

Ab Initio Electronic Structure Calculations on Chlorocarbene–Ethylene and Chlorocarbene–Benzene Complexes

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Received January 15, 1999

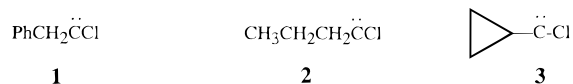
Abstract: Interaction energies for carbene–solvent complex formation have been computed at the MP2/6-311+G**//MP2/6-31G* level, including full counterpoise corrections. Our results indicate that chlorocarbenes do not form stable complexes with ethylene at ambient temperatures and react with tetramethylethylene to form cyclopropanes without an activation energy barrier. Chlorocarbenes and benzene form weakly interacting but thermally stable 1:1 and 1:2 π -type complexes. Two π -type complexes and a hydrogen-bonded ylidic structure were obtained for the 1:1 methylchlorocarbene–anisole system. The formation of carbene–solvent complexes might modulate carbenic reactivity in aromatic solvents.

Introduction

The addition of a carbene to an alkene with the formation of a cyclopropane¹ is perhaps the most fundamental of cycloaddition reactions,² as well as a basic component of the synthetic armamentarium.³ However, a significant uncertainty in the mechanistic analysis of this reaction family is introduced by the possible intervention of carbene–alkene π -complexes along the reaction coordinates.

Carbene–alkene complexes were initially postulated to account for the negative activation energies measured by laser flash photolysis for certain carbene–alkene addition reactions.⁴ Houk showed that the negative activation energies were most likely a consequence of the very high exothermicity of particular carbene–alkene additions, where activation barriers were absent on both the energy and enthalpy surfaces but arose on the free energy surfaces only because of entropic factors.^{5a,b} Results of early (1984–1985) ab initio calculations (MP2/3-21G) implied no intervention by π -complexes in reactions of dichlorocarbene (CCl₂) or more reactive carbenes with ethylene or substituted alkenes. Later calculations by Jorgensen (1989) led to the suggestion that halocarbene–alkene π -complexes could appear as broad, shallow wells in the reaction enthalpy profile, although these π -complexes did not represent minima on the free energy surfaces and would likely not persist on the enthalpy surface with di- or more substituted alkenes.⁶ Simultaneously with these developments in theoretical understanding, Liu, Bonneau, and

Tomioka reintroduced the carbene–alkene π -complex as the central feature in their explanation for the unexpected kinetic behavior of the competitive intramolecular rearrangement/intermolecular addition reactions of alkylhalocarbenes (e.g., benzylchlorocarbene, **1**).^{7,8} Alternative explanations of these results have been presented, however.^{9,10}



Although the existence of carbene–alkene complexes remains problematical, we imagined that carbene–arene complexes might be more amenable to experimental investigation. The methylene–benzene system was examined by Olah et al., who did not find theoretical support for a (singlet) methylene–benzene complex along the pathway from the reactants to the cycloheptatriene and toluene products.¹¹ However, Kahn and Goodman reported calorimetric evidence and computational support for the existence of a highly reactive transient in this reaction, identified as a π -type singlet methylene–benzene complex.¹²

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Recently, we presented evidence for the modulation of the carbenic reactivity of **1**, propylchlorocarbene (**2**), and cyclopropylchlorocarbene (**3**) by benzene and anisole.¹³ Specifically, the product ratios for rearrangement/addition (Re/Ad), corresponding to intramolecular 1,2-H (or 1,2-C) rearrangement vs intermolecular addition (to tetramethylethylene), were uniformly higher in benzene than in isoctane solvent with either photochemically or thermally generated carbenes. The Re/Ad ratio further increased in anisole. We suggested that transient carbene-arene complexes formed in benzene or anisole, which hindered the intermolecular addition reaction, extended the lifetimes of the carbenes, and favored intramolecular rearrangement. Ab initio electronic structure calculations supported the formation of the proposed complexes.¹³

Here, we present more complete details of our electronic structure studies of 1:1 chlorocarbene-arene complexes. Furthermore, we have extended the scope of the computations to include analyses of putative 1:1 carbene-alkene, 1:2 carbene-arene, and 1:2 carbene-alkene, as well as 1:1 arene-carbene-alkene complexes.

Computational Details

Electronic structure calculations were carried out with the Gaussian 94 suite of programs¹⁴ at the levels of second-order Møller-Plesset (MP2)¹⁵ and hybrid density functional theory (B3LYP)¹⁶ with basis sets developed by Pople, McLean, and co-workers.¹⁷ Geometry optimizations with the 6-31G* basis set (MP2/6-31G* or B3LYP/6-31G*) were followed by single-point calculations with the 6-311+G** basis set. Interaction energies were computed uniformly throughout this work at the MP2/6-311+G**//MP2/6-31G* level and corrected for basis set superposition errors (MP2(BSSE)) by application of the full counterpoise correction.¹⁸ For 1:1 carbene-ethylene or -benzene complexes, we have computed the vibrational zero-point energies (ZPE) and thermal energy corrections for finite temperature required to convert the purely electronic energies to internal energies at ambient temperature (298 K) at the MP2/6-31G* level. We have used data derived from B3LYP/6-31G* calculations to make these corrections for the larger complexes (1:1 carbene-anisole, 1:2 carbene-ethylene or -benzene, 1:1:1 ethylene-carbene-benzene).¹⁹ Wave functions were analyzed by using the natural orbital population scheme.²⁰

