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A R T I C L E S

What Accounts for the Difference between Singlet Phenylphosphinidene and Singlet Phenylnitrene in Reactivity toward Ring Expansion?

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Abstract: (8/8)CASSCF and (8/8)CASPT2 calculations have been performed in order to investigate the potential surface for the ring expansion of the $^1A_2$ state of phenylphosphinidene (**1c**) to 1-phospha-1,2,4,6-cycloheptatetraene (**3c**). Unlike the comparable ring expansion of the $^1A_2$ state of phenylnitrene (**1b**) to 1-aza-1,2,4,6-cycloheptatetraene (**3b**), ring expansion of **1c** to **3c** is computed to be quite endothermic. Nevertheless, cyclization of **1c**, to form the bicyclic intermediate **2c** in the ring expansion reaction, is computed to be only slightly more endothermic than the comparable cyclization reaction of **1b** to **2b**. The origins of these differences between the ring expansion reactions of **1b** and **1c** have been elucidated through the calculation of the energies of relevant isodesmic reactions.

Unlike singlet phenylcarbene (**1a**), singlet phenylnitrene (**1b**) undergoes rearrangement at low or ambient temperatures much more rapidly than it undergoes intermolecular trapping reactions.[1] The rate-determining step in the rearrangement reactions of both **1a** and **1b** is cyclization to form, respectively, bicyclo-[4.1.0]heptatrienes **2a** and **2b**, which undergo rapid electrocyclic ring opening to cycloheptatetraenes **3a** and **3b** (Scheme 1). Unlike the case in the ring expansion reaction of **1a** to **3a**, **3b** is apparently in equilibrium with singlet **1b** at low temperatures; since, on standing, **3b** forms triplet phenylnitrene, presumably by intersystem crossing in singlet **1b**.[2]

The triplet is the ground state of both phenylcarbene[3] and phenylnitrene.[4] The phosphorus analogue, phenylphoshinidene (**1c**), also appears to have a triplet ground state. The EPR spectrum of a sterically shielded derivative of triplet **1c** has been obtained by Gaspar and co-workers.[5]

The chemistry of singlet **1c**[6] has not been as well characterized as that of the lowest singlet state of either **1a** or **1b**.

Scheme 1

a, X = CH   b, X = N   c, X = P
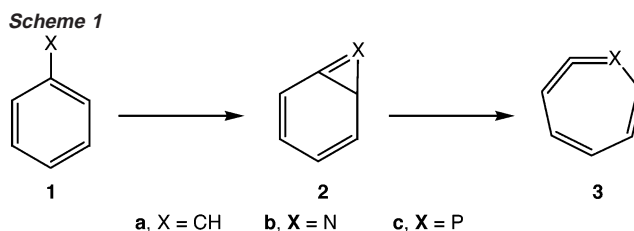
Nevertheless, there is evidence that singlet **1c** behaves much more like singlet **1a** than like singlet **1b**, since experiments by Gaspar and co-workers find that singlet **1c** undergoes intermolecular addition reactions to π bonds much faster than it undergoes intramolecular ring expansion.[7] In fact, the ring expansion reactions, seen at low temperatures for **1b** and at high temperatures for **1a**, have not been observed at all for **1c**.

Calculations have been very helpful in understanding the differences between the chemistries of **1a** and **1b**.[1,8] In the lowest singlet state of **1a**, both nonbonding electrons occupy a hybrid σ orbital that is largely localized on the carbenic carbon. This nonbonding (NB)MO is considerably lower in energy than the π NBMO, which consists of pure 2p AOs.

