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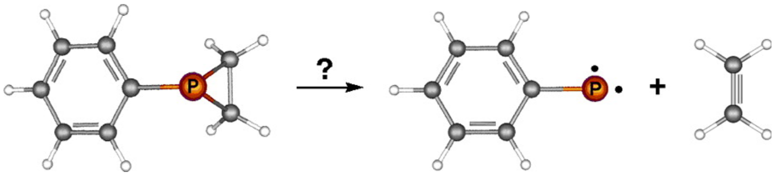

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Computational Studies of the Thermal Fragmentation of P-Arylphosphiranes: Have Arylphosphinidenes Been Generated by This Method?

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Abstract: CASSCF, CASPT2, CCSD(T), and (U)B3LYP electronic structure calculations have been performed in order to investigate the thermal fragmentation of P-phenylphosphirane (**1**) to phenylphosphinidene (PhP) and ethylene. The calculations show that generation of triplet PhP via a stepwise pathway is 21 kcal mol^{-1} less endothermic and has a 12 kcal mol^{-1} lower barrier height than concerted fragmentation of **1** to give singlet PhP. The formation of singlet PhP via a concerted pathway is predicted to be stereospecific, whereas formation of triplet PhP is predicted to occur with complete loss of stereochemistry. However, calculations on fragmentation of *anti-cis*-2,3-dimethyl-P-mesitylphosphirane (***cis*-1Me**) to triplet mesitylphosphinidene (MesP) indicate that this reaction should be more stereospecific, in agreement with the experimental results of Li and Gaspar. Nevertheless, with a predicted free energy of activation of 42 kcal mol^{-1}, the formation of MesP from ***cis*-1Me** is not likely to have occurred in an uncatalyzed reaction at the temperatures at which this phosphirane has been pyrolyzed.

Although the chemistry of phosphinidenes (R−P) has been investigated much less thoroughly than the chemistries of carbenes,[1] nitrenes,[2] and silylenes,[3] several methods for generation of transient phosphinidenes have been reported.[4−7] Nevertheless, Mathey has noted, "...generation of these transient phosphinidenes is deduced from the isolation of products, whose formation can be explained by a mechanism involving such intermediates. However, in almost every case, it is possible to conceive alternative mechanisms which do not involve phosphinidenes."[8]

Thermal and photochemical decompositions of phosphiranes have been investigated as a method for forming phosphinidenes.[4] Triplet mesitylphosphinidene ($Me_3C_6H_2P$) has, in fact, been detected by ESR spectroscopy in the photolysis of *trans*-2,3-dimethyl-1-mesitylphosphirane[9]

Photolysis and pyrolysis of P-mesitylphosphirane in the presence of 2,3-dimethylbutadiene as a trapping agent leads to the products shown in Scheme 1.[4] Evidence for free mesitylphosphinidene being formed as a reactive intermediate in these reactions included the independence of the rate of phosphirane decomposition on both the identity of the trapping agent and its concentration. In addition, in the photochemical reactions the selectivity of mesitylphosphinidene transfer to an alkyne and an alkene from four different P-mesitylphosphiranes and a P-mesityl-3-phospholene was identical within experimental error.[4c]

A similar reaction, formation of silylenes (SiR_2) by thermally induced fragmentation of siliranes, has been investigated.[10] A concerted mechanism for singlet silylene formation and a stepwise process, involving a diradical formed by homolysis of just one Si−C bond, were initially considered.[10e,f] The finding that pyrolysis of siliranes leads to stereospecific formation of

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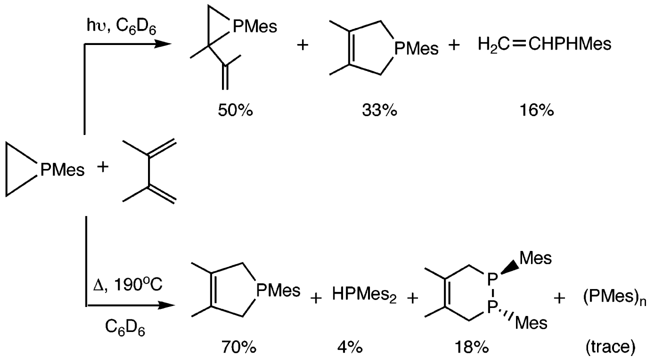
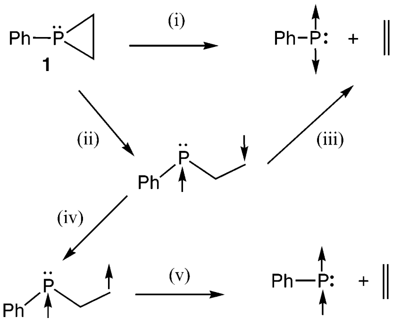
Scheme 1



Scheme 2



alkenes appears to demand a concerted mechanism.[10] However, stepwise silirane fragmentation might also lead to stereospecific alkene formation, provided that the rate of rotation about the C−C bond in the diradical intermediate were slower than the rate of cleavage of the second C−Si bond.[10a,b]

Similarly, formation of an arylphosphinidene by fragmentation of a P-arylphosphirane could also occur via either a concerted or a stepwise pathway (Scheme 2). However, arylphosphinidenes differ from silylenes in two important ways.

First, although most silylenes have singlet ground states,[3] the ground state of phenylphosphinidene is predicted to be a triplet.[11] This prediction finds support in the detection of triplet mesitylphosphinidene by EPR.[9]

Second, although the lowest singlet state of a silylene has a closed-shell configuration, in which a pair of electrons occupies the σ nonbonding orbital on silicon,[3] in phenylphosphinidene the lowest singlet state has an open-shell electronic configuration, in which one nonbonding electron occupies a 3p AO on phosphorus that lies in the plane of the benzene ring, and another nonbonding electron occupies a 3p AO of phosphorus that interacts with the π system of the benzene ring.[11] Consequently, a pathway for the fragmentation of an arylphosphirane that preserves a plane of symmetry would lead to the $^1A_1$ excited singlet state of the arylphosphinidene thus formed, rather than to the lowest singlet state ($^1A_2$). However, the conical intersection between the two lowest singlet states, which occurs along a symmetry-preserving reaction coordinate, could be avoided if the fragmentation pathway involves asynchronous bond breaking.

The open-shell configuration of the lowest singlet state of Ph-P thus raises the question of whether fragmentation of P-phenylphosphirane (**1**) is nevertheless concerted, proceeding without the formation of an intermediate (path i in Scheme 2); or whether bond breaking in **1** is so asynchronous that a singlet diradical intermediate is formed (path ii). This intermediate could fragment (path iii), with or without loss of stereochemistry, depending on the rate of scission of the second P−C bond, relative to the rate of rotation about the C−C bond in the singlet.

Alternatively, intersystem crossing (iv) to the lowest triplet state might compete with fragmentation and/or loss of stereochemistry in the singlet diradical. The triplet diradical could fragment (v), forming ethylene and the triplet ground state of PhP. If both ISC to the triplet (iv) and cleavage of the second P−C bond in the triplet diradical intermediate (v) were fast, compared to rotation about the C−C bond, extrusion of triplet PhP from **1** could be stereospecific.

