J. Am. Chem. Soc. **1994,** *116,* 3539–3542 3539

Singlet Methylcarbene: Equilibrium Geometry or Transition State?

Buyong Ma and Henry F. Schaefer, III*

Contribution from the Center for Computational Quantum Chemistry, The University of Georgia, Athens, Georgia 30602

Received November 26, 1993. Revised Manuscript Received February 14, 1994[●]

Abstract: The isomerization of singlet methylcarbene to ethylene has been studied using *ab initio* quantum mechanical methods, resulting in high-level theoretical predictions of the transition-state structure and isomerization barrier height. Basis sets as large as triple-ζ plus double polarization plus carbon atom f and hydrogen atom d functions [TZ2P(f,d)] have been used with the self-consistent-field (SCF) configuration interaction, including all single and double excitations (CISD), and coupled cluster, including all single and double substitution (CCSD) methods, as well as CCSD with the effects of connected triple excitations added perturbatively [CCSD(T)]. The geometries for ground-state singlet methylcarbene and the transition state are both of C_1 symmetry. The classical barrier is predicted to be 2.0 kcal mol^{-1}, while the activation energy (ΔE_0) is 1.2 kcal mol^{-1} at the TZ2P(f,d) CCSD(T) level at 0 K; and the free energy barrier is $\Delta G^\circ = 1.5$ kcal mol^{-1} at 298 K. The activation energy is 0.3 kcal mol^{-1} higher for fully deuterated singlet methylcarbene. Therefore singlet methylcarbene appears to be a true intermediate, consistent with some experimental deductions.

1. Introduction

Methylcarbene (CH_3CH:) is the simplest alkyl-substituted carbene. It has often been concluded that singlet methylcarbene is merely a saddle point on the ethylene ground-state surface.[1] However, recent studies, theoretical[2] and experimental,[3] may indicate that methylcarbene is a true intermediate that exists in a potential energy minimum and has a finite lifetime. The ground electronic state for methylcarbene is a triplet. However, its lowest excited state, a singlet state, is only 3–5 kcal mol^{-1} higher in energy, as indicated by recent *ab initio* studies.[4,5] Methylcarbene is generated almost exclusively in experiments[3] by photolysis of methyldiazirine. This process favors the singlet electronic state of methylcarbene. Since the rearrangement of singlet methylcarbene, via 1,2 hydrogen migration,[6] to form ethylene is so fast, it is very difficult to characterize the nascent singlet methylcarbene. An isoelectronic molecule, singlet methylnitrene (CH_3N), has essentially no barrier to prevent its rearrangement to methyleneimine, as indicated by a recent theoretical study.[7] However, in contrast singlet methylcarbene apparently has been trapped in several different experiments, as discussed by Modarelli and Platz.[3] The lifetime of methylcarbene in pentane at ambient temperature is determined to be 500 ps and the activation barrier to its isomerization to ethylene is estimated to be less than 2.3 kcal mol^{-1} experimentally.[3]

Previously, Evanseck and Houk theoretically considered the activation barrier,[2] which was found to be 0.6 kcal mol^{-1} at the MP4/6-311G**//MP+ZPE level. Since they optimized geometries via second-order perturbation theory using a modest 6-31G* basis set, it is appropriate to examine this barrier at higher theoretical levels. The critical question is whether singlet methylcarbene is a transition state or an intermediate.

2. Theoretical Methods

Three basis sets are employed in this study. The first, of double-ζ plus polarization (DZP) quality, is the standard Huzinaga–Dunning contracted Gaussian basis[8] C (9s5p/4s2p), H(9s/4s) augmented with a set of (six) d functions on the carbon atoms [$\alpha_d(C) = 0.75$] and a set of p functions on the hydrogen atoms [$\alpha_p(H) = 0.75$]. The second, designated triple-ζ plus double polarization (TZ2P), is the Huzinaga–Dunning C (10s6p/5s3p), H (5s/3p) contracted Gaussian basis[8] augmented with two sets of (five) d functions [$\alpha_d(C) = 1.50, 0.35$] on carbon atoms and two sets of p functions [$\alpha_p(H) = 1.50, 0.35$] on hydrogen atoms. The third, TZ2P(f,d), is the TZ2P basis set augmented with one set of (seven) f functions [$\alpha_f(C) = 0.80$] on the carbon atoms and a set of (five) d functions on hydrogen [$\alpha_d(H) = 1.0$].