In contrast to the case in **1a**, in **1b**, both NBMOs are formed from pure 2p AOs. In the lowest singlet state of **1b**, one nonbonding electron occupies the σ NBMO, which is largely localized on nitrogen, and the other nonbonding electron occupies a π orbital that is largely localized on the benzene ring.[9] This localization of the two nonbonding electrons to

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different regions of space in **1b** minimizes the Coulomb repulsion between these electrons.[9b]

The difference in reactivity between **1a** and **1b** has been attributed to the difference between the electronic structures of their lowest singlet states.[1,8a] The open-shell, $\sigma^1\pi^1$ configuration of the lowest singlet state of phenylnitrene (**1b**) makes it much more reactive toward intramolecular cyclization and much less reactive toward intermolecular addition to π bonds than the closed-shell σ^2 electronic configuration of the lowest singlet state of phenylcarbene (**1a**).

Hamilton and co-workers[10] and Nguyen and co-workers[11] have identified a potentially important difference between the electronic structures of **1b** and **1c**. Unlike the case in **1b**, where the open-shell, $\sigma^1\pi^1$, singlet state ($^1A_2$) is substantially lower in energy than the closed-shell, σ^2 singlet state ($^1A_1$),[9] in **1c**, these two singlet states are calculated to have nearly the same energies.[10,11] If the ordering of the lowest singlet states in **1c** were actually reversed from the ordering in **1b**, it is conceivable that **1c** might react more like **1a** than **1b**, as Gaspar's experiments have found to be the case.[7]

Hamilton et al.[10] and Nguyen et al.[11] also noted that the singlet–triplet splitting, ΔE_{ST} in **1c** is computed to be only a few kilocalories per mole smaller than ΔE_{ST} in methylphosphinidene. In contrast, calculations and experiments find that ΔE_{ST} in **1b**[9,12] is more than 10 kcal/mol lower than ΔE_{ST} in methylnitrene.[13,14] There are two contributors to this difference between the effects of the phenyl groups in **1b** and **1c** on ΔE_{ST}.

First, the larger AOs on phosphorus than on nitrogen make the repulsion between electrons of opposite spin smaller in a phosphinidene than in a nitrene.[15] Consequently, there is a smaller driving force to delocalize the nonbonding π electron into the phenyl ring in the $^1A_2$ state of **1c** than in the $^1A_2$ state of **1b**.

Second, there is a large difference between the strengths of the π bonds that can be formed with the heteroatom in **1b** and **1c**. The C–P π bond in $H_2C=PH$ has been calculated to be at least 20 kcal/mol weaker than the C–N π bond in $H_2C=NH$.[16] This large difference between the strengths of C–P and C–N π bonds means that, in all three of the low-lying electronic states, π bonding is less energetically advantageous in **1c** than in **1b**.

Differences between the strengths of C–N and C–P bonds could also affect the intramolecular reactivities of **1b** and **1c** by creating a difference between the thermochemistries of their

ring expansion reactions. As shown in Scheme 1, in the ring expansion of **1**, a new σ bond is formed to the atom that is exocyclic to the benzene ring, and especially in **1c**, a partial π bond to this atom in the reactants is replaced by a full π bond in the products. The weaker σ and π C–X bonds for X = P, relative to X = N,[16,17] should make the formation of **2c** and **3c** from **1c** less thermodynamically favorable than formation of **2b** and **3b** from **1b**.

To investigate the reason(s) for the observed difference between the intramolecular reactivities of **1b** and **1c**, we have carried out ab initio calculations. Herein we report the results of our calculations on **1c** and on its ring expansion to **3c**, via the intermediacy of **2c**.

Computational Methodology

Our computational methodology was essentially the same as that employed in our studies of phenylnitrene.[8] Geometry optimizations were performed with the 6-31G* basis set,[18] using complete active space (CAS)SCF[19] calculations. An eight-electron, eight-orbital active space, hereafter designated (8/8), was used, unless otherwise noted.

The eight orbitals in the active space for **1c** consisted of seven π MOs plus the in-plane 2p AO on phosphorus. The active-space orbitals for the transition structures (TSs) consisted of six orbitals that were mainly π in character, plus a σ/σ^* pair for the bond being formed in the TS leading from **1c** to **2c** and for the bond being broken in the TS leading from **2c** to **3c**. The same active space was used for **2c** as for the TS leading from **1c** to **2c**. The π and π^* MOs of the four double bonds comprised the active space for **3c**; and a (6/6) active space, consisting of the π and π^* MOs of the three double bonds, was used for its triene hydrogenation products (**6**).

