigated in connection with **2** and **3** (Scheme 4): **R17** leading to **DP1** *via* 1,4- H_2 elimination ($\Delta H^\ddagger(298) = 82.5 \text{ kcal mol}^{-1}$), **R18** yielding **DP3** *via* 1,1- H_2 elimination ($\Delta H^\ddagger(298) = 89.6 \text{ kcal mol}^{-1}$), **R19** corresponding to H dissociation ($\Delta H^\ddagger(298) = 94.6 \text{ kcal mol}^{-1}$), **R20** implying a CC bond cleavage thus leading first to **DP9** and then to **DP2** ($\Delta H^\ddagger(298) = 118.8 \text{ kcal mol}^{-1}$), and **R22** describing the dissociation of **3** *via* **TS(3,DP4)** ($\Delta H^\ddagger(298) = 62.2 \text{ kcal mol}^{-1}$) to **DP4** and then to **DP2**.

There is another dissociation reaction of **3**, which starts with a 1,2-H shift yielding the unstable carben **29** (**R23**: **TS(3,29)**, $\Delta\Delta H(298) = 101.1$, $\Delta H^\ddagger(298) = 77.5 \text{ kcal mol}^{-1}$), which *via* a small enthalpic barrier of $3.4 \text{ kcal mol}^{-1}$ can dissociate to **DP2**. However, carbene **29** can also rearrange *via* an even smaller barrier of $1.9 \text{ kcal mol}^{-1}$ (DFT; without geometry optimization CCSD(T) does not give a barrier) to the biradical **12** ($\Delta\Delta H(298) = 55.3 \text{ kcal mol}^{-1}$), which is linked to both **5** and **15** (see above).

5. Conclusions

The study of the the C_4H_4 PES has revealed that it is particularly rich of carbene and biradical structures, which are a result of the low H : C ratio. Some of the carbenes possess surprisingly high thermodynamic stability (**4**, **6**, **8**, **9**, **10**, **11**, **13**, **14**, **28**, **33**), however only two of them possess significant kinetic stability. According to our calculations carbenes **6**, **11**, **27a**, **27b**, **28** and **29** (the latter can rearrange with an activation enthalpy of $1.9 \text{ kcal mol}^{-1}$ or less) do not exist at all, whereas **4**, **8**, **9**, **10**, and **13** are separated from rearrangement products by enthalpic barriers of 10 up to 60 kcal mol^{-1} , respectively. Carbene **14** is a special case in so far as it can only be stable in its T ground state at low temperatures (rearrangement to **3** with an enthalpic barrier of $4.3 \text{ kcal mol}^{-1}$ provided intersystem crossing takes place). The same holds for all biradicals investigated, which can easily dissociate *via* an activation enthalpy of just $5.0 \text{ kcal mol}^{-1}$ to **DP2**. Carbenes such as **4**, **8**, **9**, **10** or **13** should be detectable in the matrix at low temperature, which has been confirmed in the case of **14**.^{60,61}

There is a manifold of reactions, which should lead beside the formation of **2** and **3**, predominantly to a dissociation of **1** to **DP1** and **DP2**. In part II, we will investigate the relevance of these observations for the chemistry of the atmosphere of Titan.

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