The structures of both the ground state of singlet methylcarbene and the transition state for the 1,2 hydrogen shift were optimized using the configuration interaction method with all single and double excitations[9] (CISD) and the couple cluster method including all single and double substitutions[10] (CCSD). The effects of connected triple excitations were added perturbatively to the CCSD method to optimize the geometries via a third correlated method [CCSD(T)]. With the CISD, CCSD, and CCSD(T) methods the two core molecular orbitals (carbon 1s-like) were kept doubly occupied in all configurations, and the two highest virtual molecular orbitals are deleted.

Harmonic vibrational frequencies were determined using analytic second derivative methods at the SCF level, and finite central differences of analytic first gradients at the CISD level. The enthalpy changes were evaluated as follows:[11]

$$\Delta H^\circ = \Delta E_e + \Delta E_v^\circ + \Delta(\Delta E_v)^{298} + \Delta E_r^{298} + \Delta E_t^{298}$$

where ΔE_v° is the difference between the zero-point vibrational energies of reactant and product at 0 K and $\Delta(\Delta E_v)^{298}$ is the change in the vibrational energy difference in going from 0 to 298 K. Entropy changes (ΔS°) have been evaluated from standard statistical mechanical relationships,[12] and free energy changes (ΔG°) are evaluated from the standard relationship $\Delta G = \Delta H - T\Delta S$. The standard state is 1 atm at 298 K.

[●] Abstract published in *Advance ACS Abstracts,* April 1, 1994.

[1] (a) Stolow, A.; Balko, B. A.; Cromwell, E. F.; Zhang, J.; Lee, Y. T. *J. Photochem. Photobiol. A: Chem.* **1992,** *62,* 285 and references therein. (b) Cromwell, E. F.; Stolow, A.; Vrakking, M. J. J.; Lee, Y. T. *J. Chem. Phys.* **1992,** *97,* 4029 and references therein.

[2] Evanseck, J. D.; Houk, K. N. *J. Phys. Chem.* **1990,** *94,* 5518.

[3] Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993,** *115,* 470 and references therein.

[4] Gallo, M. M.; Schaefer, H. F. *J. Phys. Chem.* **1992,** *96,* 1515.

[5] Khodabandeh, S.; Carter, E. A. *J. Phys. Chem.* **1993,** *97,* 4360.

[6] (a) Schaefer, H. F. *Acc. Chem. Res.* **1979,** *12,* 288. (b) Nickon, A. *Acc. Chem. Res.* **1993,** *26,* 84.

[7] Richards, C.; Meredith, C.; Kim, S.-J.; Quelch, G. E.; Schaefer, H. F. *J. Chem. Phys.* **1994,** *100,* 481.

[8] (a) Huzinaga, S. *J. Chem. Phys.* **1965,** *42,* 1293. (b) Dunning, T. H. *J. Chem. Phys.* **1970,** *53,* 2823. (c) Dunning, T. H. *J. Chem. Phys.* **1971,** *55,* 716.

[9] (a) Brooks, B. R.; Laidig, W. D.; Saxe, P.; Goddard, J. D.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980,** *72,* 4652. (b) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1986,** *85,* 963.

[10] (a) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982,** *76,* 1910. (b) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1989,** *89,* 7382.

[11] Del Bene, J. E.; Mettee, H. D.; Frisch, M. J.; Luke, B. T.; Pople, J. A. *J. Phys. Chem.* **1983,** *87,* 3279.

[12] Hout, R. F.; Levi, B. A.; Hehre, W. J. *J. Comp. Chem.* **1982,** *3,* 234.

