J. Phys. Chem. A **2006,** *110,* 367−378 **367**

Is the Mechanism of the [2+2] Cycloaddition of Cyclopentyne to Ethylene Concerted or Biradical? A Completely Renormalized Coupled Cluster Study[†]

Armağan Kınal[‡] and Piotr Piecuch*[,§]

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

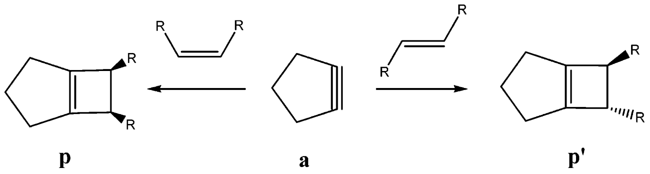
Received: March 14, 2005; In Final Form: April 27, 2005

The mechanism of the [2+2] cycloaddition reaction of cyclopentyne to ethylene has been studied using the completely renormalized coupled cluster method with singles, doubles, and noniterative triples (CR−CCSD(T)). In agreement with the experimentally observed stereochemistry, the CR−CCSD(T) method favors the concerted pathway involving a [2+1] transition state, whereas the popular CCSD(T) method, which is often regarded as the "gold standard" of electronic structure theory, and low-order multireference methods support the less probable biradical mechanism. In addition, the CCSD(T) approach produces an erroneous description of some transition states and intermediates, particularly those which have a significant biradical character. The CR−CCSD(T) calculations indicate that the reaction is a highly exothermic ($\Delta G_r^{298} = -68$ kcal/mol), predominantly concerted process with a relatively low activation barrier on the order of 13−16 kcal/mol which permits its thermal occurrence.

Introduction

According to the Woodward−Hoffmann orbital symmetry rules,[1] the [2+2] cycloaddition reactions are thermally forbidden and they are generally believed to occur stepwise by passing through a biradical intermediate. Owing to the stepwise mechanism involving biradical species, these reactions cannot be stereospecific. However, the experimental results for the [2+2] cycloaddition reactions of cyclopentyne (**a**)[2] with proper alkenes occur at modest temperatures (e.g., room temperature), producing highly stereospecific cycloadducts[3,4] which seems to contradict the Woodward−Hoffmann rules (Scheme 1). To account for this unusual behavior of cyclopentyne, several explanations have been proposed in the last twenty years. An initial explanation was due to Fitjer et al.,[3] who suggested that cyclopentyne has a singlet ground state with an antisymmetric highest-energy occupied molecular orbital (HOMO), which would make the [2+2] cycloaddition reactions of cyclopentyne with alkenes Woodward−Hoffmann allowed. This idea was supported by the early theoretical studies[5] suggesting that cyclopentyne has a significant biradical character with some electron density shifted to its acetylenic π^* MO, which is antisymmetric with respect to the C_s symmetry plane. A different explanation was offered by Gilbert and Baze,[6] who suggested that the experimentally observed stereospecificity of the reaction may be due to antarafacial participation of cyclopentyne in a concerted mechanism, which would also make the reaction thermally allowed. In a subsequent semiempirical MNDO−CI study,[7] Olivella et al. demonstrated that a [2+2] cycloaddition of cyclopentyne to ethylene (**et**) occurs via a stepwise mechanism proceeding through the formation of a biradical intermediate (structure **b** in Scheme 2) and explained the observed high stereospecificity by an extremely short lifetime of this biradical intermediate. The debate has continued, and the subsequent semiempirical AM1 calculations produced a new intermediate structure called "lumomer of cyclopentyne,"[8,9] which is consistent with the orbital symmetry rules and the concerted mechanism of the reaction. Unfortunately, this new structure could not be reproduced by more accurate ab initio calculations including electron correlation effects (MP2 and MCSCF),[10] and it was concluded that the lumomer was an artifact of the AM1 methodology. More recently, Laird and Gilbert[11] performed several experiments on the cycloaddition reactions of norbornyne with alkenes and observed that norbornyne behaves as a singlet dicarbene in its cycloaddition to alkenes with a complete retention of stereochemistry. By assuming that cyclopentyne is also a singlet dicarbene, they proposed an orbital symmetry allowed multistep mechanism passing through a concerted [2+1] transition state (structure **ac**[‡] in Scheme 2), which is in complete agreement with the experimentally observed stereospecificity.[3,4,6] Very recently, Özkan and Kinal[12] and Bachrach and Gilbert[13] explored the concerted and biradical reaction pathways for the [2+2] cycloaddition of cyclopentyne to ethylene, shown in Scheme 2, using standard ab initio and density functional theory (DFT) methods. Unfortunately, different methods used in these studies produced conflicting results. Although the DFT UB3LYP calculations reported in refs 12 and 13 predict similar barrier heights for the concerted and biradical mechanisms, slightly favoring the concerted process, the high-level ab initio calculations employing the second-order multireference perturbation theory (OVB-MP2 or CAS-MP2[14] and MC-QDPT[15] or MR-MP2[16]), based on complete active space self-consistent field (CASSCF) reference functions, and the coupled cluster method

SCHEME 1



[†] Part of the special issue "Donald G. Truhlar Festschrift".

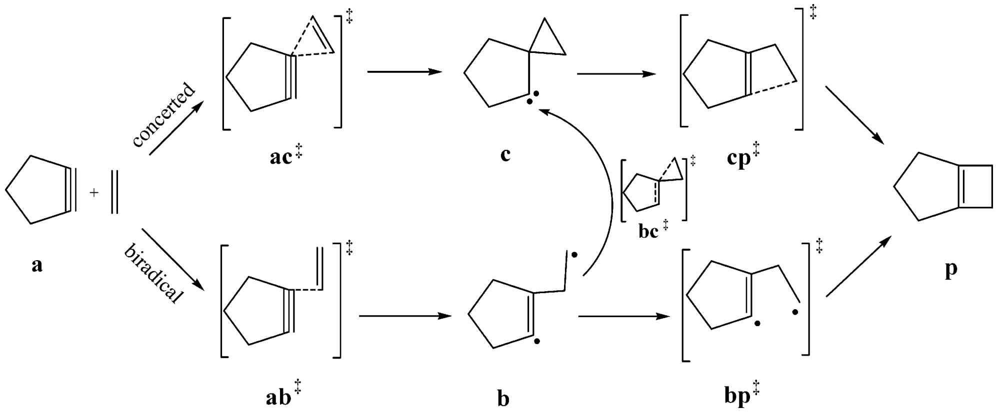
* To whom correspondence should be addressed. E-mail: piecuch@cem.msu.edu. Internet: www.cem.msu.edu/~piecuch/group_web.

[‡] NATO/TUBITAK Science Fellow.

[§] Also at: Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824.

10.1021/jp0513216 CCC: $33.50

SCHEME 2



with singles, doubles, and noniterative triples (CCSD(T)[17]), which is often regarded as the "gold standard" of electronic structure theory, favor the biradical path with no stereospecificity, contradicting the experimental findings. Thus, a theoretical explanation of the mechanism of the important [2+2] cycloaddition reaction of cyclopentyne to ethylene remains a mystery and more accurate and definitive ab initio work needs to be done in this area. The purpose of the present study is to address this unsatisfactory situation by employing the state-of-the-art ab initio methods, belonging to the new category of renormalized coupled cluster theories,[18,19] and basis sets that are much bigger than those employed in previous calculations.

The main problem with the understanding of the mechanism of [2+2] cycloaddition of cyclopentyne to ethylene lies in the presence of the biradical reaction intermediates and transition states, such as **ab**‡, **b**, and **bp**‡, on the potential energy surface (see Scheme 2), which create a significant challenge, both for experiment and for theory. The experimental characterization of such species, which typically have low thermodynamic stability, is a painstaking effort, which requires using the most advanced techniques, such as electron paramagnetic resonance.[20,21] From the theoretical point of view, biradicals are very challenging because of the manifestly multiconfigurational character of the corresponding electronic wave functions and (in some cases) the proximity of the relevant singlet and triplet potential energy surfaces (see, e.g., ref 22). The computational exploration of competing reaction pathways involving biradical species shown in Scheme 2 is particularly difficult, since one has to obtain a highly accurate and well-balanced description of reactant and product molecules, and closed-shell regions of potential energy surface, for which single-reference calculations are sufficient, and biradical intermediates and/or transition states, which typically require a multireference treatment. To obtain a uniformly accurate description of reactants, products, reaction intermediates, and transition states, one has to use methods that can properly balance the dynamic and nondynamic electron correlation effects.[23] The majority of the existing quantum chemistry methods provide an accurate description of either the dynamical correlation effects that are the dominant correlations in closed-shell molecular systems or the nondynamic correlation effects that play a significant role in quasi-degenerate (multiconfigurational) electronic states characterizing, for example, biradicals, but very few methods are capable of providing an equally accurate description of both dynamic and nondynamic correlation effects required in studies of reactive potential energy surfaces (this is particularly true for larger polyatomic molecular systems, for which the potentially most accurate multireference configuration interaction or multireference coupled cluster calculations are not feasible at this time). For example, the highly successful single-reference coupled cluster theories,[24] such as the aforementioned CCSD(T) approximation, provide an excellent description of closed-shell systems and dynamic correlation effects with relatively low computer costs,[25] but they completely fail when the potential energy surfaces involving bond breaking[18,19] and biradicals[22,23] are examined. This, in particular, applies to the [2+2] cycloaddition of cyclopentyne to ethylene, which is characterized by a potential energy surface having several biradical intermediates and transition states. As shown in this paper, the CCSD(T) approach not only favors the pathway through biradical structures **ab**‡, **b**, and **bp**‡ (see Scheme 2), but it also provides completely erroneous energy values for the intermediate **b** and transition state **bp**‡, locating the energy of the intermediate **b** below the reaction product (structure **p** in Scheme 2). A different kind of high-level coupled cluster approximation that accounts for singly, doubly, and triply excited clusters, referred to as the completely renormalized CCSD(T) (CR−CCSD(T)) method,[18,19] which can accurately and effectively deal with reactive potential energy surfaces involving single bond breaking[18,19] and biradicals,[22,23] and which has the ease-of-applicability and the relatively low computer costs of the standard CCSD(T) theory, has to be employed to obtain a reliable description of the [2+2] cycloaddition of cyclopentyne to ethylene.

