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# FIRST CARBON RING CLOSURES STARTED BY THE COMBUSTIVE RADICAL ADDITION OF PROPARGYL TO BUTADIENE. A THEORETICAL STUDY.

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## Abstract.

Formation of the first ring structure from small aliphatic molecules is often regarded as the rate-determining step (and in any case as a step of paramount importance) in the combustive growth of larger aromatic systems and soot lamellae. Among possible reactions able to start off this process, the radical addition of the propargyl radical to butadiene (diacetylene) has been recently studied theoretically [G. da Silva, A. Trevitt, *Phys. Chem. Chem. Phys.* 13 (2011) 8940] and shown to lead preferentially to a 5-membered ring intermediate. The same reaction is here addressed focusing instead on the possible formation of 6-membered rings. The large variety of partially intertwined reaction pathways is the basis for a subsequent RRKM study (carried out at different combustion temperatures). It confirms, on one hand, the favored formation of fulvenallenyl radical indicated by Da Silva and Trevitt, but also indicates the possible formation of six-membered cyclic systems as minor products. In particular, at high pressure, six-membered

ring system yields are very low, but at lower pressures a more significant yield of six-membered ring product is predicted.

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**Keywords:** 1) PAH formation; 2) first 6-ring; 3) propargyl; 4) butadiyne

**Running Title:** 6-ring closures in  $C_3H_3 + C_4H_2$

## 1. Introduction

The impact of carbonaceous particulate[1,2] and polycyclic aromatic hydrocarbons (PAHs) on the environment in general[3,4] and human health in particular is significant, because the former gives a major contribution to the overall mass of atmospheric aerosol, and the latter exhibit an ubiquitous presence. PAHs and PAH cations, PAH clusters, and amorphous carbon clusters are also of astrophysical interest, since they have been identified (to some extent tentatively) out of the terrestrial environment, namely in planetary atmospheres,[5] in the envelopes of carbon-rich stars,[6] or in the interstellar medium,[7] hence under a large variety of pressure and temperature conditions. This interest has recently prompted, for instance, combined experimental-theoretical work on cosmic-ray-mediated benzene formation.[8] On the other hand, graphene sheets, graphene nanoribbons, and synthetic ways to very large PAH systems[9] have in recent years been deemed promising from a technological point of view[10] (to build capacitors,[11] sensors,[12] transistors, circuits in general,[13] etc.).

Soot and PAHs share the same nature and origin,[14,15] and the latter are often considered as soot precursors, though other opinions have been set forth. Homann, for instance, put forward[16] that the reactions leading to PAHs could also bring about the formation of more irregular structures, called "aromers" (see ref. 16, pp 2448-2450), starting from associations between PAHs and subsequent  $H_2$  losses. These intermediate structures could grow as cages with a higher or lower H content, and get some curvature.

Since the growth mechanisms and association modes of PAHs and soot platelets are not completely clarified, we have recently attempted to give some contribution, possibly complementary to the experiment. [17,18,19]. Now, the formation of the very first (possibly aromatic) ring molecule from small aliphatics has been often seen as the rate-determining step of soot growth, and appears in any case particularly interesting.[20,21]

Since formation of aromatics and soot particles (in particular the issue of first ring formation, which is our present focus) has been reviewed and discussed by Richter and Howard in 2000,[20] and by Frenklach in 2002,[21] we will not deal at length with earlier mechanistic proposals. Among these, Bittner and Howard[22] suggested benzene formation via the butadienyl ( $CH_2=CH-CH=CH\cdot$  or  $CH_2=CH-C\equiv CH_2$ ) plus ethyne reaction. This idea was partly supported by an experiment in which butadienyl formation in a 1,3-butadiene flame was observed.[23] Then, similar mechanisms were also proposed,[24,25,26,27] such as, for instance, the sequence triggered by vinyl ( $CH_2=CH\cdot$ ) addition to (a) ethyne [ $C_2H_3\cdot + C_2H_2 \rightarrow n-C_4H_5\cdot$ ;  $n-C_4H_5\cdot + C_2H_2 \rightarrow n-C_6H_7\cdot$ ;  $n-C_6H_7 \rightarrow C_6H_6 + H\cdot$ ] or (b) to vinylacetylene ( $CH_2=CH-C\equiv CH$ ), or also (c) [ $CH_2=C\cdot-C\equiv CH + C_2H_2 \rightarrow C_6H_5\cdot$ ] the latter being however deemed unlikely in a later study.[28] Some flame studies indicated that the recombination of the propargyl radicals ( $H_2C\cdot CCH$ ) can be the dominant

pathway to first ring formation.[27,29,30] Furthermore, theoretical studies by Miller and Melius[28] and, more recently, by Miller and Klippenstein[31] showed that the addition of two propargyl radicals accounts satisfactorily for several experimental results concerning either benzene or phenyl radical formation.

First ring formation has also been the subject of more recent experimental and theoretical investigations of different ring closure processes, such as the formation of (i) several 5- and 7-membered rings in a cyclopentene flame,[32] or (ii) the phenyl radical through  $C_2 +$  buta-1,3-diene ( $C_4H_6$ ) reactions.[33] Similar studies focused also on the formation of slightly larger systems (such as naphthalene[34,35], or indene[36,37]), or consider in general the mechanism of PAH growth.[38] Along this line, we have already considered[39] the first growth steps of aromatic systems through the ring closure-radical breeding polyynes-based mechanism proposed by Krestinin[40] (polyynes had already been considered at an earlier time by Homann and Wagner[41]).

In the present paper we explore, under combustion conditions, the possible formation of 5-, 6-, or 7-membered ring intermediates, which could be involved in subsequent PAH or soot platelet growth processes. The reacting system examined is defined by the radical addition of propargyl to butadiyne ( $H-C\equiv C-C\equiv C-H$ ). Propargyl was considered originally in the mentioned studies[28,31] as a species capable in itself of generating benzene through self-addition. Other reactions, e.g. between propargyl and alkynes, are likely to play an important role in the hydrocarbon growth process. We can mention for instance that the kinetics of the related reaction between the propargyl radical and ethyne has been investigated both experimentally[42] and theoretically.[43] Both the propargyl radical and some polyynes have been recently reported to reach rather high concentrations

in the oxidation zone of premixed ethyne,[44] benzene,[45] toluene,[46] or gasoline[47] flames. Butadiyne has been detected as the highest concentration of polyynes molecules in pyrolysis or combustion.[48] The decomposition of fulvalene and fulvalenyl radical, which are expected to play an important role in the formation of PAH and soot, was recently studied both theoretically,[49] and experimentally:[50] it leads mainly to propargyl radical + butadiyne and  $C_5H_3 +$  ethyne.

This study is an extension of the da Silva and Trevitt's study[51] concerning the reactions between propargyl radical and butadiyne. We focused our attention on the formation of 6-membered rings, which could be seen as possible precursors of benzene molecules. da Silva and Trevitt calculated the energy of only one 6-membered ring (structure **6** in their work) and the transition structure for its formation. However, their computations located this intermediate 25.9 kcal mol<sup>-1</sup> above the reactants, and they consequently concluded that formation of 6-membered rings was not favored.