Most complexes were computed with considerably larger intermolecular separations at the B3LYP/6-31G* than at the MP2/6-31G* level. In accord, the interaction energies computed with the MP2 method were always much larger (i.e., more negative) than those computed with the

Table 1. Interaction Energies (kcal/mol) of CCl₂-C₂H₄ (**4**), MeCCl-C₂H₄ (**5**), C₂H₄-CCl₂-C₂H₄ (**6**), and C₂H₄-MeCCl-C₂H₄ (**7**) Species Relative to Free Carbenes and Ethylene

species	$\Delta E(\text{MP2})$			
	6-31G*	6-311+G**	(BSSE) ^a 6-311+G**	(BSSE,298) ^b 6-311+G**
4 (MIN)	-1.96	-2.79	-0.61	1.17
4 (TS)	0.80	0.53	4.01	5.33
5 (MIN)	-2.38	-2.70	-0.88	0.98
5 (TS)	-1.72	-1.96	0.78	2.34
6 (MIN)	-3.86	-5.73	-1.31	2.26
6 (TS)	-0.87	-2.54	3.12	6.19
7 (MIN)	-4.99	-5.47	-2.16	1.56
7 (TS)	-4.64	-5.18	-0.79	2.61

^a After BSSE corrections are made at the MP2 level. ^b $\Delta E(\text{MP2}(\text{BSSE},298))$ obtained by adding differential vibrational zero-point and thermal energy corrections obtained at the MP2/6-31G**//MP2/6-31G* level to the MP2(BSSE)/6-311+G**//MP2/6-31G* energy differences.

Table 2. Interaction Energies (kcal/mol) of CCl₂-C₆H₆ (**9**), MeCCl-C₆H₆ (**10**), MeCCl-C₆H₅OCH₃ (**11**), C₆H₆-CCl₂-C₆H₆ (**12**), C₆H₆-MeCCl-C₆H₆ (**13**), C₂H₄-CCl₂-C₆H₆ (**14**), and C₂H₄-MeCCl-C₆H₆ (**15**) Species Relative to Free Carbenes, Benzene, and Ethylene

species	$\Delta E(\text{MP2})$			
	6-31G*	6-311+G**	(BSSE) ^a 6-311+G**	(BSSE,298) ^b 6-311+G**
9a ^c	-3.23	-6.17	-2.00	-0.20
9b ^d	-3.19	-5.96	-1.96	<i>d</i>
9c	-3.82	-7.11	-2.32	-0.56
10	-4.78	-6.67	-3.06	-1.26
11a	-6.96	-9.48	-4.97	-3.01
11b	-5.03	-7.15	-3.30	-1.42
11c	-5.27	-5.19	-3.26	-1.33
12a	-6.28	-12.62	-4.14	-0.53
12c	-7.45	-14.62	-5.03	-1.42
13	-9.38	-14.18	-6.52	-2.82
14c	-5.63	-10.09	-3.11	0.51
15	-7.02	-9.76	-4.45	-0.77

^a After BSSE corrections are made at the MP2 level. ^b $\Delta E(\text{MP2}(\text{BSSE},298))$ obtained by adding differential vibrational zero-point and thermal energy corrections obtained at the MP2/6-31G**//MP2/6-31G* level (**9**, **10**) or B3LYP/6-31G**//B3LYP/6-31G* level (**11**-**15**) to MP2(BSSE)/6-311+G**//MP2/6-31G* energy differences. ^c First-order saddle point (transition state for interconversion of equivalent **9c** conformers). ^d Second-order saddle point.

B3LYP method; also, transition state energy barriers were higher at the B3LYP than at the MP2 level. Stabilization energies increased (and transition state energy barriers decreased) monotonically and substantially at the (BSSE uncorrected) MP2 level as the basis sets increased in size (e.g., 6-31G* → 6-311+G**), but the reverse behavior was observed at the B3LYP level. The use of the B3LYP parametrization or, more generally, most current implementations of density functional theory is questionable for the study of weakly interacting intermolecular complexes,²¹ since this methodology does not (in contrast to, for example, MP2 theory) allow for contributions to the dispersion energy.^{21a-c} The density functional theory based methods may also have difficulties in accounting properly for charge-transfer phenomena,^{21d} a second effect that could be of importance in stabilizing the complexes of interest here. Consequently, we will focus on data obtained with the MP2 method at geometries optimized at the MP2/6-31G* level. Tables 1 and 2 contain electronic energy differences obtained at the uncorrected MP2/6-31G**//MP2/6-31G* and MP2/6-311+G**//MP2/

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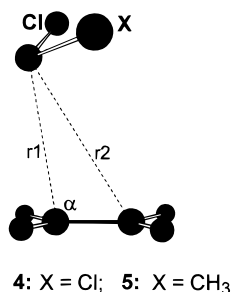
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6-31G* levels; the counterpoise corrected electronic energy differences at the MP2/6-311+G** level (denoted $\Delta E(\text{MP2}(\text{BSSE}))$) and the internal energy differences at 298 K (denoted $\Delta E(\text{MP2}(\text{BSSE}, 298))$) computed by adding the zero-point vibrational energy differences and thermal corrections (from MP2/6-31G* or B3LYP/6-31G* calculations, see above) to $\Delta E(\text{MP2}(\text{BSSE}))$. Optimized geometries at the MP2/6-31G* level are available as Supporting Information.

