J. Am. Chem. Soc. **1990**, *112*, 73-80 73

Theoretical Investigation of Intramolecular Singlet Carbene 1,4- and 1,2-Cycloadditions

J. D. Evanseck,[†] J. Mareda,[‡] and K. N. Houk*,[†]

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024, and Department of Organic Chemistry, University of Geneva, 1211 Geneva 4, Switzerland. *Received January 23, 1989*

Abstract: The intramolecular cycloaddition of singlet 2,4-cyclopentadienylcarbene to form benzvalene and reactions of related systems have been studied with ab initio molecular orbital theory. These systems were methylene plus butadiene and the intramolecular reactions of allylmethylene, 2-cyclopropenylcarbene, 2-cyclobutenylcarbene, and 2-cyclopentenylcarbene. Geometry optimizations were performed with restricted Hartree–Fock calculations and the 3-21G basis set. The effect of electron correlation was included with second-order Møller–Plesset theory with the 6-31G* basis set on the 3-21G optimized geometries. The energies of activation were found to be dependent upon ring strain and spatial orientation of the filled carbene in-plane hybrid orbital during the initial electrophilic phase of the carbene addition. A decrease in activation energy for intramolecular cycloadditions is noted for systems that approach the idealized geometry found with intermolecular additions of carbenes to alkenes.

Singlet carbenes may react with conjugated dienes to give either 1,2- or 1,4-cycloadditions. While 1,2-cycloadditions are generally favored, there are a few unusual cases, illustrated in Figure 1, in which carbenes undergo 1,4-cycloadditions with polyenes. The enforced cisoid diene conformations in cyclooctatetraene,[1] norbornadiene,[2] bismethylenecycloheptane,[3] and cyclopentadiene[4] apparently promote 1,4-additions. The potential synthetic utility of 1,4-cycloadditions and the intriguing experimental paucity of such processes have initiated experimental[5] and theoretical[6] investigations of both intermolecular and intramolecular reactions. Our interest in this subject was aroused by the work of Burger and co-workers, who proved that 1-methyl-2,4-cyclopentadienylcarbene undergoes exclusive 1,4-cycloaddition to form 1-methylbenzvalene, rather than the generally preferred 1,2-cycloaddition that would yield 2-methylbenzvalene, as shown later.

We initially investigated the reactions of 2,4-cyclopentadienylcarbene in order to understand this intriguing result but subsequently widened the scope of the study to provide a more general understanding of intramolecular carbene cycloaddition reactivity. Six unsaturated carbene systems (Figure 2) were chosen to explore the effect of imposed geometric constraints upon intramolecular carbene cycloadditions. Our model systems were chosen to illuminate the influence of ring size and rigidity upon selectivity. The intermolecular transition structures of dihalocarbenes and ethylene provide an interesting idealized geometry that is compared to the intramolecular cases described above.

Background

Anastassiou examined the reaction of cyanonitrene and cyclooctatetraene, shown in Figure 1a. The 1,4-adduct was shown to result primarily from the direct 1,4-reaction and not from the isomerization of the 1,2-adduct.[1a–c] This 1,4-addition was shown to be a nonconcerted reaction involving triplet cyanonitrene. Several workers investigated triplet carbene additions to various dienes, but only cyclopropanes were found.[1d] Fluorenylidene gives only 1,2-adducts with cyclopentadiene, cyclohexadiene, and cycloctatetrane.[1d,e]

Jefford et al. reported that the reactions of difluorocarbene and fluorochlorocarbene with norbornadiene gave significant amounts of the endo-homo-1,4-adducts.[2a] These reactions, illustrated in Figure 1b, are the first examples of 1,4-additions of singlet carbenes. An investigation of the thermal behavior of the 1,2-adducts confirms that the homo 1,4-adduct arises directly from a cheletropic reaction.[2b] Jefford attributed this to the nucleophilic character of difluorocarbene and the rigid structure of norbornadiene, which is ideally set up for the 1,4-cycloaddition. Separately, Jefford[2c] and Klumpp[2d] discussed the origins of 1,4-cycloadditions of dichlorocarbene to norbornadienes. The nucleophilic nature of the carbene postulated for the addition of difluorocarbene is not an issue with the electrophilic dichlorocarbene. The unusual formation of homo-1,4-adducts with norbornadiene and dichlorocarbene was attributed to the repulsions of chlorines and the C-5 and C-6 bridges leading to unfavorable steric interactions for normal 1,2-cyclopropanation.[2e] The influence of entropic and electronic factors on the ratio between 1,2-adducts and homo-1,4-adducts from the reaction of difluorocarbene and norbornadiene has also been addressed.[2f]

An intermolecular 1,4-addition (in miniscule yield) was reported for the reaction of dichlorocarbene and 1,2-bismethylenecyclo-

---

[†] University of California, Los Angeles.

[‡] University of Geneva.

(1) (a) Anastassiou, A. G. *J. Am. Chem. Soc.* **1965**, *87*, 5512. (b) Anastassiou, A. G. *Ibid.* **1968**, *90*, 1527. (c) Anastassiou, A. G.; Cellura, R. P. *Tetrahedron Lett.* **1970**, *60*, 5267. (d) Jones, M., Jr.; Ando, W.; Hendrick, M. E.; Kulczycki, A., Jr.; Howley, P. M.; Hummel, K. F.; Malament, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 7469. (e) Zimmerman, H. E.; Crumrine, D. S.; Döpp, D.; Huyffer, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 434.

(2) (a) Jefford, C. W.; Kabengele, n.; Kovacs, J.; Burger, U. *Tetrahedron Lett.* **1974**, *3*, 257. (b) Jefford, C. W.; Mareda, J.; Gehret, J. E.; Kabengele, N.; Graham, W. D.; Burger, U. *J. Am. Chem. Soc.* **1976**, *98*, 2585. (c) Jefford, C. W.; de los Heros, V.; Burger, U. *Tetrahedron Lett.* **1976**, *9*, 703. (d) Kwantes, P. M.; Klumpp, G. W. *Ibid.* **1976**, *9*, 707. (e) Klumpp, G. W.; Kwantes, P. M. *Ibid.* **1981**, *22*, 831. (f) Jefford, C. W.; de los Heros, V.; Gehret, J. E.; Wipff, G. *Ibid.* **1980**, *21*, 1629.

(3) Turkenburg, L. A. M.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1982**, *23*, 769.

(4) (a) Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3782. (b) Katz, T. J.; Cheung, J. J. *Ibid.* **1969**, *91*, 7772. (c) Burger, U.; Thorel, P. J.; Mentha, Y. *Chimia* **1987**, *41*, 26. (d) Burger, U.; Gandillon, G.; Mareda, J. *Helv. Chim. Acta* **1981**, *64*, 844. (e) Burger, U.; Gandillon, G. *Tetrahedron Lett.* **1979**, *44*, 4281.

