JOC Article

A Theoretical Study of the Formation of the Parent Phosphinine C_5H_5P from the Flash Vacuum Thermolysis of Diallylvinylphosphine

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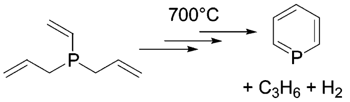

The gas-phase decomposition of diallylvinylphosphine **1** into C_5H_5P **12** is studied by DFT/6-311+G(d,p) calculations with the B3LYP functional, followed by single-point energy-only calculations at the CCSD(T)/6-311+G(d,p) level. According to these calculations, the first step involves a retro-ene elimination that yields 3-phosphahexatrienes **2Z** and **2E**. Both compounds equilibrate through the formation of 1,2- and 3,4-dihydrophosphetes **3** and **4**, and it is shown that the formation of **2Z** is favored by the exothermic formation of the 3,4-dihydrophosphinine **5** through a 6π-electrocyclization. Though **5** can easily isomerize into 2,3- (**6**) and 1,2-diyhydrophosphinines (**7**) by successive 1,5-hydrogen shifts, the formation of **12** from **5**, **6**, or **7** through an elimination of H_2 is found to be a high energy process. It is also shown that the elimination of H_2 from λ^5-phosphinine **8** following a C_{2v} pathway is a symmetry-forbidden process. Finally, 1,4-dihydrophosphinine **9**, which can be formed through a 1,4-hydrogen shift from λ^5-phosphinine **8,** is found to be a convenient precursor of **12** through a 1,4-elimination of H_2. The formation of **9** from **5** involves the intermediary formation of 3-phosphabicyclo[3.1.0]hex-2-ene **10**. The mechanism eventually proposed for the formation of **12** from **2Z** is given in Scheme 16 at the CCSD(T) level.

Introduction

Flash vacuum thermolysis (FVT) has already been proven to be a convenient method for the synthesis of sophisticated species through multistep sequences. In phosphorus chemistry, numerous studies focused on the use of stable saturated phosphorus derivatives to produce low-coordinate phosphorus compounds featuring sp- and sp^2-hybridized phosphorus atoms. Many kinetically unstable phosphalkynes and phosphaalkenes, whose synthesis through classical methods proved to be perilous, were thus easily produced and identified.[1] Due to the hardness of experimental conditions, many plausible mechanisms can be proposed to rationalize most of these transformations, and theoretical calculations are relevant tools to explore the different possible potential energy surfaces. In numerous cases, these studies shed some light on unexpected rearrangements. Recently, we reported on the mechanism of formation of the parent phosphaalkyne HCP from the pyrolysis of triallylphosphine at 700 °C.[2] This theoretical study demonstrated that a striking parallel exists between this process and the corresponding transformation that allows the synthesis of acetylene from vinyl acetylene.[3]

Herein, we wish to report on the thermal rearrangement that allows the synthesis of C_5H_5P **12** from the pyrolysis of vinyldiallylphosphine **1** at 700 °C.[1i] Initially, we proposed the following mechanism from the formation of **12** (Scheme 1).

Though the first step that involves a retro-ene elimination yielding 3-phosphahexatrienes **2Z** and **2E** is a relatively well-documented process,[4] no data relative to the 6π-electrocyclization yielding the 3,4-dihydrophosphinine **5** was available in the literature. Furthermore, the elimination of H_2 from **5**, as well as from dihydrophosphinines isomers in general, remains an unclear process.[5] All these points prompted us to reinvestigate this mechanism from a theoretical point of view.

Geometry optimizations and frequency calculations were carried out with the Gaussian 03 package at the DFT/6-311+G(d,p) level with the B3LYP functional.[6] Except when mentioned, all the energies reported below are those computed at the CCSD(T)/6-311+G(d,p) level by means of single-point energy-only calculations on the

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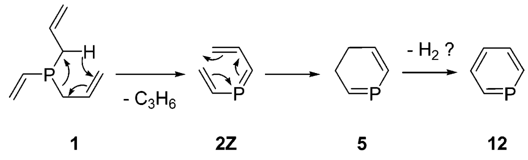
SCHEME 1

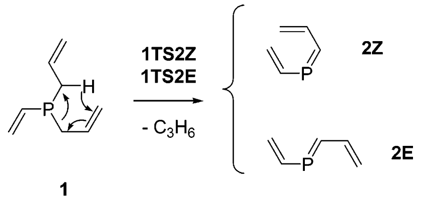


geometries optimized at the DFT level (see the Computational Details).