The electronic structure calculations, described here, were performed in order to investigate the mechanism by which phenylphosphirane (**1**) fragments to phenylphosphinidene (PhP) and ethylene.[12] Herein we report the results of our calculations on the generation of singlet and triplet PhP by pyrolysis of **1** and on the predicted stereochemistry of the alkene concomitantly formed in both reactions. We also describe the results of our calculations on the effect of the methyl groups in 2,3-dimethyl-P-mesitylphosphirane on the stereochemistry of the fragmentation reaction.

Computational Methodology

Calculations were carried out using the Gaussian 98[13] and Molcas-5.4[14] packages of programs. Geometry optimizations were performed using complete active space self-consistent-field (CASSCF)[15] calculations with the 6-31G(d) basis set.[16] A 10-electron, 10-orbital active space [(10/10)CASSCF] was used for P-phenylphosphirane (**1**) and the ring opened diradicals formed from it. The active space for **1** consisted of the bonding and antibonding orbitals of the two P−C bonds and the three bonding π orbitals of the benzene ring and their antibonding counterparts. In the products, these orbitals of **1** correlate with the π and π^* MOs of ethylene and three bonding, three antibonding, and one nonbonding π orbital of phenylphosphinidene (PhP), plus a nonbonding σ orbital on phosphorus.

CASSCF/6-31G(d) vibrational frequencies were calculated for all stationary points, to verify whether each was an intermediate or a transition state and to obtain the zero-point and thermal corrections

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needed to convert energy differences to enthalpy and free energy differences.Thermal corrections for all internal rotations were approximated using harmonic oscillator partition functions.

To include the effects of dynamic electron correlation[17] single-point CASPT2 calculations[18] were performed at each of the CASSCF stationary points.

For comparison with the CASSCF and CASPT2 energies, unrestricted (U)B3LYP calculations[19] were performed for some of the CASSCF stationary points, using the CASSCF geometries as the starting points for (U)B3LYP geometry reoptimizations. In addition, CCSD(T)[20] calculations were carried out on **1** and on triplet PhP plus ethylene at the CASSCF optimized geometries, to obtain a fourth, independent assessment of the energies of the reactant in and products of the fragmentation reaction.

Results and Discussion

Selected structural parameters for the reactants, transition states, and intermediates in the fragmentation of **1** to form singlet and triplet PhP plus ethylene are shown in Figure 1. Complete geometries are available in the Supporting Information. Enthalpies of the stationary points relative to **1** are provided in Table 1.

Table 1. Calculated CASSCF and CASPT2[a] Enthalpies (kcal mol^{-1}), Relative to P-Phenylphosphirane (**1**), of the Stationary Points in the Fragmentation of **1** to Phenylphosphinidene (PhP) and Ethylene via Stepwise and Concerted Pathways

	$\Delta H_{\mathrm{CASSCF}}$	$\Delta H_{\mathrm{CASPT2}}$	$\Delta H_{\mathrm{(U)B3LYP}}$[b]
PhP ($^1A_1$) + C_2H_4	49.1	63.3	-
PhP ($^1A_2$) + C_2H_4	46.0	59.3	-
PhP ($^3A_2$) + C_2H_4	21.8	38.0	38.7
2TS (^{1}A)	49.5	59.9	-
3aTS ($^1A''$)	37.2	42.6	-
3bTS (^{1}A)	37.6	43.1	-
3cTS ($^1A'$)	37.1	42.8	-
3d (^{1}A)	37.6	43.7	-
4a ($^3A''$)	35.7	41.1	38.9
4b (^{3}A)	37.1	42.4	39.7
5aTS (^{3}A)	43.7	49.2	47.3
5bTS (^{3}A)	43.2	47.7	46.5
6aTS ($^3A'$)	36.5	42.2	40.1
6bTS (^{3}A)	36.9	41.8	40.2

[a] CASPT2 energies at the CASSCF optimized geometries, including zero-point and thermal corrections from CASSCF calculations at 298K. [b] (U)B3LYP enthalpies at the (U)B3LYP optimized geometries at 298K.

To confirm the supposition that inclusion of dynamic electron correlation makes CASPT2 relative energies more reliable than CASSCF relative energies,[17] CCSD(T) and (U)B3LYP calculations were performed on the enthalpy of triplet PhP plus C_2H_4, relative to that of **1**. The CCSD(T) calculations at the CASSCF optimized geometries gave a relative enthalpy of 40.3 kcal mol^{-1} (see the Supporting Information). The (U)B3LYP calculations (Table 1) gave 38.7 kcal mol^{-1}. Both of these relative energies are much closer to the CASPT2 value of 38.0 kcal mol^{-1} than to the (10/10)CASSCF value of 21.8 kcal mol^{-1} (Table 1). Therefore, throughout the remainder of this paper the discussions are based on the CASPT2 energies.

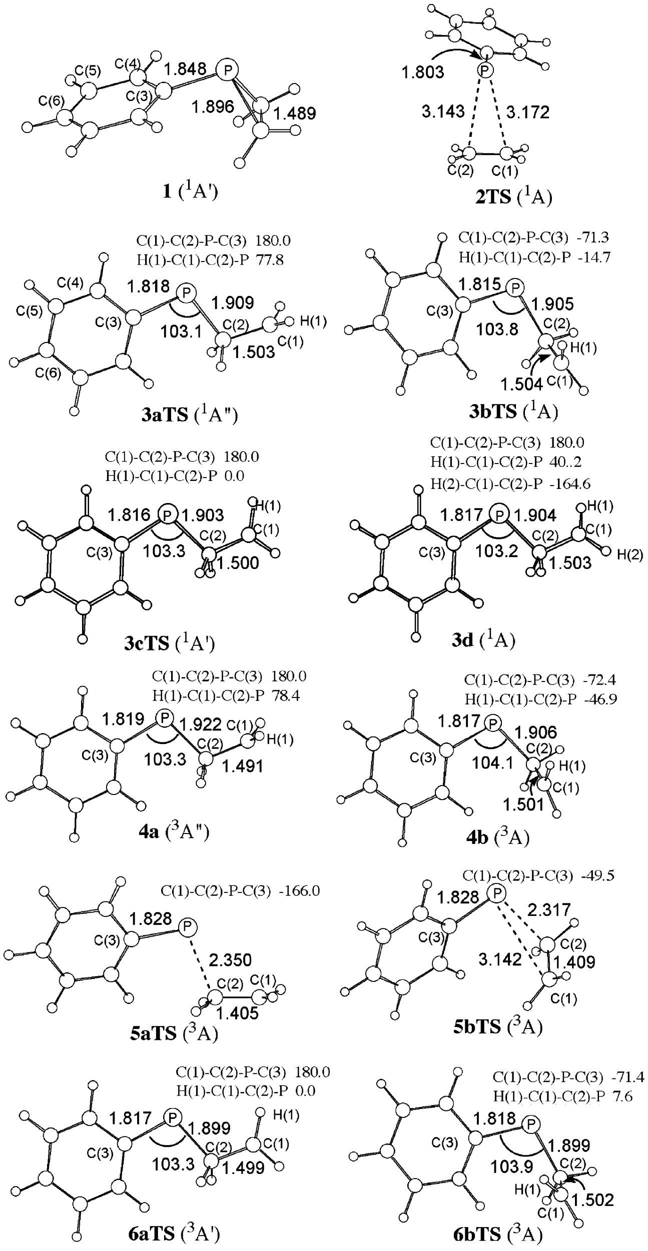

Figure 1. Selected structural parameters of the CASSCF stationary points in the fragmentation of singlet and triplet phosphinidenes from phenylphosphirane via a concerted and stepwise pathway. Bond lengths are in Å, and bond angles are in deg.