A thorough examination of the competing concerted and biradical reaction pathways characterizing the [2+2] cycloaddition of cyclopentyne to ethylene, shown in Scheme 2, with the CR−CCSD(T) approach and the comparison of the CR−CCSD(T) results with the results of CCSD(T), CAS-MP2, and DFT ((U)B3LYP) calculations are the main objectives of this study. According to our CR−CCSD(T) calculations, the [2+2] cycloaddition of cyclopentyne to ethylene is a highly exothermic process with a relatively low activation barrier enabling the reaction at modest temperatures. Unlike CCSD(T), CASSCF, and second-order multireference perturbation theory, which all support the biradical mechanism, the CR−CCSD(T) approach seems to indicate the predominantly concerted mechanism involving a [2+1] transition state. Although the stereospecificity obtained with the CR−CCSD(T) approach is slightly lower than that observed in experiment, the stereoretention resulting from the CR−CCSD(T) calculations is much closer to the experimental stereoretention than the stereoretention values resulting from other high-level ab initio calculations. The CR−CCSD(T) method seems to be the only high-level ab initio method that provides a reliable description of the mechanism of the [2+2] cycloaddition of cyclopentyne to ethylene at this time, which reasonably well agrees with experimental findings.

TABLE 1: Energies[a] (in kcal/mol) of the Stationary Points[b] along the Concerted and Biradical Reaction Paths Characterizing the [2+2] Cycloaddition of Cyclopentyne to Ethylene at Different Levels of Theory

	ab‡	**b**	**bp**‡	**bc**‡	**ac**‡	**c**	**cp**‡	**p**
CCSD(T)/6-311++G(2d,2p)[c,d]	4.2 (4.6)	−361.7	−57.2	−8.5	5.3 (6.1)	−33.6	−28.7	−81.9
CR−CCSD(T)/6-311++G(2d,2p)[c,d]	6.5 (6.0)	−15.5	−4.3	−7.7	5.0 (5.0)	−36.1	−30.8	−84.4
(U)B3LYP/6-311++G(2d,2p)[c]	4.0	−22.9	−21.5	−14.0	1.9	−34.9	−29.4	−82.5
denominator D[d,e]	1.58 (1.54)	4.95	2.59	1.54	1.51 (1.48)	1.43	1.43	1.43
% biradical character[f]	25	99	91	53	10	5	4	7

[a] Electronic energies relative to the reactants (for the CR−CCSD(T) approach, which is not strictly size extensive, the reactant energy is obtained by calculating the energy of a noninteracting complex of cyclopentyne and ethylene separated by a large distance; we used a distance of 200 Å). [b] For the explanation of the abbreviations used to label the stationary points, see ref 2 (see, also, Scheme 1 and Figure 1). [c] The (U)B3LYP/6-311G(d,p) optimized geometries were used. [d] The numbers in parentheses (**ab**‡ and **ac**‡ only) represent the results of single point coupled cluster calculations employing the geometries optimized at the UMP2/6-311G(d,p) (**ab**‡) and RMP2/6-311G(d,p) (**ac**‡) levels of theory. [e] Values of the denominator D defining the CR−CCSD(T)/6-311++G(2d,2p) method (cf. eq 2). The value of D for the **a**+**et** reactants is 1.50, when the UB3LYP/6-311G(d,p) geometry is used, and 1.51 when the RMP2/6-311G(d,p) geometry is used. [f] Percent biradical character = $(2 - n_H) \times 100$, where n_H is the occupation number of the natural orbital corresponding to the HOMO calculated at the CASSCF(6,6)/6-311G(d,p)//UB3LYP/6-311G(d,p) level. The cyclopentyne reactant has a biradical character of 21%.

As shown in this paper, the CR−CCSD(T) approach provides an accurate and well-balanced description of the biradical and closed-shell regions of the potential energy surface associated with the cycloaddition of cyclopentyne to ethylene and of the corresponding nondynamic and dynamic correlation effects, confirming similar findings in this area reported in the recent study of the Cope rearrangement of 1,5-hexadiene.[23]

Theory and Computational Details

The CR−CCSD(T) method has been developed to improve a poor description of biradicals and potential energy surfaces along bond breaking coordinates by the standard CCSD(T) approach, without making the calculations more complicated or expensive and without significantly affecting the high accuracy of the CCSD(T) results for closed-shell systems.[18,19] Although both methods originate from different formal considerations [CCSD(T) is a standard coupled cluster approximation, which belongs to a larger class of methods that combine coupled cluster and many-body perturbation theory concepts,[17] whereas CR−CCSD(T) originates from the so-called method of moments of coupled cluster equations,[18a,b,19] which is a nonperturbative formalism], the working equations defining the CCSD(T) and CR−CCSD(T) methods are very similar; in particular, both methods are single-reference coupled cluster approximations and in both cases noniterative perturbative corrections due to triply excited determinants are added to the energy obtained in the basic CCSD (coupled cluster singles and doubles[26]) calculations. Symbolically, the CCSD(T) and CR−CCSD(T) energy expressions can be written as

$$E^{\mathrm{CCSD(T)}} = E^{\mathrm{CCSD}} + N^{\mathrm{(T)}} \tag{1}$$

$$E^{\mathrm{CR-CCSD(T)}} = E^{\mathrm{CCSD}} + N^{\mathrm{CR(T)}}/D \tag{2}$$

where E^{CCSD} stands for the CCSD energy and the numerator terms $N^{\mathrm{(T)}}$and $N^{\mathrm{CR(T)}}$ and the denominator term D that are used to calculate the corrections due to triple excitations in the CCSD(T) and CR−CCSD(T) methods are defined elsewhere.[17−19] The numerator terms $N^{\mathrm{(T)}}$and $N^{\mathrm{CR(T)}}$ are quite similar to each other, so that the main difference between the standard CCSD(T) approximation and the CR−CCSD(T) method is the denominator D, which is present in the CR−CCSD(T) energy formula, eq 2, and absent in the CCSD(T) expression, eq 1. It is this denominator, which allows the CR−CCSD(T) method to improve upon the failing of the standard CCSD(T) approach in the biradical and bond breaking regions of molecular potential energy surfaces. The primary role of this denominator, which is defined through singly and doubly excited cluster amplitudes resulting from the CCSD calculations, is to damp the excessively large and unphysical values of the noniterative triples corrections $N^{\mathrm{(T)}}$ or $N^{\mathrm{CR(T)}}$ at larger internuclear separations and for biradical species.[18a−c,23] As shown in ref 23, the magnitude of the denominator D correlates, at least to some extent, with the degree of the biradical character of the molecular system in question. This is particularly true for the molecular structures characterized by the large degree of the biradical character, for which D can be 2−3 times larger than the D values characterizing the corresponding closed-shell structures (see Table 1).

The potential energy surfaces for the [2+2] cycloaddition of cyclopentyne to ethylene had been previously probed[12] with DFT, using the (U)B3LYP functional, as implemented in Gaussian 98,[27] and the 6-311G(d,p) basis set.[28] The authors of ref 12 used the (U)B3LYP/6-311G(d,p) approach to determine all of the stationary points along the concerted and biradical minimum energy paths shown in Scheme 2. The resulting structures and the selected geometric parameters defining these structures, which are particularly relevant to the understanding of the mechanism of the [2+2] cycloaddition of cyclopentyne to ethylene, are shown in Figure 1. We used the geometries of the reactant, product, and all intermediate and transition state species optimized in ref 12 to perform the single-point CCSD(T) and CR−CCSD(T) calculations. For consistency, we first used the same 6-311G(d,p) basis set as employed in ref 12 and then performed additional calculations with a larger basis set (see the discussion below). We had to rely on the geometries optimized with DFT, since the geometry optimizations at the CR−CCSD(T) level are not possible at this time. There are no analytic gradients for the CR−CCSD(T) approach, and even with the analytic gradients, these geometry optimizations would be quite expensive at this time. Although analytic gradients for the standard CCSD(T) approach have been formulated,[29] the CCSD(T) geometry optimizations would be quite expensive, too. Moreover, as shown in this paper, the CCSD(T) method provides a completely erroneous description of biradical intermediates and transition states, so that the results of geometry optimizations at the CCSD(T) level would not be particularly meaningful.

Although we were unable to reoptimize the geometries of the stationary points along the concerted and biradical pathways shown in Scheme 2 at the CR−CCSD(T) level, the use of the (U)B3LYP approach to optimize the geometries, followed by the single-point energy calculations at higher levels of theory, such as CR−CCSD(T), is a common practice, which in the case of the [2+2] cycloadditon of cyclopentyne to ethylene studied in this work can be further justified by the fact that the B3LYP functional is an effective method to obtain reliable structures