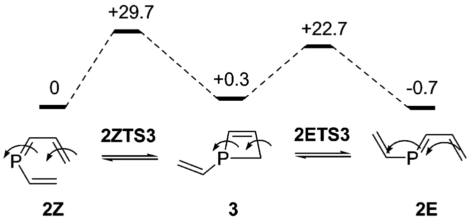
Results and Discussion

As initially proposed, the first step yielding 3-phosphahexatrienes **2E/2Z** is a classical retro-ene elimination requiring an activation energy of 42.7 kcal/mol (**1TS2E**) for the formation of **2E** and 45.8 kcal/mol (**1TS2Z**) for that of **2Z** from **1** (Scheme 2). Both processes are endothermic ($\Delta E = +22.2$ and $+22.9$ kcal/mol for **2E** and **2Z**, respectively),[7] and transition states were found to be very close in energy. In the following discussion, compound **2Z** was chosen as the zero of energy.

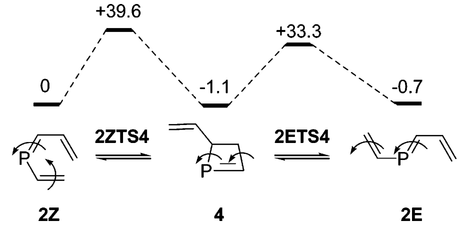
SCHEME 2



SCHEME 3



SCHEME 4



Both **2Z** and **2E** can equilibrate through a reversible 4π electrocyclic ring closure as shown in Scheme 3. As expected, this transformation proceeds through a conrotatory process and yields the 1,2-dihydro-1-vinylphosphabutene **3**. This ring closure (or ring opening) is not a highly energetically demanding process, but formation of **2E** appears to be kinetically favored.[8]

Note that both phosphaalkenes **2Z** and **2E** can also yield the 3,4-dihydrophosphete **4**, featuring a P═C double bond, through the same process. In this case, the cyclization involves the P═C double bond and the vinylic susbtituent at phosphorus. Though this transformation is equivalent to the former from a thermodynamical point of view, kinetics are different and the formation of compound **2E** is again favored (Scheme 4).

Interestingly, both dihydrophosphete isomers **3** and **4** are found to be connected through a 6 π electron phospha-Cope-type reaction.[9] Though this reaction is a relatively well-documented process in phosphorus chemistry, to the best of our knowledge no examples refer to a similar cyclic rearrangement in dihydrophosphete derivatives. Only a weak activation energy is needed to convert **3** into **4** ($\Delta E^{\ddagger} = +22.4$ kcal/mol). Therefore, compounds **2Z**, **2E**, **3**, and **4** can equilibrate (Scheme 5).

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(1) For references concerning the use of FVT or VGSR (vacuum gas solid reaction) in the synthesis of low-coordinate phosphorus compounds, see, for example: (a) Hopkinson, H. J.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *J. Chem. Soc., Chem. Commun.* **1976**, 513. (b) Guillemin, J.-C.; Denis, J.-M. *J. Chem. Soc., Chem. Commun.* **1985**, 951. (c) Fuchs, E, Hermesdorf, M. Regitz, M. *J. Organomet. Chem.* **1988**, 329. (d) Lacombe, S.; Pellerin, B.; Guillemin, J.-C.; Denis, J.-M.; Pfister-Guillouzo, G. *J. Org. Chem.* **1989**, *54*, 5958. (e) Regitz, M. *Chem. Rev.* **1990**, *90*, 191. (f) Guillemin, J.-C.; Janati, T.; Guenot, P.; Savignac, P.; Denis, J.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 196. (g) Guillemin, J.-C.; Janati, T.; Denis, J.-M. *J. Chem. Soc., Chem. Commun.* **1992**, 415. (h) Haber, S.; Le Floch, P.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1992**, 1799. (i) Le Floch, P.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1993**, 1295. (j) Haber, S.; Le Floch, P.; Mathey, F. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1993**, *1–4*, 225. (k) Guillemin, J.-C.; Cabioch, J.-L.; Morise, X.; Denis, J.-M.; Lacombe, S.; Gonbeau, D.; Pfister-Guillouzo, G.; Savignac, P.; Guenot, P. *Inorg. Chem.* **1993** *32,* 5021. (l) Guillemin, J.-C.; Janati, T.; Denis, J.-M.; Guenot, P.; Savignac, P. *Tetrahedron Lett.* **1994**, *35*, 245–248. (m) Gaumont, A.-C.; Guillemin, J.-C.; Denis, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 945. (n) Berger, D. J.; Gaspar, P. P.; Le Floch, P.; Mathey, F.; Grev, R. S. *Organometallics* **1996**, *15*, 4904. (o) Le Floch, P.; Mathey, F. In *Synthetic Methods of Organometallic and Inorganic Chemistry;* Karsch, H. H., Ed.; Thieme: Stuttgart, 1996; Vol. 3, p 8. (p) A.-C. Gaumont; Pilar, J.-F.; Denis, J.-M. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1996**, *109*, 461. (q) Guillemin, J.-C.; Janati, T.; Denis, J.-M. *J. Org. Chem.* **2001**, *66*, 7864.