(5) (a) Mislow, K.; Hellman, H. M. *J. Am. Chem. Soc.* **1951**, *73*, 244. (b) Mislow, K. *Ibid.* **1953**, *75*, 2512. (c) Hellman, H. M.; Hellman, J. W.; Mislow, K. *Ibid.* **1954**, *76*, 1175. (d) Woodworth, R. C.; Skell, P. S. *Ibid.* **1957**, *79*, 2542. (e) Skell, P. S.; Garner, A. Y. *Ibid.* **1956**, *78*, 5430. (f) Orchin, M.; Herrick, E. C. *J. Org. Chem.* **1959**, *24*, 139. (g) Franzen, V. *Chem. Ber.* **1962**, *95*, 571. (h) Frey, H. M. *Trans. Faraday Soc.* **1962**, *58*, 516. (i) Hodge, P.; Edwards, J. A.; Fried, J. H. *Tetrahedron Lett.* **1966**, *42*, 5175. (j) Derenberg, M.; Hodge, P. *J. Chem. Soc. D* **1971**, 233. (k) Nozak, H.; Yamabe, M.; Noyori, R. *Tetrahedron* **1965**, *21*, 1657. (l) Bamford, W. R.; Stevens, T. S. *J. Chem. Soc.* **1952**, 4735. (m) Powell, J. W.; Whiting, M. C. *Tetrahedron* **1959**, *7*, 305. (n) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512. (o) Storm, D. L.; Spencer, T. A. *Tetrahedron Lett.* **1967**, *20*, 1865. (p) Murayama, S. T.; Spencer, T. A. *Ibid.* **1969**, *51*, 4479. (q) Hudlicky, T.; Sheth, J. P.; Gee, V.; Barnvos, D. *Ibid.* **1979**, *51*, 4889. (r) Hudlicky, T.; Koszyk, F. J.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020. (s) Hudlicky, T.; Koszyk, F. J.; Kochwat, D. M.; Cantrell, G. L. *J. Org. Chem.* **1981**, *46*, 2911. (t) References within ref 5r.

(6) (a) Fujimoto, H.; Hoffmann, R. *J. Phys. Chem.* **1974**, *78*, 1167. (b) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395, 2511. (c) Hoffmann, R.; Woodward, R. B. *Ibid.* **1965**, *87*, 2046, 4388, 4389. (d) Hoffmann, R.; Woodward, R. B. *Acc. Chem. Res.* **1968**, *17*, 1. (e) Woodward, R. B.; Hoffmann, R. *Nagew. Chem.* **1969**, *81*, 797. (f) Schoeller, W. W.; Aktekin, N. *Chem. Commun.* **1982**, 20.

0002-7863/90/1512-73$02.50/0

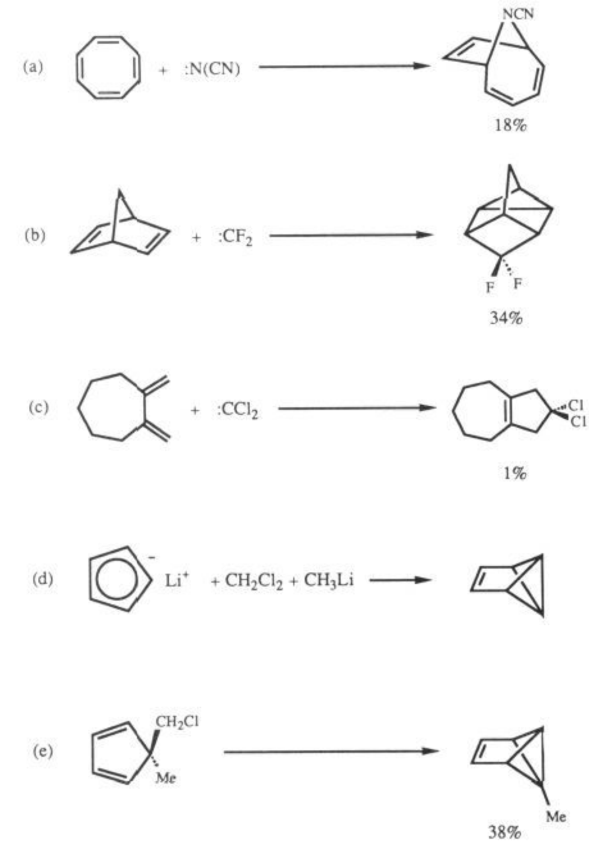


Figure 1. Experimental carbene 1,4-cycloadditions.

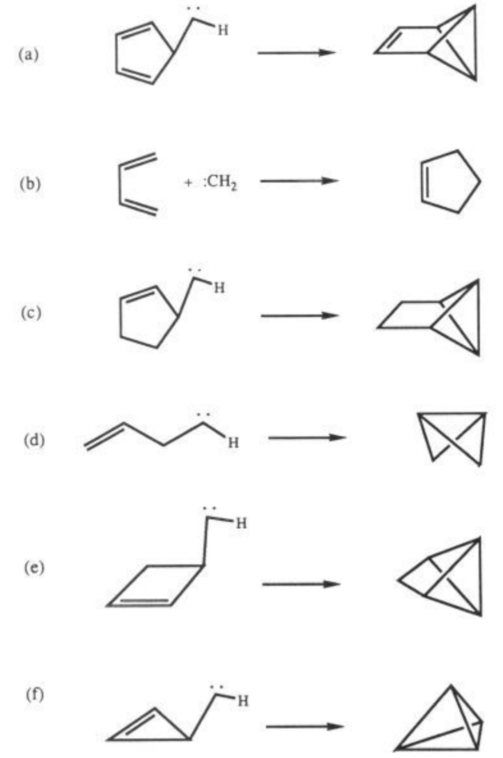


Figure 2. Reactions studied.

heptane, as shown in Figure 1c.[3]

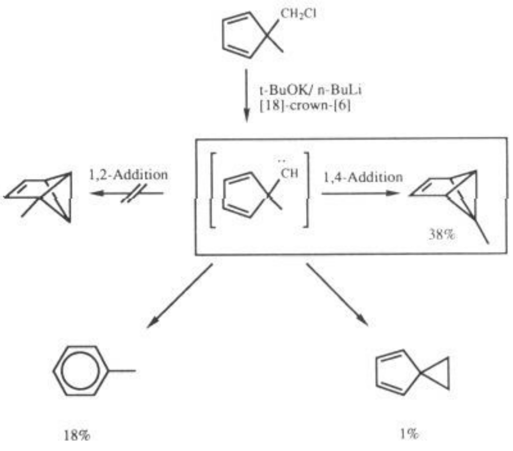
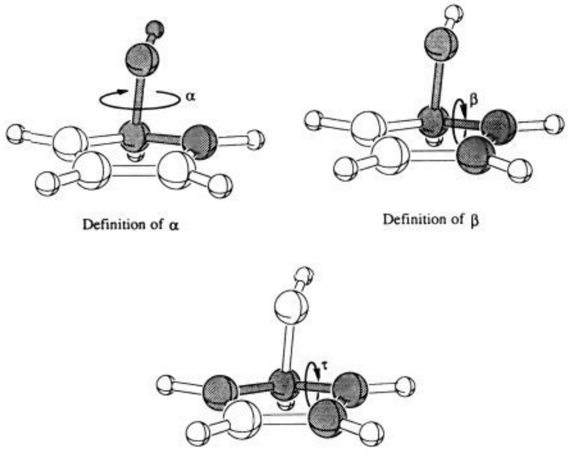


Figure 3.



Definition of α

Definition of β

Definition of τ

Figure 4.