Concerted Pathway for Formation of Singlet PhP from 1. As noted in the Introduction, there are two low-lying singlet states in PhP—one an open-shell, $\sigma^1\pi^1$, $^1A_2$ state and the other a closed-shell, $^1A_1$ state, whose dominant configuration is σ^2. Several computational studies have found that, unlike the case in phenylnitrene, where the open-shell singlet state is substantially lower in energy than the closed-shell singlet,[21] in PhP these two singlet states are close in energy.[11] Our CASPT2 calculations find that the open-shell singlet is 4.0 kcal mol^{-1} lower in enthalpy than the closed-shell singlet.

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The CASPT2 enthalpy of the fragmentation reaction, **1** → C_2H_4 + PhP ($^1A_2$), is calculated to be 59.3 kcal mol^{-1}. The large endothermicity computed for fragmentation of **1** suggests a late transition state for this reaction.

As shown in Figure 1, the lowest-energy conformation of **1** has a plane of symmetry. The closed-shell wave function of the ground state of **1** is A′ in C_s symmetry, whereas the open-shell wave function of the lowest singlet state of PhP is A″. Therefore, as noted in the Introduction, the A′ and A″ surfaces must cross somewhere along a C_s constrained reaction coordinate, and a conical intersection occurs at this point.

However, the reaction pathway of lowest energy does not pass through this intersection. Instead, the plane of symmetry, which is present in both the reactant and the products, is lost somewhere along the reaction coordinate, thus allowing the $^1A'$ state of the reactant and the $^1A''$ state of the product to mix. This mixing allows the reaction to proceed adiabatically, below the energy of the conical intersection, from the $^1A'$ reactant to the $^1A''$ product.

The transition structure (**2TS)** for the concerted loss of phosphinidene from **1** is shown in Figure 1. As expected, **2TS** has only C_1 symmetry. The phenyl ring is rotated slightly from its conformation in the reactant and the P−C(1) and P−C(2) bond lengths are slightly different. The lengths of these bonds (3.172 Å and 3.143 Å) confirm that **2TS** is indeed a late transition state.

In addition, the activation enthalpy calculated for the concerted fragmentation of **1** to $^1A_2$ PhP plus ethylene is 59.9 kcal mol^{-1}, which is nearly the same as the 59.3 kcal mol^{-1} enthalpy of the reaction. As a result, the reverse reaction, addition of $^1A_2$ PhP to ethylene to form **1** along the C_1 path, is predicted to be almost barrierless, with an enthalpy of activation of only 0.6 kcal mol^{-1}.

Nevertheless, at **2TS** the weights of the dominant configurations in the (10/10)CASSCF wave function, which are given in Table S5a of the Supporting Information, are almost the same as those in the CASSCF wave function for the $^1A'$ state of PhP, which are given in Table S6a. This indicates that, when **2TS** is reached along the C_1 reaction coordinate for the addition of $^1A''$ PhP to ethylene, the wave function has already lost the open-shell character that it has in the PhP reactant.

In **2TS** the natural orbital occupation number for 3p(σ), the 3p orbital on the phosphorus atom which lies in the plane of the phenyl ring, is a factor of 6 greater than the occupation number for 3p(π), the 3p orbital on phosphorus which lies perpendicular to the plane of the phenyl ring (Table S5b). Interestingly, in the $^1A_1$ excited state of singlet PhP, the occupancy of 3p(σ) is favored over occupancy of 3p(π) by only a factor of 3 (see Table S6b). Thus, **2TS** has more closed-shell character than $^1A_1$, the “closed-shell” singlet state of the reactant.

The preference for the selective occupancy of 3p(σ) in **2TS** is due to the orbital interactions that occur in the addition reaction between $^1A_1$ PhP and C_2H_4. They are shown schematically in the orbital interaction diagram in Figure 2. The 3p(π) AO on the P atom mixes with the filled π orbital of ethylene, and the 3p(σ) AO mixes with the empty π^* orbital of ethylene. The former interaction stabilizes the filled π orbital but destabilizes 3p(π); whereas, the latter interaction stabilizes 3p(σ). Consequently, the occupation number of 3p(σ) is greater in **2TS** than in the $^1A_1$ state of PhP.

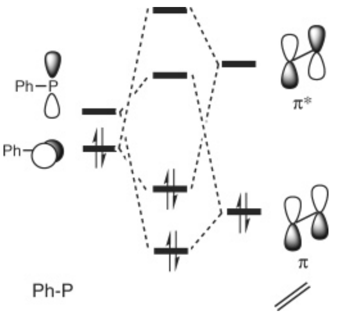

Figure 2. Schematic orbital interaction diagram between closed-shell ($^1A_1$) PhP and ethylene to form a $^1A'$ state.

The optimized geometry of **2TS** deviates only slightly from the C_s symmetry expected for the concerted addition of $^1A_1$ PhP to ethylene.[22] However, as already noted, the addition reaction on the lowest singlet surface actually involves the open-shell ($^1A_2$) state of PhP. Nevertheless, the barrier to this reaction, which involves a state crossing in C_s symmetry, is only 0.6 kcal mol^{-1}. Presumably, the small size of the energy difference between the $^1A_1$ and $^1A_2$ states[11] of PhP allows these two states to reverse order very quickly along a C_s approach to ethylene, so that, by the time **2TS** is reached along the actual C_1 addition pathway, the wave function for the lowest singlet state is largely closed-shell in character.[23]

Even though **2TS**, the transition structure for concerted fragmentation of **1**, is computed to lie only 0.6 kcal mol^{-1} above $^1A_2$ PhP plus ethylene, the products are calculated to be 59.3 kcal mol^{-1} higher in energy than **1**. Since the thermolysis of P-mesitylphosphirane (Scheme 1) was carried out at 190°, it seems highly unlikely that singlet mesitylphosphinidene could have been formed at this temperature.

We have also performed CASPT2 calculations on the fragmentation of P-mesitylphosphirane to the lowest singlet state of mesitylphosphinidene (MesP). These calculations find this reaction to be endothermic by 56.3 kcal mol^{-1}, thus eliminating the remote possibility that the three methyls on the benzene ring of the mesityl group significantly lower the endothermicity of fragmentation from that computed for the corresponding reaction of unsubstituted **1**.