Results and Discussion

MeCCl and CCl₂ Complexes with Alkenes. Minima representing 1:1 complexes between dichlorocarbene (CCl₂) and ethylene (C₂H₄, Eth), **4**(MIN), and methylchlorocarbene (MeCCl) and Eth, **5**(MIN), and corresponding transition states for cyclopropane formation (**4**(TS) and **5**(TS)) were readily located. Our MP2/6-31G* structures of **4**(MIN) and **4**(TS) agree fully with those presented previously⁶ and feature the carbene species engaging in asymmetrical π -complexation with one carbon atom of the Eth double bond. The shortest C(carbene)–C(Eth) distance, r_1 , is 3.05 Å in **4**(MIN) whereas r_2 , the longer C(carbene)–C(Eth) distance, is 3.59 Å; $\alpha = 102.7^\circ$. In **4**(TS), the corresponding distances are about 0.8 Å shorter ($r_1 = 2.22$ Å, $r_2 = 2.70$ Å) and $\alpha = 95.3^\circ$. **5**(MIN) is similar in structure to **4**(MIN) but tighter, with $r_1 = 2.94$ Å, $r_2 = 3.42$ Å, and $\alpha = 99.1^\circ$. However, **5**(TS) has $r_1 = 2.40$ Å and $r_2 = 2.79$ Å, a slightly less tight structure than that of **4**(TS), and $\alpha = 91.6^\circ$. The ethylenic bond length is virtually unchanged upon complexation with the chlorocarbenes (C(Eth)–C(Eth) = 1.336 Å in Eth, 1.338 Å in **4**(MIN), and 1.339 Å in **5**(MIN)), but some bond lengthening is noticeable in the transition states (C(Eth)–C(Eth) = 1.356 Å in **4**(TS) and 1.347 Å in **5**(TS)). The structural differences between **4**(MIN) and **4**(TS) are distinctly larger than those between **5**(MIN) and **5**(TS), as expected for the more stabilized dichlorocarbene.²



The electronic interaction energies associated with chlorocarbene–ethylene formation are small, ~ 2 – 3 kcal/mol (Table 1), and the MP2(BSSE)/6-311+G** corrected interaction energies are less than 1 kcal/mol for both **4** and **5** (-0.6 kcal/mol for **4**(MIN), -0.9 kcal/mol for **5**(MIN)). Vibrational and thermal energies favor the reactants by almost 2 kcal/mol, so that the computed interaction energies at room temperature for **4**(MIN) and **5**(MIN) are both positive and in the range of 1.0–1.2 kcal/mol. Thus, these calculations do not predict formation of stable 1:1 chlorocarbene–ethylene complexes at ambient temperatures in the gas phase.²²

The activation energy for dichlorocyclopropane formation via **4**(TS) is positive at all computed levels and takes on a significant magnitude when corrections for BSSE ($\Delta E_a = 4.0$ kcal/mol; MP2(BSSE) level) as well as vibrational and thermal effects are included ($\Delta E_a = 5.3$ kcal/mol; MP2(BSSE,298) level). Interestingly, the electronic energy of the transition state for

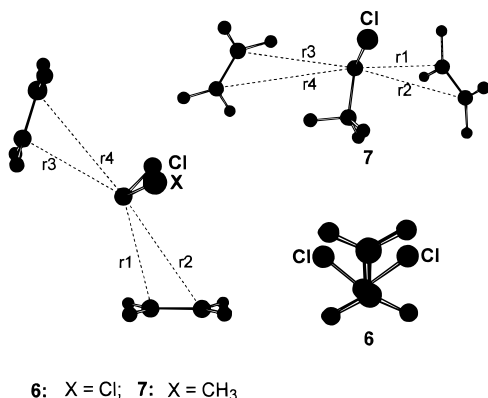
methylchlorocyclopropane formation, **5**(TS), is negative (-2.0 kcal/mol, MP2/6-311+G**) relative to the free reactants, but since the BSSE corrections are large for the compact **5**(TS) structure, the computed activation energy turns positive relative to the reactants after BSSE corrections have been made ($\Delta E_a = 0.8$ kcal/mol) and increases further to $\Delta E_a = 2.3$ kcal/mol at the MP2(BSSE,298) level. The energy difference between **5**(TS) and **5**(MIN) (~ 1.4 kcal/mol) is less than that between **4**(TS) and **4**(MIN) (~ 4.2 kcal/mol) in accordance with the structural differences between minima and transition state structures outlined above and the Hammond principle.²³