In our study, we show several other pathways bringing to more or less stable 6-membered rings, having energies close or well below that of the reactants. For this reason, we believe that the present investigation results in an interesting extension of the da Silva and Trevitt's work.

## 2. Theoretical Method

All stationary points on the energy hypersurface, *i.e.* minima and first order saddle points, corresponding to transition structures (TS), were determined by gradient procedures[52] within the Density Functional Theory (DFT),[53] and making use of the M06-2X[54] functional. This recent global hybrid meta GGA functional has shown to

successfully predict a wide range of molecular properties (energies barriers, thermochemistry and geometries).[55] The cc-pVTZ basis set[56] was used throughout in the DFT optimizations. The nature of the critical points was checked by vibrational analysis, which allowed us also the thermochemistry assessment. The optimizations were followed by CCSD(T)/cc-pVTZ[57] single-point energy computations. The DFT thermochemical corrections gave estimates of the zero point vibrational energy, by which the CCSD(T) relative energies were corrected to obtain the  $\Delta E_{ZPE}$  values reported in the schemes and discussed in the text. The thermochemistry was assessed in all cases at temperatures ranging from room T up to those typical of combustion (T in Kelvin, energetics in kcal mol<sup>-1</sup>).

Geometry optimizations and thermochemistry calculations were carried out by using the GAUSSIAN 09 system of programs.[58]

The Rice Ramsperger Kassel Marcus (RRKM) theory,[59,60] fundamental development of the unimolecular kinetic theory elaborated by Lindemann[61] and Hinshelwood[62], was then used to obtain the distribution of reaction products. In order to obtain these distributions as functions of time, RRKM and Master Equation (RRMK-ME) calculations were carried out by using Multiwell program suite.[63,64,65] It allows calculating sum and densities of states, then obtains microcanonical rate constants according to RRKM theory, and finally solves the master equation. We have used the same parameters used in the da Silva and Trevitt's paper, for sake of comparison.[51] Corrections for quantum tunneling were included for all hydrogen transfer reactions (not H dissociations) by incorporating the corrections for one-dimensional unsymmetrical Eckart barriers.[66] Internal rotations were treated as unsymmetrical hindered rotations, by using the *lamm* program, supplied

with MultiWell. The potential energy and the reduced moment of inertia as a function of dihedral angles were fitted to eight parameter functions and sum and density of states were estimated by using Meyer's algorithm.[67]

MultiWell stores densities and sums of states in double arrays: the lower part of the array consisted of 999 array elements which ranged in energy from 0  $\text{cm}^{-1}$  to 9990  $\text{cm}^{-1}$ . The higher energy part of the double array consisted of 1001 elements ranging in energy from 0  $\text{cm}^{-1}$  to 150000  $\text{cm}^{-1}$  with an energy spacing of 150  $\text{cm}^{-1}$ .

The Lennard-Jones parameters necessary for the collision frequency calculations were assumed to be the same for all the structures, were:  $\sigma = 5.9 \text{ \AA}$ , and  $\varepsilon/k_B = 488 \text{ K}$ .

Energy transfer was treated by assuming the exponential-down model for collision step-size distributions:  $E_{\text{down}} = 1000 \text{ cm}^{-1}$ , constant and independent from the temperature.[68]

Rate constants were calculated in the range 600-2000 K. In the present work, the number of stochastic trials was set to  $10^6$ , for 200 collisions, which should be sufficient to reach the Boltzmann energy distributions. Simulations were carried out at  $P = 1 \text{ atm}$  of  $N_2$  buffer gas for room pressure combustions and  $P = 0.01$  and  $40 \text{ atm}$  to simulate combustions under low[69] and high pressure[70] conditions.

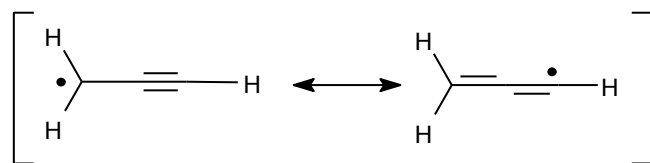
## 3. Results and discussion

### 3.1 Potential energy surface

We present briefly the initial reaction steps, already discussed in the paper by da Silva and Trevitt,[51] because they are introductory to the original part of our investigation. Four



entrance channels, due to the addition of the (to some extent) delocalized propargyl radical to the two unique positions of butadiyne are conceivable.



Resonance in the propargyl radical

However, two of them (additions to C2) have significantly higher energy barriers ( $\Delta E_{ZPE} = 16.8$  and  $19.4$  kcal mol<sup>-1</sup>) compared to the C1 additions ( $\Delta E_{ZPE} = 11.5$  and  $13.4$  kcal mol<sup>-1</sup>).

For this reason they were ruled out and no longer explored.

**Scheme 1** shows the possible pathways and relative energies ( $\Delta E_{ZPE}$ ) involving the intermediates originated by addition in C1 of butadiyne. Two intermediates could be formed, **1** and **2**, located at  $-19$  and  $-21$  kcal mol<sup>-1</sup>, respectively, with respect to the reagents. They have similar linear structures with one delocalized unpaired electron, and formation barriers ( $11.5$  and  $13.4$  kcal mol<sup>-1</sup>, respectively). Intermediate **2** could cyclize to form the 5-ring **3** (step *a* in Scheme 1). The intermediate **1** could follow a similar path (cyclization to **4**, via step *d*). Also another cyclization is possible (step *f*), leading to the 6-ring **5** ( $+21$  kcal mol<sup>-1</sup>). All these steps were already considered by da Silva and Trevitt. It has to be noted that **5** has a radical+biradical character (see a detailed analysis of its electronic structure in the Appendix).

According to da Silva and Trevitt,<sup>[51]</sup> formation of a 7-membered ring is possible but the energy barrier for this cyclization is too high ( $\Delta E_{ZPE} = +13.6$  kcal mol<sup>-1</sup>). The 5-ring isomers **3** and **4** have similar energies ( $-39$  kcal mol<sup>-1</sup>) and could both form, via a 1,2 H

shifts having barriers of ca. 12 kcal mol<sup>-1</sup>, the very stable 1-ethynylcyclopentadienyl radical intermediate (**6**, at -77 kcal mol<sup>-1</sup>), central to the da Silva and Trevitt's paper (where is called fulvenallenyl).[51] The electron delocalization occurring in 1-ethynylcyclopentadienyl (**6**) had been assumed by da Silva and Bozzelli as the major reason for its molecular stability.[71] The reaction pathways presented so far (Scheme 1: part out of the dashed box) are those proposed by da Silva and Trevitt, and our energetics are in fairly good agreement with their.[51] This is not the case for structure **5**, see Appendix.

