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Singlet and Triplet Methylene (CH_2) Plus P_4: A Computational Study

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Ab initio studies of the interaction of singlet and triplet methylene with tetrahedral P_4 (white phosphorus) are reported in which singlet methylene "reacts", giving three 1:1 species: a P−P insertion adduct, a cyclotriphosphirene product, and an apex adduct. Examination of the potential energy surface reveals the connection of the three "products" through two transition states. The structures found computationally are compared with products reported in two experimental studies of reactions of P_4 and nucleophilic (stable) carbenes. These computational results suggest that simple carbene reactions with P_4 need to be explored experimentally. Triplet methylene generally does not interact with P_4 to give any bonded structures, with one noted exception.

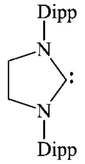
Introduction

Interesting and important, but limited, experimental and computational studies of the reactions of carbenes and tetrahedral P_4 (white phosphorus) have been reported. No work on carbenes as simple as methylene (CH_2) reacting with P_4 exists,[1–3] although other group 14 analogues such as silylenes[4] react in interesting ways, as do a number of main-group-metal and metalloid organometallics as varied as trialkylgallium,[5] gallium tetrahedral clusters,[6] cyclopentadienylaluminum,[7] (ligand)Al^I species,[8] dithallene derivatives,[9] trialkylsilyl anions,[10] and a so-called hypersilyl anion/crown ether complex.[11]

The emphases in the P_4 reactivity studies range from work in which larger phosphorus clusters are sought from smaller phosphorus fragments[1,2,11] to efforts to explore the fundamental reactivity of P_4.[1,3–9] Thus, P_4 undergoes an insertion-like reaction with tri-*tert*-butylgallium, giving a GaP_4 cluster[5] similar to reported transition-metal clusters containing cobalt,[12] zirconium,[13,14] and hafnium.[13] The gallium tetrahedral cluster $Ga_4[C(SiMe_3)_3]_4$ reacts with P_4 to give a remarkable species in which three $GaC(SiMe_3)_3$ units have inserted into P_4.[6] The resulting compound has a triangular P_3 base linked to a fourth phosphorus atom through three $GaC(SiMe_3)_3$ moieties. The hyper complex of a silyl anion and crown ethers, $(Me_3Si)_3SiK$/18-crown-6, affords a P_8 dianion with two pendant $(Me_3Si)_3Si$ groups.[11]

In reports by Bertrand and co-workers, the stabilized nucleophilic carbenes **A** and **B** react with P_4, giving interesting products.[2,3] Mechanistic studies indicate that 1 equiv of **A** reacting with $^1/_2$ equiv of P_4 produces an intermediate species whose structure is reported to be **A**=P−P=P−P=**A**, this being along the way to an isolable P_{12} cluster.[2]

A =



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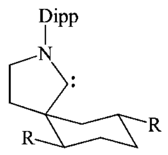
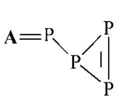


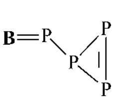
Dipp = 2,6-isoPrC_6H_3

R = isoPr

Trapping experiments with 2,3-dimethylbutadiene lead to product **C** as well as a Diels−Alder adduct. The latter structure supports the intermediacy of **A**=P−P=P−P=**A**. Reaction of **B** with $^1/_2$ equiv of P_4 leads to the *E* and *Z* isomers of **B**=P−P=P−P=**B**.[3]



C



D

Both reports give reaction path computational studies carried out at the B3LYP/6-311G(d,p) level (replacing **A** and **B** by analogues **E** and **F** for simplicity). These computational studies explore the mechanism of formation of the P_{12} cluster[2] and **B**=P−P=P−P=**B**[3] and succeed in demonstrating the intermediacy of **C** and **D**. Discussion of the mechanism leading to

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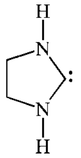
10.1021/om800011u CCC: $40.75

B═P−P═P−P═**B** emphasizes the importance of the nucleophilic nature of carbene **B** as central to the formation of **D**.[3]

