Computational View of the Mechanism of Vinylphosphirane Pyrolysis and a New Route to Phosphaalkynes

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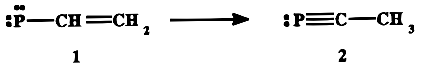
Results obtained with semiempirical MO methods support a mechanism for the pyrolysis of vinylphosphirane yielding phosphapropyne in which extrusion of ethylene leads to a vinylphosphinidene intermediate. A pathway from vinylphosphinidene to phosphapropyne involving 2*H*-phosphirene and 2-phosphapropenylidene intermediates is predicted from high level *ab initio* results to have a higher energy barrier than that for direct rearrangement. A higher energy pathway from vinylphosphirane is the migration of a hydrogen atom forming methyl(1-phosphiranyl)methylene, followed by loss of ethylene to yield the phosphaalkyne product. However, since fragmentation of 1-phosphiranylmethylene, once formed, has a low predicted barrier, its generation emerged as a new route to phosphaalkynes. (Trimethylsilyl)-(1-phosphiranyl)diazomethane was synthesized, and its pyrolysis yields $Me_3SiC{\equiv}P$.

Introduction

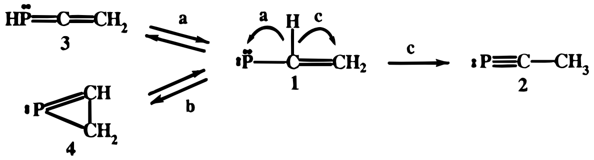
The observation that thermolysis of 1-vinylphosphirane at 700 °C leads to the formation of phosphapropyne[1] raised a number of mechanistic questions. In a previous report on the rearrangements of vinylphosphinidene,[2] computational results were presented that are in accord with the originally postulated mechanism[1] in which phosphapropyne is formed by direct rearrangement of vinylphosphinidene:



Our theoretical studies suggested the mechanism shown in Scheme 1. This rearrangement is unusual in that a hydrogen atom moves *away* from the electron-deficient neutral atom. According to these studies, vinylphosphinidene (**1**), 1-phosphaallene (**3**), and 2*H*-phosphirene (**4**) undergo rapid interconversion (Scheme 1a,b) under the Haber, LeFloch, Mathey (HLM) thermolysis conditions, but the lowest energy pathway that depletes the mixture (Scheme 1c) has a transition state resembling that for the hydrogen shift that directly converts vinylphosphinidene (**1**) to phosphapropyne (**2**).[2]

Our theoretical studies have now been extended. The rearrangements of vinylphosphinidene (**1**) have been reexamined by high level *ab initio* methods to evaluate the role of an intermediate that was slighted in our previous calculations.[2] Semiempirical methods have now been employed to explore the mechanism for the pyrolysis of vinylphosphirane in an attempt to answer the question whether pathways other than the extrusion of ethylene forming vinylphosphinidene (**1**) contribute to the formation of phosphapropyne (**2**). From the latter studies emerged a new route for the synthesis of phosphaalkynes.

Scheme 1



There was a misstatement in the introduction to our recent paper that must be corrected and that leads to one of the subjects of the present report. We stated that Yoshimine, Pacansky, and Honjou (YPH) predicted that, in a process that can be regarded as the parent reaction for the vinylphosphinidene-to-phosphaallene-rearrangement, vinylmethylene rearranges to propyne via allene. Instead, as shown in Scheme 2, YPH predicted that allene and propyne are both rearrangement products of vinylmethylene, the former via a 1,2-hydrogen migration in the expected direction (Scheme 2a) and the latter formed via a propenylidene intermediate (Scheme 2b−d).[3]

YPH predicted that cyclopropene and $CH_3HC{=}C$: are both intermediates in the rearrangement of vinylmeth-

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(1) Haber, S.; LeFloch, P.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1992**, 1799.