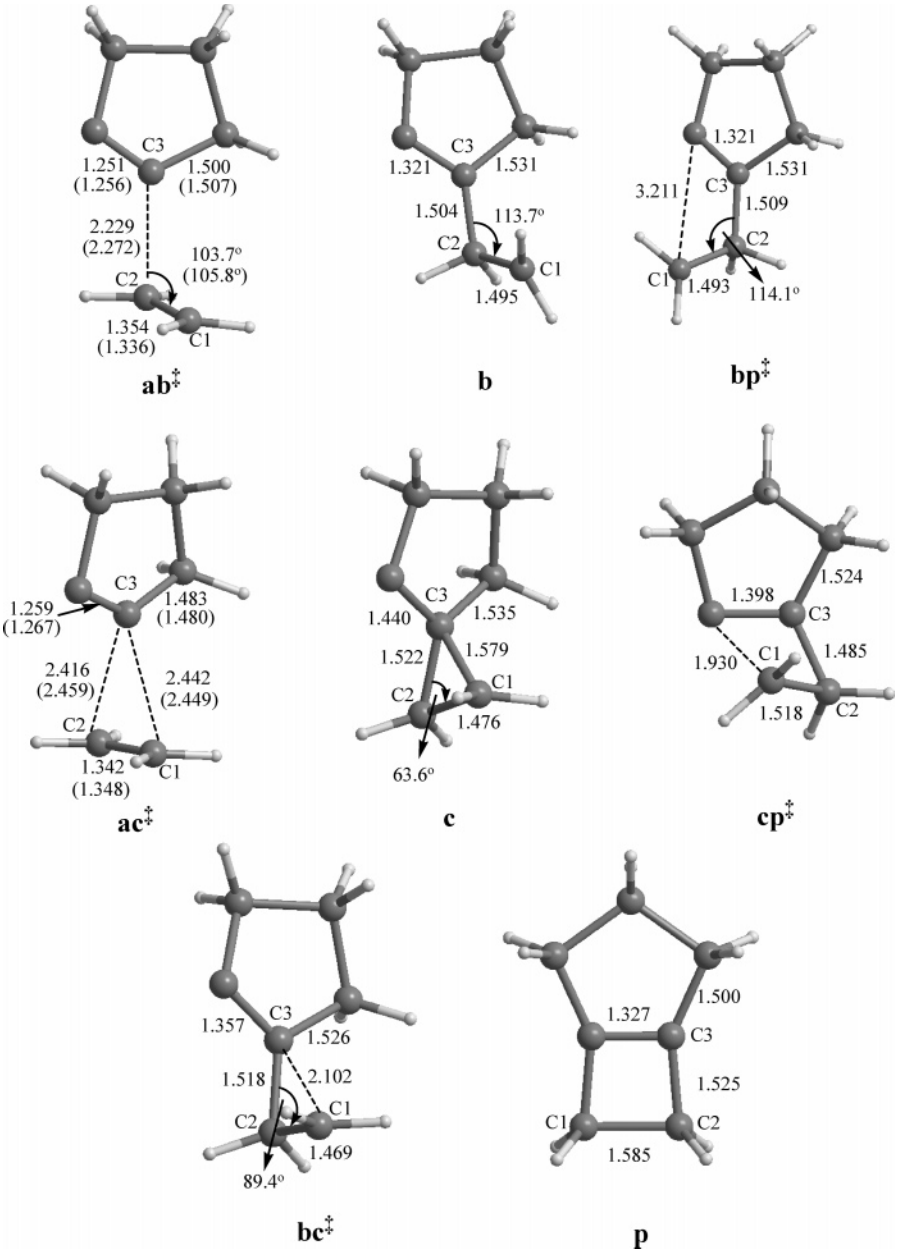


Figure 1. Selected geometric parameters for the stationary points along the concerted and biradical pathways characterizing the [2+2] cycloaddition of cyclopentyne to ethylene resulting from the (U)B3LYP/6-311G(d,p) optimizations reported in ref 12. The numbers in parentheses for transition states **ab**‡ and **ac**‡ indicate the parameters obtained in the UMP2/6-311G(d,p) (**ab**‡) and RMP2/6-311G(d,p) (**ac**‡) geometry optimizations. The dashed lines in the transition state structures indicate the new bonds that are formed after passing through these transition states.

defining the concerted and biradical reaction pathways.[30−32] To confirm that the main findings of this study are not significantly altered by the particular choice of geometries of the stationary points, we performed a few additional calculations for the initial transition states along the biradical and concerted reaction pathways (structures **ab**‡ and **ac**‡, respectively, in Scheme 2). These two transition states are the highest-energy stationary points along the biradical and concerted pathways and their relative energies define, to a large extent, the final reaction mechanism. The initial transition state for the concerted pathway, **ac**‡, has a small degree of the biradical character (see Table 1). Thus, we reoptimized the geometry of this transition state with the restricted second-order Møller−Plesset perturbation theory (RMP2), using the same 6-311G(d,p) basis set as used in the (U)B3LYP calculations of ref 12. For the initial transition state defining the biradical reaction pathway, **ab**‡, which has a somewhat larger degree of the biradical character (cf. Table 1), we performed the geometry optimization at the UMP2/6-311G(d,p) (unrestricted MP2) level. As shown in Figure 1, the differences between the geometries of the **ab**‡ and **ac**‡ transition states obtained with the (U)B3LYP and (U)MP2 methods are relatively small. The only parameter that seems to depend on the method used in the geometry optimizations somewhat more strongly is the distance between the C3 carbon atom of cyclopentyne and the C2 carbon atom of ethylene (see Figure 1), although even in this case there is a significant level of consistency between the results of the (U)B3LYP and (U)MP2 calculations (the C3−C2 distance in the biradical transition state **ab**‡ is on the order of 2.2−2.3 Å, whereas the C3−C2 ≈ C3−C1 distance in the concerted transition state **ac**‡ is approximately 2.4 Å; cf. ref 12 for further discussion). Despite these differences between the values of the C3−C2 distance obtained in the (U)B3LYP and (U)MP2 optimizations, the corresponding single point CCSD(T) and CR−CCSD(T) ener-

TABLE 2: Free Energies at 298 K[a] (in kcal/mol) of the Stationary Points[b] Defining the Concerted and Biradical Reaction Paths of the [2+2] Cycloaddition of Cyclopentyne to Ethylene at Various Levels of Theory

		ab‡	**b**	**bp**‡	**bc**‡	**ac**‡	**c**	**cp**‡	**p**
CCSD(T)	6-31G(d)[c]	13.7	−212.0	−53.4	4.4	20.1	−20.7	−14.5	−69.5
	6-311G(d,p)[d]	14.5	−280.1	−52.9	4.4	16.8	−21.2	−15.7	−68.0
	6-311++G(2d,2p)[d,e]	14.0 (13.5)	−349.5	−44.7	5.0	16.2 (14.5)	−18.4	−13.3	−65.1
CR−CCSD(T)	6-31G(d)[c]	15.4	−6.7	0.7	5.0	19.5	−23.4	−16.7	−72.0
	6-311G(d,p)[d]	16.7	−3.5	4.8	5.4	16.6	−23.7	−17.6	−70.3
	6-311++G(2d,2p)[d,e]	16.4 (15.0)	−3.2	8.2	5.8	16.0 (13.3)	−21.0	−15.3	−67.6
CAS-MP2[f]	6-31G(d)	22.7	−3.5	−0.9	13.2	24.1[g]	−12.5	−3.1	−57.7
(U)B3LYP[f]	6-311G(d,p)[d]	13.2	−12.0	−10.2	−1.6	12.6	−21.3	−15.3	−67.9
(U)B3LYP	6-311++G(2d,2p)[d]	13.9	−10.7	−9.0	−0.5	12.8	−19.8	−13.9	−65.7

[a] The CCSD(T), CR−CCSD(T), and (U)B3LYP free energies corresponding to the 6-311G(d,p) and 6-311++(2d,2p) basis sets were calculated using the ZPVE and thermal corrections obtained in the (U)B3LYP/6-311G(d,p) calculations. For the 6-31G(d) basis set (the CCSD(T) and CR−CCSD(T) methods), we used the ZPVE and thermal corrections obtained in the (U)B3LYP/6-31G(d) calculations. [b] For the explanation of the abbreviations used to label the stationary points, see ref 2 (see, also, Scheme 1 and Figure 1). [c] The (U)B3LYP/6-31G(d) geometries were used. [d] The (U)B3LYP/6-311G(d,p) geometries were used. [e] The numbers in parentheses (**ab**‡ and **ac**‡ only) represent the free energies obtained by adding the electronic energies resulting from the single point coupled cluster calculations, employing the UMP2/6-311G(d,p) (**ab**‡) and RMP2/6-311G(d,p) (**ac**‡) optimized geometries, to the ZPVE and thermal corrections obtained in the corresponding (U)MP2/6-311G(d,p) calculations. [f] Obtained by adding the CAS-MP2/6-31G(d) and (U)B3LYP/6-311G(d,p) electronic energies reported in ref 12 to the ZPVE and thermal corrections resulting from the (U)B3LYP/6-311G(d,p) calculations. [g] The RB3LYP/6-311G(d,p) optimized geometry was used.

gies (particularly, the energies obtained with the CR−CCSD(T) approach) are barely affected by the small changes in the geometries of the **ab**‡ and **ac**‡ structures resulting from different geometry optimizations. As shown in Table 1 and as discussed in the next section, the **ac**‡ structure remains the lower-energy transition state in the CR−CCSD(T) calculations, whereas CCSD(T) favors the biradical pathway through the **ab**‡ transition state, independent of the method used to optimize the **ab**‡ and **ac**‡ geometries.

To examine how the results of our calculations are affected by the particular choice of the basis set, we performed additional CCSD(T) and CR−CCSD(T) calculations (and the corresponding (U)B3LYP calculations) using the smaller 6-31G(d) basis[33] and the larger 6-311++G(2d,2p) basis.[28,34] The use of the 6-31G(d) basis set enabled us to make a meaningful comparison of the CCSD(T) and CR−CCSD(T) results obtained in this work with the previously reported[12] results of the CAS-MP2 (CASSCF-based second-order multireference perturbation theory) calculations, in which the same basis set was employed. The much larger 6-311++G(2d,2p) basis set, consisting of 289 functions (which was the largest basis set we could afford at this time, since coupled cluster calculations reported in this paper require an explicit correlation of 38 electrons after freezing the core orbitals, and several geometries have to be examined), was used to examine how the relative CCSD(T), CR−CCSD(T), and (U)B3LYP energies of the initial transiton states for the biradical and concerted pathways, **ab**‡ and **ac**‡, respectively, vary with the basis set. The careful examination of these transition states with the high-level ab initio methods and with a large basis set of the 6-311++G(2d,2p) quality is very important. Indeed, although both the concerted and biradical mechanisms of the [2+2] cycloaddition of cyclopentyne to ethylene shown in Scheme 2 are multistep mechanisms, the formation of the biradical intermediate **b** in the biradical mechanism and the formation of the carbene intermediate **c** in the concerted mechanism, which involve the initial transition states **ab**‡ and **ac**‡, respectively, are the rate-determining steps which largely determine the pathway the reaction proceeds through. One has to make sure that the role of a basis set on the relative energies of these two transition states is examined. The barriers for the formation of the product molecule **p** from the intermediates **b** and **c** (corresponding to structures **bp**‡ and **cp**‡, respectively, in Scheme 2), as well as the barrier for the conversion of **b** into **c**, are much lower, so that the conversions of intermediates **b** and **c** into product **p** should be much more rapid. It is interesting, though, that the barrier for the conversion of the biradical intermediate **b** into the reaction product **p**, defined by transition state **bp**‡, is quite sensitive to the basis set. This may have an impact on the competition between the conversions of the biradical intermediate **b** into product **p** and carbene intermediate **c** (the latter proceeding through the transition state structure **bc**‡; cf. Scheme 2). This is one more reason for examining the [2+2] cycloaddition of cyclopentyne to ethylene with the large, 6-311++G(2d,2p) basis set.