A carbene generated in solution is surrounded by several solvent molecules. Accordingly, it seems realistic to inquire whether its initial interactions with the host solvent might be better expressed as 1:2 (or higher) carbene–solvent complexes than as the 1:1 complexes considered thus far. Minima representing 1:2 CCl₂–C₂H₄ and MeCCl–C₂H₄ sandwich complexes (**6**(MIN) and **7**(MIN)) have been located. **6**(MIN) exhibits high symmetry (C_{2v}) with the carbene centrally positioned so as to bond optimally with both ethylene partners. This complex resembles the 1:1 complex **4**(MIN), with the second Eth unit symmetrically added; for example, the C(carbene)–C(Eth) distances are $r_1 = r_3 = 3.06$ Å and $r_2 = r_4 = 3.62$ Å in **6**(MIN), virtually identical with the corresponding distances in **4**(MIN) (3.05, 3.59 Å). **7**(MIN), the 1:2 MeCCl–C₂H₄ complex, may in analogous fashion be viewed as **5**(MIN) augmented with a second Eth unit, but the added Eth fragment is positioned farther away from the carbene center. For example, whereas $r_1 = 2.96$ Å and $r_2 = 3.43$ Å in **7**(MIN) (cf. $r_1 = 2.94$ Å and $r_2 = 3.42$ Å in **5**(MIN)), the C(carbene)–C(Eth) distances to the second Eth unit are $r_3 = 3.45$ Å and $r_4 = 4.14$ Å. The Me–C–Cl angle approximately bisects the Eth C–C axis in **5**(MIN), and this MeCCl orientation is maintained with respect to the closest Eth unit in **7**(MIN) as well; however, both Cl and Me are positioned on the same side of the C–C axis pertaining to the second Eth unit. The presence of the methyl hydrogens renders a symmetrical orientation of the two Eth units with respect to MeCCl impossible. Similarly, the trimer transition states for cyclopropane formation (**6**(TS) and **7**(TS)) largely resemble the dimer transition states **4**(TS) and **5**(TS) with the added Eth moieties maintaining positions where they can interact significantly with the carbene centers. For example, **6**(TS) has $r_1 = 2.21$ Å and $r_2 = 2.70$ Å (cf. $r_1 = 2.22$ Å and $r_2 = 2.70$ Å in **4**(TS)) but $r_3 = 3.05$ Å and $r_4 = 3.63$ Å, reflecting the reduced symmetry of the complex (C_s); the latter carbene–Eth distances are, however, remarkably similar to those obtained in **6**(MIN). The structure of **6**(TS) is thus an accurate composite of the appropriate relevant features of the **4**(TS) and **6**(MIN) (or **4**(MIN)) structures. Not surprisingly, the structure of **7**(TS) closely reflects the composite structures of **5**(TS) and **7**(MIN) as characterized by $r_1 = 2.41$ Å, $r_2 = 2.80$ Å, $r_3 = 3.46$ Å, and $r_4 = 3.83$ Å (**5**(TS): $r_1 = 2.40$ Å, $r_2 = 2.79$ Å; **7**(MIN): $r_3 = 3.45$ Å; $r_4 = 4.14$ Å).

Our best values for the purely electronic interaction energies of **6**(MIN) and **7**(MIN) are -1.3 and -2.2 kcal/mol (MP2(BSSE)/6-311+G**), respectively (Table 1). Since the corresponding interaction energies for the 1:1 complexes were -0.6 kcal/mol for **4**(MIN) and -0.9 kcal/mol for **5**(MIN), the apparent electronic interaction energy of the second Eth unit in **6**(MIN) is -0.7 and -1.3 kcal/mol in **7**(MIN); both values are thus slightly larger for the second Eth unit than for the first. However, at the MP2(BSSE,298) level positive interaction energies of 2.3 and 1.6 kcal/mol result for **6**(MIN) and **7**(MIN),

(22) The stationary points for **4** and **5** remain qualitatively similar to the MP2/6-31G* structures, when even larger basis sets are applied (e.g., MP2/6-311+G**).

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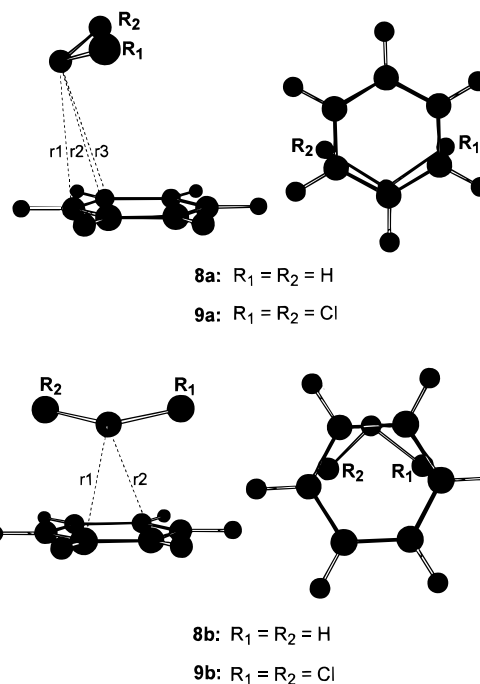
and we must conclude from these data that even 1:2 chlorocarbene–ethylene complexes should not be stable at ambient temperatures in the gas phase.