We turn now to describe, making reference to the box in Scheme 1, other cyclizations, new with respect to the previous study. Starting from **1**, a 4-ring closure (step *c*) would lead to **7**. A 6-ring closure is also possible (step *e*) to form a precursor of the *ortho*-benzyne-like structure **8**. The last reaction does not seem promising, because of the high energy barrier (22.5 kcal mol<sup>-1</sup>). In addition, structure **8** is less stable than the reactants.

More interesting is the ring closure from intermediate **2**: the reaction *b* would produce a stable *ortho*-benzyne **9** (-49 kcal mol<sup>-1</sup>) with an unpaired electron delocalized in a benzyl-like  $\pi$ -system. Its formation barrier is above the reactants (about 8 kcal mol<sup>-1</sup>). Though **9** is very stable, a direct concerted formation pathway from propargyl radical and butadiyne (**0-9**) does not exist. Any attempt to define it crosses a second order saddle point dominium (the second order saddle point itself is located at 47.1 kcal mol<sup>-1</sup>). Therefore the only way to reach **9** is going through two transition structures TS **0-2**, and TS **2-9**, (see Scheme C in the Supplementary material).

The H losses from **1** and **2**, which were already taken into account by da Silva and Trevitt, are shown in [Scheme 3](#) here and in more detail in [Scheme A](#) in the **Supplementary material**.

### 3.1.1 Other 6-membered rings formation mechanisms.

Starting from the very stable intermediate **6**, some additional pathways leading to 6-rings are conceivable ([Scheme 2](#)). The ring closure to form the bicyclic intermediate **10** (at -26 kcal mol<sup>-1</sup>) has a barrier slightly above the reactants (+1 kcal mol<sup>-1</sup>). From **10**, two distinct pathways **g** and **g'**, either via a carbene intermediate (**11**) or a 7-ring (**12**), with all relevant transition and intermediate structures well below the reference level, converge both onto the 6-ring **13**, which is a stable carbene radical (-45 kcal mol<sup>-1</sup>). Its stability can be related to one of the two resonance structures, which is of the Kekulé type (another one can of course be drawn). The transition structure connecting **11** and **13** corresponds to a concerted step which requires some explanation. The breaking of the bond *1* in **11** would form a bicyclic intermediate with condensed 6- and 3-rings). However, such a hypothetical structure is not a stable minimum, and the bond *3* is cleaves concertedly **13**. From **13**, a H shift concerted with a 3-ring closure leads, through a TS well below the reference level, to the stable intermediate **14**, which carries an aromatic 6-membered ring. It can be interesting to recall that also Kaiser *et al.*[72] mentioned the presence of **12** and **14** (as the most stable isomer) in binary collisions between one carbon atom, C(<sup>3</sup>P), with benzene.

Alternatively (pathway **h**) the breaking in **10** of the bond labeled as *1*, together with the formation a new  $\sigma$  bond (*2*), leads to a sequence of other 6-ring intermediates (**15** and

16). Then, the recoupling of two electrons in **16** produces again **14** which could subsequently interconvert to **13** or lose a hydrogen to produce the carbene **19** (not very stable). Alternative H losses from the aromatic ring of **14** were considered, but the products were even less stable. The intermediate **14** could be reached through still another pathway *i*, the sequence **6-17-18**, which entails a  $-C\equiv C-H$  group shift, followed by the closure of a 4-membered ring.

Some of the pathways just discussed could be promising: TS **6-17** (-7 kcal mol<sup>-1</sup>; compare -8, already computed by da Silva and Trevitt), TS **17-18** and TS **18-14**, though high, are still below the reference level. The H loss from **14** is high (+10 kcal mol<sup>-1</sup>). With this last exception they might be seen, at least in principle, as potentially competitive with losses of  $C_2H_2$  and other H losses from the  $C_7H_5$  radical systems (see next paragraph).

**11**, **13** and **16** are carbene radicals [adequately described by the CCSD(T) method, see Appendix].

The mechanisms of  $C_2H_2$  or H losses from the intermediates **1**, **2** and **6** are shown in [Scheme 3](#) (more details in [Schemes A](#) of the **Supplementary material**). Abstraction and loss of one hydrogen have been considered in other studies as realistic competitors of ring closures under combustion or pyrolysis condition.[73]

**3.1.2 Minor pathways.** Several other reactions could take place as a consequence of the reaction between propargyl radical and butadiyne, which involve other 4, 5, and 6-membered rings, bicycles, or linear intermediates. They have been the subject of a thesis work.[74] However, these structures and the related transition structures are characterized

by high energy barriers which make them non competitive with the pathways discussed above. For this reason, they were not included in the RRKM/master equation simulations. The full representation of the intertwined reaction pathways which originate from these radical additions is reported in the **Supplementary material (Scheme B)**. Since the RRKM phase of this study (see below) reveals that the main products can be expected to come from a subset of reaction pathways, only these have been shown here in **Schemes 1 and 2**, for clarity.

### 3.2 Master equation simulations.

The reaction yields are expressed relative to the net amount of alkyne consumed in the simulation. The simulations often show back-reaction that re-forms the original reactants from the initial adducts.[75] However, in the experiments, the effect of the back-reaction is obviously not recognizable in itself, since only the final outcome is observable. The effect of the back-reaction has been removed a posteriori. To this end, the yields reported in Figures 1-5 have been set (back reaction excluded) equal to 1, in order to allow a direct comparison with experimental results.

For each of the two entrance channels we carried out two simulations separately, then the total yields were calculated by weight-averaging [76] the two individual channels. In order to access the wide ranges of combustion or pyrolysis temperatures, the kinetic simulation was carried out at temperatures from 600 to 2000 K.

In **low pressure flames** ( $P= 0.01$  atm) up to 1700 K, the 1-ethynylcyclopentadienyl radical **6** formation is the the main outcome (see **Figure 1**). Intermediates with yields below 1% were not reported in the plots. Upon rising  $T$ , yields of **1** and **2** immediately drop

because of the fast cyclization reactions through TS **1-4** and TS **2-3**, followed by 1,2 H shifts (TS **3-6** and TS **4-6** respectively). Above 800 K, no traces of the initial adducts **1** and **2** are found. **6** is located in a very deep well, and is consequently produced in noticeably high yield. At temperature higher than 1600 K, H (**29** and **30**) and  $C_2H_2$  (**27** and **28**) losses (Scheme 3) become the dominant channels. As shown in Scheme A (supplementary material) an open-chain intermediate **23** can form from **6**. **23**, in turn, can undergo  $C_2H_2$  loss and give **28**, which is the main product. Also in the range 1000-1700 K it is produced in significant yield. H loss products **29** and **30** approach 21% and 25% respectively, only at 2000 K. Yield of **27** ( $C_2H_2$  loss from **23**) raises up to 1800 K, then remains almost constant. Though the six-ring **9** (Scheme 1, left) is very stable ( $-49 \text{ kcal mol}^{-1}$ ), it is not competitive and does not accumulate, because of its energy barrier of  $8 \text{ kcal mol}^{-1}$ . Moreover low pressure promotes the back-reaction to **2**. The other 6-ring intermediates of Scheme 1, **5** and **8**, have barriers which are too high compared to the other competitive steps and are not formed. A fraction of 6-ring structures is formed starting from the intermediate **6**, passing through the intermediates **11**, **12**, **15** and **17** reported in Scheme 2, which in the end contribute with about the same weight to the population of structure **14**. Then, H loss from **14** causes the formation of the 6-membered ring **19**. Notwithstanding the rather high energy, at  $T \approx 1800 \text{ K}$ , **19** forms as ca. 3% of the total. The yield decreases rapidly at higher and lower temperatures.