Some time ago, benzvalene was prepared by Katz.[4a,b] The "Katz reaction" to form benzvalene (Figure 1d) is believed to proceed via an exocyclic carbene or carbenoid that undergoes an intramolecular addition.[4c] Burger and co-workers[4d,e] have shown that the reaction of 1-(chloromethyl)-1-methyl-2,4-cyclopentadiene with base generates the 1-methyl-2,4-cyclopentadienylcarbene intermediate and leads to exclusive 1,4-addition, as shown in Figures 1e and 3. Formation of minute amounts of a spiro compound by CH insertion and toluene by 1,2-shift suggests that a free carbene is involved in the reaction.

There have been many experimental studies utilizing intramolecular carbene addition methodology for the preparation of tricyclo[3.1.0.0^{2,6}]hexane (Figure 2c), bicyclobutane (Figure 2d), and tricyclo[1.1.1.0^{4,5}]pentane (Figure 2e). An initial claim that a substituted tetrahedrane (Figure 2f) could be formed with a similar procedure was later retracted.[7]

Computational Methods

Ab initio molecular orbital calculations were carried out with the GAUSSIAN series of programs[8a,b] on HARRIS H-1000, Digital MicroVax II, and IBM 3090 computers.[8c] Structures were optimized with the use

---

[7] (a) Lemal, D. M.; Shim, K. S. *Tetrahedron Lett.* **1964**, *44*, 3231. (b) Closs, G. L.; Larrabee, R. B. *Ibid.* **1965**, *4*, 287. (c) Masamune, S.; Kato, M. *J. Am. Chem. Soc.* **1966**, *88*, 610. (d) White, E. H.; Maier, G. E.; Graeve, R.; Zirngibl, U.; Friend, E. W. *Ibid.* **1966**, *88*, 611. (e) Closs, G. L.; Rao, V. N. M. *J. Am. Chem. Soc.* **1966**, *88*, 4116. (f) Peterson, R. F.; Baker, R. T. K.; Wolfgang, R. L. *Tetrahedron Lett.* **1969**, *54*, 4749. (g) Lemal, D. M.; Menger, F.; Clark, G. W. *J. Am. Chem. Soc.* **1963**, *85*, 2529. (h) Baird, N. C.; Dewar, M. J. S. *J. Chem. Phys.* **1969**, *50*, 1262.

[8] (a) Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. R. GAUSSIAN/82, Release H.; Carnegie-Mellon University: Pittsburgh, PA, 1982. (b) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1983**, *13*, No. 406. (c) We thank the Office of Academic Computing at UCLA and Aeint deBoer for his time and expertise for the installation of computational chemistry code running on the 3090.

Table I. Stationary Points on the RHF/STO-3G and RHF/3-21G C_6H_6 Potential Surface for the Ring Closure of 2,4-Cyclopentadienylcarbene to Benzvalene

		RHF/STO-3G		RHF/3-21G		RMP2/6-31G*//3-21G	
system	sym	energy (hartrees)	rel (kcal/mol)	energy (hartrees)	rel (kcal/mol)	energy (hartrees)	rel (kcal/mol)
2,4-cyclopentadienylcarbene (H inward)	C_1	−227.703 46	0.0	−229.234 36	0.0	−231.256 77	0.0
2,4-cyclopentadienylcarbene (H outward)	C_s	−227.699 69	2.4	−229.227 09	4.6	−231.250 36	4.0
2,4-cyclopentadienylcarbene (H outward)	C_1	−227.702 91	0.3	−229.231 11	2.0	−231.247 96	5.5
TS (1,2-addition)	C_1	−227.676 91	16.7	−229.209 58	15.5	−231.265 94	−5.8
TS (1,4-addition)	C_1	−227.680 82	14.2	−229.214 60	12.4	−231.273 83	−10.7
2nd-order saddle (1,4-addition)	C_s	−227.679 00	15.3	−229.214 37	12.5	−231.271 93	−9.5
benzvalene	C_{2v}	−227.784 19	−50.7	−229.267 04	−20.5	−231.335 65	−49.5

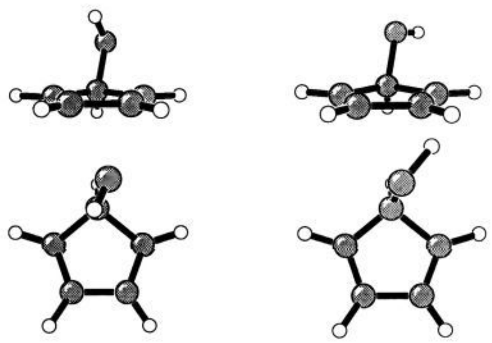
of analytical energy gradients and the STO-3G[9] or 3-21G[10] basis sets. These post Hartree–Fock calculations were carried out on the stationary points located at the RHF/3-21G geometries. These are referred to in the text as MP2/6-31G*, as a shorthand for the Pople designation MP2/6-31G*//RHF/3-21G. Electron correlation was calculated with second-order Møller–Plesset theory[11] with all core electrons included and the 6-31G* basis set.[12]

Theoretical Results

In our discussion of the formation of benzvalene and other products, we will describe the course of the reaction coordinate in terms of three torsional angles, as shown in Figure 4. The first defines the orientation of the methylenic hydrogen and is denoted as α. The second torsional angle of concern is β, which locates the carbene carbon relative to the olefin. Measurement of the nonplanar distortion of the ring was monitored by the torsional angle τ.

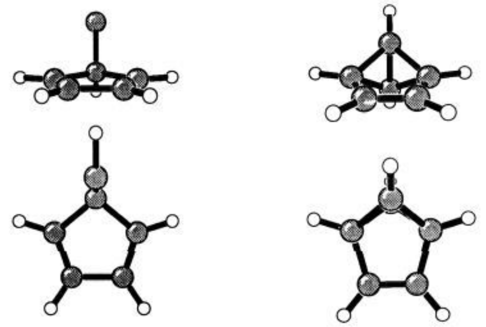
2,4-Cyclopentadienylcarbene Reactions. The ground-state conformation of 2,4-cyclopentadienylcarbene has the methylene hydrogen pointing toward the center of the ring, as shown in Figure 5a. The conformation with the methylene hydrogen facing outward (Figure 5b) is also a minimum but is less stable by 2.0 kcal/mol at the RHF level, or 5.5 kcal/mol at the MP2/6-31G* level. This preference may arise from electron–electron repulsion involving Ψ_1 of the diene moiety and the occupied hybrid orbital of the carbene. To undergo the cycloaddition, the methylene hydrogen must rotate outward, directing the filled hybrid orbital toward the center of the ring, so that the nucleophilic phase of the addition mechanism is possible. Neither of these minima have C_s symmetry, indicating that even in the reactants there is some electrophilic interaction between the carbene vacant orbital and the diene. The calculated RHF energy with the constraint of a plane of symmetry (Figure 5c) results in a 4.6 kcal/mol destabilization relative to the C_1 ground-state conformation with the hydrogen inward, or 4.0 kcal/mol at the MP2/6-31G* level. Benzvalene, the product from the carbene rearrangement, was calculated in the C_{2v} point group, as shown in Figure 5d. The energies of reaction are −50.7, −20.5, and −49.5 kcal/mol at the RHF/STO-3G, RHF/3-21G, and MP2/6-31G* levels of theory, respectively.