The geometries used in the single-point CCSD(T) and CR−CCSD(T) calculations with the smaller 6-31G(d) basis set were optimized at the corresponding (U)B3LYP/6-31G(d) level. For the largest, 6-311++G(2d,2p) basis set employed in this study, we used the geometries reported in ref 12 optimized at the (U)B3LYP/6-311G(d,p) level and, for the **ab**‡ and **ac**‡ transition states, the geometries optimized at the (U)MP2/6-311G(d,p) level.

All of the CCSD(T) and CR−CCSD(T) calculations reported in this work were performed with the highly efficient coupled cluster programs described in ref 35, which form part of the GAMESS package.[36] GAMESS was also used to optimize the geometries of the **ab**‡ and **ac**‡ transition states with the (U)MP2/6-311G(d,p) approach. The additional (U)B3LYP calculations with the 6-31G(d) and 6-311++G(2d,2p) basis sets were performed with Gaussian 98. To obtain the CCSD(T) and CR−CCSD(T) free energies for all of the stationary points defining the concerted and biradical pathways shown in Scheme 2, we added the relevant single point CCSD(T) and CR−CCSD(T) energies to the corresponding zero-point vibrational energies (ZPVE) and thermal corrections (corresponding to 298 K) that were attained by the harmonic frequency calculations at the (U)B3LYP and (for **ab**‡ and **ac**‡ only) (U)MP2 levels.

Results and Discussion

We begin our discussion by examining the electronic and Gibbs free energies (relative to the reactants) of the stationary points defining the concerted and biradical pathways for the [2+2] cycloaddition of cyclopentyne to ethylene given in Tables 1 and 2, respectively. In addition to electronic energies, Table 1 includes the information about the values of the denominator D defining the CR−CCSD(T) method, eq 2, and the percent biradical character,[37] for all of the species involved in the concerted and biradical mechanisms. The free energy profiles at 298 K, defining the concerted and biradical pathways for the

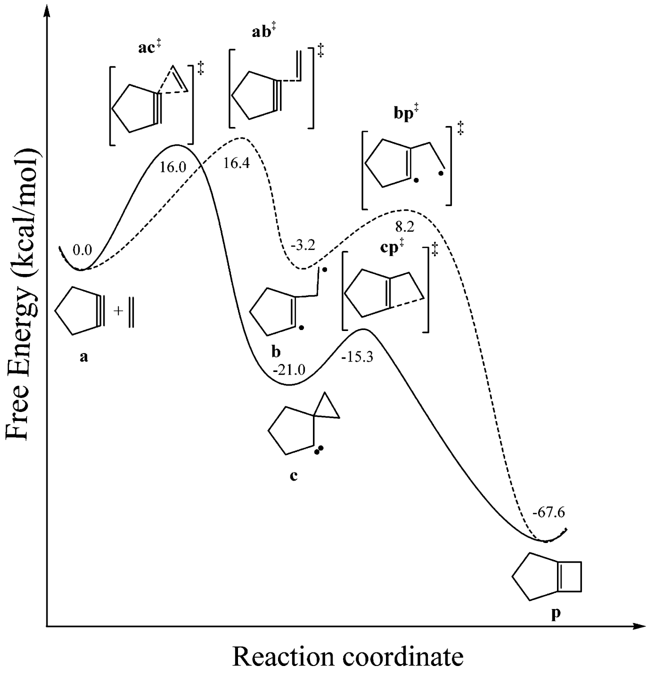


Figure 2. Free energy profiles for the concerted and biradical pathways characterizing the [2+2] cycloaddition of cyclopentyne to ethylene at 298 K. The free energy values were obtained by adding the ZPVE and thermal corrections corresponding to 298 K, obtained in the (U)B3LYP/6-311G(d,p) calculations, to the electronic energies obtained in the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations. The use of the (U)MP2/6-311G(d,p) geometries, ZPVEs, and thermal corrections and the CR−CCSD(T)/6-311++G(2d,2p)//(U)MP2/6-311G(d,p) electronic energies changes the free energy values for **ab**‡ and **ac**‡ to 15.0 and 13.3 kcal/mol, respectively.

[2+2] cycloaddition of cyclopentyne to ethylene, resulting from the highest-level CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations performed in this work are also depicted in Figure 2. As mentioned in the previous section, the selected geometric parameters of the stationary points along both pathways, resulting from the (U)B3LYP/6-311G(d,p) optimizations reported in ref 12 and the (U)MP2/6-311G(d,p) optimizations for the initial transition states **ab**‡ and **ac**‡ performed in this work, are shown in Figure 1. These structures clearly reflect the nature of various bond rearrangements along the biradical and concerted pathways shown in Scheme 2. The biradical pathway (**a**+**et** → **ab**‡ → **b** → **bp**‡ → **p**) begins with the formation of the C3−C2 bond in the biradical intermediate **b** via the asymmetric transition state **ab**‡. This step is followed by the rotation of the C3−C2−C1 fragment in **b** around the axis defined by the C3−C2 bond that leads to the formation of the cycloadduct **p** through the transition state **bp**‡. The concerted pathway (**a**+**et** → **ac**‡ → **c** → **cp**‡ → **p**) starts with the virtually symmetric approach of the C3 carbon atom of cyclopentyne by the ethylene molecule and the synchronous formation of the C3−C2 and C3−C1 bonds in the carbene intermediate **c** via the [2+1] transition state **ac**‡. This step is followed by the dissociation of the C3−C1 bond in **c** synchronized with the rotation of the C2−C1 fragment around the C3−C2 bond that leads to the formation of the new bond between the C1 carbon atom of ethylene and the carbon atom adjacent to C3 via the transition state **cp**‡. There is also a possibility of going from the biradical intermediate **b** to carbene intermediate **c** through the transition state **bc**‡. This step involves the formation of the C3−C1 bond, mostly by the reduction of the C3−C2−C1 angle (from 114° in **b**, through 89° in **bc**‡, to 64° in **c**). We refer the reader to the earlier papers[12,13] for further discussion of the geometrical features in the stationary points defining the cycloaddition of cyclopentyne to ethylene shown in Figure 1.

Before discussing which reaction mechanism is more probable, let us analyze the relative ability of high-level coupled cluster methods employed in this work to characterize the species involved in the biradical pathway. As mentioned in the Introduction, biradical species are very difficult to describe by the majority of ab initio methods. The strongly biradical species **b** and **bp**‡ create a severe situation for the electronic structure approaches, particularly for the CCSD(T) method. Indeed, as shown in Table 1, the CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculation predicts the energy of biradical **b**[38] relative to the reactants at the completely erroneous value of −361.7 kcal/mol. The unphysical nature of the CCSD(T) result can be best seen by comparing the CCSD(T) energy for the biradical intermediate **b** with the energy of the product species **p**, which is around (−84) to (−82) kcal/mol. If we believed the CCSD(T) approach, we would have to conclude that the biradical intermediate **b** is much more stable than the product, so that the reaction would never go to completion. It is, therefore, quite obvious that the CCSD(T) method fails to describe the biradical species **b**. A similar failure is observed for the **bp**‡ transition state, which also has a significant biradical character. In this case, the CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculation produces a large negative energy value of −57.2 kcal/mol. These failures of CCSD(T) are a consequence of the inability of the CCSD(T) method to describe biradicals. When the electronic state of interest has a significant biradical character and when the nondynamic correlation effects become important, the noniterative triples correction $N^{(T)}$obtained with the CCSD(T) approach assumes unphysically large negative values.[18,19,23] This means that we cannot fully trust CCSD(T) in studies of reaction mechanisms involving a competition between biradical and concerted mechanisms. For example, although the CCSD(T) method performs reasonably well for the transition state **ab**‡, which is an initial and highest energy transition state for the biradical pathway that determines the rate of the biradical mechanism, the degree of the biradical character of **ab**‡ is significantly higher than the degree of the biradical character of the initial and highest energy transition state for the concerted pathway, **ac**‡, which determines the rate of the concerted mechanism (see Table 1). Since the CCSD(T) approach produces unphysical energy lowerings whenever the biradical character of the electronic wave functions becomes significant, it also artificially favors the biradical transition states over the transition state structures that have a smaller degree of the biradical character. Thus, as one might expect, the CCSD(T) and CR−CCSD(T) results for the concerted transition state **ac**‡, which has a small degree of the biradical character, agree very well (cf. Tables 1 and 2), but there are significant, ∼2 kcal/mol, differences between the CCSD(T) and CR−CCSD(T) results for the transition state **ab**‡, which has a higher degree of the biradical character, since the CCSD(T) approach artificially lowers the energy of **ab**‡ relative to **ac**‡. In consequence, we cannot rely on the CCSD(T) method when it predicts the biradical mechanism for the [2+2] cycloaddition of cyclopentyne to ethylene, since the energy of the more biradical transition state **ab**‡ resulting from the CCSD(T) calculations is artificially lowered relative to the energy of the less biradical concerted transition state **ac**‡. As already mentioned, the CCSD(T) approach traps the cyclopentyne+ethylene system in the biradical intermediate structure **b**, which makes the CCSD(T) calculations even less trustworthy.

TABLE 3: Energies[a] (in kcal/mol) of the Stationary Points[b] along the Concerted and Biradical Reaction Paths Characterizing the [2+2] Cycloaddition of Cyclopentyne to Ethylene Calculated with the CCSD(T), CR−CCSD(T), and CAS-MP2 Approaches and the 6-31G(d) Basis Set

	ab‡	**b**	**bp**‡	**bc**‡	**ac**‡	**c**	**cp**‡	**p**
CCSD(T)[c]	4.0	−222.5	−65.7	−8.3	6.7	−35.7	−30.0	−86.5
CR−CCSD(T)[c]	5.7	−17.2	−11.6	−7.7	6.1	−38.4	−32.2	−89.0
CAS-MP2[d]	12.8	−15.7	−13.5	−0.3	13.2	−27.6	−18.5	−74.5

[a] Electronic energies relative to the reactants (for the CR−CCSD(T) approach, which is not strictly size extensive, the reactant energy is obtained by calculating the energy of a noninteracting complex of cyclopentyne and ethylene separated by a large distance; we used a distance of 200 Å). [b] For the explanation of the abbreviations used to label the stationary points, see ref 2 (see, also, Scheme 1 and Figure 1). [c] The (U)B3LYP/6-31G(d) geometries were used. [d] From ref 12.