In atmospheric pressure flames ( $P=1 \text{ atm}$ , Figure 2) the behavior is different. **1** and **2** are efficiently thermalized and are present with relevant yields up to 1200 K. From 900 K to 2000 K, the intermediate **6** is the main product. The importance of H (**29**, and **30**) or

$C_2H_2$  (**27** and **28**) losses rises slowly: they represent at most 20% of the total product (T = 2000 K). 6-rings **9** and **19** are produced with yields of 0.2% at T=1600 K, and 1% at T=2000 K respectively (not reported in the [Figure 2](#)). It is apparent that the pressure of the buffer gas plays a relevant role on the kinetics, and product yields and distribution.

Estimated absolute rate constants for the main products (H and  $C_2H_2$  losses, and **19**) are plotted in [Figure 3](#). The rate constants were calculated by multiplying the yields of each species by  $k_{\infty}(T)$ , the high pressure limit rate constant for propargyl + butadiyne recombination reaction. Rate constants for each of the two channels were summed to obtain the overall rate constants reported below. In the **Supplementary material** ([Table A](#)) the rate constants were fitted by using a modified Arrhenius equation  $k = A T^n \exp(-E_a/RT)$ .

Due to the uncertainty on the barrier calculations, the rate constants estimated by RRKM/ME have to be considered only qualitatively.

In the range 800-2000 K our rate constants ( $k_a$ ) for the H losses (formation of **29** and **30**) are similar to those calculated by da Silva and Trevitt ( $k_b$ ): the ratio  $k_a/k_b$  is in between 5.6 (**30**, 600 K) and 0.4 (**30**, 2000 K). The rate constant for the  $C_2H_2$  losses (formation of **27** and **28**) are almost identical (ratio = 1.7) at 2000 K but at low temperature they are significantly different (up to 3 orders of magnitude). As concerns the 5-ring **6**, it shows an opposite behaviour: the rate constants agree at 600 K, but they are dissimilar [77] at high temperature.

In **high pressure flames** ([Figure 4](#)), which simulate the situation of the combustion chamber in modern engines, thermalization is even more effective: **1** and **2** are found in

relevant yields up to 1800 K. The yield of intermediate **6** becomes dominant over **1500 K** and the importance of H losses (labeled as **29** and **30**) raises, over **1700 K**.

Other products are present in traces only. In particular, 6-rings **9** and **19** are produced with yields of only 0.4% and 0.1% respectively within the range 1800 K- 2000 K.

Cumulative 6-ring yields (for **5**, **8**, **9**, **14** and **19**) at different pressures are shown in **Figure 5**. Relatively higher yields (close to 3%) are found under low pressure conditions, whereas at pressure of 1 atm or above, 6-rings represent only 0.6-1% of the total reaction products. Structures **19** and **9**, which have aromatic character, are the main 6-ring intermediates, and have aromatic character.

## 4. Conclusions

The present study on the propargyl + butadiyne reaction focuses on the combustion pathways leading to the formation of 6-membered rings (aromatic or non aromatic). Several pathways are found, at first sight promising when  $\Delta E_{ZPE}$  is considered, since keep below the reference  $E_{ZPE}$  level defined by the reagents. However, the subsequent RRKM part of this study shows that only some of them could play a role in the reaction, and that this role is of limited importance. Structure **9** (**Scheme 1**), which bears an aromatic ring, forms directly from the adduct **2**, and is a very stable structure (-52 kcal mol<sup>-1</sup>). However, its formation barrier is close to the  $E_{ZPE}$  reference level and its formation results consequently marginal. Structures **5** and **8** (non-aromatic 6-rings, see **Scheme 1**) lie above the reactants and do not play any role. Other 6-membered ring intermediates like **13** (-45 kcal mol<sup>-1</sup>) and **16** (-15 kcal mol<sup>-1</sup>), which present some aromatic character, or **15** (-23 kcal



mol<sup>-1</sup>), non-aromatic, (all in [Scheme 2](#)) could form during the combustion process, but they quickly transform to the more stable aromatic structure **14** (-62 kcal mol<sup>-1</sup>). This one is connected, through H loss, to the closed shell aromatic product **19** (10 kcal mol<sup>-1</sup>).

According to the kinetic study, at **room pressure**, the 5-membered ring **6** is the main product, as already stressed by da Silva and Trevitt, along with some amount of the initial adducts **1** and **2**, and the products of H and C<sub>2</sub>H<sub>2</sub> losses, depending on the temperature range. Under these conditions, the formation of the intermediate **19** is still possible but in low yield (about 1% at 2000 K). On the other hand, in low pressure flames, the intermediates **1** and **2** react to form about 3% of the 6-membered ring **19**, and only 0.1% of **9**. At high pressure, **9** reaches about 0.1%; **1**, **2** and **6** are the main products.

## 5. Appendix

Some intermediates (**5**, **13** and **16**) seem to present complex electronic structures that could be not properly treated by CCSD(T) and require a multireference method. Therefore, their energies were recalculated by the CASPT2 method which includes both the dynamical and non-dynamical electron correlation energies and consequently provides a reliable reference. Moreover, through the inspection of the occupation number of the active orbitals, whether a structure presents some diradicaloid character can be assessed. So, the energies of the intermediates cited above, and of **1** (added for sake of comparison) were calculated with respect to the intermediate **6** at the CASPT2(13,13)[78]/cc-pVTZ//M06-2X/cc-pVTZ level. The active space [n electrons in m orbitals define the label (n,m)] derives from that of the reactants, which must include all the Pi orbitals of the butadiyne (8,8), the Pi orbitals (5,5) of the propargyl radical [79]. The calculations were performed by the MOLCAS 7 [80] program.

Intermediate **5** might be seen as a triradical. It actually exhibits a radical+diradicaloid character. In fact its doublet wavefunction is strongly contaminated by the quartet multiplicity. The contamination is testified by the UHF total spin operator expectation value  $\langle S^2 \rangle = 2.59$  (for the uncontaminated doublet wavefunction  $\langle S^2 \rangle = 0.75$ ). The CCSD(T) method does not completely eliminate spin-contamination.[81] Multireference methods allow a more instructive inspection of its electronic structure.