E =


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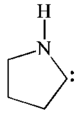


While stable singlet carbenes typically have adjacent electron-donating substituents like nitrogen making them σ donors, most carbenes are not nucleophilic but react by either electrophilic stepwise or so-called biphilic concerted pathways.[15–20] Among the latter is singlet methylene, whose chemistry is dominated by an empty, electrophilic p orbital and, thus, addition/insertion reactivity.[15,16,19] Ground-state methylene is a triplet with a singlet−triplet gap of ~9 kcal/mol.[15,16,19] Bertrand and co-workers' comments[3] concerning the nucleophilic nature of carbene **B** as well those indicating differences in reactivity[2] for carbenes prompts this report, since our computational studies of singlet and triplet methylene and P_4 reveal surprising results that are not attributable to nucleophilic carbene behavior.

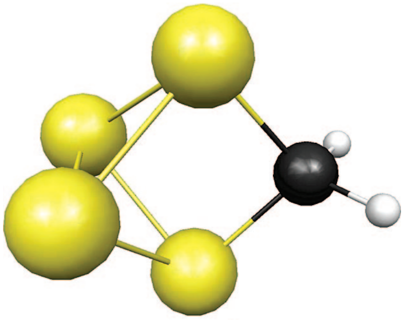
Computational Methods

Several computational methods were used to evaluate the systems considered herein. Energies were computed from geometry-optimized structures obtained without symmetry constraints using either density functional theory (DFT) with the B3LYP exchange-correlation functional[21–23] or Møller−Plesset second-order perturbation theory (MP2);[24] the two basis sets used were 6-311++G(d,p)[25] and 6-311++G(3df,3p).[26–29] Relative energies are reported in the body of this paper, while explicit energy data from the B3LYP/6-311++G(3df,3p)//L3LYP/6-311++G(3df,3p), B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p), MP2/6−311++G(3df,3p)//MP2/6-311++G(3df,3p), and MP2/6-311++G(d,p)//MP2/6-311++G(d,p) studies can be found in the Supporting Information. Frequency calculations and zero point energy corrections (ZPC) were carried out by standard techniques on the optimized structures. Products **1**−**3** are local minima (no "imaginary" frequency). The transition states[30,31] found were connected using intrinsic reaction coordinate (IRC) methodology, as discussed later.[32]

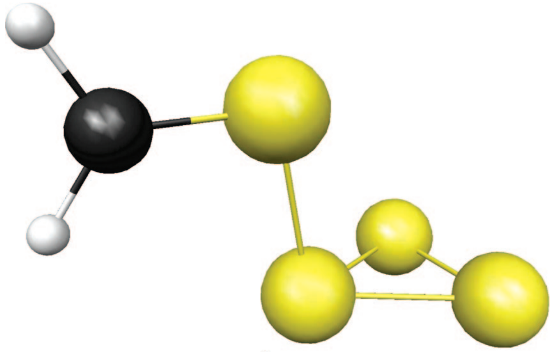
All computations were carried out using the GAMESS suite of programs,[33] with MacMolPlot[34] being used to visualize the molecular structures.

Results and Discussion

Geometry optimizations in which singlet methylene has been placed in various initial orientations and at various distances from P_4 have been conducted without symmetry constraints. Three structures (**1**−**3**) have been found with relative energies of 0 (**1**), ~22 (**2**), and ~42 kcal/mol (**3**) in B3LYP/6-31++G(3df,3p)//B3LYP/6-31++G(3df,3p)[35] computations (zero point energy corrected). Additional studies at the MP2/6-311++G(3df,3p)//MP2/6-311++G(3df,3p)[35] level give zero point energy corrected relative energies of 0, ~32, and ~41 kcal/mol for **1**−**3**. Examination of these structures reveals some interesting features in terms of their geometries and the conditions under which they are found computationally.