The presence of a second, solvating Eth unit reduces the purely electronic activation energy barriers for cyclopropane formation (Table 1, MP2(BSSE)). A preferential TS stabilization energy of 0.9 kcal/mol is obtained from a comparison of **6**(TS) and **4**(TS), a value slightly exceeding (by ~ 0.2 kcal/mol) the interaction energy obtained for the second Eth in **6**(MIN). Similarly, a preferential TS stabilization of 1.6 kcal/mol is obtained from the analogous comparison of **7**(TS) and **5**(TS), a value 0.3 kcal/mol larger than the interaction energy predicted for the second Eth unit in **7**(MIN). At room temperature the predicted activation energy for dichlorocyclopropane formation within the 1:2 complex is $\Delta E_a = 6.2$ kcal/mol, however, well into positive territory. Interestingly, with the substantial stabilization of **7**(TS) the purely electronic activation energy for the formation of methylchlorocyclopropane is actually computed to be *negative*, $\Delta E_a = -0.8$ kcal/mol, relative to the free reactants. Yet, at room temperature we compute a small but positive ΔE_a of 2.6 kcal/mol at the MP2(BSSE,298) level.

Despite numerous and lengthy attempts, we were not able to locate stationary points for the reaction systems consisting of CCl₂ or MeCCl and tetramethylethylene (TME). All our extensive searches of the potential energy surfaces using different trial reactant geometries, initial freezing of selected structural variables, and other “guiding” approaches ultimately led only to the cyclopropane products. The addition of either chlorocarbene species to TME appears to proceed without the presence of a barrier on the electronic energy surface (uncorrected for BSSE).²⁴

CCl₂ and MeCCl Complexes with Benzene. The two favorable interaction geometries identified by Kahn and Goodman for the parent CH₂–C₆H₆ complex (**8a**, **8b**)¹² show the carbene center interacting either directly with a specific benzene (Bz) carbon atom (**8a**) or with the π -electron cloud above a C–C bond (**8b**). Kahn and Goodman found both **8a** and **8b** (X = H) to be stationary points, stabilized by 7.2 and 5.8 kcal/mol (MP2/6-31G**//HF/6-31G*; no BSSE, vibrational or thermal corrections), respectively, relative to the isolated methylene (singlet) and Bz species.²⁵ The calculated dissociation energy for **8a** was similar to the measured enthalpy deposition (8.7 ± 3.1 kcal/mol) for an experimentally detected transient.¹²

Structures akin to **8a** and **8b** provided initial guesses for our investigations of CCl₂–C₆H₆ (**9**). Surprisingly, structure **9a** (C_s) with $r_1 = 3.14$ Å, $r_2 = r_3 = 3.49$ Å was found to be a transition state ($\nu = 31i$ cm⁻¹, a'' symmetry), and **9b** (C_s) was a second-order saddle point with two imaginary frequencies ($\nu = 8i$ and



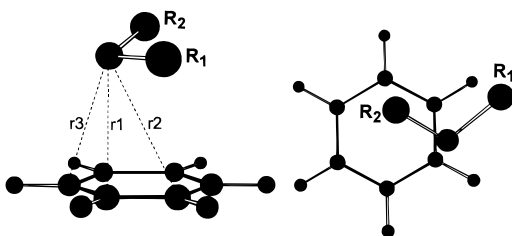
30i cm⁻¹; a'') at the MP2/6-31G* level. Both **9a** and **9b** lie approximately 2 kcal/mol below free CCl₂ + Bz (MP2(BSSE)/6-311+G**, Table 2). The minimum energy configuration for the CCl₂–C₆H₆ system at the MP2/6-31G* level **9c** presents no overall molecular symmetry.²⁶ In **9c**, the carbenic carbon remains situated nearly above a Bz carbon atom (as in **9a**) at a distance of $r_1 = 3.00$ Å (next nearest distances $r_2 = 3.35$ Å, $r_3 = 3.36$ Å), but the CCl₂ unit is rotated so that, relative to the Bz π -system, one Cl atom is oriented “in” toward the center of the Bz ring and one Cl is pointed “away”. The Cl–C–Cl angle is approximately bisected by the underlying Bz C–C bond and, locally, the interaction site in **9c** therefore looks very similar to the CCl₂–C₂H₄ interaction site in **4**(MIN), an alignment that maximizes π -type interactions.^{2c,d} The interaction energy (MP2-(BSSE)/6-311+G**, Table 2) is considerably larger in **9c** ($\Delta E = 2.3$ kcal/mol) than in **4**(MIN) ($\Delta E = 0.6$ kcal/mol). Further analysis shows that **9a** is the transition state for CCl₂ rotation around the C(carbene)–C(Bz) axis between two equivalent **9c**-type minima. Overall, there are many points on this potential energy surface of similar stabilization energy (~ 2 kcal/mol) and the CCl₂ unit does not appear to be strongly trapped in any particular location above the perimeter of the Bz ring.