In general, as shown in Table 1, there is a clear correlation between the degree of failure of the CCSD(T) approach and the percent biradical character of a transition state or intermediate of interest. On the other hand, the CR−CCSD(T) method, whose primary success originates from the improvement of the CCSD(T) results through a well-balanced description of triples corrections to CCSD energies in the presence of strong nondynamic correlation effects[18,19,22,23] (which the CCSD(T) approach cannot provide), produces uniformly accurate results for all stationary points defining the biradical and concerted pathways. The improvements offered by the CR−CCSD(T) approach can largely be understood if we examine the values of the denominator D, which “renormalizes” the triples corrections to CCSD energies, for all of the stationary points listed in Tables 1−3. As shown in Table 1, the denominator D entering eq 2 becomes large when the percent biradical character obtained, for example, by calculating the occupation number for the highest occupied natural orbital of CASSCF, becomes large. Thus, whenever the biradical character of the transition state or intermediate in question becomes significant, as is the case for the **b** and **bp**‡ structures, the excessively large negative triples correction of the CCSD(T) theory, which causes the failure of the CCSD(T) approach in such situations, is damped by the correspondingly large denominator D (cf., also, our recent study of the Cope rearrangement of 1,5-hexadiene[23] for similar findings). For the structures with small biradical character, such as **ac**‡, **c**, **cp**‡, or **p**, for which D is relatively small, the CR−CCSD(T) results agree reasonably well with those obtained with the CCSD(T) method, since in these cases there is very little or no need to damp triples corrections (see Tables 1−3). For strong biradicals, such as **b** or **bp**‡, for which the standard CCSD(T) method fails, the CR−CCSD(T) results are in reasonably good agreement with the results of multireference CAS-MP2 calculations (see Table 3). Indeed, as shown in Table 3, the energy estimates provided by the CR−CCSD(T) and CAS-MP2 methods for the strongly biradical **b** and **bp**‡ structures differ by only 1.5 and 1.9 kcal/mol, respectively. For structures with small or moderate degree of biradical character, for which the CR−CCSD(T) and CCSD(T) methods agree with each other, the differences between the CR−CCSD(T) and CAS-MP2 results are bigger, but we must remember that, compared to CCSD(T) or CR−CCSD(T), CAS-MP2 offers a lower-order treatment of dynamic correlation effects, which should be described at the relatively high level and balanced with nondynamic correlation effects to obtain a uniformly accurate description of reactive potential energy surfaces. For reactions involving biradical transition states and intermediates, the CR−CCSD(T) approach offers a more accurate and more balanced description of dynamic and nondynamic correlation effects when compared to the second-order multireference perturbation theory calculations, as demonstrated in the recent studies of the isomerizations of bicyclopentene and tricyclopentane into cyclopentadiene[22] and the Cope rearrangement of 1,5-hexadiene.[23] At least for the medium-size molecular systems of the type of the system studied in this work, the CR−CCSD(T) approach preserves a highly accurate description of dynamic correlation effects offered by the CCSD(T) approach in regions characterized by a small degree of configuration quasi-degeneracy, while providing a balanced description of dynamic and nondynamic correlation effects, which can often compete with the best multireference approaches, in regions characterized by large quasi-degeneracy effects, including biradicals.[18,19,22,23] This observation plus the use of large basis sets, such as 6-311++G(2d,2p), in this study make us believe that the CR−CCSD(T) results for the [2+2] cycloaddition of cyclopentyne to ethylene reported in this paper are more accurate than the results of earlier ab initio calculations for the same reaction, including the multireference CAS-MP2 and MR-MP2 results described in refs 12 and 13, respectively.

In view of the above discussion and based on the results of the CR−CCSD(T) calculations, we believe that the [2+2] cycloaddition of cyclopentyne to ethylene largely proceeds through a concerted pathway shown in Scheme 2. According to the CR−CCSD(T) calculations with the largest, 6-311++G(2d,2p) basis set used in this study, employing the geometries, ZPVEs, and thermal corrections obtained with the (U)B3LYP/6-311G(d,p) approach, the free energies of the initial transition states along the biradical and concerted pathways, **ab**‡ and **ac**‡, respectively, which are the highest energy transition states defining the rate determining steps for the biradical and concerted mechanisms, are 16.4 and 16.0 kcal/mol, respectively. The elementary kinetic arguments (cf. eqs 3−5 below), based on calculating the ratio of the rate constants corresponding to the **a**+**et**→ **b** and **a**+**et**→ **c** initial processes that proceed through **ab**‡ and **ac**‡, respectively,[39] enable us to conclude that the 0.4 kcal/mol difference between the free energies of **ab**‡ and **ac**‡ obtained in the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculation is sufficient to produce the relatively high stereoretention of 83%. Indeed, if we realize that the reactants that follow the concerted pathway must retain the stereochemistry and if we assume that at the same time the reactants that follow the biradical pathway cause the stereorandomization (due to the almost unhindered rotation of the CH_2 end group of ethylenic fragment in biradical **b** about the corresponding single bond), we can write[39]

$$\%\ \text{Stereoretention} = \left[1 - \frac{1}{2(k_{\mathbf{c}}/k_{\mathbf{b}} + 1)}\right] \times 100 \qquad (3)$$

where, according to transition state theory, the ratio of the rate constants $k_{\mathbf{c}}$ to $k_{\mathbf{b}}$ for the **a**+**et**→ **c** and **a**+**et**→ **b** processes that proceed through **ac**‡ and **ab**‡, respectively, can be estimated as follows:

$$\frac{k_{\mathbf{c}}}{k_{\mathbf{b}}} = \exp\left(-\frac{\Delta\Delta G^{\ddagger}}{RT}\right) \qquad (4)$$

Here

$$\Delta\Delta G^{\ddagger} = \Delta G_{\mathbf{ac}^{\ddagger}} - \Delta G_{\mathbf{ab}^{\ddagger}} \qquad (5)$$

is the difference between the free energies for **ac**‡ and **ab**‡, respectively. If, as implied by the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations, the

TABLE 4: Free Energy Differences (kcal/mol) and Rate Constant Ratios for the a+et→ c and a+et→ b Initial Processes of the Concerted and Biradical Mechanisms that Proceed through the ac‡ and ab‡ Transition States, Respectively, and the Corresponding Values of the Percent Stereoretention Calculated at Different Levels of Theory

level of theory	$\Delta\Delta G^{\ddagger}$	$k_{\mathbf{c}}/k_{\mathbf{b}}$	% stereoretention[a,b]
CCSD(T)/6-311++G(2d,2p)[c,d]	2.2 (1.0)	0.03 (0.19)	51[e] (58)
CASSCF(6,6)/6-31G(d)	only biradical path	0	50[e]
CAS-MP2/6-31G(d)[f]	1.4	0.09	54[e]
CR−CCSD(T)/6-311++G(2d,2p)[c,d]	−0.4 (−1.7)	2.0 (16.4)	83 (97)
(U)B3LYP/6-311G(d,p)	−0.6	2.8	87
(U)B3LYP/6-311++G(2d,2p)[c]	−1.1	5.9	93

[a] Experimental stereoretention is 99%. [b] Calculated using eq 3. [c] The CCSD(T), CR−CCSD(T), and (U)B3LYP free energies corresponding to the 6-311++(2d,2p) basis set were calculated using the ZPVE and thermal corrections obtained in the (U)B3LYP/6-311G(d,p) calculations. [d] The numbers in parentheses are based on the free energies obtained by adding the electronic energies resulting from the single point coupled cluster calculations, employing the UMP2/6-311G(d,p) (**ab**‡) and RMP2/6-311G(d,p) (**ac**‡) optimized geometries, to the ZPVE and thermal corrections obtained in the corresponding (U)MP2/6-311G(d,p) calculations. [e] Complete or almost complete stereorandomization. [f] Based on the CAS-MP2 results reported in ref 12, where the authors used the CASSCF(6,6)/6-31G(d) optimized geometry for **ab**‡ and the RB3LYP/6-311G(d,p) optimized geometry for **ac**‡ (the CASSCF(6,6)/6-31G(d) optimization for **ac**‡ failed to converge).

free energy difference $\Delta\Delta G^{\ddagger} = \Delta G_{\mathbf{ac}^{\ddagger}} - \Delta G_{\mathbf{ab}^{\ddagger}}$ is −0.4 kcal/mol, so that the ratio of $k_{\mathbf{c}}$ to $k_{\mathbf{b}}$ is very close to 2, eq 3 gives the percent stereoretention of 83% (see Table 4). This value is not as high as the 99% stereoretention observed experimentally, but several factors have to be considered when comparing the theoretical stereoretention of 83%, resulting from the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations, with the experimental value of 99%. Let us discuss some of these factors.