1



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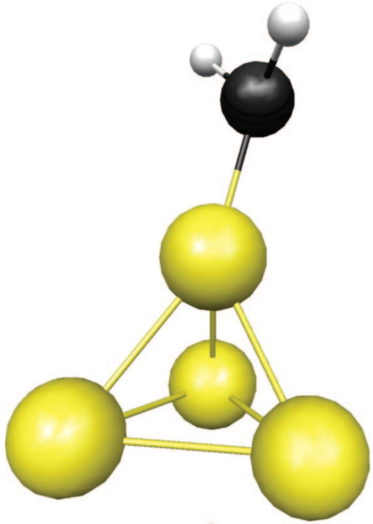

3

The lowest energy structure **1** is located when singlet CH_2 is juxtaposed with respect to P_4 with the empty p orbital of CH_2 (sp^2-hybridized carbon) pointed toward the P−P edge. The resulting structure is a highly symmetrical cage. All its C−P−P bond angles are equal (~88°), as are the four adjacent P−P bonds (2.25 Å) forming the "bicylic" P_4 base (geometric parameters are from the B3LYP/6-311++G(3df,3p) computations). The C−P bonds are 1.88 Å, and the P−P bond joining the phosphorus atoms not bound to carbon is slightly shorter than other P−P bonds at 2.20 Å. The H−C−H bond angle is

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~109°. To compare, the P−P bond length in P_4 is 2.21 Å,[36] a typical C−P distance is 1.86 Å,[37] and the H−C−H bond angle of free singlet methylene is ~102°.[16,19] Similar insertion structures with bridging gallium,[5] cobalt,[12] zirconium,[13,14] hafnium,[13] and silicon[4] have been reported.

Structure **2** has been found in optimizations beginning with various orientations of singlet methylene. In each of these cases, CH_2 migrates to the P_4 apex before continuing to **2**. Structure **2** has a H−C−H bond angle of ~116°, C−P and $P_{exocyclic}$-P_{cyclic} bond distances of 1.67 and 2.24 Å, and ring P−P bond distances of 2.25, 2.25, and 2.01 Å. The shortened C−P and ring P−P bonds suggest both a C=P bond and the P=P of a triphosphirene ring (no isolated triphosphirenes are known).[2] Typical C=P and P=P bond distances are 1.63 and 2.02 Å.[36]

The highest energy structure, **3**, was found in optimizations where singlet CH_2 initially is positioned near a P_4 apex. Structure **3** has an H−C−H bond angle of ~117°, a C−P bond distance of 1.68 Å (close to that expected for C=P), and ring P−P bond distances ranging between 2.13 and 2.20 ($P_{\text{triangular base}}$−$P_{\text{apex}}$) and 2.25−2.29 Å ($P_{\text{triangular base}}$−$P_{\text{triangular base}}$). The slight distortion of the P_4 cluster results from its bond to CH_2. No examples of structures analogous to **3** have been reported. Transition state **4** is ~49 kcal/mol above insertion product **1**, with transition state **5** being ~29 kcal/mol higher in energy than cyclotriphosphirene **2**. Numerous attempts to locate possible transition states along the entrance channels from CH_2 plus P_4 to either **1** or **3** failed, possibly because these transition states do not exist. They would probably not be very much higher in energy than the entrance channel energy, if they exist, and would be difficult to locate in this high-energy regime, particularly given the high exothermicity of the left- and right-hand channels (~46 and ~90 kcal/mol) to **3** and **1**. In contrast, computations by Bertrand and co-workers modeling the reaction of **F** and P_4 at B3LYP/6-311G(d,p) indicate an ~18 kcal/mol exothermicity to the their cyclotriphosphirene product, that found over a small barrier (~4 kcal/mol).[3] The barrier from **1** to **2** is ~49 kcal/mol and is not easily surmounted. That between **3** and **2** is much smaller (~9 kcal/mol), suggesting that **3** might easily convert to the cyclotriphosphirene **2**. A TS connecting two rotational isomers of **2** about the C−P bond has been found as well. The two rotomers differ in energy by ~2 kcal/mol, with a barrier of ~2 kcal/mol separating the higher (its CH_2 is above the P_3 ring) from the lower (its CH_2 points away from the P_3 ring) energy rotomer.