Stepwise Pathway for the Formation of Triplet PhP from 1. The triplet ($^3A_2$) is the ground state of PhP and is computed to be 21.3 kcal mol^{-1} lower in energy than the lowest singlet state ($^1A_2$).[11] Thus, formation of triplet PhP in the fragmentation of **1** is calculated to be endothermic by only 38.0 kcal mol^{-1}, making formation of the triplet considerably less unfavorable thermodynamically than formation of singlet PhP.

Formation of triplet PhP from singlet **1** requires intersystem crossing (ISC). ISC is most likely to occur in the singlet diradical, formed by cleavage of one P−C bond in **1**, because the lowest singlet and triplet energy surfaces are expected to be closest in energy at diradical geometries. In fact, our attempts to find a lower energy intersection between the singlet and triplet potential energy surface proved unsuccessful. Therefore, the lowest energy pathway for formation of triplet PhP from **1** presumably consists of the three steps shown in Figure 1—(ii)

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(23) The change in orbital occupancy in **2TS** compared to PhP may be regarded as coming about through the mixing of the second $^1A_1$ state of PhP into the $^1A_1$ state of lowest energy.

ring opening of phosphirane **1** by homolytic cleavage of one phosphorus−carbon ring bond, (iv) ISC to a triplet diradical, and (v) fragmentation of the triplet diradical to form triplet PhP and ethylene.

Ring Opening of 1 to a Singlet Diradical by Cleavage of One P−C Bond. We began by investigating step (ii), ring opening of **1** to a singlet diradical. Three transition structures, **3aTS**, **3bTS**, and **3cTS** were found for homolytic cleavage of one P−C bond in **1**. As shown in Figure 1, **3aTS** has C_s symmetry, with the H−C−H plane of the radical center at C(1) lying perpendicular to the P−C(2) bond, thus allowing the singly occupied AO on C(1) to hyperconjugate with the P−C(2) bond. The singly occupied 3p AO on phosphorus is conjugated with the π system of the benzene ring.

As a result of this conjugation between the radical center on phosphorus and the π system of the benzene ring, following the transition vector from **3aTS** leads to the formation of a second C_s conformer of phosphirane **1**. In this conformer, unlike the case in the C_s conformer shown in Figure 1, the plane of the phenyl ring bisects the three-membered ring. The energy difference between this bisected conformer and the C_s conformer shown in Figure 1 is quite small, with the latter computed to be only 0.4 kcal mol^{-1} lower in energy than the former.

Figure 1 shows that transition structure **3bTS** has no element of symmetry. As in **3aTS**, in **3bTS** the singly occupied 3p AO on phosphorus is conjugated with the π system of the benzene ring and is nearly orthogonal to the singly occupied 2p AO on C(1). However, unlike **3aTS**, in which the C(1)−C(2) bond is *anti*-periplanar to the P−C(3) bond, in **3bTS** the C(1)−C(2) bond is nearly perpendicular to the P−C(3) bond. The C(1)−C(2)−P−C(3) dihedral angle is −71.3° in **3bTS**, and the terminal CH_2 group is rotated ca. 90° from its geometry in **3aTS**, so that the singly occupied 2p AO on C(1) is nearly orthogonal to the P−C(2) bond.

Hyperconjugation of the radical center at C(1) with the P−C(2) bond makes **3aTS** slightly lower in energy than **3bTS.** As shown in Table 1, **3aTS** and **3bTS** are calculated to be, respectively, 42.6 and 43.1 kcal mol^{-1} higher in energy than phosphirane **1**.

The single imaginary frequency for **3aTS** (48.5i cm^{-1}) corresponds to rotation about the P−C(2) bond, while the single imaginary frequency for **3bTS** (183.9i cm^{-1}) corresponds to rotation about the C(1)−C(2) bond. In each transition structure the vibration with the imaginary frequency begins to align the singly occupied AOs at C(1) and P for bond formation, leading to reclosure of the singlet diradical to **1**.

Although **3aTS** and **3bTS** are both transition structures for stereomutation of **1** by P−C bond cleavage, passage over each transition structure leads to a different stereochemical outcome. Passage over **3aTS**, which involves rotation about the P−C bond, preserves the stereochemistry about the C−C bond in **1**, but leads to both of the hydrogens that were cis to the phenyl group in the reactant becoming trans to it in the product and vice versa. In contrast, rotation about the C−C bond in **3bTS** exchanges the environments of only the hydrogens on the CH_2 group that rotates.

A third transition structure was located in which the rotation about the C−P bond in **3aTS** is combined with rotation about the C−C bond in **3bTS**. (10/10)CASSCF optimization of a C_s geometry in which the phenyl group attached to P and the hydrogens attached to C(1) all lie in the P−C(2)−C(1) plane gave a stationary point (**3cTS)** with one imaginary frequency. The imaginary frequency corresponds to a vibration that both pyramidalizes and rotates the C(1) methylene group; so this transition state must connect two mirror-image diradical intermediates.

Carefully following the transition vector in one direction does, in fact, lead to one of these two, very shallow, CASSCF energy minima (**3d**). As shown in Figure 1, in **3d** C(1) is pyramidalized and rotated, so that the singly occupied orbital on C(1) can hyperconjugate with one of the C−H bonds at C(2). At the (10/10)CASSCF level, **3d** is 0.3 kcal mol^{-1} lower in energy than **3cTS**, but at the CASPT2 level of theory the relative energies of **3cTS** and **3d** are essentially the same.

The one additional vibrational mode with a real frequency in **3d** than in **3cTS** makes the zero-point energy and heat capacity of **3d** greater than those of **3cTS**. Consequently, Table 1 shows that, in the localized harmonic oscillator approximation, the enthalpy of **3d** is actually computed to be greater than that of **3cTS** at both the CASSCF and CASPT2 levels of theory.

In analogy with the potential energy surface for cyclopropane ring opening,[24] dynamic electron correlation probably simplifies the potential surface for ring opening of **1**, so that, at the CASPT2 level of theory, **3cTS**, lies on the reaction pathway for conrotatory C−P bond breaking.[25] However, the slightly lower enthalpy of **3aTS** than **3cTS** indicates that the hyperconjugation of one radical center with the P−C bond in **3aTS** is sufficiently stabilizing to overcome the preference in the trimethylene diradical for a geometry like that of **3cTS**, in which both radical centers are hyperconjugated with the C−H bonds at C(2).[24]

The CASPT2 energies in Table 1 suggest that there are no singlet diradical intermediates, but only transition structures, on the potential energy surface for ring opening of **1**. If intersystem crossing (ISC) were to occur, it would presumably occur in the flat region of the singlet potential energy surface where the three singlet diradical transition structures (**3aTS**−**3cTS)** are located. As shown in Table 1, all three structures lie within 0.5 kcal mol^{-1} of each other in energy.