Only one stationary point could be located for the MeCCl–C₆H₆ (**10**) complex. It has a “c-type” structure with the carbenic CH₃ group pointing “in” toward the center of the Bz ring and the Cl “away” from the Bz ring. The shortest C(carbene)–C(Bz) distances are $r_1 = 3.01$ Å, $r_2 = 3.32$ Å, and $r_3 = 3.49$ Å, similar to those encountered in **9c**. The purely electronic interaction energy in **10** at the MP2(BSSE)/6-311+G** level is 3.1 kcal/mol, somewhat larger than the interaction energy computed for **9c** (2.3 kcal/mol). These electronic interaction energies may well be sufficiently large to support the formation of stable complexes even at ambient temperatures, since **9c** and **10c** are computed to be stable to dissociation by 0.6 and 1.3 kcal/mol, respectively, at the MP2(BSSE,298) level (Table 2).

(25) We have almost completed a comprehensive (re)investigation of the methylene–benzene energy surface (to be submitted for publication).

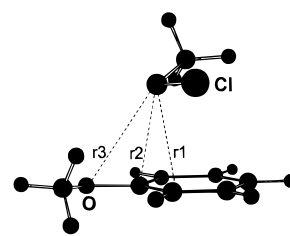
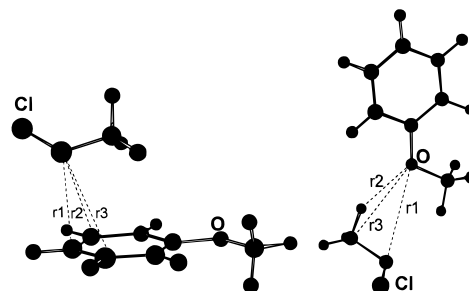
(26) At the HF/6-31G**//HF/6-31G* level, structure **9b** represents, however, a minimum whereas **9a** is a transition state. At the B3LYP/6-31G**//B3LYP/6-31G* level, both structures **9a** and **9b** represent minima.

(24) Cyclopropane formation also occurs without any activation energy barriers on the B3LYP/6-31G* energy surfaces.

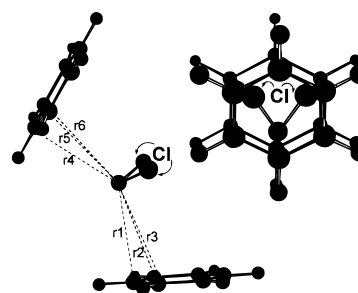
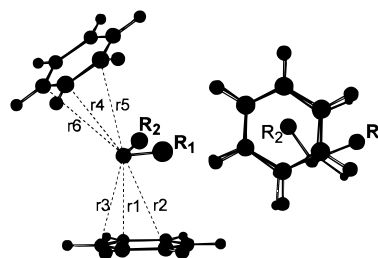
**9c:** $R_1 = R_2 = \text{Cl}$ **10c:** $R_1 = \text{Cl}; R_2 = \text{CH}_3$

Even more strongly bound carbene–arene complexes could be expected from more strongly coordinating solvents such as anisole ($\text{C}_6\text{H}_5\text{OCH}_3$). Indeed, we have located three minima on the 1:1 $\text{MeCCl}-\text{C}_6\text{H}_5\text{OCH}_3$ surface. One structure, **11a**, is a π -type complex with the carbenic carbon located above an ortho carbon of the benzene ring ($r_1 = 2.89 \text{ \AA}$, $r_2 = 3.26 \text{ \AA}$, $r_3 = 3.70 \text{ \AA}$). A second π -type complex, **11b**, has the carbenic carbon located nearly above the para carbon of the benzene ring ($r_1 = 2.96 \text{ \AA}$, $r_2 = 3.36 \text{ \AA}$, $r_3 = 3.38 \text{ \AA}$). In both structures, the methyl group is situated “in” and the Cl is pointing “away” from the benzene ring. The third minimum, **11c**, is a hydrogen-bonded ylidic structure in which the carbene engages in both hydrogen bonding and charge-transfer-type interactions with the anisole oxygen atom. In **11c**, the carbenic center is located in the anisole plane and the Cl atom is oriented almost perpendicular to this plane. Hence the formally empty p-orbital on the carbenic center is able to engage in an ylidic acceptor–donor interaction with the oxygen atom ($r_1 = 3.43 \text{ \AA}$). In addition, this p-orbital hyperconjugates with one of the methyl hydrogen atoms, increasing its charge, so that a weak hydrogen bond is formed to the methoxy oxygen atom ($r_2 = 2.33 \text{ \AA}$, $r_3 = 3.34 \text{ \AA}$, $\angle \text{O} \cdots \text{H}-\text{C} = 163.3^\circ$). The strongly electron-donating methoxy group increases the π -density at both ortho and para positions, but more so at the ortho position. In accordance, the interaction energy for the ortho π -type complex **11a** ($\Delta E = -5.0 \text{ kcal/mol}$, MP2(BSSE)/6-311+G**) is larger than those for the para π -type complex **11b** ($\Delta E = -3.3 \text{ kcal/mol}$, MP2(BSSE)/6-311+G**) and the hydrogen-bonded, ylidic complex **11c** (also $\Delta E = -3.3 \text{ kcal/mol}$, MP2(BSSE)/6-311+G**). After zero-point energy and thermal corrections have been included, the computed interaction energy for **11a** is $\Delta E = -3.0 \text{ kcal/mol}$, considerably larger than that computed above for **10** ($\text{MeCCl}-\text{C}_6\text{H}_6$; $\Delta E = -1.3 \text{ kcal/mol}$). Complexes **11b** and **11c** are also computed to be stable to dissociation by 1.4 and 1.3 kcal/mol, respectively.