0002-7863/94/1516-3539$04.50/0

Table 1. The Geometries for the Equilibrium Geometry of Singlet Methylcarbene (Figure 1a)[a]

	r_e					θ_e						τ
theoretical levels	C_1–C_2	C_2–H_3	C_1–H_4	C_1–H_5	C_1–H_6	4–1–5	4–1–2	2–1–5	1–2–3	6–1–2	6–1–5	6–1–2–3
DZP SCF	1.486	1.099	1.102	1.090	1.085	106.4	100.1	117.0	106.9	113.8	111.1	195.8
TZ2P(f,d) SCF	1.475	1.094	1.100	1.086	1.081	106.4	99.9	116.7	107.1	114.2	111.2	194.7
DZP CISD	1.484	1.113	1.112	1.096	1.091	106.2	96.4	118.9	105.3	114.5	111.9	195.1
TZ2P CISD	1.471	1.100	1.107	1.087	1.082	106.5	95.9	118.5	106.0	114.8	112.1	194.4
TZ2P(f,d) CISD	1.466	1.101	1.107	1.088	1.083	106.2	95.9	118.7	105.8	114.9	112.1	194.1
DZP CCSD	1.490	1.119	1.116	1.100	1.096	106.1	96.8	118.8	104.9	114.4	111.8	194.6
TZ2P CCSD	1.477	1.106	1.112	1.091	1.086	106.6	95.8	118.7	105.4	114.8	112.2	194.0
TZ2P(f,d) CCSD	1.470	1.106	1.112	1.091	1.086	106.1	95.4	119.0	105.7	115.0	112.2	193.9
DZP CCSD(T)	1.489	1.120	1.119	1.101	1.097	106.1	95.7	119.3	104.9	114.6	112.0	194.3
TZ2P CCSD(T)	1.478	1.108	1.114	1.092	1.087	106.0	95.3	118.8	105.2	114.9	112.2	193.7

[a] Bond distances are in Å, and angles are in deg.

Table 2. Stationary Point Geometries for the Transition State for the Isomerization of Singlet Methylcarbene to Ethylene (Figure 1b)[a]

	r_e						θ_e				τ	
theoretical levels	C_1–C_2	C_2–H_3	C_1–H_4	C_1–H_5	C_1–H_6	C_2–H_6	4–1–2	2–1–5	5–1–4	1–2–3	4–1–2–3	6–1–2–3
DZP SCF	1.386	1.091	1.088	1.083	1.327	1.275	125.8	119.6	114.5	109.1	–6.5	100.5
TZ2P(f,d) SCF	1.376	1.086	1.084	1.079	1.317	1.276	125.5	119.4	114.5	109.4	–6.8	99.9
DZP CISD	1.409	1.103	1.016	1.091	1.274	1.316	126.1	119.2	114.4	106.7	–7.0	97.7
TZ2P CISD	1.395	1.092	1.086	1.082	1.264	1.317	125.6	119.5	114.7	107.4	–7.7	96.8
TZ2P(f,d) CISD	1.393	1.092	1.087	1.082	1.258	1.319	125.6	119.5	114.8	107.5	–7.4	96.6
DZP CCSD	1.418	1.109	1.100	1.095	1.266	1.336	126.2	119.1	114.5	106.0	–7.4	96.8
TZ2P CCSD	1.404	1.098	1.090	1.085	1.268	1.328	125.5	119.8	114.4	106.9	–8.1	95.7
TZ2P(f,d) CCSD	1.402	1.098	1.091	1.086	1.250	1.340	125.6	119.3	114.7	106.9	–7.9	95.7
DZP CCSD(T)	1.425	1.112	1.102	1.097	1.257	1.352	126.2	119.0	114.5	105.6	–7.5	96.0
TZ2P CCSD(T)	1.413	1.101	1.092	1.087	1.253	1.350	125.7	118.8	115.1	106.2	–8.4	95.2

[a] Bond distances are in Å, and angles are in degrees.

Table 3. Total Energies (hartrees) for Singlet Methylcarbene and Its Transition State to Ethylene

theoretical levels	ground state	transition state
DZP SCF	–77.942 61	–77.923 83
TZ2P(f,d) SCF	–77.956 71	–77.940 73
DZP CISD	–78.211 02	–78.202 91
TZ2P CISD	–78.248 01	–78.241 09
TZ2P(f,d) CISD	–78.273 90	–78.268 21
DZP CCSD	–78.234 66	–78.227 20
TZ2P CCSD	–78.274 77	–78.268 28
TZ2P(f,d) CCSD	–78.302 92	–78.297 82
DZP CCSD(T)	–78.242 73	–78.237 00
TZ2P CCSD(T)	–78.286 14	–78.281 56
TZ2P(f,d) CCSD(T)[a]	–78.315 67	–78.312 52

[a] Single-point energies using the geometries determined at the TZ2P CCSD(T) level.