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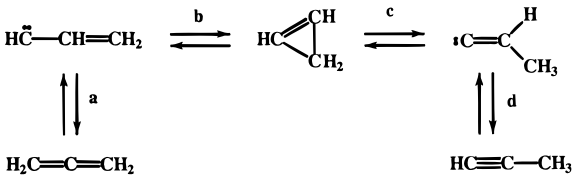
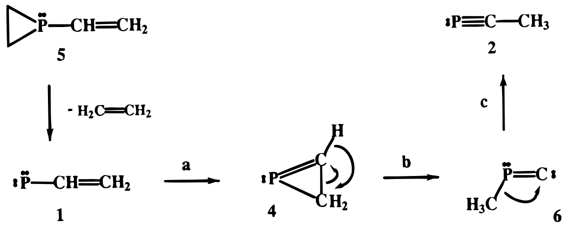
Scheme 2



Scheme 3



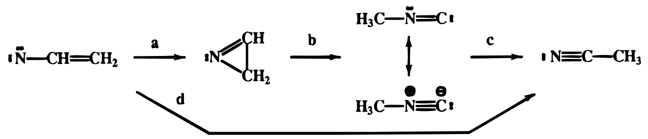
ylene to propyne but that allene is a side product. This paper evaluates several alternative mechanisms for phosphapropyne formation from vinylphosphirane, including the phosphapropenylidene route shown in Scheme 3. This mechanism, involving ring closure of vinylphosphinidene (**1**) to 2*H*-phosphirene (**4**) (Scheme 3a), ring opening of **4** with hydrogen migration to form 2-phosphapropenylidene (**6**) (Scheme 3b), and, ultimately, migration of a methyl group from a π-bonded P-atom to a carbene center Scheme 3c), was not discussed in our recent report.[2]

The high energy of 2-phosphapropenylidene (**6**) indicated by our previous studies suggested that it would *not* be an important intermediate in the formation of phosphapropyne (**2**). The results from semi-empirical methods reported previously[2] predicted that rearrangement of vinylphosphinidene **1** to 2*H*-phosphirene (**4**) is a facile process with an enthalpy barrier of only 1.9 kcal/mol, but 2-phosphapropenylidene (**6**) was predicted to have an enthalpy only 0.8 kcal/mol below that of the transition state which converts the equilibrating mixture of **1**, **3**, and **4** to phosphapropyne (**2**).

The mechanism of Scheme 3 seemed quite unfavorable, since the barrier for the formation of 2-phosphapropenylidene (**6**) from 2*H*-phosphirene (**4**) is predicted by MNDO methods to be 35.9 kcal/mol higher than the highest barrier along the route from **4** to phosphapropyne (**2**) via vinylphosphinidene (**1**) (Scheme 1). Therefore it seemed that a pathway via 2-phosphapropenylidene (**6**) makes at most only a minor contribution to the formation of **1** under the HLM thermolysis conditions.

A closer look at the energetics of Scheme 3 seemed necessary, however, given the experimental evidence for the intermediacy of propenylidene in the thermal conversion of cyclopropenes to acetylenes (Scheme 2)[4] and the prediction based on *ab initio* methods with correlation corrections[5] that methylisonitrile is an intermediate in the rearrangement of singlet vinylnitrene to acetonitrile, as shown in Scheme 4. Prudence suggested reexamination with the aid of high-level *ab initio* methods of the role of 2-phosphapropenylidene **6** in the rearrangement of vinylphosphinidene **1** to phosphapropyne **2**, and we do so in this report.

Scheme 4



For the rearrangement of singlet vinylnitrene to acetonitrile, depicted in Scheme 4, the isonitrile intermediate corresponding to 2-phosphapropenylidene (**6**) is stabilized by delocalization. This may be represented by a major contribution from a zwitterionic resonance structure that lends triple-bond character to the C—N bond and makes the unsaturated carbon atom less “carbene-like”. By contrast, 2-phosphapropenylidene (**6**) is *more* “alkylidene-like” due to a smaller contribution of a triple-bonded zwitterionic resonance structure and, hence, *less* stable.

The instability of phosphavinylidenes, also called phosphaisonitriles, R—P═C:, relative to phosphaacetylenes or phosphanitriles R—C≡P:, has been attributed to “orbital nonhybridization”,[6] also known as the “inert-pair effect”.[7] Rapid rearrangement of R—P═C: intermediates to R—C≡P: in solution has been inferred by several groups.[8-10] While no phosphavinylidene has been isolated, a transition metal complex has been prepared.[11]

The isonitrile intermediate in the rearrangement of vinylnitrene to acetonitrile (Scheme 4) was found by Lohr, Hanamura, and Morokuma (LHM) to be more stable than 2*H*-azirine, and there are significant barriers for its formation from 2*H*-azirine (Scheme 4b) and for its rearrangement ot acetonitrile (Scheme 4c).[5] The barrier for formation of the isonitrile (Scheme 4b) was found to be higher in energy than the barrier for its rearrangement to acetonitrile (Scheme 4c). Both these transition states were predicted to be lower in energy than the lowest singlet state of vinylnitrene, which undergoes ring closure to 2*H*-azirine (Scheme 4a) with no appreciable barrier.