First of all, it is quite possible that the actual free energy difference $\Delta\Delta G^{\ddagger}$, eq 5, is more negative than that obtained in the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations. Indeed, the use of the (U)MP2/6-311G(d,p) geometries, ZPVEs, and thermal corrections and the CR−CCSD(T)/6-311++G(2d,2p) single-point energies leads to the increase of the difference between the free energies of **ab**‡ and **ac**‡ from 0.4 to 1.7 kcal/mol (see Table 2). The 1.7 kcal/mol difference between the free energies of **ab**‡ and **ac**‡ ($\Delta\Delta G^{\ddagger} = -1.7$ kcal/mol) is sufficient to increase the percent stereoretention, calculated using eq 3, to 97% (see Table 4). Although there is a 14% difference between the stereoretention values calculated with the (U)B3LYP/6-311G(d,p) and (U)MP2/6-311G(d,p) geometries and harmonic frequencies, both sets of the CR−CCSD(T)/6-311++G(2d,2p) calculations for **ab**‡ and **ac**‡ carried out in this work provide the relatively large values of the percent stereoretention, which are in much better agreement with experiment than those obtained with other ab initio methods, clearly pointing to the predominantly concerted mechanism of the cycloaddition of cyclopentyne to ethylene. One should, however, continue to examine this aspect of our and earlier calculations further. We hope to be able to perform the relevant CR−CCSD(T) geometry optimizations and frequency calculations in the not-too-distant future, when the suitable computer codes are developed. Second, the computational studies of the [2+2] cycloaddition of cyclopentyne to alkenes discussed in this article involve an unsubstituted ethylene and there is no steric hindrance in the intermediate **b** formed from an unsubstituted ethylene that could, for example, prevent the fast establishment of the rotational equilibrium. The actual experimental studies of the stereochemistry of the [2+2] cycloaddition of cyclopentyne to alkenes are conducted by using substituted ethylenes. The intermediate **b** formed from a substituted ethylene will clearly be more “packed” compared to an unsubstituted one. This should make the rotation around the broken C2−C1 π bond in the ethylenic fragment in **b** more difficult, resulting in a further increase of stereoretention. Third, the observed stereospecificity may be affected by the lifetime of the biradical intermediate **b**. The 83% value obtained in the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations is essentially the minimum value of the percent stereoretention, which is obtained if the lifetime of the biradical intermediate **b** is long enough to reach the rotational equilibrium with its rotamer **b′**, randomizing the stereochemistry of the molecules proceeding through the biradical pathway (see Figure 3a). However, if the lifetime of **b** is shorter than the lifetime needed to reach the rotational equilibrium **b**↔**b′**, there will be no or very little stereorandomization and the stereochemistry of the molecules proceeding along the biradical path will be largely preserved, independent of whether they proceed via the **b**→**c**→**p** or **b**→**p** channel, leading to 100% stereoretention (see Figure 3b). Furthermore, some additional stereoretention may result from the conversion of the biradical intermediate **b** into the carbene intermediate **c** if the lifetime of **b** is short (so that the stereospecificity is not lost), since, according to our CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations, the free energy barrier for the internal conversion of biradical **b** into carbene **c** (corresponding to the transition state **bc**‡) is considerably lower than the barrier for the formation of the reaction product **p** from **b** (defined by the free energy of the transition state **bp**‡; see Table 2; cf., also, ref 13 for related remarks). Finally, the difference between the CR−CCSD(T) energy of structure **ab**‡, which is the rate determining initial transition state that defines the biradical mechanism and which has a higher degree of the biradical character when compared to the [2+1] concerted transition state **ac**‡ (cf. Table 1) and the CR−CCSD(T) energy of structure **ac**‡, which is the less biradical initial transition state defining the concerted mechanism, seems to increase with the basis set size (see Table 5). Thus, we may expect that the difference between the CR−CCSD(T) energies of **ab**‡ and **ac**‡ extrapolated to the limit of the infinite basis set is somewhat larger than that obtained in the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations, increasing the percent stereoretention above 83%. It would be useful to perform the CR−CCSD(T) calculations with a sequence of the correlation consistent basis sets[40] in the future to verify this suggestion (we are unable to perform such calculations now, since we would have to consider basis sets of cc-pVQZ or cc-pV5Z quality, which are too large for us at this time when systems as large as cyclopentyne plus ethylene are considered). Interestingly enough, a similar pattern is observed in the CR−CCSD(T) calculations for the transition states **bp**‡ and **bc**‡. The free energy of the more biradical transition state **bp**‡, which defines the formation of the reaction product **p** from the biradical intermediate **b,** significantly increases with the size of the basis set, whereas the free energy of the transition state **bc**‡, which has a smaller degree of the

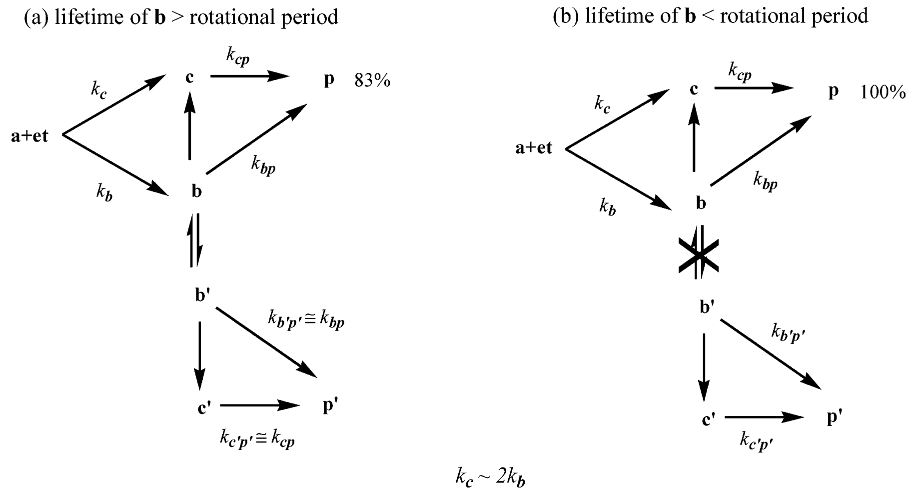


Figure 3. Schematic representation of the biradical and concerted pathways for the [2+2] cycloaddition of cyclopentyne to ethylene. (a) The situation where the lifetime of biradical intermediate **b** is considerably longer than its rotational period, allowing the rotational equilibrium **b**↔**b′** to be reached. (b) The situation where the lifetime of intermediate **b** is shorter than its rotational period, preventing the rotational equilibrium **b**↔**b′** from being reached. Numerical values in % represent the percent stereoretention values (calculated for case (a) with eq 3, using the results of the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations; if we relied on the CR−CCSD(T)/6-311++G(2d,2p)//(U)MP2/6-311G(d,p) calculations for **ab**‡ and **ac**‡, the ratio of k_c to k_b and the corresponding percent stereoretention would be 16.4 and 97%, respectively).

TABLE 5: Energies[a] (in kcal/mol) of Structures ab‡ and ac‡ (Transition State Structures Defining the Rate Determining Steps of Biradical and Concerted Mechanisms, Respectively)[b] Obtained with the CCSD(T), CR−CCSD(T), and (U)B3LYP Methods and Various Basis Sets

	CCSD(T)		CR−CCSD(T)		(U)B3LYP	
	ab‡	**ac**‡	**ab**‡	**ac**‡	**ab**‡	**ac**‡
6-31G(d)	4.0	6.7	5.7	6.1	1.7	0.3
6-311G(d,p)	4.6	5.9	6.9	5.7	3.3	1.7
6-311++G(2d,2p)[c]	4.2 (4.6)	5.3 (6.1)	6.5 (6.0)	5.0 (5.0)	4.0	1.9

[a] Electronic energies relative to the reactants (for the CR−CCSD(T) approach, which is not strictly size extensive, the reactant energy is obtained by calculating the energy of a noninteracting complex of cyclopentyne and ethylene separated by a large distance; we used a distance of 200 Å). [b] The (U)B3LYP/6-311G(d,p) geometries from ref 12 were used in the calculations with the 6-311G(d,p) and 6-311++G(2d,2p) basis sets. For the 6-31G(d) basis set, the geometries were obtained in the (U)B3LYP/6-31G(d) calculations performed in this work. [c] The numbers in parentheses represent the results of single point coupled cluster calculations employing the geometries optimized at the UMP2/6-311G(d,p) (**ab**‡) and RMP2/6-311G(d,p) (**ac**‡) levels of theory.

biradical character compared to **bp**‡ and which defines the conversion of biradical **b** into carbene **c**, remains almost insensitive to the basis set size. Thus, we may expect that in the limit of the infinite basis set the barrier for the conversion of **b** into **c** may become even lower relative to the barrier for the formation of the reaction product **p** from the biradical intermediate **b**, compared to the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculation. We can conclude that the concerted mechanism is the dominant pathway for the [2+2] cycloaddition reaction of cyclopentyne to ethylene, leading to high stereoretention which can be further enhanced by the steric and lifetime factors described above. As a matter of fact, according to the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations, the entire biradical pathway is considerably higher in energy than the concerted pathway (see Figure 2).

Although the percent stereoretention obtained in the CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations is not as high as that observed experimentally (cf., however, the CR−CCSD(T)/6-311++G(2d,2p)//(U)MP2/6-311G(d,p) results in Table 4), the large scale CR−CCSD(T) calculations with the sizable 6-311++G(2d,2p) basis set are the only high-level ab initio calculations at this time which suggest that the concerted mechanism for the [2+2] cycloaddition of cyclopentyne to ethylene (a mechanism consistent with the orbital symmetry rules) is entirely possible. The CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations provide a high degree of stereoretention which is relatively close to experiment (see Table 4). The CR−CCSD(T)/6-311++G(2d,2p)//(U)MP2/6-311G(d,p) calculations for the transition states **ab**‡ and **ac**‡ lead to even better agreement between the theoretical and experimental stereoretention values. This should be contrasted with the CCSD(T), CASSCF(6,6), and CAS-MP2 calculations which clearly favor the biradical mechanism and low stereoretention. As mentioned earlier, the CCSD(T) method favors the biradical mechanism by artificially lowering the energy of the transition state **ab**‡ which has a partly biradical character, relative to the concerted transition state **ac**‡ which has a very small degree of biradical character. Interestingly enough, this finding seems to be independent of the method used to optimize the geometries of the initial, rate-determining transition states **ab**‡ and **ac**‡. Indeed, as shown in Tables 2 and 4, the free energy difference $\Delta\Delta G^{\ddagger}$ between **ac**‡ and **ab**‡, eq 5, obtained at the CCSD(T)/6-311++G(2d,2p)//(U)MP2/6-311G(d,p) level, which in the CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations is 2.2 kcal/mol, remains positive and large enough to produce the low stereoretention of only 58% (see Table 4). As shown in Table 5, the CCSD(T) results do not change too much with the basis set either, favoring the biradical mechanism all along. In fact, the overall description of the biradical pathway by the CCSD(T) method, where the intermediate **b** has an energy below the energy of a product, is rather poor, so that we do not think that one can trust the CCSD(T) predictions regarding the mechanism of the [2+2] cycloaddition of cyclopentyne to ethylene too much. The CASSCF(6,6) and CAS-MP2 methods favor the biradical mechanism too, which is a consequence of the imbalanced description of the biradical and concerted transition states and intermediates by these methods, particularly in the former case. The CASSCF method describes the nondynamic correlation effects only and it is impossible to obtain an accurate and well-balanced description of reactive potential energy surfaces when the dynamical correlation effects are neglected. CAS-MP2 describes dynamic correlation effects, but, as mentioned earlier, this is a low-order description of these effects which can only be adequate when the biradical character is strong and when the nondynamic correlation effects dominate. For weak biradicals or structures that have no biradical character, CAS-MP2 provides a considerably less accurate description of dynamic correlation effects, which dominate in such situations (cf., e.g., the large differences between the CAS-MP2 and CCSD(T) or CR−CCSD(T) energies for the product **p** molecule or the **cp**‡ transition state, which are largely closed-shell systems, shown in Table 3). Thus, CAS-MP2 and other low-order multireference perturbation theory techniques may have difficulty in providing a well-balanced description of biradical and closed-shell regions of the potential energy surface, favoring biradical structures which the CAS-MP2 approach describes in a relatively accurate manner compared to closed-shell species. As a matter of fact, we could not find the concerted transition state **ac**‡, which is an initial transition state defining the concerted pathway, in the underlying CASSCF(6,6) calculations that precede the calculations of the CAS-MP2 energy.[41] This can be a purely numerical problem or a problem with CASSCF. In any case, we have a situation here where either the transition state **ac**‡ does not exist on the CASSCF(6,6) surface or, if we rely on the (U)B3LYP/6-311G(d,p) geometries, the CASSCF(6,6) and CAS-MP2 energies of the biradical transition state **ab**‡ are lower than those of the concerted transition state **ac**‡. In either case, the CASSCF(6,6) approach and the corresponding CAS-MP2 method favor the biradical mechanism and low stereoretention, which seem to disagree with the experiment. Moreover, according to CAS-MP2 calculations reported in ref 12, the formation of the product molecule **p** from the biradical intermediate **b** is strongly favored, when compared to the internal conversion of the biradical intermediate **b** into the carbene intermediate **c**, making the concerted mechanism even less probable, in contrast to the predictions offered by the accurate CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations, which show that the internal **b**→**c** conversion that precedes the final **c**→**p** step has a considerably lower barrier than the **b**→**p** step (see Table 2).