(8/8)CASSCF/6-31G* vibrational frequencies were calculated for all stationary points, to verify whether each was an intermediate or a transition state. The unscaled (8/8)CASSCF frequencies were also used to compute zero-point vibrational corrections to the energies. The CASSCF calculations were performed using the Gaussian 98 suite of programs.[20] The geometries, absolute energies, and vibrational corrections for all the stationary points are available as Supporting Information.

The effects of dynamic electron correlation[21] were included by performing single-point (8/8)CASPT2/6-31G* calculations[22] at the (8,8)-CASSCF/6-31G* stationary point geometries. The (8/8)CASPT2 calculations were carried out with MOLCAS.[23]

Results and Discussion

Low-Lying States of Phenylphosphinidene. Hamilton and co-workers performed CISD/6-31G* calculations on the low-

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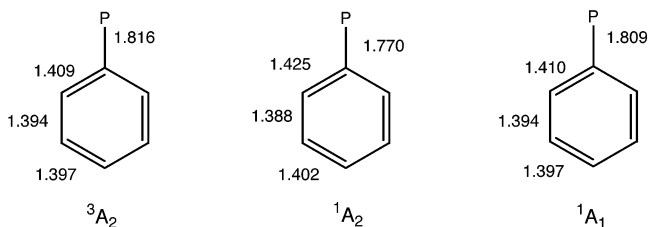
Figure 1. (8/8)CASSCF/6-31G* bond lengths (Å) for the triplet ground state and two low-lying singlet states of phenylphosphinidene (**1c**)

Table 1. Calculated (8/8)CASSCF and (8/8)CASPT2 Energies (kcal/mol) of the Stationary Points on the C_6H_5P Potential Energy Surface, Relative to the Energy of the $^3A_2$ State of **1c**, Including Differences between Zero-Point Energies

|	(8/8)CASSCF	(8/8)CASPT2
$^1A_2$-**1c**	24.2	21.3
$^1A_1$-**1c**	27.3	25.4
TS1	36.4	32.1
2c	33.0	26.2
TS2	53.8	45.3
3c	33.7	37.5

lying states of **1c**, using a two-configuration reference for the $^1A_1$ state and adding the Davidson correction for neglected quadruple excitations.[10] At this level of theory, the $^3A_2$ state was computed to be lower in energy than the $^1A_1$ state by 20.7 kcal/mol, and $^1A_1$ was computed to be 3.5 kcal/mol lower in energy than $^1A_2$.

Using an atomic natural orbital (ANO) basis set, the CASPT2 calculations of Nguyen and co-workers found the energy difference between $^1A_1$ and $^3A_2$ to be 22.3 kcal/mol, with $^1A_2$ lower than $^1A_1$ by 0.8 kcal/mol.[11] However, the $^3A_2$ geometry was used to compute the $^1A_2$ energy. Thus, 0.8 kcal/mol is a lower limit to the CASPT2/ANO energy difference between $^1A_2$ and $^1A_1$ at the optimized geometry of each state.

We were able to optimize the geometries of all three low-lying states of **1c** at the (8/8)CASSCF level of theory. The optimized geometries are shown in Figure 1. As in the case of phenylnitrene (**1b**), in the $^1A_2$ state of phenylphosphinidene (**1c**), the bond to the heteroatom is shorter and the benzene ring shows more bond alternation than in either the $^1A_1$ or $^3A_2$ states. However, the differences between the geometries of $^1A_2$ and the other two low-lying states are much smaller in **1c** than in **1b**, reflecting the fact that π bonds to phosphorus are weaker than π bonds to nitrogen.[16] The weaker π bond to the phosphorus in the $^1A_2$ state of **1c** is the major reason $^1A_1$ is much closer in energy to $^1A_2$ in **1c**[10,11] than in **1b**.[9]

As shown in Table 1, both our (8/8)CASSCF/6-31G* and (8/8)CASPT2/6-31G* calculations place $^1A_2$ below $^1A_1$. After corrections for zero-point energies, the (8/8)CASPT2 energies of $^1A_1$ and $^1A_2$, relative to that of $^3A_2$, are, respectively, 25.4 and 21.3 kcal/mol.