The computations were performed using the program PSI developed by this research group.[14]

3. Results and Discussion

A. The Conformations of Singlet Methylcarbene. The structures of the ground state of singlet methylcarbene and the transition state for rearrangement appear in Figure 1, and the geometrical parameters determined at the different theoretical levels appear in Tables 1 and 2, respectively. Both the ground state and the transition state contain no elements of symmetry (i.e. point group C_1) at all theoretical levels employed here.

Khodabandeh and Carter[5] recently studied the effects of hyperconjugation on singlet methylcarbene. Using the generalized valence bond (GVB) method they reported that the C_s symmetry conformation (Figure 1c) is lower in energy than the C_1 conformation (Figure 1a) for singlet methylcarbene. However, in the present study, the C_s symmetry conformation (Figure 1c) is 0.3 kcal mol^{-1} higher in energy in the TZ2P(f,d) SCF level and 0.5 kcal mol^{-1} higher in energy at the TZ2P CCSD level than the C_1 conformation (Figure 1a) of theory. Our C_s conformation also has different bond distances than those obtained by the Carter group. For example, their C–C bond distance is 1.53 Å whereas ours is only 1.49 Å at the TZ2P CCSD level.

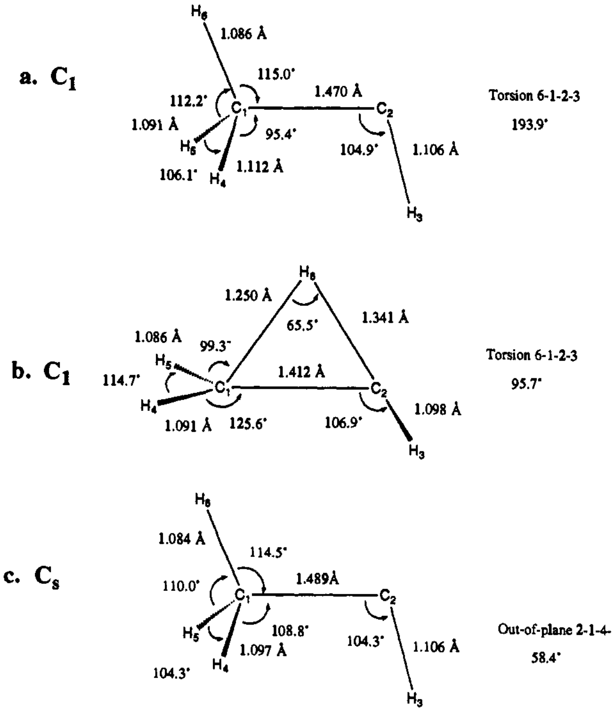

Figure 1. Stationary point geometries for singlet methylcarbene for (a) the minimum at the TZ2P(f,d) CCSD level of theory, (b) the transition state at the TZ2P(f,d) CCSD level of theory, and (c) a local minimum with C_s symmetry at the TZ2P CCSD level. For the geometrical parameters at other theoretical levels, see Tables 1 and 2.

B. The Barrier for the Isomerization of Singlet Methylcarbene to Ethylene. The total energies for singlet methylcarbene and the transition state for the 1,2 hydrogen shift are summarized in Table 3. The thermochemical data for the activation barrier are

---

(13) Grev, R. S.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1991**, *95*, 5128.

(14) Yamaguchi, Y.; Frisch, M. J.; Gaw, J. F.; Schaefer, H. F.; Binkley, J. S. *J. Chem. Phys.* **1986**, *84*, 2262.