The transition states for both the 1,2- and 1,4-modes of cycloaddition were located with the Baker routines[13] incorporated into the GAUSSIAN 82 program. As a first step, a second-order saddle point was located along the C_s reaction path. The lowest normal mode had a frequency of 614i cm^{-1} with A′ symmetry. As depicted in Figure 6a, this mode leads to the 1,4-cycloaddition. The other imaginary frequency of 165i cm^{-1} has A″ symmetry and corresponds to a symmetry-breaking motion, as pictured in Figure 6b. Starting from this geometry, searches for transition structures with reduced symmetry were conducted. A two-dimensional reaction coordinate search was initiated, adjusting and examining the internal coordinate forces on the torsional angle, α, and bond angle involving the methylene carbon to the olefin of addition. Both the 1,4- and the 1,2-addition modes were located in this manner. Energetics are presented in Table I. Parts c and d of Figure 6 illustrate the geometries and the transition vectors corresponding to the imaginary frequencies for the 1,4- and 1,2-cycloaddition transition structures, respectively. As pictured in Figure 6d, in the 1,2-reaction, the methylene unit has tilted toward the adjacent olefinic center with an angle of 71°, compressed from 95° in the reactant. This structure is strained for a typical intramolecular rearrangement, since the occupied hybrid orbital is directed away from the olefinic carbon necessary for 1,2-ring closure. The lower strain required to have the filled hybrid orbital point toward the olefinic carbon to complete the reaction in the 1,4-manner is the reason for absence of the 1,2-adduct in the 1-methyl-2,4-cyclopentadienylcarbene cycloaddition. The short and long bond-forming distances in the 1,2-transition structure are 1.820 and 2.169 Å, respectively. The corresponding distances for the 1,4-transition structure are 1.886 and 2.066 Å. The distance in the 1,4-transition structure from the methylenic center to the olefinic carbon involved in the completion of the 1,2-addition is 2.655 Å, 0.49 Å further away than the corresponding 1,4-closure distance. The large advancement along the reaction coordinate reflects the lateness of the 1,2-transition state, with the carbon



(a) 2,4-Cyclopentadienylcarbene Hydrogen Inward

(b) 2,4-Cyclopentadienylcarbene Hydrogen Outward



(c) 2,4-Cyclopentadienylcarbene C_s Symmetry

(d) Benzvalene C_{2v} Symmetry

Figure 5.

---

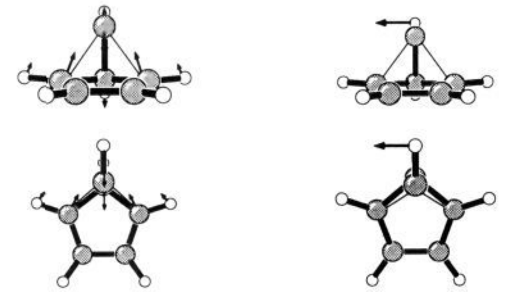
(9) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(10) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

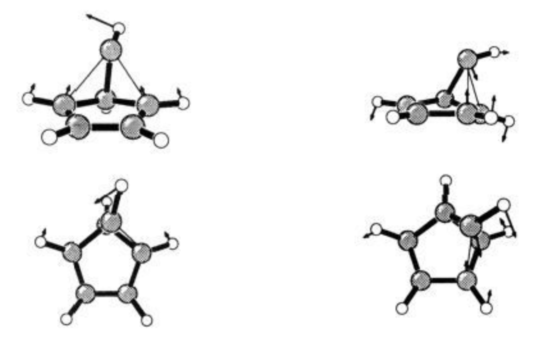
(11) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Binkley, J. S.; Pople, J. A. *Int. J. Quant. Chem.* **1975**, *9*, 229.

(12) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(13) Baker, J. *J. Comput. Chem.* **1986**, *7*, 385.



(a) Stationary Point 614i cm^{-1} C_s Symmetry (b) Stationary Point 165i cm^{-1} C_s Symmetry



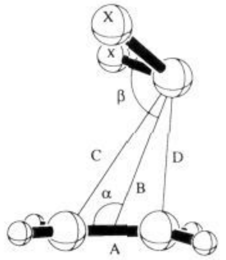
(c) 1,4-Transition Structure 650i cm^{-1} (d) 1,2-Transition Structure 401i cm^{-1}

Figure 6.

skeleton achieving a highly distorted configuration of $\beta = 74°$, which is 35° from the ground-state carbene. In comparison, $\beta = 97°$ for the 1,4-transition state, only 12° from the reactant geometry.

The 1,4 activation energy is predicted by RHF/3-21G to be 3.1 kcal/mol lower than that of the 1,2-addition. MP2/6-31G* single points gave negative activation energies, and the concerted 1,4-addition process was favored by 4.9 kcal/mol over the 1,2-addition mechanism. The influence of correlation energy, lowering the activation energy and hence causing it to disappear, is observed quite generally in calculations for unstabilized carbenes. In spite of the absence of an energetic barrier for these carbene reactions, there is likely to be an entropy decrease as the reaction proceeds and a finite free energy barrier. The magnitude of the free energy barrier is primarily determined by the relative energies of different processes, as we have described in detail earlier.[14]

To understand the difference between 1,2- and 1,4-selectivity in general, the description of transition structures previously calculated for intermolecular carbene reactions is necessary. Earlier work by Rondan et al. with disubstituted halocarbenes has led to interesting transition structures for the 1,2-cycloaddition to ethylene.[14] Recently, higher level calculations by Blake et al. produce a similar geometry for the addition of dichlorocarbene to ethylene.[15] A summary of critical geometric parameters for various substituents, ranging from electrophilic CCl_2 to nucleophilic $C(OH)_2$, is given in Figure 7. A characteristic geometric feature of these transition structures is that the so-called electrophilic bond-forming distance is larger than the nucleophilic one. This holds for the intermolecular addition of either electrophilic or nucleophilic carbenes.[14] The electrophilic distance is defined as the difference between the methylenic center and the ethylenic carbon that is directly in the path of the empty p orbital on the carbene. Rondan et al. utilized the ratio of electrophilic to nucleophilic distances to describe the character of the transition state.



X	Level	A	B	C	D	α	β
Cl†	MP2/6-31G*	1.354	2.219	2.703	2.219	111.7°	109.1°
Cl	RHF/STO-3G	1.356	2.013	2.292	1.941	105.8°	107.8°
F	RHF/STO-3G	1.379	1.900	2.220	1.800	108.8°	107.1°
OH	RHF/STO-3G	1.425	1.852	2.227	1.707	112.8°	107.9°

† - Reference 15
All other work reference 14

Figure 7. Transition structures for stabilized carbene cycloadditions.

Table II. Single Points on the RHF/3-21G Potential Surface of 1-Methyl-2,4-cyclopentadienylcarbene Ring Closure to 1-Methylbenzvalene and 2-Methylbenzvalene[a]

		RHF/3-21G	
system	pt gp sym	energy (hartrees)	rel (kcal/mol)
1-methyl-2,4-cyclopentadienylcarbene (H inward)	C_1	−268.056 69	0.0
1-methyl-2,4-cyclopentadienylcarbene (H outward)	C_1	−268.053 21	2.2
TS (1,2-addition)	C_1	−268.030 76	16.3
TS (1,4-addition)	C_1	−268.038 77	11.2
1-methylbenzvalene	C_1	−268.091 33	−21.7
2-methylbenzvalene	C_1	−268.088 82	−20.2

[a] All geometries were taken from the 2,4-cyclopentadienylcarbene optimized RHF/3-21G structures, and a standard methyl was attached.