To establish the energy of the triplet, relative to the singlet potential surface at these geometries, (10/10)CASPT2 single-point triplet calculations were performed at the geometries of **3aTS**−**3cTS**. The energies of the triplets at these singlet geometries were, respectively 2.1, 0.8, and 0.7 kcal mol^{-1} lower than those of the corresponding singlet states. Since the singlet surface lies above the triplet surface at all three of these geometries, the activation enthalpy of 42−43 kcal mol^{-1} for the ring opening of **1** via these three transition structures should provide an upper limit to the enthalpy of activation necessary for ISC from the singlet to the triplet to occur.

Triplet Diradical Intermediates and Their Fragmentation. Upon optimizing the geometries of **3aTS** and **3bTS** with triplet

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(24) Isborn, C.; Hrovat, D. A.; Borden, W. T. *J. Phys. Chem. A* **2004**, *108*, 3024 and references therein.

(25) Ring opening of **1** by conrotatory C−C bond breaking leads to formation of a 1,3-dipolar intermediate, with an enthalpy that we computed to be 1.5 kcal mol^{-1} less than that of **3cTS**. A similar 1,3-dipolar intermediate was also located on the potential energy surface for ring opening of unsubstituted phosphirane, but this intermediate was computed to be 17.5 kcal mol^{-1} lower in energy than the transition structure for its formation.[12a] Therefore, in the ring opening of **1**, although the 1,3-dipolar intermediate, is computed to be slightly lower in enthalpy than **3cTS**, it is quite likely that C−P bond cleavage via **3cTS** has a much lower activation enthalpy than C−C bond cleavage to form this 1,3-dipolar intermediate.

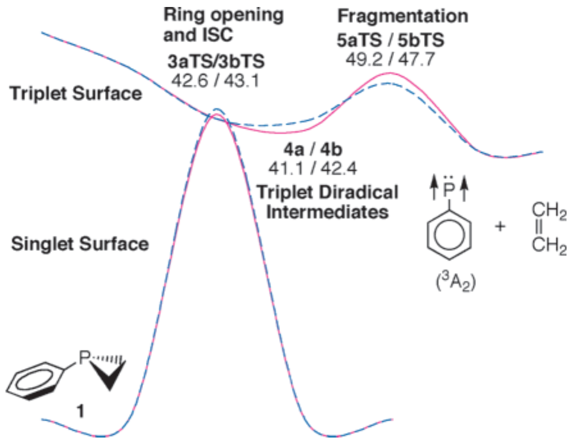


Figure 3. Schematic depiction of and CASPT2 enthalpies (kcal mol^{-1}) for generation of triplet Ph-P by stepwise P−C bond cleavage. The solid line corresponds to formation of triplet diradical intermediate **4a** and the broken line to formation of **4b**.

wave functions, two triplet diradical intermediates (**4a** and **4b**) were found. The geometries of the triplet intermediates were very similar to those of the singlet transition structures (Figure 1). The triplet intermediates **4a** and **4b** are, respectively, 1.5 and 0.7 kcal mol^{-1} lower in enthalpy than their singlet counterparts. Since ISC cannot take place below the energies of the triplet intermediates, 41−42 kcal mol^{-1} provides a lower limit to the energy at which ISC from the singlet to the triplet can occur.

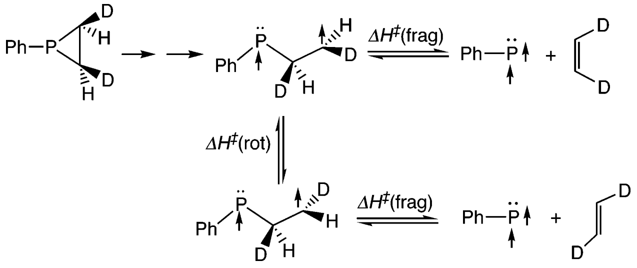
It is of some interest that the P−C(2) bond length in triplet **4a** (1.922Å) is longer than that in singlet **3aTS** (1.909Å), whereas the P−C(2) bond lengths in triplet **4b** and singlet **3bTS** are essentially the same and only slightly shorter than that in **3aTS**. In both **3aTS** and **4a**, the 2p orbital on the radical center at C(1) is hyperconjugated with the P−C(2) bond. The hyperconjugated resonance structure, PhP plus C_2H_4, is lower in energy for triplet PhP than for singlet PhP; so this resonance structure contributes more for **4a**, which is a triplet, than for **3aTS**, which is a singlet.

Evidence in favor of this explanation of the longer P−C(2) bond length in **4a** than in **3aTS** comes from the C(1)−C(2) bond length in **4a**, which is shorter than the C(1)−C(2) bond length in **3aTS**, as well as in **3bTS** and **4b**. If the hyperconjugated resonance structure, PhP plus C_2H_4, contributes more to **4a** than to **3aTS**, **3bTS**, and **4b**, then the C(1)−C(2) bond length should be more ethylene-like in **4a**.

Following formation of triplet diradical intermediate **4a**, cleavage of the P−C(2) bond generates triplet PhP and C_2H_4, which completes the fragmentation of **1**. However, cleavage of the P−C(2) bond in triplet diradical **4b** requires an additional rotation about the C(1)−C(2) bond.

The transition structures, respectively, **5aTS** and **5bTS**, for breaking the P−C(2) bond in **4a** and **4b** are depicted in Figure 1. The P−C(1) distances in **5aTS** and **5bTS** are longer by 0.428 and 0.411 Å than in the corresponding triplet diradical intermediates. Table 1 shows that **5aTS** and **5bTS** are computed to be, respectively, 49.2 kcal mol^{-1} and 47.7 kcal mol^{-1} higher in energy than reactant **1**. Figure 3 gives a schematic energy profile for the generation of triplet PhP via pathways involving the intermediacy of triplet diradicals **4a** and **4b**. Assuming that ISC occurs near the singlet transition structures, the barrier for forming the triplet diradicals is predicted to be about 43 kcal mol^{-1}. Fragmentation of the triplet diradical intermediates, to form the triplet PhP and C_2H_4 via **5bTS**, is predicted to require an additional 5 kcal mol^{-1}. The overall barrier to fragmentation of **1** to triplet PhP by stepwise P−C bond cleavage is computed to be 47.7 kcal mol^{-1}, which is 12.2 kcal mol^{-1} lower than the barrier for formation of singlet PhP by concerted cleavage of both C−P bonds in **1**.

Scheme 3



Stereospecificity of the Fragmentation of 1 to Triplet PhP Plus Ethylene. An interesting question, which we addressed computationally, is whether fragmentation of **1**-2,3-d_2 to triplet PhP and ethylene-1,2-d_2 could possibly be stereospcific. Alternatively, one might ask the same question about the reverse reaction, addition of triplet PhP to cis- or *trans*-ethylene-1,2-d_2.