The transition state (TS)[30,31] structure connecting **1** and **2** has been found (TS-**4**), as has that between **2** and **3** (TS-**5**). These connections have been verified by moving in both directions from transition states **4** and **5** (Figure 1) along the intrinsic reaction coordinate.[32]

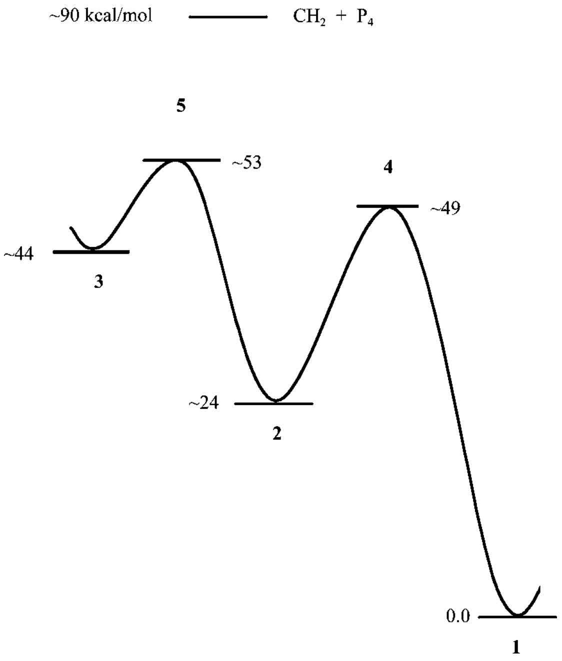
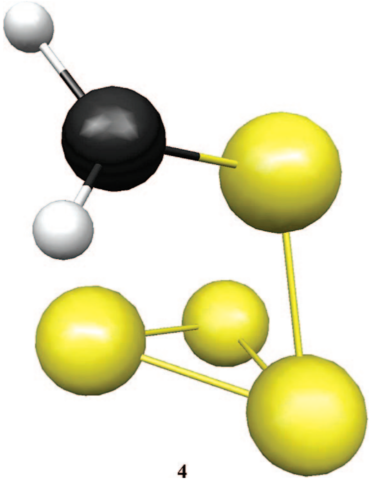
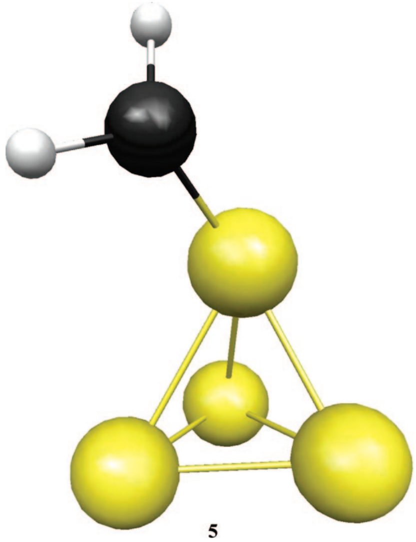


Figure 1. Reaction coordinate relative to **1** in kcal/mol. Energies have been determined at B3LYP/6-311++G(3df,3p)//B3LYP/6-311++G(3df,3p).