1-Methyl-2,4-cyclopentadienylcarbene Reactions. Replacement of a hydrogen on the optimized C_6H_6 stationary points with a standard methyl group[16] magnifies the 1,4-addition preference, as summarized in Tables I and II. The energy of activation for the 1,2-addition increased 0.8 kcal/mol for the RHF/3-21G single-point energy and decreased 1.2 kcal/mol for the 1,4-transition state. The preference for the 1,4-adduct increases to 5.1 kcal/mol, as compared to the 3.1 kcal/mol in the unsubstituted case.

Methylene–Butadiene Reactions. The difference between the intramolecular and intermolecular cases is demonstrated by the calculations of 1,3-butadiene plus methylene. A local minimum for a methylene–butadiene complex was located (C_s) 2.6 kcal/mol below the reactants (Figure 8a). The energy was found to be slightly above that of the reactants with inclusion of electron correlation and probably would not be a stable entity if adequate correlation were included and geometry optimization were carried out at that level.

The search for a transition structure constrained to C_s symmetry results in the location of a second-order stationary point with two imaginary frequencies. The first corresponds to the 1,4-addition at 582i cm^{-1} with A′ symmetry, as shown in Figure 8b. The second vibration reduces the symmetry, as shown in Figure 8c. The product from the 1,4-addition, cyclopentene, is shown in Figure

---

(14) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555. Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770. Houk, K. N.; Rondan, N. G.; Mareda, J. *Ibid.* **1984**, *106*, 4291.

(15) Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 1919.

(16) The standard methyl used had C–C of 1.5407 Å, C–H of 1.0849 Å, and C–C–H angles of 111.74°, with CH bonds staggered with respect to the vicinal bonds.

Table III. Stationary Points for the Reactions of 1,4-Addition of Singlet Methylene to 1,3-Butadiene (Energies Relative to Methylene plus *s-trans*-Butadiene)

		RHF/STO-3G		RHF/3-21G		RMP2/6-31G*//3-21G	
system	pt gp sym	energy (hartrees)	rel (kcal/mol)	energy (hartrees)	rel (kcal/mol)	energy (hartrees)	rel (kcal/mol)
methylene	C_{2v}	-38.37230		-38.65185		-38.96986	
s-trans-butadiene	C_{2h}	-153.01744		-154.05394		-155.42069	
CH_2 + *s-trans*-butadiene	C_1	-191.38974	0.0	-192.70579	0.0	-194.39055	0.0
ion-dipole complex	C_s	-191.39125	-0.9	-192.70995	-2.6	-194.38900	1.0
2nd-order saddle (1,4-addition)	C_s	-191.35225	23.5	-192.68451	13.4	-194.39152	0.6
cyclopentene	C_s	-191.67366	-178.2	-192.90199	-123.1	-194.61583	-141.4
cis-vinylcyclopropane	C_s	-191.59859	-131.1	-192.85178	-91.6	-194.60033	-131.6
trans-vinylcyclopropane	C_s	-191.60583	-135.6	-192.85588	-94.2	-194.60314	-133.4

Table IV. Stationary Points on the RHF/STO-3G and RHF/3-21G C_6H_8 Potential Surfaces for the Ring Closure of 2-Cyclopentenylcarbene to Tricyclo[3.1.0.0^{2,6}]heptane

		RHF/STO-3G		RHF/3-21G		RMP2/6-31G*//3-21G	
system	pt gp sym	energy (hartrees)	rel (kcal/mol)	energy (hartrees)	rel (kcal/mol)	energy (hartrees)	rel (kcal/mol)
2-cyclopentenylcarbene (H outward)	C_1	-228.91967	0.0	-230.42004	0.0	-232.47901	0.0
TS (1,2-addition)	C_1	-228.90224	10.9	-230.40988	6.4	-232.49577	-10.5
tricyclo[3.2.0.0^{2,6}]heptane	C_{2v}	-229.01975	-62.8	-230.47356	-33.6	-232.58277	-65.1

Table V. Stationary Points on the RHF/STO-3G and RHF/3-21G C_4H_6 Potential Surfaces for the Ring Closure of Allylmethylene to Bicyclobutane (Energies Relative to the C_1 Point Group for Allylmethylene)

		RHF/STO-3G		RHF/3-21G		RMP2/6-31G*//3-21G	
system	pt gp sym	energy (hartrees)	rel (kcal/mol)	energy (hartrees)	rel (kcal/mol)	energy (hartrees)	rel (kcal/mol)
cis-allylmethylene	C_s	-152.90353	0.8	-153.93497	0.5	-155.29553	0.8
trans-allylmethylene	C_s	-152.90214	1.7	-153.93350	1.4	-155.29418	1.7
allylmethylene	C_1	-152.90479	0.0	-153.93570	0.0	-155.29683	0.0
TS (1,2-addition)	C_1	-152.89508	6.1	-153.92983	3.7	-155.32195	-15.8
bicyclobutane	C_{2v}	-153.00195	-61.0	-153.98664	-32.0	-155.40632	-68.7

Table VI. Energies of 2-Cyclobutenylcarbene and Tricyclo[1.1.1.0^{4,5}]pentane

		RHF/STO-3G		RHF/3-21G		RMP2/6-31G*//3-21G	
system	pt gp sym	energy (hartrees)	rel (kcal/mol)	energy (hartrees)	rel (kcal/mol)	energy (hartrees)	rel (kcal/mol)
2-cyclobutenylcarbene	C_1	-190.28743	0.0	-191.5437	0.0	-193.25901	0.0
tricyclo[1.1.1.0^{4,5}]pentane	C_{2v}	-190.36819	-50.7	-191.59044	-29.3	-193.35001	-57.1

8d. The reaction was found to be 141 kcal/mol exothermic at the MP2/6-31G* level. The energies for the different stationary points are summarized in Table III.

Relaxation of the symmetry constraints for the determination of the transition states for both the 1,2- or the 1,4-additions was problematic. Neither 1,2- nor 1,4-transition states could be located at either the RHF/STO-3G or the RHF/3-21G levels of theory. Earlier calculations have shown that methylene, without additional stabilization by substituents, does not form the characteristic π-complexes found for stabilized carbenes at the RHF level.[14] The surface for the reaction of singlet methylene with ethylene has been thoroughly investigated by Zurawski and Kutzelnigg.[17] The potential energy surface was similar to the one reported by Hoffmann[18] with a semiempirical treatment, except that no barrier for addition was observed. The energy decreased monotonically as a function of reaction coordinate, leading to cyclopropanation without a detectable activation barrier. The concerted 1,4-addition of methylene to *cis*-butadiene has also been computed to have an activation barrier of 28 kcal/mol by the semiempirical MINDO/3 method[19] but 15 kcal/mol higher in energy than the corresponding activation energy found with the RHF/3-21G level of theory.