According to Skell's rule, addition of singlet carbenes to olefins can occur stereospecifically, by a concerted pathway, but triplet carbene addition, which involves formation of a triplet diradical intermediate, should be nonstereospecific.[26] However, it was subsequently pointed out by Gaspar and Hammond that stepwise carbene addition might or might not be nonstereospecific, depending on the relative rates of ring closure and C−C bond rotation in the diradical intermediate.[27]

In 1964, Hammond and co-workers reported that, in the addition of triplet methylene to cis- and *trans*-2-butene in solution, rotation about the C−C bond in the presumed triplet diradical intermediate must be faster than ring closure, because cyclopropane formation is not stereospecific.[28] However, it has been found that hyperconjugation with the C−Si bond to a silyl substituent, β to a carbon radical center, results in an increase in the barrier height to rotation about the C_α-C_β bond.[29] A sufficiently large increase in the barrier height to rotation could lead, at least in principle, to stereospecific addition of a triplet silylene to 2-butene, resulting in a violation of Skell's rule.

In the fragmentation of **1** to triplet PhP, if ISC from the singlet to the triplet potential energy surface occurs faster than loss of stereochemistry in the singlet diradical, the stereospecificity of the fragmentation of **1**-2,3-d_2 to triplet PhP and ethylene-1,2-d_2 would depend on the relative rates of rotation and fragmentation in the triplet diradical intermediate (Scheme 3). Thus, fragmentation of **1**-2,3-d_2 could be then stereospecific, if hyperconjugation of the radical center at C(1) with the C(2)−P

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(26) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496.

(27) Gaspar, P. P.; Hammond, G. S. The spin states of carbenes. In *Carbene Chemistry*, 1st ed.; Kirmse, W., Ed.; Academic: New York, 1964; pp 235−274; Spin states in carbene chemistry. In *Carbenes* Vol. II, Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; pp 207−362.

(28) (a) Koepecky, K. R.; Hammond, G. S.; Leermakers, P. A. *J. Am. Chem. Soc.* **1961**, *83*, 2397. (b) Koepecky, K. R.; Hammond, G. S.; Leermakers, P. A. *J. Am. Chem. Soc.* **1962**, *84*, 1015.

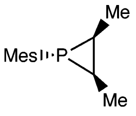
(29) (a) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846. (b) Kawamura, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 648. (c) Kawamura, T.; Meakin, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 8065.

bond in triplet diradical **4a** made the barrier to rotation larger than the barrier to fragmentation.

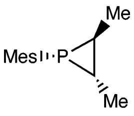
To predict the stereochemical outcome of alkene formation in the stepwise fragmentation of **1** to triplet PhP, the barriers to rotation around the $C_{\alpha}-C_{\beta}$ bond in the triplet diradical intermediates **4a** and **4b** were computed. The transition structures (**6aTS** and **6bTS**) for rotation about C(1)−C(2) bonds in, respectively, **4a** and **4b** are shown in Figure 1. The P−C(2) bond shortens and the C(1)−C(2) bond lengthens in going from **4a** to **6aTS**, because the 2p orbital on the C(1) radical center does not have the correct orientation to hyperconjugate with the $P-C_{\alpha}$ bond in **6aTS**.

The barrier to rotation about the C(1)−C(2) bond in **4a**, via **6aTS**, is 1.1 kcal mol^{-1}, which is much smaller than the barrier to fragmentation of **4a** via **5aTS** (8.1 kcal mol^{-1}) or via **5bTS** (6.6 kcal mol^{-1}). After inclusion of zero-point and thermal corrections to the enthalpy, the barrier to rotation in **4b** via **6bTS** is actually computed to be negative (−0.6 kcal mol^{-1}). This is nonsense of course, but it does indicate that the fragmentation of **1**-2,3-d$_2$ to triplet PhP plus ethylene-1,2-d$_2$ should be completely stereorandom.

Stereospecificity of the Fragmentation of 2,3-Dimethyl-P-mesitylphosphirane to Triplet MesP and 2-Butene. Experiments on the stereochemistry of thermal P-arylphosphirane fragmentation have been carried out by Li and Gaspar with anti-*cis*-2,3-dimethyl-P-mesitylphosphirane (***cis*-1Me**) and *trans*-2,3-dimethyl-1-mesitylphosphirane (***trans*-1Me**).[30] The reactions were found not to be stereospecific, but only ca. 10% of the "wrong" stereoisomer was formed in each case. Thus, product formation was much more stereospecific than would have been expected, based on the results of our calculations on the fragmentation of **1** to triplet PhP and ethylene.



***cis*-1Me**



***trans*-1Me**

A possible explanation of this difference is that the presence of methyl groups on three phenyl and two ring carbons in ***cis*-1Me** increases the barrier to rotation in and/or decreases the barrier to fragmentation of the triplet diradical intermediate, formed from ***cis*-1Me**. To test this hypothesis, we carried out calculations on the competition between rotation in and fragmentation of this triplet diradical.

Because of the size of this diradical and the presence of five nearly freely rotating methyl groups in it, (10/10)CASSCF geometry optimizations were prohibitive, due to the amount of computer time they consumed. Therefore, we took advantage of our finding that the (U)B3LYP optimized geometries for the species in Table 1 were, in general, quite close to the CASSCF optimized geometries (see Table S7 in Supporting Information). Consequently, we used (U)B3LYP optimized geometries for CASPT2 single-point calculations on the fragmentation of ***cis*-1Me** to triplet MesP and 2-butene.

Table 2. Calculated (U)B3LYP, and CASPT2 Enthalpies[a] and Free Energies[b] (kcal mol^{-1}), Relative to Those of ***cis*-1Me**, of the Stationary Points in the Fragmentation of ***cis*-1Me** to Triplet MesP Plus 2-Butene via Triplet Diradical Intermediates ***cis*-4aMe** and ***cis*-4bMe**

	$\Delta H_{(U)B3LYP}$	ΔH_{CASPT2}	ΔG_{CASPT2}
Triplet MesP + cis-2-butene	31.9	37.9	-
Triplet MesP + trans-2-butene	30.5	36.3	-
***cis*-4aMe** (^{3}A)	41.8	43.6	37.8
***cis*-4bMe** (^{3}A)	41.5	43.3	38.4
***cis*-7MeTS** (^{3}A)	42.9	45.2	42.7
***cis*-5aMeTS** (^{3}A)	45.1	47.8	42.4
***cis*-5bMeTS** (^{3}A)	44.1	46.2	41.2
6aMeTS (^{3}A)	42.9	44.7	40.5
6bMeTS (^{3}A)	43.1	44.9	42.1
***trans*-4aMe** (^{3}A)	40.5	42.4	36.8
***trans*-4bMe** (^{3}A)	40.9	42.4	37.4
***trans*-5aMeTS** (^{3}A)	43.9	46.6	41.7
***trans*-5bMeTS** (^{3}A)	42.9	44.7	40.2

[a] CASPT2 energies at the (U)B3LYP optimized geometries, including (U)B3LYP zero-point and thermal corrections at 298K. [b] CASPT2 energies at the (U)B3LYP optimized geometries, including (U)B3LYP zero-point. thermal, and entropic corrections at 433K, the upper end of the temperature range in which the experiments in ref 4c were performed.