In addition to the stepwise rearrangement of vinylnitrene from its lowest $n^2\pi^2$ singlet state, LHM found an excited closed-shell π^4 singlet state of vinylnitrene lying 12.4 kcal/mol above the lowest singlet state. This π^4 singlet vinylnitrene can rearrange directly to acetonitrile (Scheme 4d) via a hydrogen shift *away from* the electron-deficient nitrogen, a process similar to, but with a transition-state geometry rather different from, that of the direct rearrangement of vinylphosphinidene (**1**) to phosphapropyne (**2**).

Recent theoretical studies by Doughty, Bacskay, and Mackie (DBM) on the interconversion of C_2H_3N species are largely in agreement with the LHM results, when differences in the levels of theory and the basis sets employed are taken into account.[12] But DBM found

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(4) Walsh, R.; Wolf, C.; Untiedt, S.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1992**, 421.

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(8) Yoshifuji, M.; Niitsu, T.; Inamoto, N. *Chem. Lett.* **1988**, 1733.

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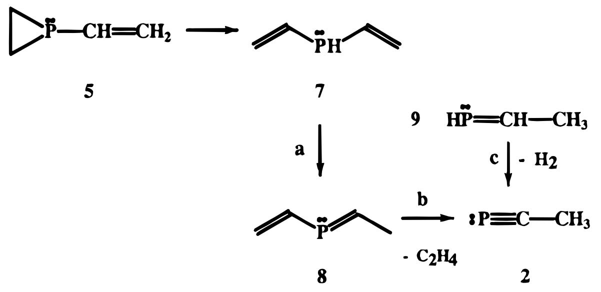
Scheme 5



that the transition state for formation of methyl isonitrile (Scheme 4b) lies 12.1 kcal/mole *above* the lowest singlet state of vinylnitrene and is the highest point along the methyl isonitrile pathway from vinylnitrene to acetonitrile. Below this transition state by 4.3 kcal/mol DBM found a transition state for direct rearrangement of vinylnitrene to acetonitrile (Scheme 4d). The transition state found by DBM for direct arrangement of vinylnitrene to acetonitrile (Scheme 4d) resembles that reported previously by us for direct rearrangement of vinylphosphinidene (**1**) to phosphapropyne (**2**).[2] DBM made no choice between the two mechanisms: direct rearrangement of vinylnitrene to acetonitrile and stepwise rearrangement via 2*H*-azirine and methyl isonitrile.

This report has three sections: (A) Examination by *ab initio* methods of the role of 2-phosphapropenylidene (**6**) in the rearrangement of vinylphosphinidene (**1**) to phosphapropyne (**2**); (B) a survey at the semiempirical level of the pyrolysis of vinylphosphirane (**5**), including alternative mechanisms for the formation of phosphapropyne (**2**) that do not involve vinylphosphinidene (**1**) (our previous report did *not* scrutinize the fragmentation pathways for vinylphosphirane); (C) a new route to phospha-alkynes suggested by one of the alternative mechanisms that emerged from the semiempirical studies. While we do not believe that this particular pathway operates under the HLM conditions, its feasibility has been established by experiments described here.

An alternative mechanism shown in Scheme 5, not involving vinylphosphinidene (**1**) for the formation of phosphapropyne (**2**) from vinylphosphirane (**5**), emerged from *ab initio* studies by Nguyen, Landuyt, and Vanquickenborne (NLV) on ring-chain rearrangements of unsubstituted phosphirane.[13]

NLV noted that HLM had found divinylphosphine (**7**) as the major product at 500 °C, at which temperature no phosphapropyne (**2**) was observed. NLV pointed out that **2** could be formed from **7** by a 1,3-H-shift forming 3-phospha-1,3-pentadiene (**8**) (Scheme 5a), followed by elimination of ethylene (Scheme 5b). This mechanism was thought by those workers to be less likely than loss of ethylene directly from vinylphosphirane (**5**) under the HLM thermolysis conditions.

NLV found that elimination of H_2 from 1-phosphapropene (**9**) forming phosphapropyne **2** (Scheme 5c) has a high predicted barrier, and they pointed out that the elimination of ethylene from divinylphospine (Scheme 5a,b) might be similarly disfavored. Scheme 5 predicts the formation of $P{\equiv}CCH_2D$ from $(H_2C{=}CH)_2PD$ if loss of ethylene from **8** is a 1,2-elimination. HLM reported that only a trace of $P{\equiv}CCH_2D$ was formed upon pyrolysis of $(H_2C{=}CH)_2PD$,[1] but equilibration of divinylphosphine and vinylphosphirane would scramble the hydrogens, and ignoring isotope effects, this scrambling would lower the yield of $P{\equiv}CCH_3$ to less than 43%. The contribution of the **5** → **7** → **8** → **2** pathway under the HLM pyrolysis conditions has been assessed via semiempirical studies and is discussed below.