(2) Le Floch, P.; Mathey, F. *J. Org. Chem.* **2004**, *69*, 5100.

(3) For examples illustrating the analogy between phosphorus and carbon, see: Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998.

(4) (a) Martin, G.; Ocando-Mavarez, E. *Heteroatom Chem.* **1991**, *2*, 651; (b) Martin, G.; Ocando-Mavarez, E.; Osorio, A.; Canestrari, M. *Heteroatom Chem.* **1992**, *3*, 395.

(5) For a general review on the chemistry of phosphinines and their derivatives, see: (a) Le Floch, P. In *Phosphorus–Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Pergamon: Oxford, 2001; p 485. (b) Nyulaszi, L. *Chem. Rev.* **2001**, *101*, 1229.

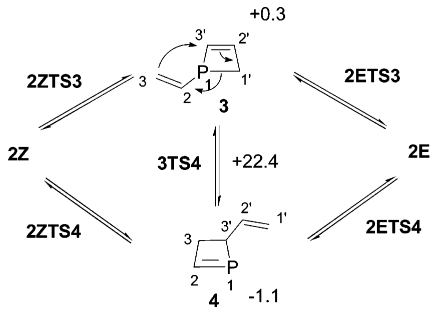
(6) Gaussian 03, Revision B.05, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 2003.

(7) Since the number of molecules changes during the reaction, free energies are more relevant tools to measure the feasibility of the reaction. According to Gibbs free energies at 1000 K, calculated at the B3LYP/6-311+G(d,p) level, both reactions are exergonic: $\Delta G = -22.4$ kcal/mol (**2Z**), $\Delta G = -25.4$ kcal/mol (**2E**).

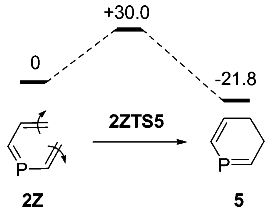
(8) For references concerning phosphabutadienes and their thermally induced conrotatory ring closing, see: (a) Bachrach, S. M.; Liu, M. *J. Am. Chem. Soc.* **1991**, *113*, 7929. (b) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 209. (c) Bachrach, S. M.; Liu. M., *J. Org. Chem.* **1992**, *57*, 2040.

(9) (a) Appel, R.; Kochta, J.; Winkhaus, V. *Chem. Ber.* **1988**, *121*, 631. (b) Tran Huy, Marinetti, A.; N. H.; Ricard, L.; Mathey, F. *Organometallics* **1992**, *11*, 1438. (c) Salzner, U.; Bachrach, S. M. *J. Org. Chem.* **1995**, *60*, 7101–7109.

SCHEME 5



SCHEME 6



On the basis of these results, how can we rationalize the formation of the 3,4-dihydrophosphinine derivative which was proposed as the key intermediate of our mechanism? Indeed, as can be seen in Schemes 3 and 4, the formation of phosphahexatriene **2Z** is not favored and the overall equilibrium should be kinetically shifted toward the formation of phosphahexatriene **2E**. The fact that the equilibrium is indeed shifted toward **2Z** became evident after computing the disrotatory 6π-electrocyclization process. As can be seen in Scheme 6, this transformation was found to be significantly exothermic ($\Delta E = -21.8$ kcal/mol), and a rather weak activation energy ($\Delta E^{\ddagger} = +30.0$ kcal/mol) is needed to promote the cyclization. A view of the transition **2ZTS5** is presented in Figure 1 together with the most relevant bond distances and bond angles.

Having shown that the first part of the overall mechanism relies on the formation of dihydrophosphinine **5**, we had to tackle the difficult problem of the elimination of H_2 to form phosphinine **12**. Various mechanisms can account for the formation of **12**. First, one may consider that a (3,4) elimination of H_2 directly occurs from compound **5** (Scheme 7) in a trans fashion (see Scheme 11). Note that the activation energy for this reaction step was evaluated at the CASSCF(2,2) + MP2//DFT(B3LYP) level because the transition-state structure **5TS12trans** was shown to have a strong diradical character (see the Computational Details). This elimination process requires an important activation energy ($\Delta E^{\ddagger} = +76.8$ kcal/mol).