Table 4. Barrier Heights for the Isomerization of the Singlet Methylcarbene to Ethylene[a]

theoretical levels	classical barrier ΔE_e	ΔE_0	ΔH°	ΔG°	ΔS°	comments
DZP SCF	11.8	11.3 (11.3)	11.0 (11.0)			ZPVE at the DZP SCF level
TZ2P(f,d) SCF	10.0	9.3 (9.6)	9.1 (9.2)	9.6 (9.9)	−1.5 (−2.2)	ZPVE at the TZ2P(f,d) SCF level
DZP CISD	5.1	4.3 (4.6)	4.1 (4.3)	4.6 (5.0)	−1.5 (−2.2)	ZPVE at the DZP CISD level
TZ2P CISD	4.3	3.5 (3.8)	3.3 (3.5)	3.8 (4.2)		ZPVE at the DZP CISD level
TZ2P(f,d) CISD	3.6	2.9 (3.2)	2.7 (2.8)	3.2 (3.5)		ZPVE at the DZP CISD level
DZP CCSD	4.7	3.9 (4.2)	3.7 (3.9)	4.2 (4.6)		ZPVE at the DZP CISD level
TZ2P CCSD	4.1	3.3 (3.6)	3.1 (3.3)	3.6 (4.0)		ZPVE at the DZP CISD level
TZ2P(f,d) CCSD	3.2	2.5 (2.8)	2.3 (2.4)	2.8 (3.1)		ZPVE at the DZP CISD level
DZP CCSD(T)	3.6	2.8 (3.1)	2.6 (2.8)	3.1 (3.5)		ZPVE at the DZP CISD level
TZ2P CCSD(T)	2.9	2.1 (2.4)	1.9 (2.1)	2.4 (2.8)		ZPVE at the DZP CISD level
TZ2P(f,d) CCSD(T)[b]	2.0	1.2 (1.5)	1.0 (1.2)	1.5 (1.9)		ZPVE at the DZP CISD level

[a] The values of ΔH and ΔG are in kcal mol^{-1}, and ΔS values are in cal/(K·mol). The standard state is 1 atm at 298 K. The results in parentheses refer to fully deuterated species. [b] Single-point energies using the geometries at the TZ2P+d CCSD(T) level.

Table 5. Harmonic Vibrational Frequencies and IR Intensities for Singlet Methylcarbene and Its Transition State to Ethylene at the DZP CISD Level of Theory

	ground state					transition state				
no.	mode	ω (cm^{-1})	ω (cm^{-1}) (scaled)[a]	IR intensity (Km/mol)	IR relative intensity	mode	ω (cm^{-1})	ω (cm^{-1}) (scaled)[a]	IR intensity (Km/mol)	IR relative intensity
1	C_1–H_6	3226	3064	35.5	0.49	C_1–H_5	3244	3081	22.1	0.32
2	C_1–H_5	3148	2990	39.6	0.55	C_1–H_4	3143	2985	37.2	74.4
3	C_1–H_4	3027	2875	72.0	1.00	C_2–H_3	3101	2945	68.5	1
4	C_2–H_3	3011	2860	1.3	0.02	H_6–C_1	2322	2205	7.6	0.11
5	H_6–C_1–H_5	1560	1482	6.5	0.09	C_2–C_1–H_5	1596	1516	5.3	0.08
6	H_4–C_1–H_5	1435	1363	5.2	0.07	C_1–C_2	1415	1344	25.4	0.37
7	H_4–C_1–H_5	1369	1300	28.0	0.39	C_1–C_2	1321	1254	12.5	0.18
8	C_1–C_2–H_3	1306	1240	10.2	0.14	C_1–C_2–H_3	1305	1239	40.7	0.59
9	C_1–C_2	1128	1071	5.2	0.07	H_6–C_1–C_2	1185	1125	16.7	0.24
10	H_6–C_1–C_2	978	929	23.0	0.32	H_4–C_1–C_2	1103	1047	52.8	0.77
11	H_4–C_1–C_2	588	558	4.0	0.06	H_5–C_1–C_2	982	932	32.8	0.48
12	H_5–C_1–C_2	484	459	65.0	0.90	$C_1 \cdots H_6$	1029i	977i	23.8	

[a] The vibrational frequencies were scaled by a factor 0.95 to account for anharmonicity and higher level correlation effects; see ref 13.

reported in Table 4. Harmonic vibrational frequencies and IR intensities are reported in Table 5.

Singlet methylcarbene may be compared with the X $^1A_1$ state of vinylidene[15] (H_2CC) in that the potential energy surfaces for both species are connected, via 1,2 hydrogen shift, with a stable and well-characterized structural isomer—ethylene in the former case and acetylene in the latter. On the basis of rigorous geometry optimizations at the TZ2P CCSD level of theory, Gallo, Hamilton, and Schaefer recently predicted a classical barrier to rearrangement of 3.0 kcal mol^{-1} for the vinylidene–acetylene 1,2 hydrogen shift. Their theoretical results, together with experimental observations and deductions,[16] confirm that the vinylidene does indeed exist as a bound molecule.