Table 1. CCSD(T) *ab Initio* Energies and Enthalpies of Several Isomers of C_2H_3P Relative to Phosphapropyne (2) (kcal/mol)

	ΔE		ΔH_0	
molecule	DZP	TZPF	DZP	TZPF
vinylphosphinidene (**1**)	57.7	51.9	57.4	51.6
phosphapropyne (**2**)	0.0	0.0	0.0	0.0
1-phosphaallene (**3**)	21.3	19.1	18.9	16.7
2*H*-phosphirene (**4**)	22.9	21.3	22.5	20.9
2-phosphapropenylidene (**6**)	70.2	68.0	68.5	66.3
1*H*-phosphirene (**13**)	33.7	35.4	31.5	33.1
ethynylphosphine (**14**)	27.3	24.3	23.8	20.7

Computational Details

1. *Ab Initio* Methods. These have been described.[2] For internal consistency we extend our previous results by reoptimizing all the geometries of the singlet states at the singles and doubles coupled cluster level of theory (CCSD) using the polarized double-ζ basis set (DZP). For those structures that had previously been optimized at the CISD level of theory, the largest geometry change was 0.016 Å in bond length and 0.6° in bond angle.

Relative (to phosphapropyne (**2**)) energies and relative enthalpies shown in Table 1 were obtained by adding on scaled SCF (or TCSCF) zero-point vibrational energies. Selected energies and enthalpies of activation are given in Table 2. The final energies were obtained at the DZP CCSD optimized geometries using the CCSD(T) method, which includes a perturbative estimate of connected triple excitations.[14] Two basis sets were used here: the DZP basis set and a larger basis set of TZ(2df,2p) quality. Specifically, we used density matrix averaged natural orbital basis sets for hydrogen (8s,4p) → [3s2p], carbon (14s9p4d3f) → [4s3p2d1f], and phosphorus (17s12p5d4f) → [5s4p2d1f].[15]

2. Semiempirical Methods. Semiempirical studies were performed using MNDO[16] as implemented by the MOPAC package, versions 5.0 and 6.0,[17] and by HyperChem, Release 3.[18] Except when otherwise specified, calculations were at the RHF level. When employed, limited configuration interaction at optimized geometries combined all microstates involving excitations from the three highest occupied MO's to the three lowest unoccupied MO's of the ground state.

Transition states were fully optimized whenever possible by eigenvector following[19] at the RHF-SCF level in MOPAC 6.0, after having been obtained either as saddle points along the MOPAC-generated reaction coordinate between two fully

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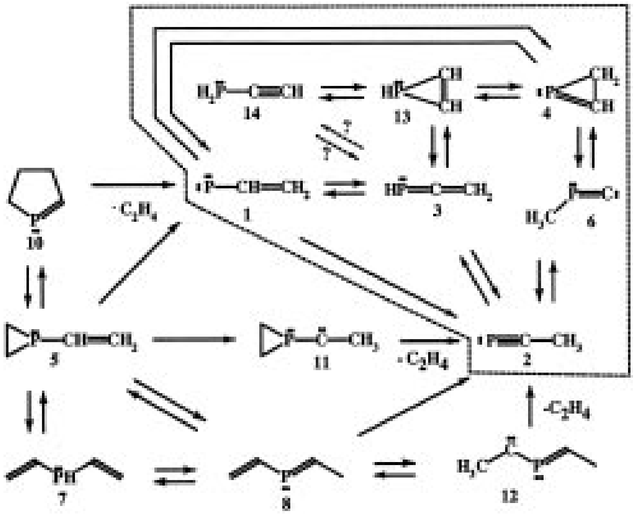
Table 2. CCSD(T) *ab Initio* Energies and Enthalpies of Transition States for Selected Elementary Reactions of Scheme 6 Relative to Phosphapropyne (2) and Energies and Enthalpies of Activation (kcal/mol)