At the CASPT2 level, **5** is located  $92.9 \text{ kcal mol}^{-1}$  above **6** (see [Table 1](#)). Populations of the three singly occupied orbitals are 1.00, 1.37 and 0.63, (the other ten orbitals are substantially doubly occupied or empty) and testify the radical+diradicaloid character. In fact, CCSD(T) overestimates the energy by  $7 \text{ kcal mol}^{-1}$  and seems inadequate to describe

triradical structures with non-negligible static (structure dependent) correlation. Anyway, even using multireference methods, **5** formation remains not competitive compared to the other processes.

Intermediates **13** and **16** are carbene radicals. However, in these cases, the diradicaloid character is less marked (the populations of the active orbitals are close to 2, 1 or 0), in such a way that they can be treated by single reference wavefunction methods. In fact, for these structures, as for the adduct **1**, CCSD(T) energies are close to the CASPT2(13,13) energies. By comparing single point CASPT2 energies based on M06-2X/cc-pVDZ geometries with CASPT2/cc-pVDZ//CASPT2/cc-pVDZ for some structures (Table 2), the agreement between the two sets of data is apparent. Therefore we deduced that DFT(M06-2X) gives reasonably reliable geometries for CASPT2 calculations. For this validation cc-pVDZ basis set was used because CAS(13,13)PT2/cc-pVTZ optimizations were computationally too demanding.

Thermodynamic and kinetic data were used to validate the computational level chosen for this study [CCSD(T)/cc-pVTZ//DFT(M06-2X)/cc-pVTZ for energies; DFT(M06-2X)/cc-pVTZ for geometries and thermochemistry]. Five reactions were first considered, and a comparison between the relevant experimental and computational reaction enthalpies drawn (Table 3). Reaction #1 is the formation of the benzyl radical from propargyl and but-1-ene-3-yne. Reaction #2 is the formation of benzene starting with two propargyl radicals (see the studies reported in the Introduction). Reaction #3 is ethyne trimerization to give benzene.[82] Reaction #4 sees seven ethyne molecules put into relation with two benzyl radicals: it is not to be considered as a real reaction, yet it allows a

“reaction” enthalpy comparison. Reaction #5 is the radical coupling of propargyl with atomic hydrogen, to get propyne.

Then, the rate constants for the propargyl radical + ethyne reaction were calculated at the same level by using TST theory, at four different temperatures, and compared to experimental data.[83] Calculated rate constants show a very good agreement with the experimental rate constants, as reported in [Table 4](#).

## Acknowledgments

This work was conducted in the frame of EC FP6 NoE ACCENT and ACCENT-PLUS projects (Atmospheric Composition Change, the European NeTwork of Excellence). Financial support has been provided by the Italian MIUR, within the *Programma di Ricerca Scientifica di Rilevante Interesse Nazionale* “Studi fondamentali ed interdisciplinari di chimica ionica e neutra in fase gassosa” (PRIN 2009).

**Supplementary material available:** it includes RRKM simulations carried out by using  $E_{\text{down}} = 500 \text{ cm}^{-1}$ , the rate constants, the geometries, energetics, vibrational frequencies, moments of inertia of all the structures, and a complete description of the reaction pathways studied.

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ref. 45:  $6.3 \times 10^{-3}$  (butadiyne) and  $2.4 \times 10^{-3}$  (propargyl)  
ref. 46:  $4.4 \times 10^{-3}$  (butadiyne) and  $2.8 \times 10^{-3}$  (propargyl)  
ref. 47:  $2.3 \times 10^{-3}$  (butadiyne) and  $3.1 \times 10^{-3}$  (propargyl)
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**Scheme 1.** The prominent steps of the propargyl radical ( $C_3H_3$ ) + butadiyne ( $C_4H_2$ ) reaction.  $\Delta E_{ZPE}$  energies in kcal mol<sup>-1</sup>. In parentheses the energies reported in ref 51.

**Scheme 2.** 6-Membered rings formation from the intermediate **6**.  $\Delta E_{ZPE}$  energies in kcal mol<sup>-1</sup>. Figures in parentheses are energies reported in Ref 51.

**Scheme 3.**  $C_2H_2$  or H losses.  $\Delta E_{ZPE}$  energies in kcal mol<sup>-1</sup>. In parentheses the energies reported in ref 51.

**Figure 1.** Product distribution of the propargyl radical + butadiyne at P = 0.01 atm as a function of T. **27** and **28** are open chain products from  $C_2H_2$  loss. **29** and **30** are H loss open-chain products. **19** is a H loss 6-membered ring products from **14** (both are 6-rings). **1** is the open-chain initial intermediate. **6** is a 5-membered ring.

**Figure 2.** Product distribution of the propargyl radical + butadiyne in function of T, at P = 1 atm. **27** and **28** are  $C_2H_2$  loss open-chain products. **29** and **30** are H loss open-chain products. **1** and **2** are the open-chain initial intermediates. **4** and **6** are 5-membered rings.

**Figure 3.** Calculated rate constants in molec<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup> of the most relevant products as a function of T, at P = 1 atm. **6** is a 5-membered ring. **27** and **28** are  $C_2H_2$  loss open-chain products. **29** and **30** are H loss open-chain products. **19** is a 6-ring produced by H loss products from **14**.

**Figure 4.** Product distribution of the propargyl radical + butadiyne as a function of T, at P = 40 atm. **29** and **30** are H loss open-chain products. **1** and **2** are the open-chain initial intermediates. **3**, **4** and **6** are 5-membered rings.

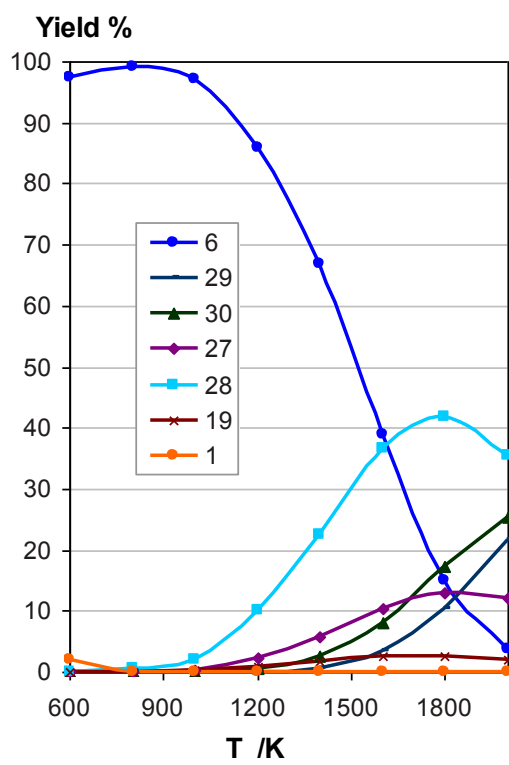
**Figure 5.** Total 6-membered ring formation (cumulative yield of **5**, **8**, **9**, **14** and **19**) as a function of T, at three pressures (0.01, 1 and 40 atm).