The formation of the 1,2-cycloaddition product *trans*-vinylcyclopropane is exothermic by 133.4 kcal/mol at the MP2/6-31G* level. The cis conformation of vinylcyclopropane is destabilized by 2.6 kcal/mol with RHF/3-21G and 1.8 kcal/mol with the inclusion of electron correlation as compared to the trans conformation.

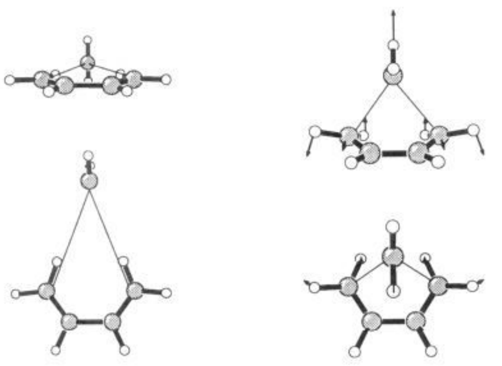
2-Cyclopentenylcarbene Reaction. The ground state of 2-cyclopentenylcarbene is shown in Figure 9a. The relaxation of the ring allows more interaction of the carbene with the π-bond of the alkene. The angle β = 95° is 14° closer to the 1,2-transition state than observed for the rigid diene structure. The puckering of the five-membered ring is τ = 19°, significantly different from the diene value of 3°.

The 1,2-transition state, Figure 9b, is less strained than the diene case. The degree of twisting of the ring is measured by τ = -38°, which is 14° more than the diene 1,2-transition-state geometry. The additional ring flexibility allows the transition structure to become more similar to an intermolecular transition-state geometry. Considerable elongation of both electrophilic and nucleophilic bond-making distances as compared to the 2,4-cyclopentadienylcarbene transition structure is observed along with a corresponding decrease in activation energy. Calculations predict that E_a = 6.4 kcal/mol at the RHF/3-21G level, 9.1 kcal/mol below that evaluated for the corresponding diene (Table IV). The energy of reaction for the formation of tricyclo[3.1.0.0^{2,6}]hexane (Figure 9c) was determined to be -65.1 kcal/mol by MP2/6-31G* single-point calculations.

2-Cyclopropenylcarbene Reaction. The reduction in the rigidity of the diene moiety has been demonstrated to lower substantially

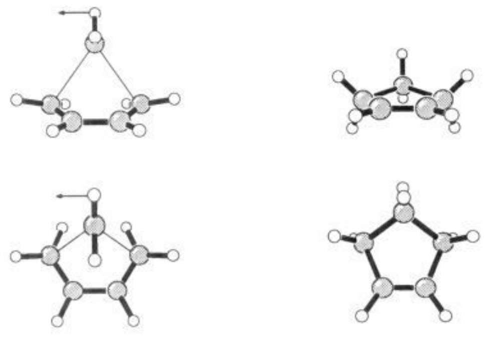
---

(17) Zurawski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1978**, *100*, 2654.
(18) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.
(19) Schoeller, W. W.; Yurtsever, E. *J. Am. Chem. Soc.* **1978**, *100*, 7548.



(a) Methylene-Butadiene Complex C_{2v} Symmetry

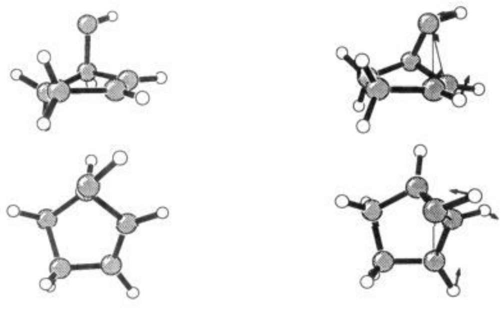
(b) Second Order Saddle Point 582i cm^{-1} C_s Symmetry



(c) Second Order Saddle Point 425i cm^{-1} C_s Symmetry

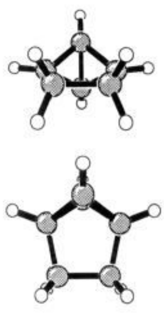
(d) Cyclopentene C_s Symmetry

Figure 8.



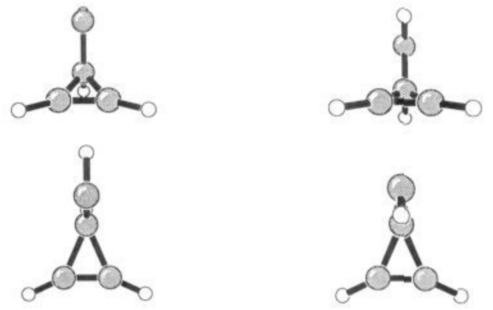
(a) 2-Cyclopentenylcarbene C_1 Symmetry

(b) 1,2-Transition Structure 355i cm^{-1}



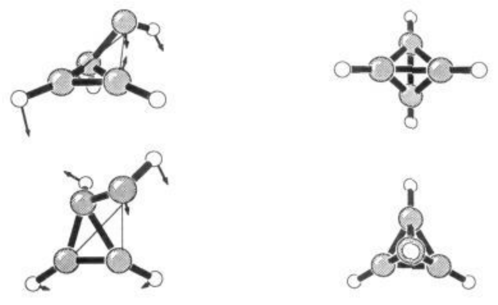
(c) Tricyclo[3.1.0.0^{2,6}]hexane C_{2v} Symmetry

Figure 9.



(a) 2-Cyclopropenylcarbene hydrogen outward C_s symmetry

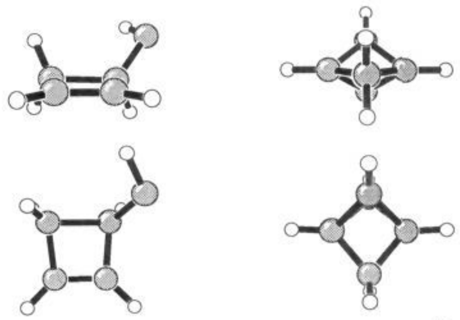
(b) 2-Cyclopropenylcarbene hydrogen inward C_s symmetry



(c) 1,2-Transition Structure 412i cm^{-1}

(d) Tetrahedrane T_d symmetry

Figure 10.



(a) 2-Cyclobutenylcarbene C_1 symmetry

(b) Tricyclo[1.1.1.0^{4,5}]pentane C_{2v} symmetry

Figure 11.

the activation energy for the 1,2-addition. The 1,2-cycloaddition of 2-cyclopropenylcarbene to form tetrahedrane (Figure 10d) was also examined in order to probe the influence of ring size on activation energy. The ground-state species is shown in Figure 10a. Unlike the other carbenes studied, the preferred π-complex geometry has C_s symmetry. A slight preference for the occupied hybrid orbital to be facing outward away from the ring was observed at the RHF/3-21G level, as shown in Figure 10b. At the MP2/6-31G* level, the conformer with the hydrogen inward over the ring is 0.5 kcal/mol less stable. The results are summarized in Table V. The formation of tetrahedrane is much less exothermic than the other carbene cycloadditions. The energy of reaction was found to be −32.1 kcal/mol at the RHF/STO-3G, −11.8 kcal/mol at the RHF/3-21G, and −36.8 at the MP2/6-31G* levels of computation. Other workers have examined the stability of tetrahedrane and have reported similar energies of reaction.[20]