Thus, the calculations of Hamilton,[10] Nguyen,[11] and those reported herein, all agree that the two lowest singlet states of phenylphosphinidene both lie 20−25 kcal/mol above the triplet. However, the CISD calculations, used by Hamilton and co-workers, and the CASPT2 calculation, used by Nguyen and co-workers and by us, disagree as to which singlet state is lower in energy. It is likely that (8/8)CASPT2 is prejudiced toward favoring the open-shell singlet ($^1A_2$) over the closed-shell ($^1A_1$) singlet;[24] but this fact does not settle the issue of which singlet state actually does lie lower in **1c**.
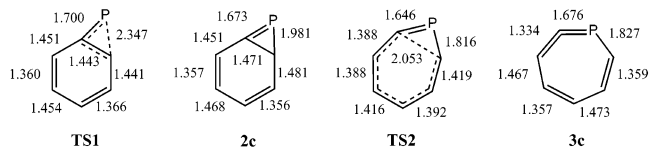
Figure 2. (8/8)CASSCF bond lengths (Å) of the transition structures, the intermediate **2c**, and the product in the ring expansion of the $^1A_2$ state of phenylphosphinidene (**1c**) to 1-phospha-1,2,4,6-heptatetraene (**3c**).

Fortunately, the question of which of the two singlet states really is lower in energy is not of critical importance to the potential surface for ring expansion of **1c**, because the TS for the cyclization of **1c** to **2c** (**TS1** in Figure 2) has no element of symmetry. Therefore, the energetic proximity of the two low-lying singlets in the C_{2v} reactant means that they will be mixed strongly in the C_1 TS for cyclization. Consequently, whether $^1A_1$ or $^1A_2$ is actually lower in energy in **1c** should not have a profound effect on the electronic structure of the TS leading to **2c**.

Comparison of the Energetics of the Ring Expansion Reactions of 1b and 1c. As shown in both Table 1 and Figure 3, at the (8/8)CASPT2/6-31G* level of theory, cyclization of the $^1A_2$ state of **1c** to **2c** is computed to be endothermic by 4.9 kcal/mol and to require passage over a TS 10.8 kcal/mol higher in energy than the reactant. At the same level of theory, the potential energy surface for cyclization of **1b** to **2b** is rather similar, with the reaction being computed to be endothermic by 1.6 kcal/mol and to require passage over a barrier of 8.6 kcal/mol.[8a] The seemingly small differences of $\Delta\Delta H = 3.3$ kcal/mol and $\Delta\Delta H^{\ddagger} = 2.2$ kcal/mol between the cyclization steps in the ring expansion reactions of **1b** and **1c** do not appear likely to be the principal reason the ring expansion of **1b** occurs readily, whereas that of **1c** has never been observed.

However, the energetics are very different for the ring opening of phosphirene **2c** to 1-phospha-1,2,4,6-cycloheptatetraene (**3c**) than for the ring opening of azirine **2b** to 1-aza-1,2,4,6-cycloheptatetraene (**3b**). The former reaction is computed to require passage over a barrier of 19.1 kcal/mol and to be endothermic by 11.3 kcal/mol. In contrast, at the same level of theory, ring opening of **2b** to **3b** involves passage over a barrier of only 5.2 kcal/mol and is *exothermic* by 2.9 kcal/mol.[8a]

Thus, as illustrated graphically in Figure 3, both reactions in the ring expansion of singlet **1c** to **3c** are predicted to be endothermic, making the overall endothermicity of the ring expansion of **1c** to **3c** 16.2 kcal/mol. In contrast, the second step of the ring expansion of singlet phenylnitrene (**1b**) to 1-aza-1,2,4,6-cycloheptatetraene (**3b**) is sufficiently favorable energetically to make the overall rearrangement of **1b** to **3b** exothermic by 1.3 kcal/mol.