Another interesting possibility would be to envisage the isomerization of **5** into its 2,3-dihydrophosphinine **6** and 1,2-dihydrophosphine **7** isomers. These reactions rely on successive symmetry-allowed (1,5) sigmatropic shifts of a hydrogen atom. The first process that leads to **6** was found to be slightly exothermic ($\Delta E = -3.7$ kcal/mol) and requires an activation energy of $\Delta E^{\ddagger} = +40.7$ kcal/mol. Then, a second (1,5) sigmatropic shift from **6** can lead to the 1,2-dihydrophosphinine **7** that features a P–H functionality through an activation energy of 33.7 kcal/mol (Scheme 8).

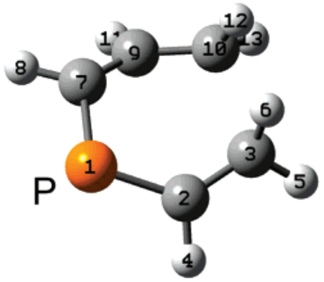
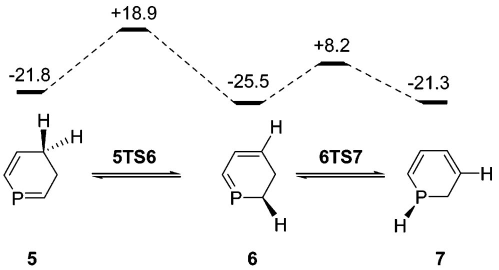


FIGURE 1. Transition state **2ZTS5** (6π-electrocyclization). Most significant bond distances (Å) and bond angles (deg): P1–C2, 1.745; C2–C3, 1.393; P1–C7, 1.757; C7–C9, 1.390; C9–C10, 1.399; C3–C10, 2.220. C10–C9–C7, 125.9; C9–C7–P1, 127.6; C7–P1–C2, 103.1; P1–C2–C3, 129.0; C2–C3–C10, 107.9.

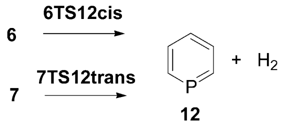
SCHEME 7

Scheme 7

SCHEME 8



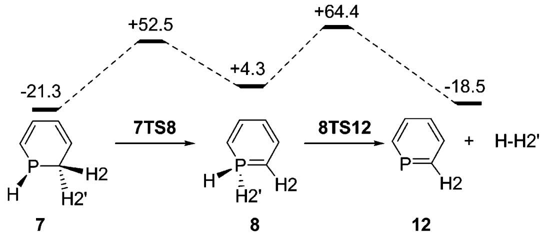
SCHEME 9



The possible formation of **6** and **7** offers two other interesting possibilities to generate phosphinine **12** through the elimination of H_2 (Schemes 9 and 11). A similar elimination of H_2 has already been envisioned to explain the formation of a 3,4-dimethylphosphinine by vacuum gas solid reaction (VGSR) but no detailed mechanism has been proposed.[1p] However, for both compounds, these eliminations require important activation energies ($\Delta E^{\ddagger} = 103.1$ kcal/mol for the (2,3) cis elimination from **6** and 90.1 kcal/mol for the (1,2) trans elimination from **7**) which make these pathways excluded on energetic grounds.

To explore a last possibility, we also studied the formation of a λ^5-phosphinine **8** featuring two H atoms at phosphorus from dihydrophosphinine **7**. This type of (1,2) shift has already been proposed in the literature to rationalize the formation of phosphinines from 1,2-dihydrophosphinines at high temperatures (about 250–300 °C). Indeed, it is well-known that 1-R,R′-λ^5-phosphinines rearrange at high temperature to yield phosphinines and one molecule of R–R′.[10] However, a significant energetic activation energy of 73.8 kcal/mol is needed to promote this rearrangement which was found

SCHEME 10



to be endothermic (see Scheme 10). In a second step, the elimination of H_2 from compound **8** is found to be exothermic and kinetically more favorable ($\Delta E^{\ddagger} = 60.1$ kcal/mol) than those previously studied from **5** and **6** and **7**. However, it is quite clear that the overall process is still highly energetically demanding.