		$\Delta E(\ddagger)^a$		$\Delta H(\ddagger)^a$		$\Delta E(\ddagger)(I\rightarrow F)$		$\Delta H(\ddagger)(I\rightarrow F)$		$\Delta E^\ddagger(F\rightarrow I)$		$\Delta H^\ddagger(F\rightarrow I)$	
init pt	final pt	DZP	TZPF	DZP	TZPF	DZP	TZPF	DZP	TZPF	DZP	TZPF	DZP	TZPF
1	**2**	69.2	65.7	64.5	61.1	11.5	13.8	7.1	9.5	69.2	65.7	64.5	61.1
1	**3**	62.3	56.9	57.9	52.6	4.6	5.0	0.5	1.0	41.0	37.8	39.0	35.9
2	**3**	81.5	77.1	77.8	73.4	81.5	77.1	77.8	73.4	60.2	58.0	58.9	56.7
2	**6**	73.8	70.5	71.6	68.3	73.8	70.5	71.6	68.3	3.6	2.5	3.1	2.0
3	**13**	87.1	84.1	81.3	78.3	65.8	65.0	62.4	61.6	53.4	48.7	49.8	45.2
4	**6**	74.4	72.4	71.2	69.2	51.5	51.1	48.7	48.3	4.2	4.4	2.7	2.9
4	**13**	84.5	79.8	79.5	74.8	61.6	58.5	57.0	53.9	50.8	44.4	48.0	41.7
13	**14**	88.1	84.5	82.2	78.6	54.4	49.1	50.7	45.5	60.8	60.2	58.4	57.9

[a] Relative to phosphapropyne (**2**).

Scheme 6



optimized local minima[20] or by optimization of points along an arbitrarily selected coordinate.

Vibrational analysis was performed on each transition state to confirm that it had only one imaginary frequency and that the frequency corresponded to the probable reaction coordinate. The imaginary vibrational frequency was also visually examined, using HyperChem Release 3, in order to confirm the reasonableness of the transition states.

Results and Discussion

Computational Results. The full set of reactions that was considered in this work is shown in Scheme 6. All the reactions were examined via semiempirical methods. The other reactions in Scheme 6 are interconversions of C_4H_7P molecules and their fragmentation processes. The reactions of C_2H_3P species studied by *ab initio* methods are within the dotted borders. The transition state for the interconversion of **1** and **3**, as well as that for **1** and **2**, as determined by *ab initio* methods, was reported in our previous publication.[2] DZP CCSD geometry-optimized structures for **2**, **3**, **4**, **6**, **13**, and **14** are displayed in Figure 1. DZP CCSD structures for the transition states for conversion of **6** to phosphapropyne (**2**) and 2*H*-phosphirene (**4**) are given in Figure 2, along with DZP CCSD transition state structures **2/3**, **3/13**, **4/13**, and **13/14**. *Ab initio* structures for **1**−**4**, **13**, and **14**, all but the first at the SCF and CISD levels, have been presented previously.[2]

MNDO heats of formation for the transition states connecting the species included in Scheme 6 and enthalpies of activation in both directions are given in Table 3. Heats of formation for the species included in Scheme 6, as predicted by MNDO semiempirical methods, are presented in Table 4. MNDO-optimized structures for those species in Scheme 6 other than those presented in our previous report (**1**−**4**, **6**, **13**, **14**)[2] are displayed in Figure 3. Those transition state geometries from semiempirical studies that have not been previously published are shown in Figures 4 and 5. Semiempirical transition state structures **1/2**, **1/3**, **1/4**, **2/3**, **3/13**, **3/14**, **4/13**, and **13/14** are in the previous report.[2]

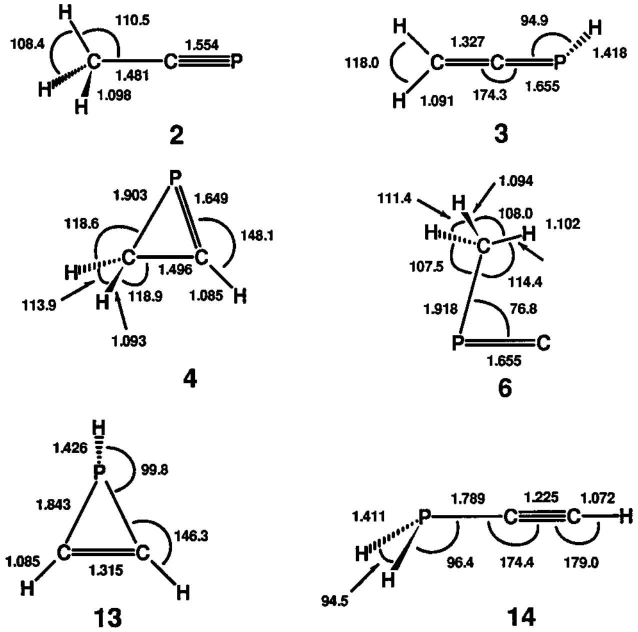


Figure 1. *Ab initio* DZP CCSD-optimized geometries for **2**−**4**, **6**, **13**, and **14**.