The molecular size and possibly low point group symmetry of 1:2 carbene–Bz complexes prevented us from carrying out extensive searches of their potential energy surfaces at the MP2/6-31G* level. We have located stationary points resulting from the addition of a Bz unit to **9a** and **9c** in a symmetrical fashion (**12a** (C_{2v} symmetry) and **12c** (C_s symmetry), respectively). We also carried out one very lengthy calculation starting from a conformation where the carbene initially was arbitrarily “sandwiched” between the two planes of two benzene units with no symmetry restrictions imposed; ultimately, this calculation converged to a **12c** structure. In **12c**, the carbene carbon shows closest interaction distances $r_1 = r_4 = 3.00 \text{ \AA}$ to a carbon atom on each Bz ring and next nearest distances of $r_2 = r_5 = 3.35 \text{ \AA}$ and $r_3 = r_6 = 3.36 \text{ \AA}$; one C–Cl bond is oriented “in and above” and the other is “outside” with respect to the Bz π -electron surfaces. The interaction energy in **12c** is 5.03 kcal/mol, slightly more than twice the stabilization energy of **9c** (2.31 kcal/mol). Similarly, the stabilization energy of **12a** ($r_1 = r_4$

**11a****11b****11c**

$= 3.14 \text{ \AA}$, $r_2 = r_3 = r_5 = r_6 = 3.50 \text{ \AA}$) is computed at 4.14 kcal/mol, essentially twice that of **9a** (2.00 kcal/mol).²⁷

**12a****12c:** $R_1 = R_2 = \text{Cl}$ **13:** $R_1 = \text{Cl}; R_2 = \text{CH}_3$

The stationary point located for a Bz– MeCCl –Bz complex (**13**) shows the anticipated configuration that would result from maximization of both individual sets of MeCCl –Bz interactions. The shortest C(carbene)–C(Bz) distances are $r_1 = 3.14 \text{ \AA}$, $r_2 = 3.41 \text{ \AA}$, and $r_3 = 3.59 \text{ \AA}$ to one Bz unit and $r_4 = 3.02 \text{ \AA}$, $r_5 = 3.27 \text{ \AA}$, and $r_6 = 3.56 \text{ \AA}$ to the other unit; hence, in this 1:2 complex the carbene is located with slight asymmetry at distances comparable to those of the 1:1 complex. Consequently, the computed dimer stabilization energy of 6.52 kcal/mol is approximately twice the monomer stabilization energy (3.06 kcal/mol).

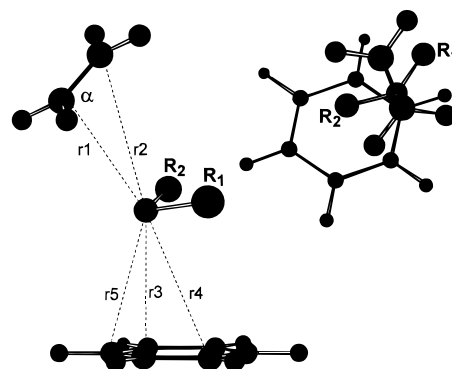
(27) The exact nature of **12a** on the MP2/6-31G* surface is not known to us, since we could not perform the required normal-mode analysis, but **12a** is a minimum on the B3LYP/6-31G* surface.

In summary, we calculate that MeCCl always engenders larger solvent stabilization energies than does CCl₂, and that complexation with Bz (or anisole) is more favorable than is complexation with Eth. These trends may be readily rationalized through arguments based on simple electrostatics. MeCCl possesses a larger permanent dipole moment (~2.2 D; MP2/6-31G*) than does CCl₂ (~1.2 D; MP2/6-31G*). Thus, electric dipole interactions with permanent or induced multipole moments of the complexation partner (Eth, Bz or anisole) should be larger for MeCCl. Neither Eth nor Bz possess a permanent dipole moment but anisole does (~1.4 D, MP2/6-31G*); hence, it is quite understandable that the largest interaction energy is computed for the 1:1 MeCCl–anisole complex **11a** (Table 2). The carbene furthermore complexes preferentially at the ring site of largest electron density. Since Bz has a substantial permanent quadrupole moment and a larger molecular polarizability than Eth, halocarbene complexes with Bz will be more stable than complexes with Eth. The structural finding that the CH₃ group in MeCCl always points “in” over the Bz ring may indicate the presence of weakly stabilizing hydrophobic interactions between CH₃ and the Bz ring. Actual charge transfer between the interacting units appears minimal. For example, NBO analysis of the MP2/6-31G* wave functions for **9c**, **10**, and **11a** predict a net transfer of 0.02–0.03 electrons from the carbene to the arene unit.