The structure of the transition state **8TS12** is particulary interesting, and a view of the optimized geometry is presented in Figure 2. As can be seen, the elimination of H_2 does not proceed in a synchronous fashion, and one hydrogen atom is closer to the phosphorus atom than the second one (P11−H13, 1.431 Å; P11−H12, 1.820 Å with a H13−H12 distance of 1.309 Å). This unexpected geometry will be further rationalized by considering the molecular orbital diagram of λ^3- and λ^5-phosphinines.

At this stage of the discussion, let us recall some important features of the molecular orbital diagram of λ^3-phosphinines (Scheme 11). Both the HOMO and the LUMO bear a significant coefficient on the phosphorus and the C4 atom (para). The HOMO is bonding between phosphorus and α-carbon atoms (C2′−P−C2) as well as between C3 and C4 (C3′−C4−C3) and antibonding between C2 and C3. On the other hand, the LUMO is antibonding between phosphorus and C2 as well as between C3 and C4.

If we consider now the different possibilities to add H_2 onto phosphinines to form dihydrophosphinines, it is clear that the addition will only be allowed in certain cases. To develop stabilizing two-electron interactions between the frontier orbitals (HOMO and LUMO) of the reagents, H_2 will add in a *cis*-fashion on the C2−C3 bond to yield 2,3-dihydrophosphinines and also in a 1,4-*cis*-fashion to yield a 1,4-dihydrophosphinine. Note that this addition would probably be kinetically favored because of the important size of the coefficients at phosphorus and C4 in both the HOMO and the LUMO. On the other hand, 1,2- and 3,4-*trans*-addition of H_2 (with H_2 located in the plane perpendicular to the ring) would be conceivable to yield the 1,2- and the 3,4-dihydrophosphinine derivatives exclusively (Scheme 11).

Now, how can we rationalize the surprising geometry of the transition state **8TS12**? At first sight, one may propose that the elimination of H_2 can take place according to the least motion concerted C_{2v} pathway. However, on examining the symmetry of the molecular orbitals of the reactants and the product, it rapidly appears that this process is symmetry forbidden: there are different numbers of a_1- and b_1-occupied orbitals in the λ^5-phosphinine **8** (reactant) and the phosphinine + H_2 (products). Many avoided crossings are present in the correlation diagram, and as can be seen in the simplified representation given in Scheme 12, the HOMO of **8** actually correlates with the LUMO of **12** and the LUMO +1 of **8** with the HOMO-2 of **12** which describes the lone pair at phosphorus. Such an orbital crossing associated with the highest symmetry pathway is similar to that found for the elimination of X_2 from CX_2Y_2[11a] (or for the addition of methylene to ethylene).[11b] This observation fully rationalizes why the thermal elimination of H_2 follows a less symmetrical pathway.

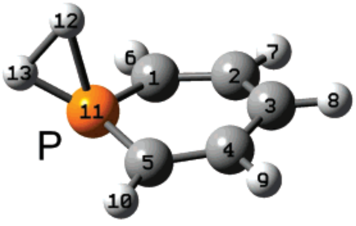
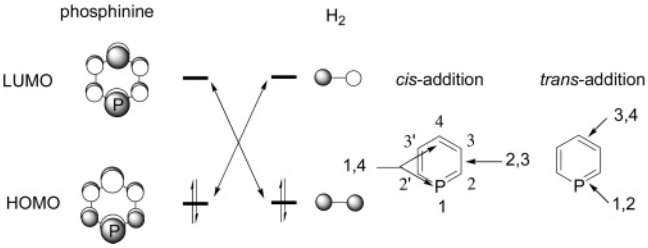
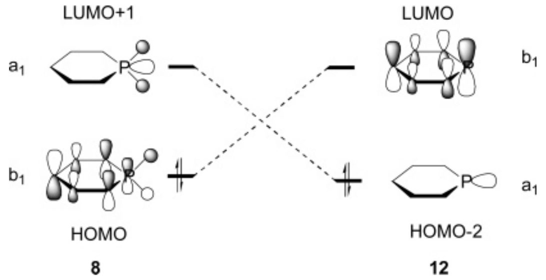


FIGURE 2. Transition state **8TS12** (elimination of H_2 from λ^5-phosphinine **8**). Most significant bond distances (Å) and bond angles (deg): P11−C1, 1.734; C1−C2, 1.387; C2−C3, 1.402; C3−C4, 1.403; C4−C5, 1.387; C5−P1, 1.734; P11−H13, 1.431; H13−H12, 1.309. P11−C1−C2, 117.2; C1−C2−C3, 125.8; C2−C3−C4, 122.5; C3−C4−C5, 125.8; C4−C5−P11, 117.2; C5−P11−C1, 108.3.