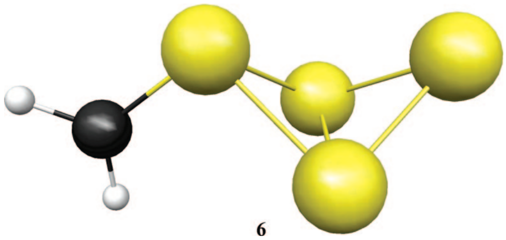


4



5

Restricted open-shell Hartree−Fock (ROHF)[32] computations of triplet methylene indicate that P_4 and CH_2 generally do not interact to form bonds in optimizations with one exception (several tries at both MP2/6-31++G(d,p) and B3LYP/6-311++G(3df,3p)). Most optimizations begin with different orientations of CH_2 and P_4 but lead to optimized structures where CH_2 and P_4 moieties have moved to nonbonding distances of ~4−5 Å. The H−C−H angle is ~134° at B3LYP/6-311++G(3df,3p) in all of these optimizations, nearly the same as free triplet CH_2 estimates of ~134−137°.[16,19,38] The one successful triplet result (optimization at the B3LYP/6-311++G(3df,3p) level) gave structure **6** although the same input geometry at MP2/6-31++G(d,p) disclosed no bonding interaction. This is another example of a basis set effect on row 3 elements in which the 6-311++G(3df,3p) basis produces optimized structures that are not found with smaller bases.[26–29] The course of the optimization leading to **6** is tortuous, with many early geometry iterations affording no C−P bonding. The initial orientation of CH_2 and P_4 has linear CH_2 poised over a P_3 triangle with the carbon centered. During the optimization the CH_2 slowly approaches a P apex with a sidewise, not head-on, orientation. Eventually, a bond between C and P is made from the side with a simultaneous scission of a P−P bond, the result being structure **6** in which the H−C−H bond is ∼117°. The two highest occupied molecular orbitals of **6** contain one electron each in essentially p orbitals, one localized on carbon and the other on the distant, two-coordinate phosphorus. The energy of structure **6** is ∼19 kcal/mol higher than that of structure **1**. The general lack of triplet "reactivity" may seem surprising, given the well-known reaction and chemiluminescence of dioxygen (O_2) and white phosphorus (P_4). Closer scrutiny, however, indicates that the chemiluminescence of P_4 is quite complicated and, in fact, does not occur in pure dioxygen.[39,40]



6

The computations reported here relate to various mechanistic studies of P_4 with organometallic reagents as well as with nucleophilic carbenes. Although structures analogous to **1** have been observed for gallium,[5] cobalt,[12] zirconium,[13,14] hafnium,[13] and silicon,[4] Bertrand and co-workers have reported no such structural analogues in their nucleophilic carbene studies.[2,3] This raises questions of (1) whether finding **1** in these computations is an artifact resulting from the initial placement of methylene with respect to P_4 or (2) whether methylene and nucleophilic carbenes have fundamentally different reactivities. The second question can only be examined by further experimentation, but we favor the latter possibility, notably because the zwitterionic group 14 silylene studied by Driess and co-workers gives only a structure analogous to **1** on reaction with P_4.[4] On the other hand, experimental and computational studies of the reaction of nucleophilic carbenes and P_4 not only suggest the intermediacy of structures analogous to **2**[2,3] but show that such species can be trapped.[2] Finally, structure **3** has been neither suggested nor observed in reactions with P_4, possibly because its energy is too high to be accessed. This seems surprising, since it suggests that the nonbonding electrons located on phosphorus are less accessible to the empty p orbital of singlet methylene than are the electrons on an edge P−P bond. This may be consistent with (1) our observations that bonding occurs on a P−P edge in geometry optimizations leading to **1** and **2** and (2) the greater number of η^2 as compared to η^1 ligand attachments of P_4 to transition metals.[36] It is noteworthy, on the other hand, that the first ionization energies (IE) of P_4 (adiabatic IE of 9.2 eV)[41] and various phosphines (adiabatic IEs of Me_3P, Me_2PH, $MePH_2$, and PH_3 are 8.11, 8.47, 9.12, and 9.96 eV)[42] are similar, which seems inconsistent if the nonbonding electrons in P_4 are remarkably less available. Whatever the mechanistic details, experimentation focused on the reactivity of the simple singlet carbene, CH_2, with P_4 needs to be explored.

Acknowledgment. Thanks go to Professor G. Barney Ellison for helpful discussions on triplet methylene and its possible relationship to singlet oxygen in reactions of P_4, to Professor C. H. DePuy for useful comments on reading an early draft, to Professor John S. Stanton for engaging in helpful discourse on the importance of describing the reaction coordinate using density functional theory, and to Professor Mark S. Gordon for discussions about techniques to locate transition states. R.D. also thanks the University of Colorado Denver for providing sabbatical support for this work.

Supporting Information Available: Tables containing the absolute and relative energies for the species reported as well as Cartesian coordinates for their input and optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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