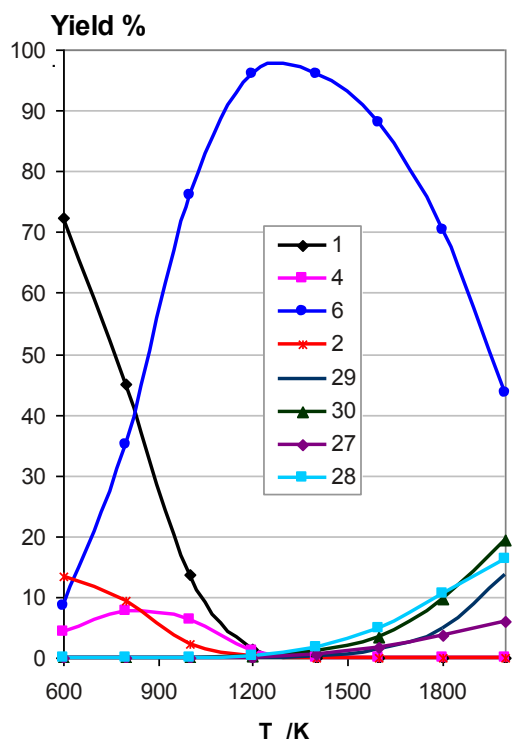
**Table 1.** Comparison of the CASPT2 and CCSD(T) energies for structures with diradicaloid character.<sup>a</sup>

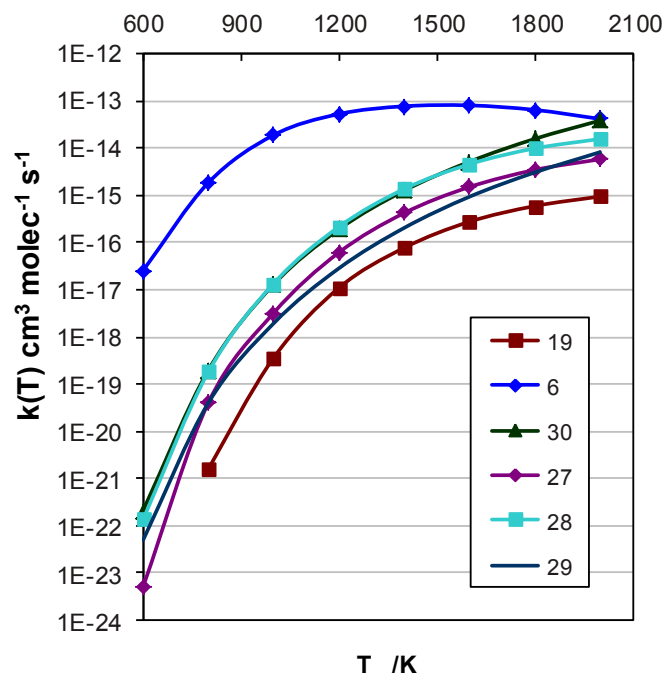
**Table 2.** Effect of the M06-2X geometries on the CASPT2 energies.<sup>a</sup>

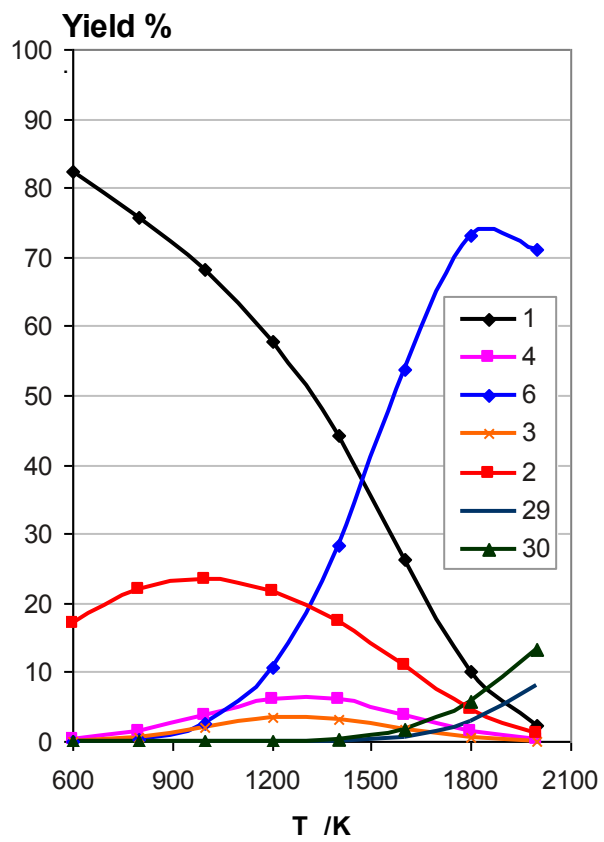
**Table 3.** Experimental vs. theoretically assessed reaction enthalpies for cases 1-5.

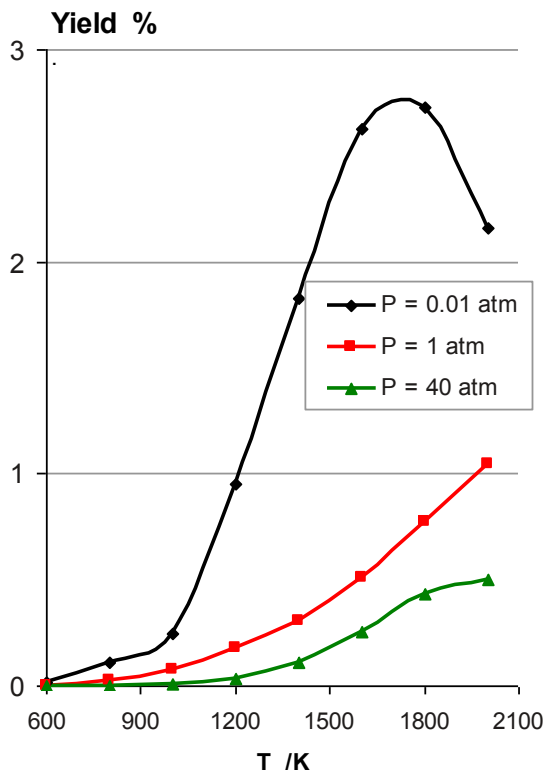
**Table 4.** Experimental vs. theoretically assessed rate constants for the propargyl radical + ethyne reaction.