A. Examination by *ab Initio* Methods of the Role of 2-Phosphapropenylidene (6) in the Rearrangement of Vinylphosphinidene (1) to Phosphapropyne (2). *Ab Initio* Structures and Transition States. It was the question whether 2-phosphapropenylidene (**6**) is an intermediate in the formation of phosphapropyne (**2**) under the HLM thermolysis conditions that led us to carry out *ab initio* studies on **6** and the transition states for its interconversion with the proximal species in Scheme 6, phosphapropyne product **2** and 2*H*-phosphirene (**4**). For none of the species in Scheme 6 that had previously been the subjects of *ab initio* studies (**1**−**4**, **13**, and **14**)[2] had large differences in geometry from those predicted by semiempirical methods been found. Bond angles differed by 5° or less in all cases.

For 2-phosphapropenylidene (**6**), however, the DZP CCSD structure displayed in Figure 1 is quite unusual

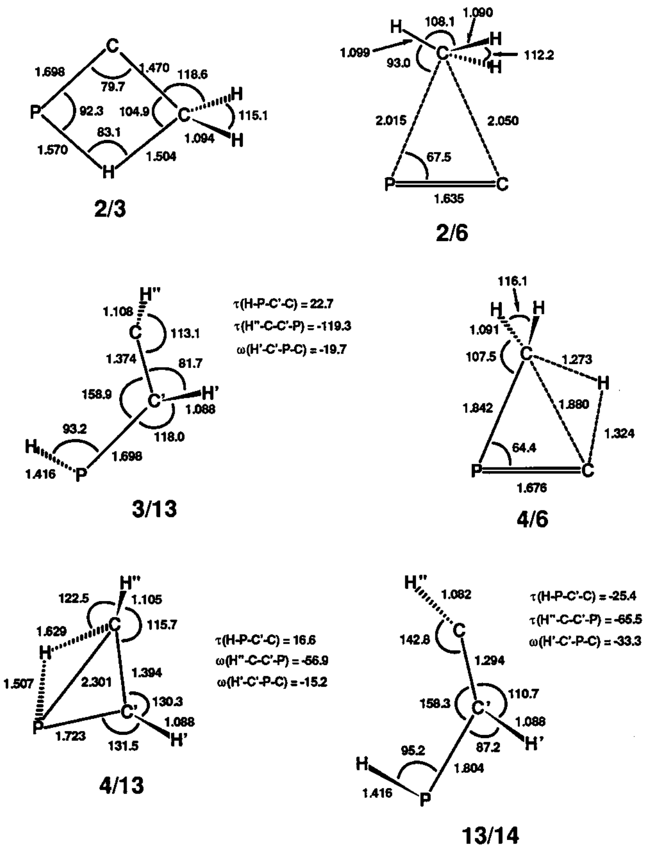


Figure 2. *Ab initio* DZP CCSD-optimized geometries for transition states **2**/**3**, **2**/**6**, **3**/**13**, **4**/**6**, **4**/**13**, and **13**/**14**. τ are torsional angles, and $\bar{\omega}$ are out-of-plane or improper torsional angles.

Table 3. MNDO Heats of Formation for Transition States and Enthalpies of Activation for the Elementary Reactions of Scheme 6

init pt	final pt	$\Delta H_f(\ddagger)$ (kcal/mol)	$\Delta E^{\ddagger}$ (kcal/mol) init → final	final → init	ref
1	**2**	106.2	29.8	82.5	2
1	**3**	92.0	15.6	51.0	2
1	**4**	78.2	1.8	35.1	2
2	**3**	144.6	120.9	103.7	2
2	**6**	135.9	112.2	30.6	*a*
3	**13**	119.4	78.4	65.9	2
3	**14**	123.1	82.1	79.3	2
4	**6**	142.1	99.0	36.8	*a*
4	**13**	111.9	68.8	58.5	2, *a*, *b*
5	**1**	92.3	86.0	irreversible	*a*
5	**7**	76.2	69.9	60.9	*a*
5	**8**	84.4	78.1	75.5	*a*
5	**10**	77.7	71.4	91.1	*a*
5	**11**	92.1	85.8	20.9	*a*
7	**8**	79.1	63.8	70.2	*a*
8	**2**	123.8	114.9	irreversible	*a*
8	**12**	90.9	82.0	22.6	*a*
10	**1**	94.6	108.0	irreversible	*a*
11	**2**	71.2	0	irreversible	*a*
12	**2**	112.3	44.0	irreversible	*a*
13	**14**	102.7	49.3	58.9	2

[a] This work. [b] These recalculated values differ significantly from those reported in ref 2.