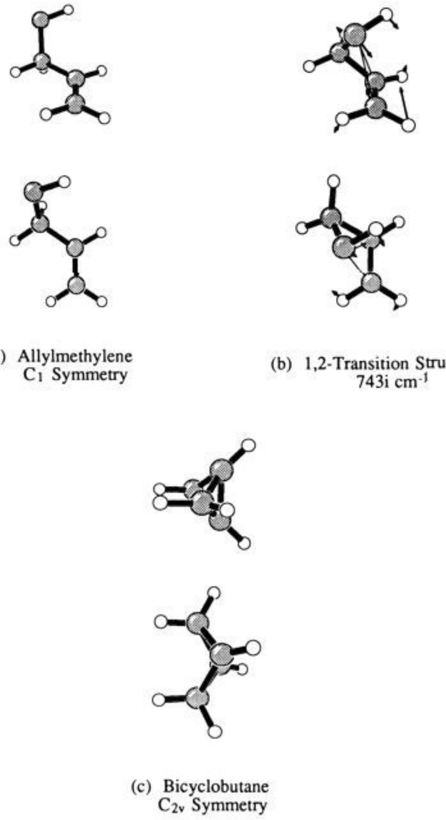
The transition structure, Figure 10c, is 8.2 kcal/mol above the ground state. This is destabilized by 1.8 kcal/mol as compared to the energy of activation for the 2-cyclopentenylcarbene rearrangement at the RHF/3-21G level of theory. The 1,2-transition-state geometry is highly contorted from its original ground-state structure, but only in such a way as to increase both the

---

[20] (a) Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 2617. (b) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 865.

Table VII. Stationary Points on the RHF/STO-3G and RHF/3-21G C_4H_4 Potential Surfaces for the Ring Closure of 2-Cyclopropenylcarbene to Tetrahedrane

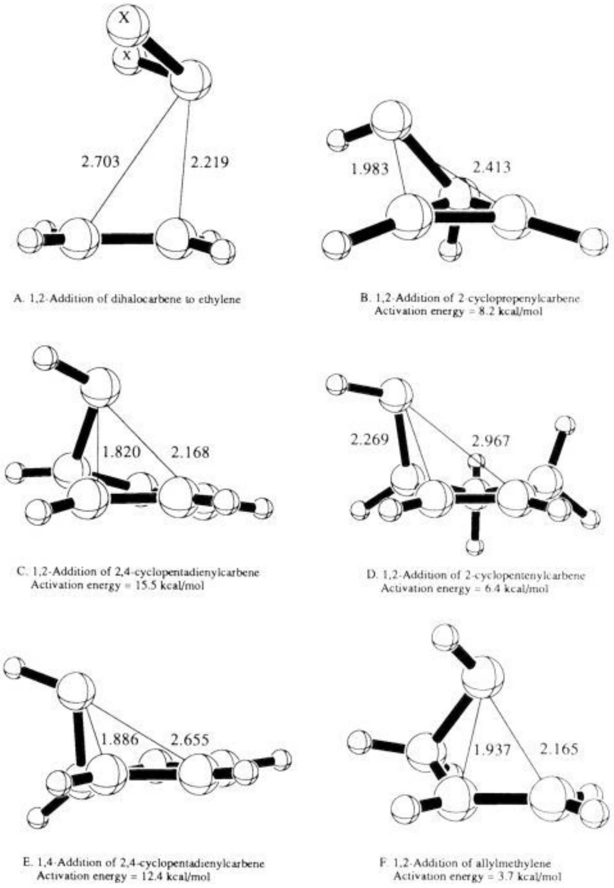
		RHF/STO-3G		RHF/3-21G		RMP2/6-31G*//3-21G	
system	pt gp sym	energy (hartrees)	relative (kcal/mol)	energy (hartrees)	relative (kcal/mol)	energy (hartrees)	relative (kcal/mol)
2-cyclopropenylcarbene (H outward)	C_s	−151.656 65	0.0	−152.689 53	0.0	−154.067 38	0.0
2-cyclopropenylcarbene (H inward)	C_s	−151.656 33	0.2	−152.689 86	−0.2	−154.066 56	0.5
TS (1,2-addition)	C_1	−151.638 47	11.4	−152.676 49	8.2	−154.077 24	−6.2
tetrahedrane	C_{2v}	−151.707 82	−32.1	−152.708 36	−11.8	−154.126 03	−36.8


(a) Allylmethylene C_1 Symmetry

(b) 1,2-Transition Structure 743i cm^{-1}

(c) Bicyclobutane C_{2v} Symmetry

Figure 12.



A. 1,2-Addition of dihalocarbene to ethylene

B. 1,2-Addition of 2-cyclopropenylcarbene Activation energy = 8.2 kcal/mol

C. 1,2-Addition of 2,4-cyclopentadienylcarbene Activation energy = 15.5 kcal/mol

D. 1,2-Addition of 2-cyclopentenylcarbene Activation energy = 6.4 kcal/mol

E. 1,4-Addition of 2,4-cyclopentadienylcarbene Activation energy = 12.4 kcal/mol

F. 1,2-Addition of allylmethylene Activation energy = 3.7 kcal/mol

Figure 13.

electrophilic and nucleophilic distances, as shown in Figure 13b.

2-Cyclobutenylcarbene Reaction. The 1,2-cycloaddition transition state for 2-cyclobutenylcarbene was not located, but the reactant and product (Figure 11a,b) were optimized. The energy of reaction is −29.3 kcal/mol at the RHF/3-21G level of theory and −57.1 kcal/mol with the inclusion of electron correlation.

Allylmethylene Reaction. Allylmethylene (Figure 12a) has added geometric flexibility, and the intramolecular reaction is more facile. The characteristic positioning for the stabilizing electrophilic interaction with the π-system was not observed for the ground-state carbene. In fact, the methylenic hydrogen was pointed almost directly into the olefinic centers, allowing for staggering of the occupied hybrid orbital and the adjacent σ_{C-H} bonds. The cis and trans conformations of allylmethylene were held in C_s symmetry and optimized. The geometries are 0.5 and 1.4 kcal/mol, respectively, higher in energy than the C_1 minima. This additional relaxation of the carbon skeleton removes the carbenic center from the electron-rich π-system, such that the electrophilic interaction no longer occurs. For allylmethylene, the electrophilic distance is 2.580 Å, whereas in 2-cyclopentenylcarbene it is decreased to 2.270 Å, and for 2,4-cyclopentadienylcarbene (H-outwards) the distance is 2.252 Å. The same situation is apparent for 2-cyclopropenylcarbene, since only a C_s structure could be located with an electrophilic distance was elongated to 2.553 Å, comparable to the length for allylmethylene.

The 1,2-transition state, Figure 12b, for the allylmethylene reaction was reminiscent of the others found in this investigation, except that it most closely resembles the intermolecular structure as compared to the other intramolecular cases examined. The ratio of electrophilic to nucleophilic distances is 0.9, whereas in the intermolecular case this ratio is 1.2. The reduction in the energy of activation to 3.7 kcal/mol as compared to higher values in cyclic cases reflects only a small amount of riing strain in this transition structure.