Contributors to the Enthalpy Difference between 1b → 3b and 1c → 3c. The difference between the 16.2 kcal/mol endothermicity of the ring expansion of **1c** to **3c** and the 1.3 kcal/mol exothermicity of the ring expansion of **1b** to **3b** makes the isodesmic reaction in eq 1 endothermic by 17.5 kcal/mol.

(24) See, for example, the comparison between the experimental singlet−triplet energy difference in methylene and the values, computed at different levels of theory, in Table 1 of: Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F. *J. Org. Chem.* **1996**, *61*, 7030. The larger energy diffence between the nonbonding orbitals in methylene than in **1c** makes the $^1A_1$ state of methylene more of a "closed-shell" singlet than the $^1A_1$ state of **1c**.
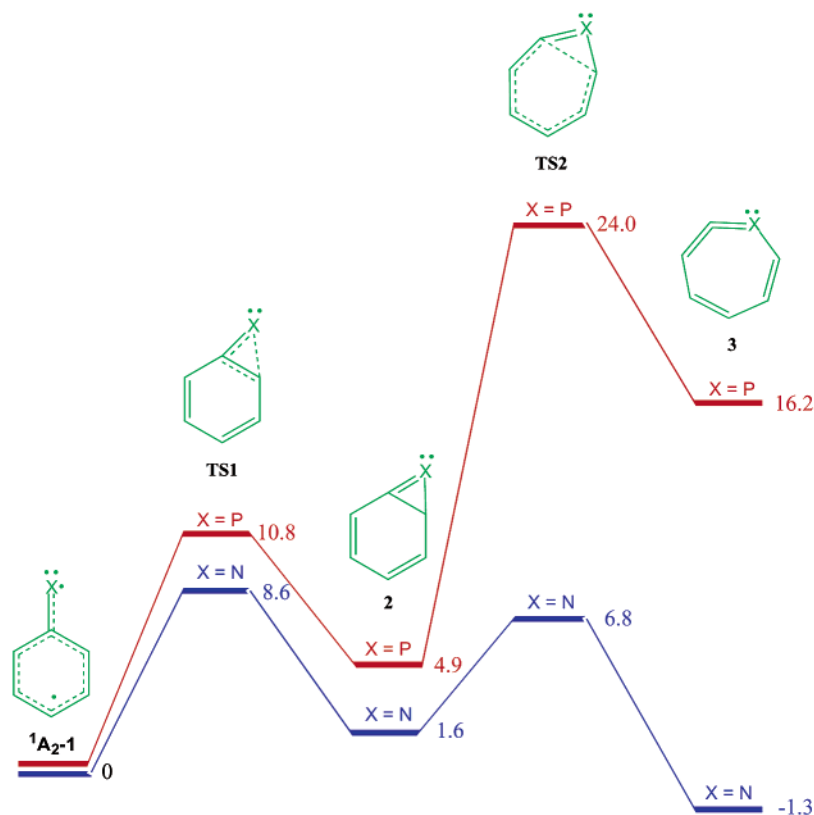
Figure 3. Zero-point inclusive, (8/8)CASPT2, relative energies (kcal/mol) of the transition structures, the intermediate **2** and the product **3** in the ring expansion of the $^1A_2$ state of phenylnitrene (**1b**) and of phenylphosphinidene (**1c**).