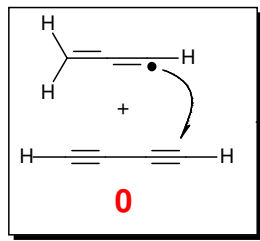




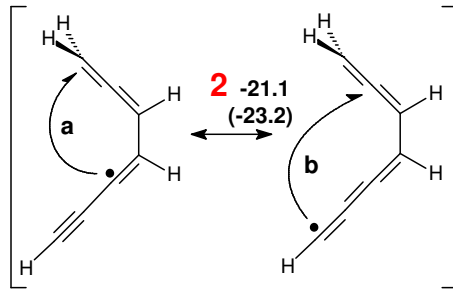




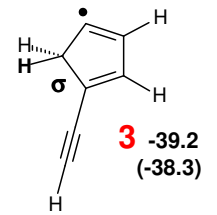




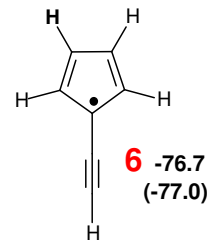
**channel 2**  
13.4  
(10.7)



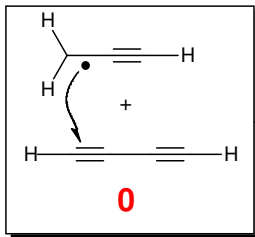
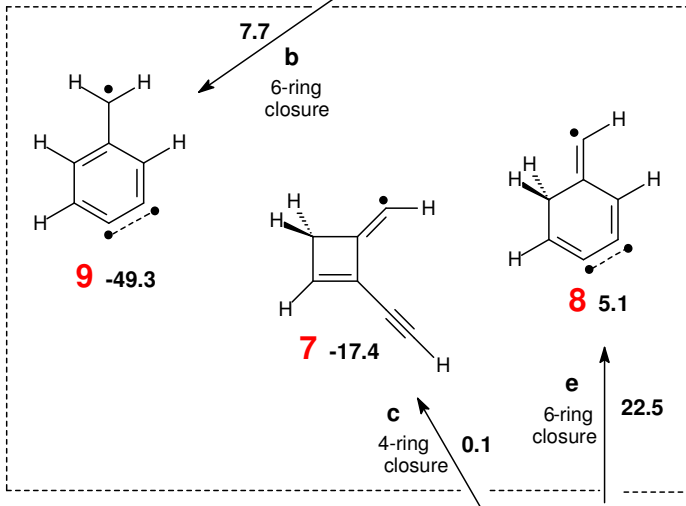
-4.7  
(-7.3)  
**a**  
5-ring  
closure



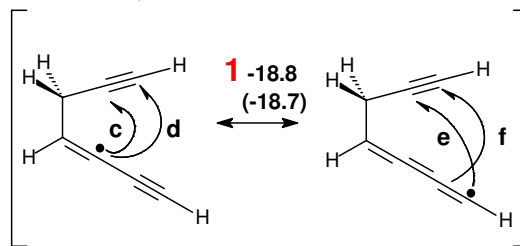
1,2 H shift  
-12.3  
(-12.5)



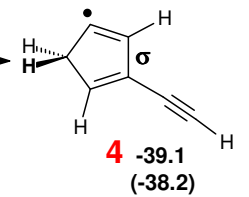
1,2 H shift  
-11.6  
(-12.1)



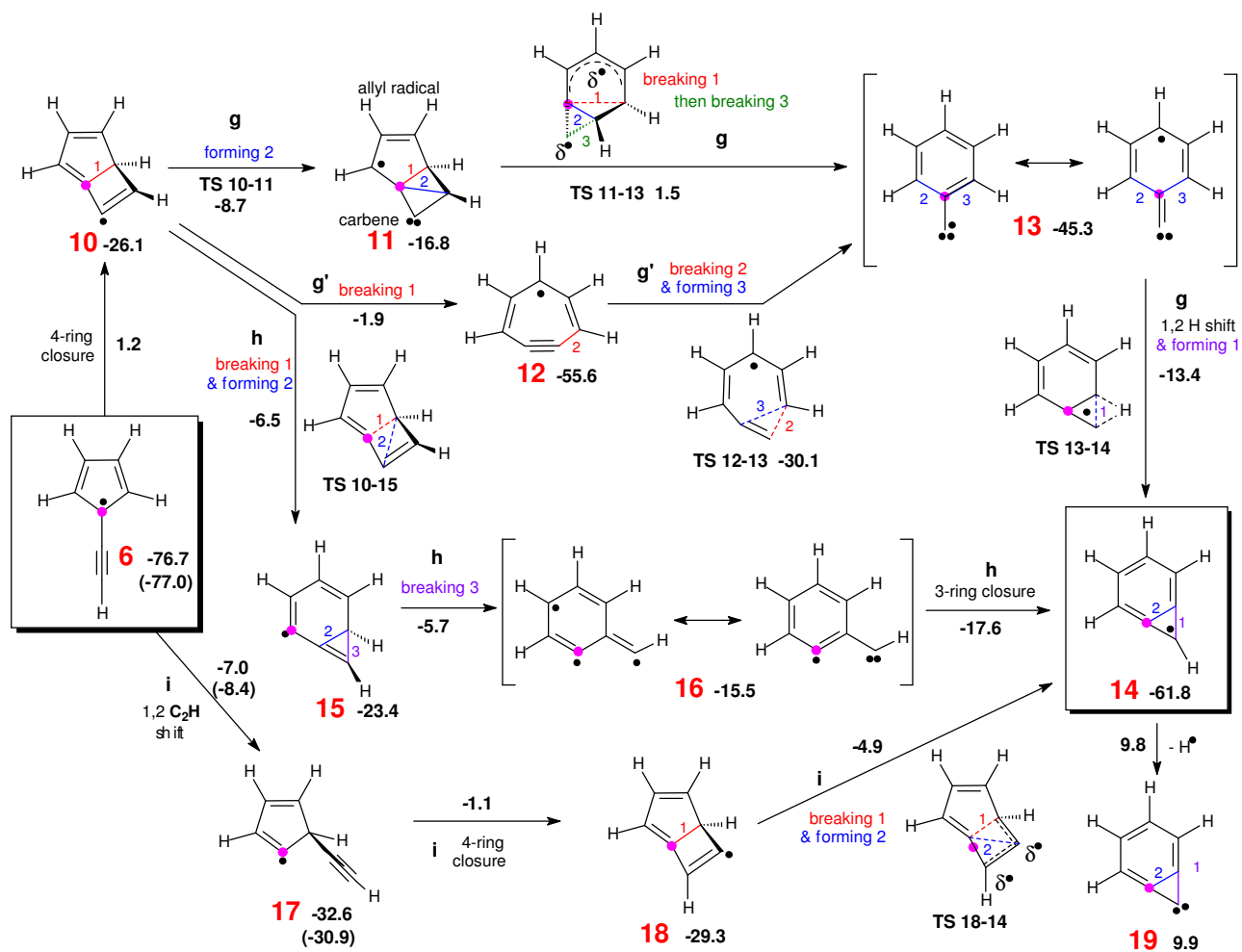
**channel 1**  
11.5  
(8.4)