Remarkably, the only other method that seems to agree reasonably well with the CR−CCSD(T) calculations is the DFT (U)B3LYP approach. Our simple modeling of the percent stereoretention, based on eq 3 and the (U)B3LYP/6-311G(d,p) results, leads to the 87% stereoretention, in reasonable agreement with experiment. The (U)B3LYP/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculation increases this value to 93%. Although DFT methods are not always trustworthy, the (U)B3LYP approach seems to be able to balance dynamic and nondynamic correlation effects for reactions involving biradical species reasonably well (cf., e.g., refs 22, 23, and 42). The activation free energies for the biradical and concerted pathways, defined by the **ab**‡ and **ac**‡ transition states, of 13.2 and 12.6 kcal/mol, respectively, obtained with the (U)B3LYP/6-311G(d,p) approach, and 13.9 and 12.8 kcal/mol, respectively, obtained with the (U)B3LYP/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) approach, are lower than those obtained with the CR−CCSD(T)/6-311G(d,p)//(U)B3LYP/6-311G(d,p) or CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) methods, which give 16.7 and 16.6 or 16.4 and 16.0 kcal/mol, respectively, but this reflects the fact that DFT methods underestimate activation barriers in many cases,[43] whereas the CR−CCSD(T) approach may slightly overestimate them.[18g,23] On the other hand, the CR−CCSD(T)/6-311++G(2d,2p) values of the free energies of **ab**‡ and **ac**‡ obtained with the geometries and harmonic frequencies calculated at the (U)MP2/6-311G(d,p) level, of 15.0 and 13.3 kcal/mol, respectively, although still higher than the corresponding (U)B3LYP values, are in better agreement with the results of the (U)B3LYP/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) calculations. Based on our best calculations employing the single-point CR−CCSD(T)/6-311++G(2d,2p) and (U)B3LYP/6-311++G(2d,2p) energies, we can conclude that the [2+2] cycloaddition of cyclopentyne to ethylene is a predominantly concerted process, with an activation barrier between 13 and 16 kcal/mol. The CR−CCSD(T)/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) and (U)B3LYP/6-311++G(2d,2p)//(U)B3LYP/6-311G(d,p) results for the free energy of the reaction under study in this work agree very well, producing the reaction free energy at $T = 298$ K on the order of (−68) to (−66) kcal/mol.

Conclusion

The mechanism of the [2+2] cycloaddition of cyclopentyne to ethylene has been studied using the standard and completely renormalized coupled cluster methods with singles, doubles, and noniterative triples (CCSD(T) and CR−CCSD(T)). To examine the dependence of the results on the basis set, a few basis sets, including the large, 6-311++G(2d,2p) basis, have been employed. The results of coupled cluster calculations have been analyzed and compared with those obtained earlier with the DFT and low-order multireference methods. We have shown that the CR−CCSD(T) method makes the concerted pathway, which is allowed by the orbital symmetry rules, and the high stereoretention observed experimentally entirely possible, but we had to use larger basis sets to obtain this finding. The CR−CCSD(T) results largely agree with the results of the DFT (U)B3LYP calculations. The popular CCSD(T) method and low-order multireference methods favor the less probable biradical mechanism and low stereoretention, which do not agree with experimental data. We have provided an explanation why the CCSD(T) and low-order multireference methods may produce the results that cannot be reconciled with experiment. We have also shown that the standard CCSD(T) approach produces an erroneous description of some transition states and intermediates, particularly those which have a significant biradical character. The CR−CCSD(T) calculations indicate that the reaction is a highly exothermic ($\Delta G_r^{298} \cong -68$ kcal/mol), predominantly concerted process with a relatively low activation barrier on the order of 13−16 kcal/mol which enables its thermal occurrence.

As indicated in this study, the greatest advantage of CR−CCSD(T) over CCSD(T) is the high accuracy of the CR−CCSD(T) approach in describing biradical transition states and intermediates, which cannot be described by the standard CCSD(T) method. We have demonstrated that the CR−CCSD(T) approach provides an accurate and balanced description of biradical and closed-shell regions of reactive potential energy surfaces. We have observed similar behavior in other studies of organic reaction mechanisms.[22,23] In addition to the high accuracies in describing biradicals that the CR−CCSD(T) method offers, the CR−CCSD(T) approach is characterized by the ease-of-applicability, which can only be matched by the standard single-reference "black box" methods. The CR−CCSD(T) method does not require choosing active orbitals on a molecule-by-molecule basis or using other elements of multireference calculations. However, as the calculations for the biradical intermediate **b** show, one has to make sure that the underlying solution of the CCSD equations represents the same physical solution as those defining other regions of a given molecular potential energy surface. This remark is important, since biradical regions are characterized by larger cluster amplitudes and one has to make sure that the properly converged values of these amplitudes are obtained.

Acknowledgment. This work has been supported by the NATO-B1 research fellowship, directed by The Scientific and Technical Research Council of Turkey (TUBITAK), and by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy (Grant No. DE-FG02-01ER15228). The calculations were performed on a 64-processor Altix 3700 system provided by the High Performance Computing Center at Michigan State University and on 32- and 16-processor Origin systems in the Department of Chemistry at Michigan State University funded through a grant from the National Science Foundation, Chemical Instrumentation Program (Grant No. CHE-9974834), and Michigan Center for Biological Information.

Supporting Information Available: The CR−CCSD(T), CCSD(T), and (U)B3LYP energies of all stationary points along the biradical and concerted pathways of the [2+2] cycloaddition reaction of cyclopentyne to ethylene. The Cartesian coordinates of the (U)B3LYP/6-31G(d) optimized geometries of all stationary points and the (U)MP2/6-311G(d,p) optimized geometries of the reactants and transition states **ab**‡ and **ac**‡ are included too. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Woodward, R. B.; Hoffmann, R. Angew. *Chem., Int. Ed. Engl.* **1969**, *8*, 781−853.

(2) The following abbreviations are used throughout this paper: **a**, alkyne reactant (in the present paper, cyclopentyne); **b**, biradical intermediate; **c**, carbene intermediate; **p**, product (cycloadduct). Ethylene is labeled by **et**. The transition states are labeled by combining the letter codes of the associated minima on the potential energy surface. For example, **ab**‡ designates a transition state connecting the alkyne reactant **a** with the biradical intermediate **b**, which is the initial transition state along the biradical pathway for the **a**+**et** → **p** reaction, whereas **ac**‡ designates a transition state connecting alkyne **a** with the carbene intermediate **c**, which is the initial transition state along the concerted pathway for the **a**+**et** → **p** reaction. Other examples of transition states discussed in this paper include **bp**‡, **cp**‡, and **bc**‡, which connect the biradical intermediate **b** with the product **p**, the carbene intermediate **c** with the product **p**, and the biradical and carbene intermediates **b** and **c**, respectively.

(3) Fitjer, L.; Kliebisch, V.; Wehle, D.; Modaressi, S. *Tetrahedron Lett.* **1982**, *23*, 1661−1664.

(4) Fitjer, L.; Modaressi, S. *Tetrahedron Lett.* **1983**, *24*, 5495−5498.

(5) Olivella, S.; Pericas, M. A.; Riera, A.; Sole, A. *J. Am. Chem. Soc.* **1986**, *108*, 6884−6888.

(6) Gilbert J. C., Baze M. E. *J. Am. Chem. Soc.* **1984**, *106*, 1885−1886.

(7) Olivella, S.; Pericas, M. A.; Riera, A.; Sole, A. *J. Chem. Soc., Perkin Trans. 2*, **1986**, 613−617.

(8) Gilbert, J. C.; Kirschner, S. *Tetrahedron Lett.* **1993**, *34*, 599−602.

(9) Gilbert, J. C.; Kirschner, S. *Tetrahedron Lett.* **1993**, *34*, 603−606.

(10) Johnson R. P.; Daoust K. J. *J. Am. Chem. Soc.* **1995**, *117*, 362−367.

(11) Laird, D. W.; Gilbert J. C. *J. Am. Chem. Soc.* **2001**, *123*, 6704−6705.

(12) Özkan, I.; Kinal, A. *J. Org. Chem.* **2004**, *69*, 5390−5394.

(13) Bachrach, S. M.; Gilbert J. C. *J. Org. Chem.* **2004**, *69*, 6357−6364.

(14) McDouall, J. J.; Peasley, K.; Robb, M. A. *Chem. Phys. Lett.* **1988**, *148*, 183−189.

(15) (a) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983−7992. (b) Nakano, H. *Chem. Phys. Lett.* **1993**, *207*, 372−378.

(16) (a) Hirao, K. *Chem. Phys. Lett.* **1992**, *190*, 374−380. (b) Hirao, K. *Chem. Phys. Lett.* **1992**, *196*, 397−403. (c) Hirao, K. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 517−526. (d) Hirao, K. *Chem. Phys. Lett.* **1993**, *201*, 59−66.

(17) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479−483.