What differences between the two ring expansion reactions contribute to the 17.5 kcal/mol difference between their overall energies?
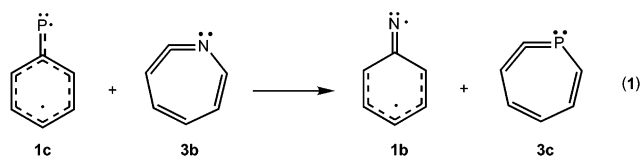

In both reactions—forming **3b** from **1b** and **3c** from **1c**—a second σ bond between carbon and the heteroatom is created. In addition, in the latter reaction, a full C−P π bond in the product replaces partial C−P and C−C π bonds in the reactant. Thus, a very significant contributor to the difference between the overall enthalpies of the two ring expansion reactions is likely to be the difference between the strengths[16,17] of these σ and π bonds.

The differences between the changes in bonding that occur in the ring expansion reactions of **1b** to **3b** and of **1c** to **3c** should be largely mirrored in the isomerization of the lowest singlet state ($^1A''$) of 3-azaphenylphosphinidene (**4**) to the lowest singlet state ($^1A''$) of 3-phosphaphenylnitrene (**5**). Therefore, one might expect that, like the isodesmic reaction in eq 1, the isomerization reaction in eq 2 would be computed to be quite
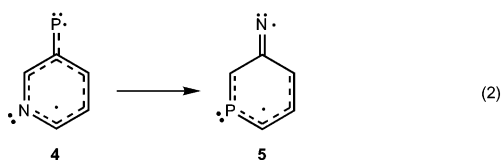
endothermic. In fact, the endothermicity of 22.3 kcal/mol for the reaction in eq 2 is actually 4.8 kcal/mol larger than the endothermicity of 17.5 kcal/mol for the reaction in eq 1.

One possible explanation of the finding that the isodesmic reaction in eq 2 is more endothermic than the isodesmic reaction in eq 1 is that **3b** and **3c** are heterocumulenes, in which the cumulated double bonds are both twisted and bent. These deformations might exact a higher energetic cost from **3b** than from **3c**. To test this hypothesis, we computed the energy of the isodesmic reaction in eq 3, which compares the heats of
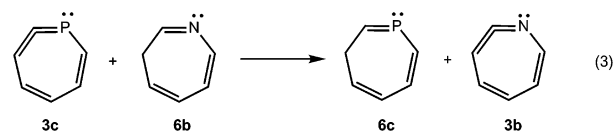

hydrogenation of the cumulated C−C double bond in **3b** to form **6b** with the formation of **6c** from **3c**.

The energy change of 7.5 kcal/mol that is computed for the isodesmic reaction in eq 3 indicates that the presence of the bent and twisted cumulated double bonds does, indeed, apparently destabilize azacycloheptatetraene **3b** more than phosphacycloheptatetraene **3c**. Based on the energy of the isodesmic reaction in eq 3, the energy of destabilization of **3b**, relative to **3c**, is actually 2.7 kcal/mol larger than the estimate of 4.8 kcal/mol that is based on the difference between the energies of the isomerization reaction in eq 2 and the isodesmic reaction in eq 1. Given the differences between the two ways of estimating the energy of destabilization of **3b**, relative to **3c**, it is not surprising that the two estimates differ. Nevertheless, it is probably safe to conclude that, without the selective destabiliza-

tion of **3b**, relative to **3c**, the difference between the enthalpies of the ring expansion reactions of **1b** and **1c** would be 5−8 kcal/mol larger than the (8/8)CASPT2/6-31G* value of 17.5 kcal/mol for the isodemic reaction in eq 1.

Differences between the Overall Energetics of Ring Expansion and the Energetics of the Ring Closure Step. As already noted, the difference of 3.3 kcal/mol between the energies of the ring closure steps in the ring expansions of **1b** and **1c** is very much smaller than the difference of 17.5 kcal/mol between the energies of the overall reactions. Thus, despite the fact that **2b** and **3b** each contain a doubly bonded nitrogen and **2c** and **3c** each contain a doubly bonded phosphorus, the isodesmic rection in eq 4 is endothermic by 14.2 kcal/mol.