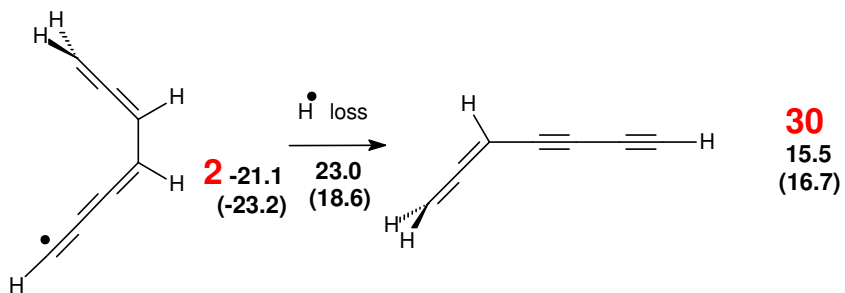
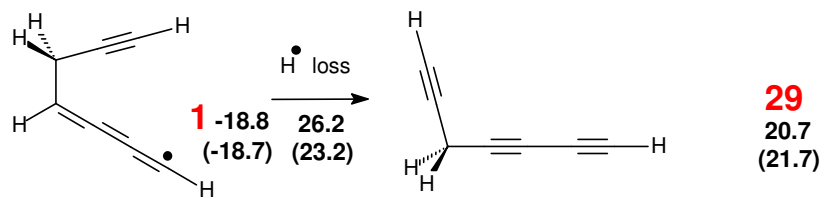
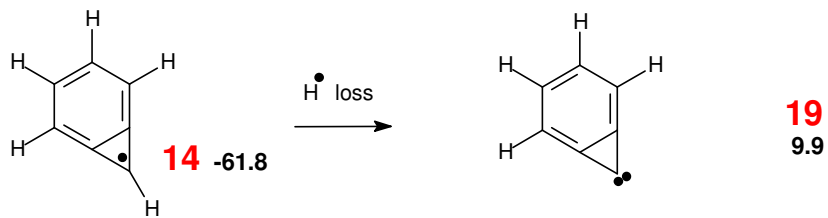
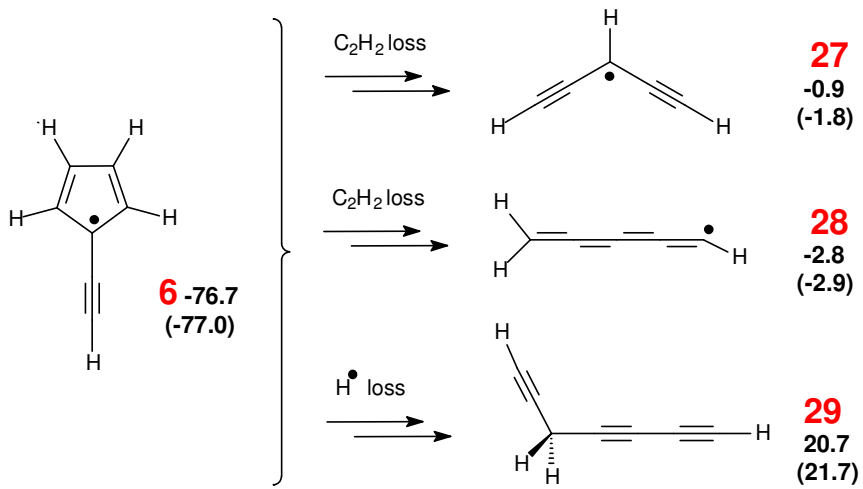


-3.4  
(-4.5)  
**d**  
5-ring  
closure









	CASPT2 <sup>b</sup>	CCSD(T) <sup>c</sup>
<b>6</b>	0.0	0.0
<b>1</b>	61.9	60.5
<b>5</b>	92.9	99.5
<b>13</b>	28.7	30.5
<b>16</b>	61.0	60.7

<sup>a</sup>  $\Delta E$  in kcal mol<sup>-1</sup>, with respect the intermediate **6**.

<sup>b</sup> CAS(13,13)PT2/cc-pVTZ//M06-2X/cc-pVTZ

<sup>c</sup> CCSD(T)/cc-pVTZ//M06-2X/cc-pVTZ

	M06-2X <sup>b</sup>	CASPT2//M06-2X <sup>c</sup>	CASPT2 <sup>d</sup>
<b>6</b>	0.0	0.0	0.0
<b>5</b>	93.3 <sup>e</sup>	89.4	89.1
<b>13</b>	28.6	26.2	26.5
<b>16</b>	57.6	57.5	57.7

<sup>a</sup>  $\Delta E$  in kcal mol<sup>-1</sup>, with respect the intermediate **6** <sup>b</sup> M06-2X/  
cc-pVDZ optimization. <sup>c</sup> CAS(13,13)PT2/cc-pVDZ//M06-2X/  
cc-pVDZ. <sup>d</sup> CAS(13,13)PT2/cc-pVDZ optimization. <sup>e</sup> Spin-  
Projected energy.[81]

Reaction	$\Delta H(\text{exp.})/\text{kcal mol}^{-1}$	$\Delta H(\text{theor.})/\text{kcal mol}^{-1}$	
		DFT(M06-2X) <sup>g</sup>	CCSD(T) <sup>h</sup>
1	$-101.9 \pm 1.5$ <sup>a,b,d</sup>	-103.7	-101.9
2	$-142.20 \pm 1.43$ <sup>a,c</sup>	-148.2	-147.8
3	$-142.77 \pm 0.22$ <sup>f,c</sup>	-148.1	-144.9
4	$-280 \pm 1$ <sup>f,d</sup>	-290.7	-282.1
5	$-88.78 \pm 1.02$ <sup>a,e,f</sup>	-91.1	-90.9
	<i>Mean Signed Error</i>	-5.23	-2.39
	<i>Mean Unsigned Error</i>	5.23	2.39

<sup>a</sup>propargyl radical: ref 84; <sup>b</sup>but-1-ene-3-yne: ref 85;  
<sup>c</sup>benzene: ref 86; <sup>d</sup>benzyl radical: ref 84; <sup>e</sup>propyne: ref 87;  
<sup>f</sup>hydrogen atom and ethyne: ref 88; <sup>g</sup>geometry optimization and thermochemistry at this level of theory; <sup>h</sup>CCSD(T)/cc-pVTZ//M06-2X/cc-pVTZ energy plus M06-2X/cc-pVTZ thermochemistry.

T /K	k / molec <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup>		
	experiment <sup>a</sup>	DFT(M06-2X) <sup>b</sup>	CCSD(T) <sup>c</sup>
800	7.25 x 10 <sup>-16</sup>	3.04 x 10 <sup>-16</sup>	1.53 x 10 <sup>-16</sup>
<b>900</b>	1.46 x 10 <sup>-15</sup>	9.40 x 10 <sup>-16</sup>	5.11 x 10 <sup>-16</sup>
<b>1000</b>	2.55 x 10 <sup>-15</sup>	2.38 x 10 <sup>-15</sup>	1.38 x 10 <sup>-15</sup>
1100	4.03 x 10 <sup>-15</sup>	5.21 x 10 <sup>-15</sup>	3.16 x 10 <sup>-15</sup>

<sup>a</sup> ref 83; <sup>b</sup>geometry optimization and thermochemistry at DFT(M06-2X)/cc-pTVZ level; <sup>c</sup>single-point energy at CCSD(T)/cc-pVTZ //DFT(M06-2X)/cc-pVTZ, plus M06-2X/cc-pVTZ thermochemistry.