The relative (U)B3LYP and CASPT2 enthalpies of the triplet intermediates and transition structures in the fragmentation of ***cis*-1Me** to triplet MesP and 2-butene are given in Table 2; and selected structural parameters for these UB3LYP stationary points are shown in Figure 4. In the table and figure the triplet diradical intermediates and the transition structures for fragmentation of and rotation in them are labeled as **4aMe** and **4bMe**, **5aMeTS** and **5bMeTS**, and **6aMeTS** and **6bMeTS**, respectively. The designations cis and trans at the beginning of the labels refer to the orientation of the two methyl groups on C(1) and C(2).

Two triplet intermediates (***cis*-4aMe** and ***cis*-4bMe**) were found, in which the pair of methyl groups on C(1) and C(2) are cis to each other. Inspection of Table 2 shows that ***cis*-4aMe** is computed to have a 0.3 kcal mol^{-1} higher enthalpy than ***cis*-4bMe**, despite the fact that the preferred conformation (**4a**) of the triplet diradical, lacking the five methyl groups, is much more like that in ***cis*-4aMe** than that in ***cis*-4bMe**. Inspection of Figure 4 shows that in ***cis*-4aMe** an *ortho*-methyl group and the methyl group at C(2) are close enough to interact with each other. Rotation about the P−C(2) bond, to give ***cis*-4bMe**, alleviates this destabilizing interaction and is presumably responsible for the slightly lower enthalpy computed for ***cis*-4bMe** than for ***cis*-4aMe**.

As shown in Table 2, fragmentation of ***cis*-4bMe** via ***cis*-5bMeTS** is computed to require 2.9 kcal mol^{-1}, whereas rotation to ***trans*-4bMe** via **6bMeTS** is computed to require 1.6 kcal mol^{-1}. The comparable activation enthalpies for fragmentation and rotation of unsubstituted **4a** in Table 1 are, respectively, 6.6 and 0.7 kcal mol^{-1}. Thus, the methyl groups in ***cis*-4bMe** result in a net decrease of 4.6 kcal mol^{-1} in the difference between the enthalpies of activation for fragmentation and rotation. This decrease is due to a 3.7 kcal mol^{-1} decrease in the barrier to fragmentation and a 0.9 kcal mol^{-1} increase in the barrier to rotation in ***cis*-4bMe**, compared to **4a**.

Comparing Figures 1 and 4, the *ortho*-methyl groups on the benzene ring can be seen to change the preferred conformation of this ring in both ***cis*-4aMe** and ***cis*-4bMe** from that in **4a** and **4b**, where the phenyl can stabilize the electron in the singly occupied orbital of phosphorus. The less favorable phenyl conformation in triplet ***cis*-4bMe** is presumably the reason that the barrier to its fragmentation is 3.7 kcal mol^{-1} lower than the barrier to fragmentation of **4a**. The lower barrier heights to

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(30) Trieber, D. A., II.; d'Avignon, D. A.; Lam, W. H., Davidson, E. R. Borden, W. T.; Gaspar, P. P. Manuscript in preparation.

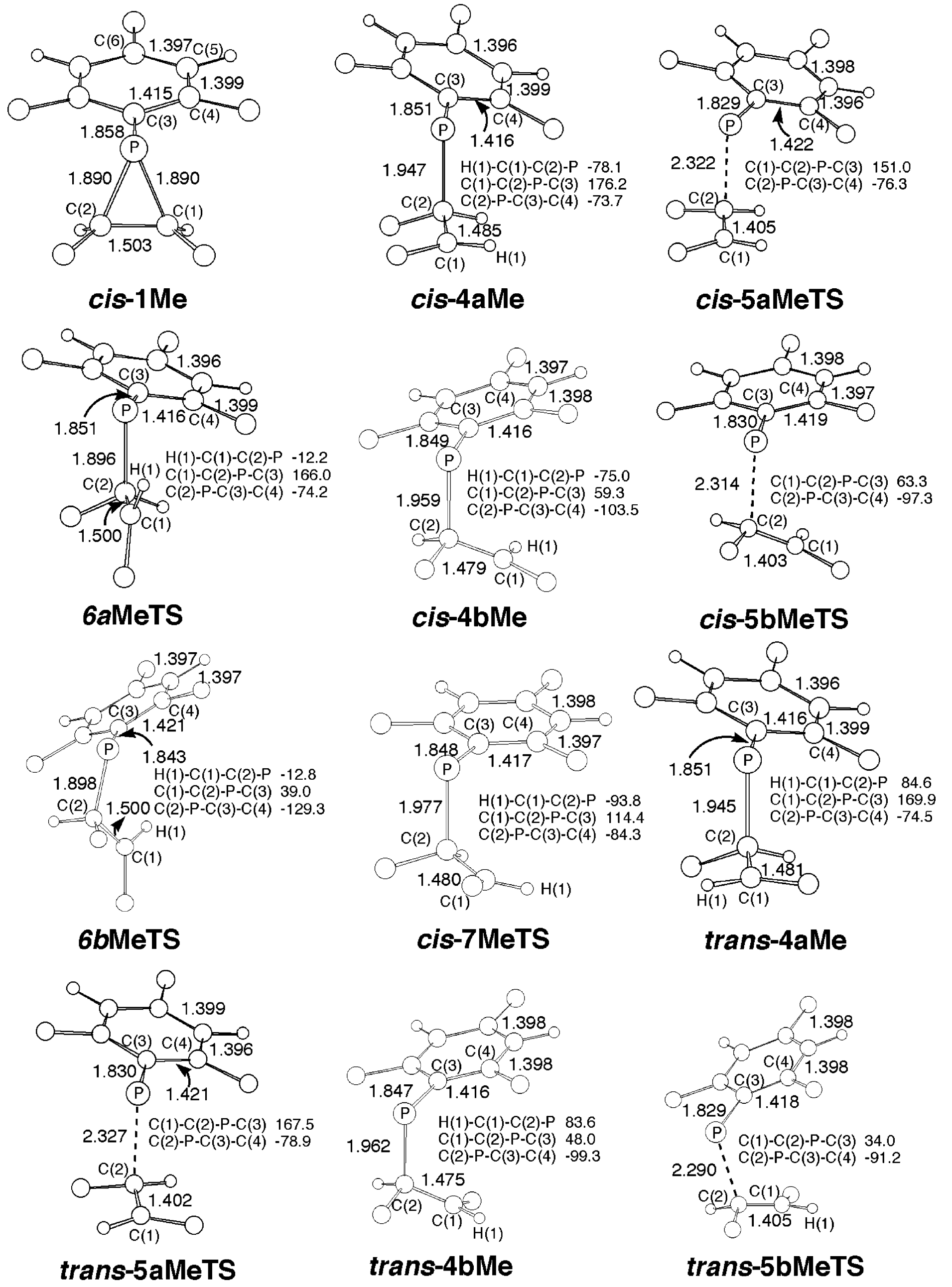

Figure 4. Selected structural parameters of the (U)B3LYP stationary points in Table 2. Bond lengths are in Å, and bond angles are in deg. Methyl hydrogens have been deleted for clarity.

fragmentation of all four of the methylated triplet diradical intermediates in Table 2, compared to the two unmethylated diradical intermediates in Table 1, are consistent with the longer P−C(2) bonds in the methylated triplet diradicals (Figure 4) than in their unmethylated counterparts (Figure 1).