SCHEME 11



SCHEME 12



As explained above, one may expect that the 1,4-dihydrophosphinine **9** could be a suitable precursor of **12** through a 1,4-elimination of H_2.[12] One possible way to rationalize the formation of **9** is to propose that the λ^5-phosphinine **8** can undergo a 1,4-hydrogen shift from the phosphorus atom to the C4 carbon atom. This process which is symmetry allowed requires an activation energy of +23.6 kcal/mol and is exothermic. Interestingly, we

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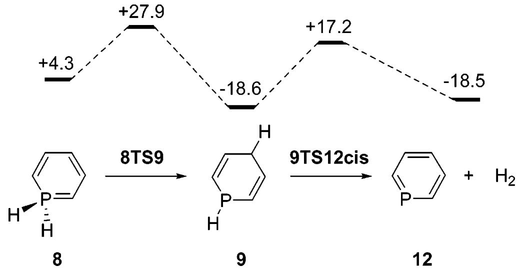
(10) See, for example: (a) Dimroth, K.; Städe, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 981. (b) Dimroth, K.; Hettche, A.; Städe, W.; Steuber, F. W. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 776.1 (c) Hettche, A.; Dimroth, K. *Tetrahedron Lett.* **1972**, 829. (d) Dimroth, K.; Hettche, A.; Kanter, H.; Städe, W. *Tetrahedron Lett.* **1972**, 835. (e) Kanter, H.; Mach, W.; Dimroth, K. *Chem. Ber.* **1977**, *110*, 395. (f) Märkl, G.; Hock, K. *Tetrahedron Lett.* **1983**, *24*, 5051. (g) Märkl, G.; Matthes, D. *Tetrahedron Lett.* **1974**, 4381. (h) Märkl, G.; Hock, K.; Matthes, D. *Chem. Ber.* **1983**, *116*, 445.

(11) (a) Cain, S. R.; Hoffmann, R.; Grant, E. R. *J. Phys. Chem.* **1981**, *85*, 4046. (b) Hoffmann, R.; Hayes, D. H.; Skell, P. *J. Phys. Chem.* **1972**, *76*, 664.

SCHEME 13



found that the *cis* 1,4 elimination of H_2 from **9** should easily proceed because of a relatively weak activation energy ($\Delta E^{\ddagger} = +35.8$ kcal/mol) (Scheme 13). A view of the structure optimized for the transition state **9TS12cis**, which adopts a boatlike conformation, is shown in Figure 3 together with the most significant theoretical parameters.

Though this sequence (1,4-hydrogen shift followed by 1,4-elimination) seemed reasonable at first sight, a significant energetic barrier is required to form **8**. Therefore, we focused our study on other mechanisms accounting for the formation of the 1,4-dihydrophosphinine **9** from dihydrophosphinines. Upon examining the potential energy surface between **5** to **9** (corresponding to thermally forbidden 4-electron-1,3-hydrogen shifts according to the Woodward–Hoffmann rules), transition state **5TS10** was found to be energetically accessible. Interestingly, by following the reaction path by the conventional IRC procedure, we found that this transition state does not connect **5** to **9** through a 1,3-hydrogen shift but to the 3-phosphabicyclo[3.1.0]hex-2-ene **10**. A view of this optimized transition state is shown in Figure 4. The conversion of **5** into **10** involves a 1,2-hydrogen shift of one hydrogen atom and the formation of a cyclopropane. To the best of our knowledge, no similar mechanism has been reported so far,[13] although this conversion might be related either to the vinylcyclopropane–cyclopentene or the vinylphosphirane–phospholene conversions.[14] This process can be related to a 1,5-hydrogen shift involving six electrons, two electrons being given by the C–H bond and four electrons by the π-system of 2-phosphabutadienyl part of the molecule. This transformation involves an activation barrier of 55.2 kcal/mol (Scheme 14). Interestingly, bicycle **10** can be easily converted in 1,4-dihydrophosphinine **9** through a kind of 1,5-sigmatropic shift involving one hydrogen atom, one double bond and the ring opening of the cyclopropane (Scheme 14). This transformation is slightly exothermic and requires an activation energy of 42.4 kcal/mol. This pathway appears to be kinetically favored with respect to the conversion of **7** into **12** through compound **8**.[15]