Mixed Complexes of MeCCl and CCl₂ with Ethylene and Benzene. In reactions between a carbene and an alkene carried out in benzene solution,¹³ we might imagine that an initial benzene–carbene–benzene sandwich complex (e.g., **12c** or **13**) would have to be replaced by a less stable benzene–carbene–alkene complex before carbene–alkene addition could occur. In this way, the 1:2 carbene–benzene complex might interfere with intermolecular addition, prolong the lifetime of the carbene, and enhance its intramolecular rearrangement/intermolecular addition product distribution.¹³ We have succeeded in locating stationary points corresponding to Eth–CCl₂–Bz (**14**) and Eth–MeCCl–Bz (**15**) complexes. Not surprisingly, the stabilizing interactions in **14** are a composite of those observed in **4(MIN)** and **9c**. Thus, the CCl₂ unit straddles the alkene double bond with C(carbene)–C(Et) distances of $r_1 = 3.09 \text{ \AA}$, $r_2 = 3.69 \text{ \AA}$ and $\alpha = 116.1^\circ$ (cf. 3.05 \AA , 3.59 \AA , and 102.7° in **4(MIN)**) and C(carbene)–C(Bz) distances of $r_3 = 3.02 \text{ \AA}$, $r_4 = 3.31 \text{ \AA}$, and $r_5 = 3.44 \text{ \AA}$ (cf. 3.00 , 3.35 , and 3.36 \AA in **9c**). The computed interaction energy of -3.11 kcal/mol (Table 2) approximates the sum of the interaction energies in **4(MIN)** and **9c** (-0.61 and -2.32 kcal/mol , respectively). Similarly, **15** resembles the union of **5(MIN)** and **10c** in geometry, but has an interaction energy (-4.45 kcal/mol) slightly larger than the sum (-3.94 kcal/mol) of the interaction energies computed for **5(MIN)** and **10c** (-0.88 and -3.06 kcal/mol , respectively). Interestingly, all attempts to use TME as the alkene in such mixed complexes led readily to the formation of a cyclopropane with a free benzene unit split off to a large intermolecular separation.

Concluding Remarks

The calculated stabilization energies are larger and the activation energy barriers for cyclopropane formation are smaller with MeCCl as the carbene than with CCl₂, but the data do not support the existence of stable complexes between simple chlorocarbenes and ethylene on either the internal energy (Table



14: R₁ = R₂ = Cl

15: R₁ = Cl; R₂ = CH₃

1) or enthalpy²⁸ surfaces. The presence of the solvent appears to reduce the barrier to cyclopropane formation, since the computed activation energies are smaller in the 1:2 carbene–ethylene complexes than in the 1:1 complexes.

The calculations suggest that more significant interactions occur between chlorocarbenes and arenes. We find that the carbene–Bz interaction energies are considerably larger than the carbene–Eth interaction energies, and that many highly accessible conformations show appreciable stabilization. Consequently we propose that such π -complexes form in the liquid phase. The interaction energies presented in Table 2 suggest that, when formed, carbene–arene complexes should have more than a fleeting lifetime and hence should be capable of influencing carbenic reactivity, in particular with respect to intra- vs intermolecular reactivity. To complete the addition of chlorocarbenes to Bz would involve a considerable energy cost from the loss of Bz aromaticity, and would require surmounting a considerable barrier. With Eth as the solvent, there is only a small barrier for cyclopropane formation; carbene–TME interactions are so strong that product formation occurs with no barrier and, of course, no penalty from loss of aromaticity.

We also note that the interaction energies involving one carbene and two solvent molecules are approximately twice, but typically slightly more than twice, those computed for one carbene and one solvating molecule. We cannot discern whether truly nonadditive effects are at play here, because of the approximations imposed to arrive at the interaction energies (limited correlation treatment (MP2), BSSE corrections, etc.), but we do find this to be an interesting, final observation.

Acknowledgment. We thank the National Science Foundation for financial support. We acknowledge the Center for Computational Neuroscience for a generous grant of computer time, and we appreciate helpful advice from Professors I. Tobias and E. R. Davidson.

Supporting Information Available: Tables containing the MP2/6-31G* optimized geometries and total energies of most of the structures discussed (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(28) Enthalpy differences at 298 K may be obtained from the $\Delta E(\text{MP2-BSSE}, 298)$ values by deducting $RT = 0.59 \text{ kcal/mol}$ for 1:1 complexes and $2RT = 1.18 \text{ kcal/mol}$ for 1:2 complexes.