(18) (a) Piecuch, P.; Kowalski, K. In *Computational Chemistry: Reviews of Current Trends*; Leszczyński, J., Ed.; World Scientific: Singapore, 2000; Vol. 5, pp 1−104. (b) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2000**, *113*, 18−35. (c) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2000**, *113*, 5644−5652. (d) Kowalski, K.; Piecuch, P. *Chem. Phys. Lett.* **2001**, *344*, 165−175. (e) Piecuch, P.; Kucharski, S. A.; Špirko, V.; Kowalski, K. *J. Chem. Phys.* **2001**, *115*, 5796−5804. (f) McGuire, M. J.; Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2002**, *117*, 3617−3624. (g) McGuire, M. J.; Piecuch, P.; Kowalski, K.; Kucharski, S. A.; Musiał, M. *J. Phys. Chem. A* **2004**, *108*, 8878−8893. (h) Kowalski, K.; Piecuch, P. *J. Chem. Phys.* **2005**, *122*, 074107−1−074107−12.

(19) (a) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O.; Kucharski, S. A. In *Low-Lying Potential Energy Surfaces*; Hoffmann, M. R., Dyall, K. G., Eds.; ACS Symposium Series, Vol. 828; American Chemican Society: Washington, DC, 2002; pp 31−64. (b) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O.; McGuire, M. J. *Int. Rev. Phys. Chem.* **2002**, *21*, 527−655. (c) Piecuch, P.; Pimienta, I. S. O.; Fan, P.-D.; Kowalski, K. In *Progress in Theoretical Chemistry and Physics*, Vol. 12; *Advanced Topics in Theoretical Chemical Physics*; Maruani, J., Lefebvre, R., Brändas, E., Eds.; Kluwer: Dordrecht, The Netherlands, 2003; pp 119−206. (d) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O.; Fan, P.-D.; Lodriguito, M.; McGuire, M. J.; Kucharski, S. A.; Kuś, T.; Musiał, M. *Theor. Chem. Acc.* **2004**, *112*, 349−393.

(20) Hu, Y.; Hirai, K.; Tomioka, H. *J. Phys. Chem. A*, **1999**, *103*, 9280−9284.

(21) Itakura, H.; Mizuno. H.; Hirai, K.; Tomioka, H. *J. Org. Chem.* **2000**, *65*, 8797−8806.

(22) Özkan, I.; Kinal, A.; Balci, M. *J. Phys. Chem. A* **2004**, *108*, 507−514.

(23) McGuire, M. J.; Piecuch, P. *J. Am. Chem. Soc.* **2005**, *127*, 2608−2614.

(24) (a) Coester, F. *Nucl. Phys.* **1958**, *7*, 421−424. (b) Coester, F.; Kümmel, H. *Nucl. Phys.* **1960**, *17*, 477−485. (c) Čížek, J. *J. Chem. Phys.* **1966**, *45*, 4256−4266. (d) Čížek, J. *Adv. Chem. Phys.* **1969**, *14*, 35−89.

(25) (a) Bartlett, R. J. In *Modern Electronic Structure Theory*, Part I; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; pp 1047−1131. (b) Paldus, J.; Li, X. *Adv. Chem. Phys.* **1999**, *110*, 1−175. (c) Crawford, T. D.; Schaefer III, H. F. *Rev. Comput. Chem.* **2000**, *14*, 33−136. (d) Gauss, J. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; Wiley: Chichester, U.K., 1998; Vol. 1, pp 615−636.

(26) (a) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910−1918. (b) Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F., III *J. Chem. Phys.* **1987**, *86*, 2881−2890. (c) Scuseria, G. E.; Janssen, C. L.; Schaefer III, H. F. *J. Chem. Phys.* **1988**, *89*, 7382−7387. (d) Lee, T. J.; Rice, J. E. *Chem. Phys. Lett.* **1988**, *150*, 406−415. (e) Piecuch, P.; Paldus, J. *Int. J. Quantum Chem.* **1989**, *36*, 429−453.

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(28) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650−654.

(29) (a) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718−8733. (b) Watts, J. D.; Gauss, J.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *200*, 1−7. (c) Lee, T. J.; Rendell, A. P. *J. Chem. Phys.* **1991**, *94*, 6229−6236. (d) Scuseria, G. E. *J. Chem. Phys.* **1991**, *94*, 442−447.

(30) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036−6043.

(31) Houk, K. N.; Beno, B. R.; Nendel, M.; Black, K.; Yoo, H. Y.; Wilsey, S.; Lee, J. K. *THEOCHEM* **1997**, *169*, 398−399.

(32) Hrovat, D. A.; Beno, B. R.; Lange, H.; Yoo, H. Y.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 7456−7460.

(33) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261.

(34) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265−3269. (b) Clark, T.; Chandrasekhar, J.; Schleyer, P.v. R. *J. Comput. Chem.* **1983**, *4*, 294−301.

(35) Piecuch, P.; Kucharski, S. A.; Kowalski, K.; Musiał, M. *Comput. Phys. Commun.* **2002**, *149*, 71−96.

(36) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.;

Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

(37) (a) The percent biradical character has been calculated by using the natural orbitals obtained with the CASSCF(6,6)/6-311G(d,p)//UB3LYP/6-311G(d,p) calculations performed with GAMESS. We followed the procedure proposed by Jensen (see ref 37b), in which we determine the biradical index BR defined as $\mathrm{BR} = 2 - n_{\mathrm{H}}$, where n_{H} is the occupation number of the natural orbital corresponding to the HOMO, and calculate the percent biradical character by multiplying BR by 100%. (b) Jensen, F. *J. Am. Chem. Soc.* **1989**, *111*, 4643−4647.

(38) The routine single point CCSD calculations at the U3BLYP-optimized geometry of the biradical intermediate **b**, which precede the corresponding CCSD(T) and CR−CCSD(T) calculations of triples energy corrections, converge to an unphysical solution, which is located approximately 63 kcal/mol above the physical one (causing the corresponding CR−CCSD(T) energy to be 89 kcal/mol above the correct value when the 6-311G(d,p) basis set is employed). This is a consequence of the nonlinear character of coupled cluster theory, which may result in the existence of multiple solutions. In regular cases, the standard CCSD algorithms converge to the desired physical solutions. However, the biradical intermediate **b**, which is characterized by the very large values of the doubly excited cluster amplitudes, is not a regular case and one cannot rely on routine calculations with default initial guesses for cluster amplitudes to obtain the correct energy values. To obtain the physically meaningful solution of the CCSD equations and the correct values of the CCSD(T) and CR−CCSD(T) energies, which belong to the same potential energy surface as the CCSD(T) and CR−CCSD(T) energies of the remaining structures shown in Scheme 2, we first obtained a few geometries along the UB3LYP/6-311G(d,p) intrinsic reaction coordinate (IRC) path connecting the transition state $\mathbf{ab}^{\ddagger}$ and the biradical intermediate **b**. These IRC calculations were performed with Gaussian 98. Next, we performed the CCSD calculations for each of the points on the IRC path connecting $\mathbf{ab}^{\ddagger}$ and **b**, continuing the CCSD solution obtained at the geometry of $\mathbf{ab}^{\ddagger}$ toward the intermediate **b** by using the converged cluster amplitudes obtained at the previous geometry as an initial guess for the CCSD calculations at the next geometry (this was done with the CCSD restart option described in ref 35 and available in GAMESS). Once the correct CCSD solution at the geometry of the intermediate **b** was determined, we could calculate the corresponding CCSD(T) and CR−CCSD(T) energies in a usual way.

(39) Equation 3 has been obtained as follows: Reactants that follow the concerted pathway retain stereochemistry. Reactants that follow the biradical pathway do not retain stereochemistry due to the almost unhindered rotation of the CH_2 end group of ethylenic fragment in biradical **b** about the corresponding single bond. Suppose the barrier for the concerted pathway is infinitely high compared to the barrier for the biradical pathway ($\Delta G_{\mathbf{ac}^{\ddagger}} \gg \Delta G_{\mathbf{ab}^{\ddagger}}$). In this case, $k_{\mathbf{c}}/k_{\mathbf{b}} = 0$ and, due to complete stereorandomization, the percent stereoretention is 50%, in agreement with eq 3. Suppose both pathways have identical activation barriers, i.e., the free energies of $\mathbf{ab}^{\ddagger}$ and $\mathbf{ac}^{\ddagger}$ are identical ($\Delta G_{\mathbf{ac}^{\ddagger}} = \Delta G_{\mathbf{ab}^{\ddagger}}$) and $k_{\mathbf{c}}/k_{\mathbf{b}} = 1$. In this case, the percent stereoretention should be 75% (the 50% of the molecules that follow the concerted path give a 100% stereoretention and the other 50% of the molecules that follow the biradical path give a 50% stereoretention) and eq 3 gives 75% when $k_{\mathbf{c}}/k_{\mathbf{b}} = 1$. When the rate determining step of the concerted path $\mathbf{a}+\mathbf{et} \rightarrow \mathbf{c}$ is twice as fast as the rate determining step of the biradical path $\mathbf{a}+\mathbf{et} \rightarrow \mathbf{b}$, i.e., $k_{\mathbf{c}}/k_{\mathbf{b}} = 2$, the number of molecules following the concerted path must be twice the number of molecules following the biradical path. In this case, two-thirds of the molecules that follow the concerted path give a 100% stereoretention and the remaining one-third of the molecules give a 50% stereoretention. This results in the percent stereoretention of 83%, in agreement with eq 3 for $k_{\mathbf{c}}/k_{\mathbf{b}} = 2$.

(40) (a) Dunning, T. H., Jr. *J. Chem. Phys*. **1989**, *90*, 1007−1023. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys*. **1992**, *96*, 6769−6806.

(41) Despite several attempts, we failed to locate the transition state $\mathbf{ac}^{\ddagger}$, which defines the concerted pathway, with the CASSCF(6,6)/6-31G(d) approach. This may be a purely numerical issue or a real problem with CASSCF, which may not have this transition state on the corresponding potential energy surface. We had no problem whatsoever with locating the transition state $\mathbf{ab}^{\ddagger}$, which defines the biradical pathway, in the CASSCF(6,6)/6-31G(d) calculations.

(42) (a) Kraka, E.; Cremer, D. *J. Am. Chem. Soc*. **2000**, *122*, 8245−8264. (b) McGuire, M. J.; Piecuch, P. in preparation.

(43) Laird, A.; Ross, R. B.; Zeigler, T. *Chemical Applications of Density Functional Theory*; American Chemical Society: Washington, DC, 1996.