(4)
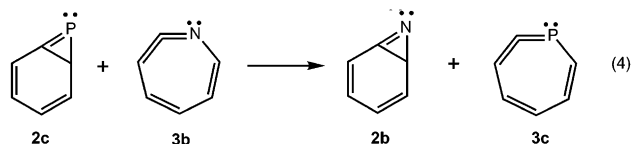
An obvious contributor to the 14.2 kcal/mol difference in energies between the opening of **2b** to **3b** ($\Delta E = -2.9$ kcal/mol) and of **2c** to **3c** ($\Delta E = 11.3$ kcal/mol) is the difference in strain between the three-membered rings in **2b** and **3b**. Bond angles at nitrogen are, in general, larger than bond angles at phosphorus. For example, the C−N−C bond angles of 110.7° in **3b** and 121.9° in **6b** are, respectively, 14.6° and 17.4° larger than the bond angles of 96.1° in **3c** and 104.5° in **6c**. Therefore, incorporation of $C = X-C$ into a three-membered ring should induce more strain for X = N than for X = P,[25] thus making opening of **2b** to **3b** more thermodynamically favorable than opening of **2c** to **3c**.

The contribution of the difference between the strain energies of the three-membered rings in **2b** and **2c** to the energy of the reaction in eq 4 can easily be assessed by computing the difference between adding hydrogens to the bridgehead carbons in these two compounds and cleaving the C−C bond between these carbons. Therefore, the isodesmic reaction that defines the difference between the strain energies of the three-membered rings in **2b** and **2c** is given by eq 5. The energy of this reaction

(5)
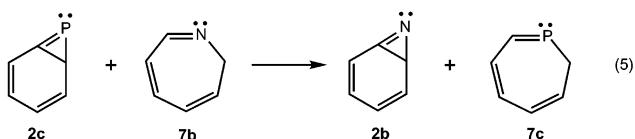
is computed to be 11.7 kcal/mol. Thus, the larger strain in **2b** than in **2c** does, indeed, make the major contribution to the 14.2 kcal/mol difference between the enthalpies of the ring opening reactions of **2b** to **3b** and **2c** to **3c**, which is given by the energy of the isodesmic reaction in eq 4.

Differences between the Energies of Trienes 6 and 7. The remaining 2.5 kcal/mol of the endothermicity of the isodesmic reaction in eq 4 is given by the difference between the isodesmic reactions in eqs 4 and 5. The difference between these two reactions is the isodesmic reaction in eq 6.

(25) The 6−7 kcal/mol lower strain energy computed for phosphirane than for cyclopropane has been attributed to the same type of difference between unstrained C−P−C and C−C−C bond angles: (a) Bachrach, S. M. *J. Phys. Chem.* **1989**, *93*, 7780. (b) Lammertsma, K.; Wang, B.; Hung, J.-T.; Ehlers, A. W.; Gray, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 11650.

(6)
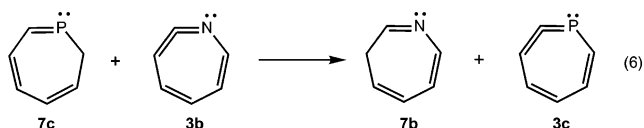
The hydrogen exchange reaction in eq 6 is not the same as the hydrogen exchange reaction in eq 3, because the diene groups in heterocycloheptatrienes **6b** and **6c** are conjugated with the heteroatom end of the C−X double bonds, whereas the diene groups in **7b** and **7c** are conjugated with the carbon end of the C−X double bonds. The isomerization of **6b** to **7b** is computed to be endothermic by 3.5 kcal/mol, and the isomerization of **6c** to **7c** is computed to be exothermic by 6.5 kcal/mol.