In the intramolecular cases examined, the alkyl tether forces even longer nucleophilic distances, as compared to the electrophilic length. As the strain in the system decreases and the ratio of electrophilic to nucleophilic distances approaches that of the intermolecular case, a corresponding decrease in activation energy is observed. Therefore, as the intramolecular transition structure approaches that of a intermolecular geometry, a lowering of activation energy is computed; this is illustrated in Figure 13.

Summary

Although there are a number of 1,4-addition products resulting from the reactions of carbenes with polyenes, only a few documented direct 1,4-cycloadditions have been reported, one via a triplet mechanism and others through the singlet mode. The closure of 2,4-cyclopentadienylcarbene to 1-methylbenzvalene has been shown to result from the geometric strain in the 1,2-cycloaddition transition state. The positioning of the carbene HOMO to complete its nucleophilic attack in the 1,2-mode of addition diverts the preferred reaction pathway to 1,4 in this intramolecular case.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work and to F. A. L. Anet and D. Farrelly for helpful discussions and assistance. Dr. M. D. Miller provided the graphics routines for Figures 4–13.

Registry No. 2,4-Cyclopentadienylcarbene, 65312-66-5; benzvalene, 659-85-8; methylene, 2465-56-7; butadiene, 106-99-0; allylmethylene, 90566-94-2; 2-cyclopropenylcarbene, 61281-66-1; 2-cyclobutenylcarbene, 112879-11-5; 2-cyclopentenylcarbene, 123811-71-2; 1-methyl-2,4-cyclopentadienylcarbene, 74130-26-0; 1-methylbenzvalene, 74130-27-1; 2-methylbenzvalene, 74130-29-3; cyclopentene, 142-29-0; vinylcyclopropane, 693-86-7; tricyclo[3.2.0.0^{2,6}]heptane, 30907-83-6; bicyclobutane, 157-33-5; tricyclo[1.1.1.0^{4,5}]pentane, 333-17-5; tetrahedrane, 157-39-1.

Supplementary Material Available: Structures and listings of bond lenths and bond angles (5 pages). Ordering information is given on any current masthead page.

Structure and Bonding in $Cr(CO)_5H_2$ and $Cr(CO)_4(H_2)_2$ Complexes

Gianfranco Pacchioni

Contribution from the Dipartimento di Chimica Inorganica e Metallorganica, Centro CNR, Università di Milano, via Venezian 21, 20133 Milano, Italy.

Received February 15, 1989

Abstract: The electronic structure of $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$ complexes has been investigated using ab initio electronic wave functions and effective core potentials. In $Cr(CO)_5(H_2)$ η^2-H_2 coordination is found to be energetically preferred, in agreement with experimental results. The formation of the dihydride form is an energy-demanding process; this explains why under D_2 pressure no isotope exchange is observed. $Cr(CO)_4(H_2)_2$ contains two coordinated hydrogen molecules; polyhydrogen forms are found to be highly unstable. A mechanism is proposed to explain the observed formation of $Cr(CO)_5(HD)$ during H_2/D_2 exchange in $Cr(CO)_4(H_2)_2$; it implies the formation of a dihydrogen–dihydride complex. The calculations predict also the possible existence of a stable open H_3 ligand in the hypothetical $[Cr(CO)_5(H_3)]^+$ complex.

The recent discovery of transition-metal complexes where the H_2 molecule is stably coordinated to a metal center[1] without giving oxidative addition has opened new opportunities to study one of the most fundamental molecular activations in organometallic complexes as well as in metal surfaces.[2] Since the first example of a stable dihydrogen complex, $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$, where η^2-H_2 denotes side-on bonding, was reported by Kubas in 1984,[1a] an increasing number of similar compounds have been synthesized.[3] The original Kubas complex has been characterized in the solid state by both X-ray and neutron diffraction techniques,[1] showing an H–H distance of 0.75 Å (X-ray) and 0.84 Å (neutron); a similar H–H distance has been observed in the $[Fe(H)(H_2)(dppe)_2]^+$ complex.[3a,b] The existence of other η^2-H_2 complexes has been inferred mainly by spectroscopic measurements.[2,3]

This is the case of the $Cr(CO)_5H_2$ complex where the existence of coordinated molecular hydrogen has been deduced from ν_{H-H} IR data.[4,5] Simple theoretical arguments[6] as well as experimental evidence[4] support the view of an H_2 complex with low stability toward H_2 loss and low-energy pathways for the $H_2 \rightarrow D_2$ exchange. Indeed, under pressure of D_2, $Cr(CO)_5H_2$ thermally reacts to form $Cr(CO)_5D_2$.[5] However, different from Kubas' compound where isotope exchange occurs giving within a few days a statistical mixture of H_2, D_2, and HD species[1b,1c], under pressure of D_2, the only species observed with the Cr complex are $Cr(CO)_5H_2$ and $Cr(CO)_5D_2$ with no evidence for any $Cr(CO)_5HD$.[5] The latter is observed in a mixture of $Cr(CO)_5(D_2)$ and $Cr(CO)_4(D_2)_2$ under H_2 pressure.[5] This exchange is of considerable interest for the understanding of the interaction of H_2 with metal centers. A proposed mechanism for the exchange implies the simultaneous coordination of both H_2 and D_2 molecules according to the scheme $Cr(CO)_6 + 2H_2 - 2CO \rightarrow Cr(CO)_4(H_2)_2 + D_2 - H_2 \rightarrow Cr(CO)_4(H_2)(D_2) \rightarrow Cr(CO)_4(HD)_2 + CO - HD \rightarrow Cr(CO)_5(HD)$. The rate-determining step will involve the cleavage of H–H and D–D bonds and the formation of a new HD ligand, but the mechanism is not clear. It has been suggested that the exchange can occur through the formation of transient species where polyhydrogen "mass spectrometer molecules" like H_3 or H_4 are stabilized by bonding to the metal center.[7,8]

In this paper we present the results of an ab initio MO–LCAO study of $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$ complexes. We will analyze the relative stabilities of η^1-H_2 and η^2-H_2 as well as the seven-coordinated dihydride forms of $Cr(CO)_5(H_2)$ and of a number of possible geometrical isomers of $Cr(CO)_4(H_2)_2$. The bonding of molecular hydrogen with transition-metal complexes has been already the subject of theoretical studies based on qualitative arguments.[6–9] However, ab initio approaches, different

---

(1) (a) Kubas, G. J.; Ryan, R. R.; Svanson, B. J.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J.; Ryan, R. R.; Wroblewski, D. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (c) Kubas, G. J.; Unkefer, C. J.; Swanson, B. J.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

(2) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(3) (a) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (b) Ricci, G. S.; Koetzle, P. F.; Bautista, M.; Hoffstede, T.; Morris, R. H.; Sawyer, J. F. ACA Meeting, Philadelphia, June 1988; Series 2, Vol. 16, p 4. (c) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (d) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (e) Crabtree, R. H.; Lavin, M.; Bonneviot, L. J. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (f) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. (g) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124. (h) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

(4) Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374.

(5) Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc* **1986**, *108*, 3645.

(6) Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(7) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakoff, M.; Turner, J. J.; Upmacis, R. *Inorg. Chem.* **1987**, *26*, 3054.

(8) Burdett, J. K.; Pourian, M. *Organometallics* **1987**, *6*, 1684.

(9) Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* **1986**, *108*, 6587.

0002-7863/90/1512-80$02.50/0