Table 4. MNDO Heats of Formation of Several Isomers of C_2H_3P and C_4H_7P (kcal/mol)

vinylphosphinidene (**1**)	76.4[a]
phosphapropyne (**2**)	23.7[a]
1-phosphaallene (**3**)	41.0[a]
2*H*-phosphirene (**4**)	43.1[a]
vinylphosphirane (**5**)	6.3
2-phosphapropenylidene (**6**)	105.3
divinylphosphine (**7**)	15.3
trans-3-phospha-1,3-pentadiene (**8**)	8.9
1-phosphacyclopentene (**10**)	−13.4
methyl(1-phosphiranyl)methylene (**11**)	71.2[b]
trans-3-phospha-3-penten-2-ylidene (**12**)	74.3
1*H*-phosphirene (**13**)	53.4[a]
ethynylphosphine (**14**)	43.8[a]

[a] Previously reported in ref 2. [b] This energy is from a single-point RHF calculation at the geometry optimized at the UHF level.

and is significantly different from that found by semiempirical methods, the *ab initio* C−P−C angle of 76.8° differing dramatically from the semiempirical value of 159°![2] The *ab initio* structure of **6** is very similar to that of the transition state **2**/**6**, shown in Figure 2, for rearrangement of **6** to phosphapropyne (**2**) via shift of a methyl group. The semiempirical structure for **2**/**6** shown in Figure 4 is in good agreement with the structure of this transition state. The geometry of the semiempirical transition state **4**/**6** (Figure 4) also agrees with the *ab initio* structure (Figure 2).

2-Phosphapropenylidene (**6**) is predicted by the CCSD(T) studies to be only a shallow local minimum (<3 kcal/mol). This was presaged by the similarity of its structure to that of the transition state for rearrangement of **6** to 2*H*-phosphirene (**4**), structure **4**/**6** of Figure 2, as well as to that of transition state **2**/**6**. The similarity of *ab initio* structures **6**, **2**/**6**, and **4**/**6** is mirrored by the extremely low activation barriers predicted by the CCSD(T) studies of the transformation **6** → **2** and **6** → **4**, 3 and 4 kcal/mol, respectively, given in Table 2. The transition state for rearrangement of 2-phosphapropenylidene (**6**) to phosphapropyne (**2**) is in accord with a 1,2-methyl shift, for which there is considerable precedent in the chemistry of vinylidenes.[21]

The DZP CCSD harmonic vibrational frequency analysis of **6** predicts that the C−P−C bending vibration has the smallest vibrational frequency, 215 cm^{-1}. This vibration is even softer at semiempirical levels, with a frequency of 48 cm^{-1} predicted by the MNDO parametrization. Other parametrizations give bending frequencies nearer the *ab initio* prediction, AM1 predicting a 117° bond angle and 159 cm^{-1} frequency, while PM3 predicts a 180° bond angle and 160 cm^{-1} frequency. AM1 and PM3 both predict higher heats of formation for **6** than MNDO (118.9 and 109.5, respectively, vs 105.3), and the MNDO values are employed in the discussion of the semiempirical results below.

For the parent phosphavinylidene HP=C:, multireference CASSCF theoretical studies by Goldstein, Jin, Carrillo, and Cave (GJCC) predicted that linear HP=C: is unstable toward bending and rearranges without a barrier to HC≡P:.[22] By contrast GJCC found that at the MP2 level linear HP=C: *is* a local minimum but with only a 2−3 kcal/mol barrier for rearrangement. On this basis GJCC were unable to reach a firm conclusion regarding the existence of HP=C: as a metastable species and noted merely that the potential surface is quite flat in the vicinity of HP=C:.

Previous work by Nguyen and Ha found a local minimum for HP=C: at HF/3-21G, but at all higher levels of theory, linear HC≡P: was the only minimum

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(21) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.
(22) Goldstein, E.; Jin, S.; Carrillo, M. R.; Cave, R. J., *J. Comput. Chem.* **1993**, *14*, 186.
(23) Nguyen, M. T.; Ha, T.-K. *J. Mol. Struct.* **1986**, *139*, 145.