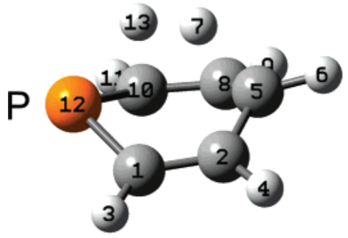


FIGURE 3. Transition state **9TS12** (elimination of H_2 from 1,4-dihydrophosphinine **9**). Most significant bond distances (Å) and bond angles (deg): P12–C1, 1.792; C1–C2, 1.356; C2–C5, 1.448; C5–C8, 1.448; C8–C10, 1.356; C10–P12, 1.792; P12–H13, 1.801; H13–H7, 0.955; H7–C5, 1.497. P12–C1–C2, 118.9; C1–C2–C5, 119.2; C2–C5–C8, 118.5; C5–C8–C10, 119.2; C8–C10–P12, 118.9; C10–12–H13, 82.3; P12–H13–H7, 121.3, H13–H7–C5, 133.0.

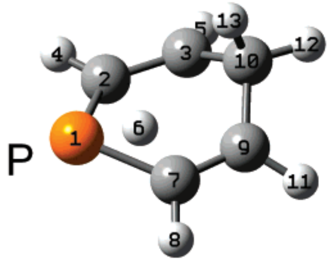
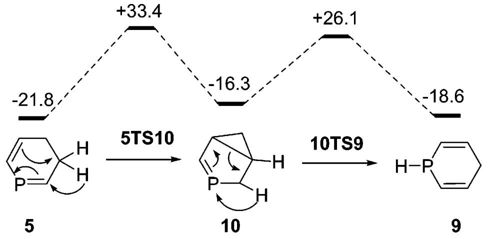


FIGURE 4. Transition state **5TS10** (hydrogen atom H6 going from C3 to C2). Most significant bond distances (Å) and bond angles (deg): P1–C7, 1.801; C7–C9, 1.352; C9–C10, 1.520; C10–C3, 1.484; C3–C2, 1.447; C2–P1, 1.799; C2–H6, 1.194; C3–H6, 1.525; C3–C9, 2.418. P1–C7–C9, 125.3; C7–C9–C10, 120.3; C9–C10–C3, 107.2; C10–C3–C2, 118.2; C3–C2–P1, 124.4; C2–H6–C3, 62.9.

SCHEME 14



We also checked whether the same sequence could apply for the conversion of dihydrophosphinine **7** into the 6-Phospha-bicyclo[3.1.0]hex-2-ene **11** which features a phosphirane ring. The transformation of **7** into **11** would involve the same type of rearrangement, leading to the displacement of one double bond and the formation of a phosphirane ring as depicted in the Scheme 15. However, this process which is slightly endothermic requires a significant activation energy ($\Delta E^{\ddagger} = +68.3$ kcal/mol) which compares in magnitude to the transformation of

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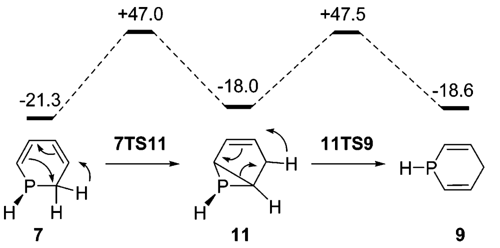
(12) For 1,4-elimination from 1,4-dihydrophosphinines, see, for example: (a) De Koe, P.; Bickelhaupt, F. P. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 567. (b) Märkl, G.; Fischer, D. E.; Olbrich, H. *Tetrahedron Lett.* **1970**, 645. (c) Ashe, A. J., III. *J. Am. Chem. Soc.* **1971**, *93*, 3293. (d) Jongsma, G.; Vermeer, H.; Bickelhaupt, F.; Schäfer, W.; Schweig, A. *Tetrahedron* **1975**, *31*, 2931. (e) Märkl, G.; Kneidl, F. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 931. (f) Märkl, G.; Kees, F.; Hofmeister, P. Soper, C. *J. Organomet. Chem.* **1973**, *173*, 125. (g) De Graaf, H. G.; Bickelhaupt, F. *Tetrahedron* **1975**, *31*, 1097.

(13) Some ring opening from similar bicycles to phosphinines or dihydrophosphinines are known but they involve different mechanisms; see, for example: (a) Holand, S.; Ricard, L.; Mathey, F. *J. Org. Chem.* **1991**, *46*, 5031. (b) Keglevich, G.; Ujszaszi, K.; Kowacs, A.; Töke, L. *J. Org. Chem.* **1993**, *58*, 977.