In contrast to the case in the triplet intermediates, in the transition structures for rotation about the C−C bond the P−C(2) bond has about the same length in both the methylated and unmethylated triplet diradicals. Rotation of the radical center at C(1), so that hyperconjugation with the P−C(2) bond is lost in the transition structure, is more costly in the methylated triplet diradicals, where the P−C(2) bond is weaker and therefore provides more hyperconjugative stabilization of the radical center at C(1) than in the unmethylated triplet diradicals. Thus, we believe that the slightly higher barriers to rotation in the methylated triplets, like the substantially lower barriers to fragmentation in these diradicals, are attributable to the change in the preferred conformation in them when the phenyl group in **4** is replaced by the mesityl group in **4Me**.

Although the enthalpic barrier to rotation is still computed to be 1.3 kcal mol^{-1} lower than the enthalpic barrier to fragmentation in ***cis*-4bMe**, it is, of course, not the relative enthalpies, but the relative free energy barriers, that determine the relative rates of rotation and fragmentation. We computed the free energies of all the species in Table 2 at 433 K, the upper end of the temperature range in which Li and Gaspar performed their experiments.[4c]

The free energy of activation for the fragmentation of ***cis*-1Me** by a pathway involving formation of triplet diradical ***cis*-4bMe** as an intermediate was computed to be $\Delta G^{\ddagger} = 41.2$ kcal mol^{-1}. This free energy of activation is 5.0 kcal mol^{-1} smaller than the enthalpy of activation, due to a positive entropy of activation of $\Delta S^{\ddagger} = 11.8$ cal mol^{-1} K^{-1}.

The entropy of ***cis*-5bMeTS**, the transition structure for fragmentation of ***cis*-4bMe**, is 5.4 cal mol^{-1} K^{-1} higher than that of **6bMeTS**, the transition structure for rotation about the C(1)−C(2) bond in ***cis*-4bMe**. This large difference in activation entropies makes the calculated free energy barrier to fragmentation of ***cis*-4bMe** 0.9 kcal mol^{-1} lower than that for rotation. Consequently, unlike the case in unmethylated triplet diradical **4a**, our calculations predict that fragmentation of ***cis*-4bMe** should be competitive with rotation about the bond between C1 and C2.

Another possible reaction of triplet diradical ***cis*-4bMe** is rotation about the P−C bond to form ***cis*-4aMe**. In the latter, extended conformation of the triplet diradical, loss of stereochemistry by rotation about the C−C bond via **6aMeTS** is computed to have a 1.9 kcal/mol lower free energy of activation than fragmentation via ***cis*-5aMeTS**. Thus, isomerization of ***cis*-4bMe** to ***cis*-4aMe** should lead to substantial loss of stereochemistry in the 2-butene formed via passage over ***cis*-5aMeTS**.

However, in ***cis*-4bMe** rotation about the C−C bond, to form ***trans*-4bMe** via **6bMeTS**, and rotation about the P−C bond, to form ***cis*-4aMe** via ***cis*-7MeTS**, are both entropically disfavored. Rotation about either bond leads to a decrease in entropy, due to loss of a low-frequency vibrational mode, which becomes the reaction coordinate in each TS. Consequently, as shown in Table 2, rotation about the P−C bond in ***cis*-4bMe** via ***cis*-7MeTS** is computed to have a free energy of activation that is 1.5 kcal/mol higher than fragmentation to triplet MesP and *cis*-2-butene via ***cis*-5bMeTS**. Thus, if ***cis*-4bMe** is, indeed, the triplet diradical intermediate that is originally formed by ring opening of phosphirane ***cis*-1Me**, our calculations predict that it should fragment slightly faster than it loses stereochemistry.

This computational result is in good qualitative agreement with the results of Li and Gaspar, who found only about 10% loss of stereochemistry in the fragmentation of ***cis*-1Me**.[4c] Of course, whether this agreement is just fortuitous depends on whether the thermal fragmentation of ***cis*-1Me** really does proceed via the intermediacy of triplet diradical intermediate ***cis*-4bMe**.

Conclusions

The calculations described here show that generation of triplet PhP from **1** via a stepwise pathway is not only thermodynamically but also kinetically favored over concerted fragmentation of **1** to ethylene plus singlet PhP. Formation of triplet PhP is 21.2 kcal mol^{-1} less endothermic and has a 12.2 kcal mol^{-1} lower barrier height than formation of singlet PhP.

The formation of singlet PhP via a concerted pathway should be stereospecific, whereas formation of triplet PhP via a stepwise pathway is predicted to occur with complete loss of stereochemistry. However, our calculations on the stepwise fragmentation of anti-*cis*-2,3-dimethyl-1-mesitylphosphirane (***cis*-1Me**) to triplet MesP indicate that the rotation barrier increases slightly and the fragmentation barrier decreases substantially in triplet diradical ***cis*-4bMe**, compared to the unmethylated triplet diradical, **4a**. We attribute both changes to the *ortho*-methyls of the mesityl group in ***cis*-4bMe** altering the preferred conformation of the benzene ring from that in **4a**. Thus, the presence of the methyl groups, particularly the *ortho*-methyls on the benzene ring, is predicted to make the fragmentation reaction of ***cis*-1Me** much more stereospecific than that of **1**.

Our finding that fragmentation of ***cis*-4bMe** is calculated to have a free energy barrier that is about 1 kcal mol^{-1} lower than the free energy barrier for isomerization to ***trans*-4bMe** is in apparent agreement with the experimental results of Li and Gaspar on the stereochemistry of the fragmentation of ***cis*-1Me**. However, with a calculated free energy barrier of $\Delta G^{\ddagger} = 41.2$ kcal mol^{-1}, fragmentation of ***cis*-1Me** via triplet diradical ***cis*-4bMe** is calculated to have a rate constant of only $k = 10^{-8}$ s^{-1} at 433 K. If ISC to form ***cis*-4bMe** from ***cis*-1Me** were rate determining, the fragmentation reaction would be slower still.

Thus, fragmentation of ***cis*-1Me** to triplet MesP is calculated to be far too slow to have been ca. 30% complete in 30 min at the reaction temperatures used by Li and Gaspar.[4a] Formation of singlet MesP from ***cis*-1Me** is even less likely to have occurred at these temperatures.

Therefore, the results of our calculations suggest that, under the reaction conditions used by Li and Gaspar, either the fragmentation of ***cis*-1Me** was catalyzed and/or, as suggested by Mathey for P-arylphosphirane fragmentation reactions in general,[8] free MesP was not generated in this reaction. The results of additional experiments and calculations that bear on the question of the mechanism by which these fragmentation reactions occur will be reported in due course.[30]

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Supporting Information Available: Optimized geometries, energies, and thermal corrections for all compounds in the text, and complete refs 13 and 14. This information is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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