In both cases, the more thermodynamically stable triene isomer is the one in which the diene group is connected to the C−X double bond by the shorter single bond. This isomer is favored because the shorter single bond to the diene group gives it the larger π-conjugation energy. The difference between the two modes of connection is greater for C=P than for C=N, since the difference of 0.368 Å between the P−diene single bond length in **6c** (1.824 Å) and the C−diene single bond length in **7c** (1.456 Å) is much larger than the difference of 0.075 Å between the C−diene single bond length in **7b** (1.475 Å) and the N−diene single bond length in **6b** (1.400 Å).[26]

The energy change of 3.5 + 6.5 = 10.0 kcal/mol for the isomerization of the trienes in eq 7 is equal to the sum of the

(7)
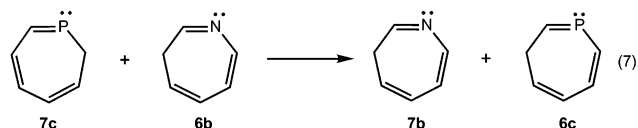
energy changes of 7.5 kcal/mol for the isodesmic reaction in eq 3 and 2.5 kcal/mol for the isodesmic reaction in eq 6. This must be the case, since the pair of isomerization reactions in eq 7 is just the sum of the reactions in eqs 3 and 6.

Conclusions

The results of our calculations provide a simple rationalization of the experimental observation that, unlike phenylnitrene (**1b**), phenylphosphinidene (**1c**) does not undergo a ring expansion reaction. The ring expansion reaction of **1b** to **3b** is computed to be slightly exothermic.[8] whereas the same type of calculations find the ring expansion of **1c** to **3c** to be very endothermic. Our calculations indicate that the difference between the energies of these two reactions can be attributed to the differences between the strengths of the σ bonds formed to nitrogen and to phosphorus in these reactions, plus the fact that a full C−P π bond in **3c** replaces a partial C−P π bond in **1c**.

(26) Professor Ken Houk has suggested in a private communication that differences in homoaromaticity may play a role in our finding that 1-phosphacycloheptatriene is lower in enthalpy than 2-phosphacyclohep-tatriene but that 2-azacycloheptatriene is lower in enthalpy than 1-azacy-cloheptatriene. Evidence in favor of this proposal comes from comparison of the B3LYP and CASSCF optimized geometries. Because the CASSCF calculations do not include the effects of dynamic electron correlation,[21] if homoaromaticity does contribute to these enthalpic preferences, the distance between C-1 and C-6 should be larger in the CASSCF than in the B3LYP optimized geometries. This is, in fact, the case. Moreover, the difference between the CASSCF and B3LYP bond distances amounts to 0.082 Å in 2-azacycloheptatriene but only 0.023 Å in 1-azacycloheptatriene and 0.125 Å in 1-phosphacycloheptatriene but only 0.067 Å in 2-phosphacyclohep-tatriene.

Despite the occurrence of the same changes in bonding in the cyclization reactions of **1b** and **1c**, the cyclization of **1c** to **2c** is computed to be only slightly more endothermic than that of **1b** to **2b**. Our calculations show this finding is the result of the much lower strain in the three-membered ring in **2c**, compared to **2b**. This difference in strain energies, which compensates for the differences in the strengths of unstrained C−N and C−P σ bonds, is the result of unstrained bond angles being smaller for C−P−C than for C−N−C.

The cyclization of **1c** to **2c** is computed to be endothermic by only 4.9 kcal/mol and to require an activation energy of only 10.8 kcal/mol. These findings offer the hope that it might prove possible to trap **2c** chemically with reagents that react with **2c** but not with **1c**. This possibility seems worthy of experiments directed toward the goal of trapping **2c**.

Supporting Information Available: (8/8)CASSCF/6-31G* optimized geometries, (8/8)CASSCF and (8/8)CASPT2/6-31G* energies, and (8/8)CASSCF zero-point energies and thermal corrections for: the three low-lying electronic states of **1c**, **TS1**, **2c**, **TS2**, **3b**, **3c**, **4**, **5**, **6b**, **6c**, **7b**, and **7c**. This material 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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