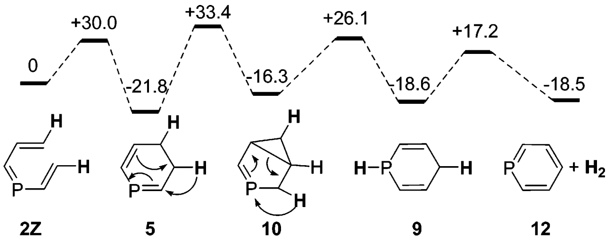
(14) (a) Houk, K. N.; Nendel, M.; Wiest, O.; Storer, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 10545. (b) Davidson, E. R.; Gajewski, J. J. *J. Am. Chem. Soc.* **1997**, *119*, 10543. (c) Bulo, R. E.; Ehlers, A. W.; Grimme, S.; Lammertsma, K. *J. Am. Chem. Soc.* **2002**, *124*, 13903.

(15) The diradical character of **5TS10** and **5TS9** was tested by CASSCF(2,2) calculations (see the Computational Details). The one-electron density matrix, however, indicates occupancies of 1.75 and 1.80, respectively, for the first orbital. Related to this point, see, for example: (a) Nendel, M.; Sperling, D.; Wiest, O.; Houk, K. N. *J. Org. Chem.* **2000**, *65*, 3259. (b) Suhrada, C. P.; Houk, K. N. *J. Am. Chem. Soc.* **2002**, *124*, 8796.

SCHEME 15



SCHEME 16



7 into **8**. Additionally, it was also found that the second step, which can be assimilated to 1,5-shift of hydrogen (like the transformation of **10** into **9**) also involves an important energetic barrier ($\Delta E^{\ddagger} = +65.5$ kcal/mol). Therefore, it is more difficult to form **9** from **7** than from **5** (Scheme 15).

Thus, the thermal decomposition of vinyldiallylphosphine into phosphinine is shown to be more complicated than initially proposed and several possible processes can account for the formation of the parent phosphinine **12**. Though the two first steps leading to the dihydrophosphinines **5**−**7** are rather low energy processes, it was shown that the elimination of H_2 is a complicated process that cannot proceed directly from these dihydrophosphinines. According to our results, the transient formation of λ^5-phosphinine **8**, though attracting from a mechanistic point of view, can be likely ruled out on energetical grounds. Therefore, the isomerization of dihydrophosphinine **5** into the bicyclic compound **10** is found to be the most realizable pathway and the formation of **12** from phosphahexatriene **2Z** is summarized in Scheme 16 in which the two eliminated hydrogen atoms are shown in bold.[16]

In conclusion, we have shown that the thermal decomposition of vinyldiallylphosphine into phosphinine involves as a kinetically determining step the transient formation of a 3-Phosphabicyclo[3.1.0]hex-2-ene. Additionally, we also demonstrated that the most plausible way to yield C_5H_5P from the corresponding λ^5-phosphinine C_5H_7P involves the transient formation of the 1,4-dihydrophosphinine and that the elimination of H_2 following a C_{2v} symmetry pathway is a symmetry-forbidden process. Further studies which are currently under progress in our laboratory focus on the case of functional derivatives.

Computational Details

Calculations were performed with the GAUSSIAN 03 series of programs.[6] Density functional theory (DFT)[17,18] was applied with the B3LYP functional[19−21] for geometry optimizations and frequencies calculations using the 6-311+G(d,p) basis set. The diradical character of the twenty-one transition states was tested by means of CASSCF(2,2) single-point calculations.[22] Twenty of them came out to be essentially single reference structures. The energy of these transition states and that of all the minima they connect were recomputed at the CCSD(T) level[23] in order to get accurate values for the energetic profiles (CCSD(T)//B3LYP/6-311+G(d,p) level of theory). The **5TS12trans** transition state was, however, found to have a diradical nature with similar weights of two electronic configurations. The energetic results given by single-reference methods being hazardous in such case, the activation energy of the reaction step going through this transition state (Scheme 7) was computed by single point calculation at the CASSCF(2,2) + MP2 level.[22] Since this reaction step was eventually eliminated on energetic grounds, the final reaction mechanism proposed in Scheme 16 involves only CCSD(T) energies.

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Supporting Information Available: View, Cartesian coordinates, and frequencies of all structures presented in this work (**1**−**12** and transition states). Energies are given at the CCSD(T) level and at the CASSCF(2,2) + MP2 level for **5**, **5TS12trans**, and **12** (see the Computational Details). This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] It should be noted that the last step (departure of H2) is exergonic considering Gibbs free energies at 1000 K calculated at the B3LYP/6-311+G(d,p) level: $\Delta G = -34.4$ kcal/mol.

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