The transition state for the singlet methylcarbene to ethylene reaction involves the migration of one of the hydrogen atoms as the reaction coordinate (Figure 1b). It may be seen from Table 4 that the activation barrier does not vanish. The activation energy, at our highest level [TZ2P(f,d) CCSD(T)], is ΔE_0 = 1.2 kcal mol^{-1} at 0 K and the free energy barrier ΔG° = 1.5 kcal mol^{-1} at 298 K.

A direct comparison between the classical barriers predicted at similar levels of theory for methylcarbene and related species is of interest, as we examine the question "Is methylcarbene a true equilibrium geometry?" At the TZ2P CISD level, the classical barriers for methylcarbene and vinylidene are 4.3 and 7.1 kcal mol^{-1}, respectively. The TZ2P CCSD barriers are closer, 4.1 (methylcarbene) and 6.1 kcal mol^{-1} (vinylidene). Since the exact classical barrier for vinylidene (synthesized from a comparison of theory[15] and experiment[16]) is about 3 kcal mol^{-1}, this comparison suggests an ultimate classical barrier of about 1 kcal mol^{-1} for singlet methylcarbene.

Theoretical[17] and experimental[18] results also exist for the fluorovinylidene system. There the TZ2P CCSD(T) barrier is predicted to be 2.4 kcal mol^{-1}, compared to the present methylcarbene result at the same level of theory, 2.9 kcal mol^{-1}. Since fluorovinylidene has been well characterized experimentally[18] and the theoretical methylcarbene classical barrier is 0.5 kcal mol^{-1} higher, we are hopeful that the latter molecule will also succumb to detailed spectroscopic identification and analysis.

An interesting point made by the referee is that the basis set dependence of the predicted barriers is in some cases greater for methylcarbene than for either vinylidene or fluorovinylidene. For example, going from DZP to TZ2P lowers the CCSD barrier by 0.6 kcal mol^{-1} for methylcarbene but only 0.5 kcal mol^{-1} for vinylidene;[4] for fluorovinylidene,[17] the barrier is *increased* by 0.1 kcal mol^{-1} from DZP CCSD to TZ2P CCSD. However, the addition of f functions at the CISD level lowered the vinylidene barrier[4] by 1.8 kcal mol^{-1}, while the analogous barrier lowering here for methylcarbene is only 0.7 kcal mol^{-1}.

Consistent with the experimental result[3] that deuteration leads to a longer lifetime of the photogenerated carbene, there is an isotope effect on the isomerization barrier. The activation energy ΔE_0 is 0.3 kcal mol^{-1} higher for the isomerization of the fully deuterated methylcarbene (Table 4). There is a significant entropy contribution to the free energy barrier (ΔG°). Even though the absolute value for this contribution is small, being only 0.5 kcal mol^{-1} at 298 K, it is substantial considering the small size of the overall barrier.

C. Conclusions. The activation barrier for the isomerization of singlet methylcarbene to ethylene has been examined at high *ab initio* theoretical levels. Vibrational frequency analyses have confirmed that the singlet methylcarbene is a genuine minimum

---

(15) Gallo, M. M.; Hamilton, T. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1990**, *112*, 8714 and references therein.

(16) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Chem. Phys.* **1989**, *91*, 5974.

(17) DeLeeuw, B. J.; Fermann, J. T.; Xie, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1993**, *115*, 1039.

(18) Gilles, M. K.; Lineberger, W. C.; Ervin, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 1031.

and that there exist a true transition state on the potential energy surface. The activation energy, at the highest level of theory employed in this study, is $\Delta E_0 = 1.2$ kcal mol^{-1} at 0 K and the free energy barrier is $\Delta G^\circ = 1.5$ kcal mol^{-1} at 298 K. On this basis, singlet methylcarbene is a true intermediate with a finite lifetime.

Acknowledgment. We thank Dr. Cynthia Meredith for helpful discussions and for a careful reading of the manuscript. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant No. DE-FG09-87ER13811.