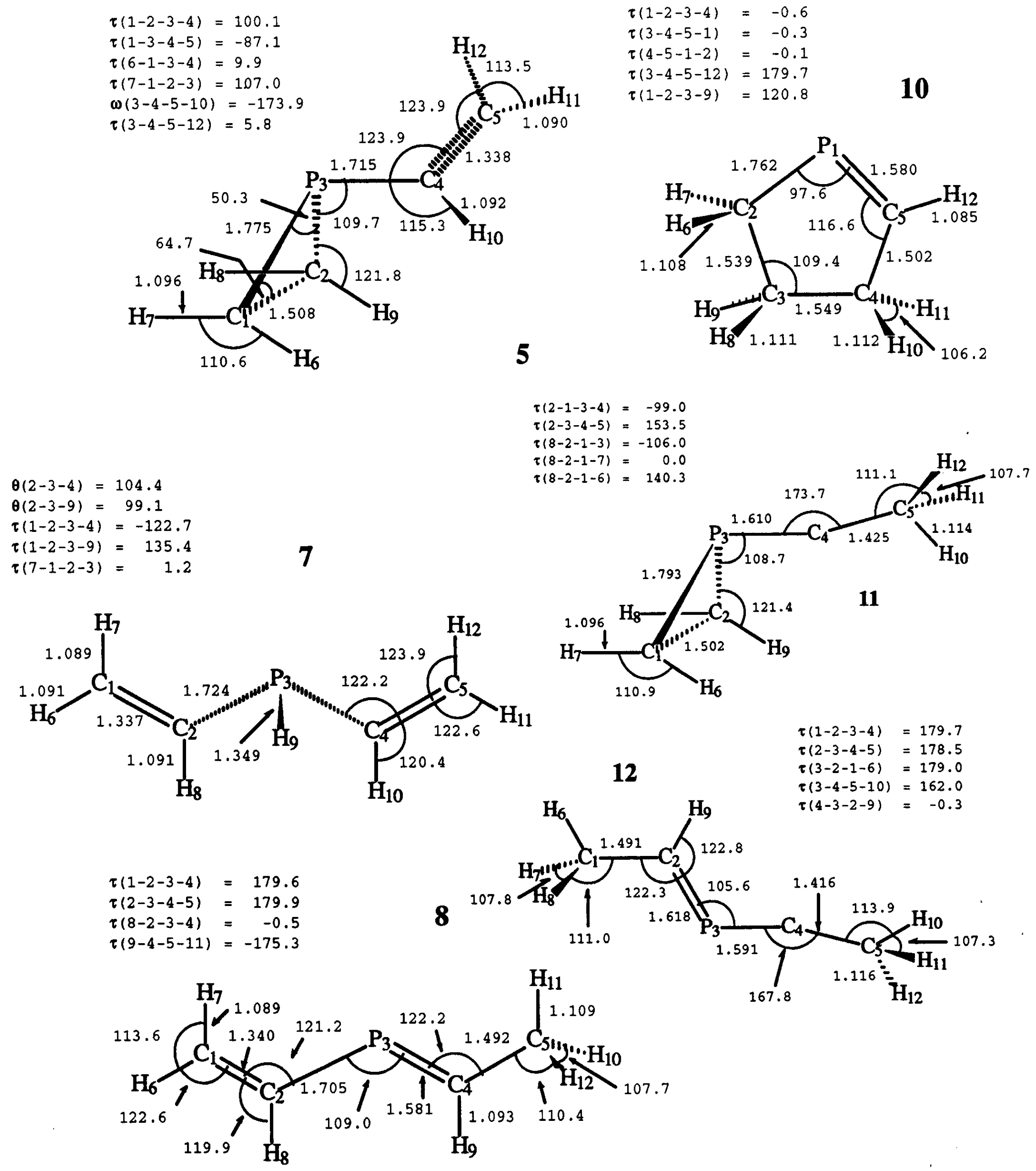

Figure 3. MNDO RHF-optimized geometries for selected molecules of Scheme 6. τ are torsional angles, and ω is an out-of-plane or improper torsional angle.

located.[23] The HF/3-21G predicted structure for metastable HP=C: has an 87.8° H−P−C angle.

Given the variations among the predictions for HP=C: at the highest *ab initio* levels, the difference between the various semiempirical predictions for **6** are understandable without undermining confidence in the results for other species participating in Scheme 6.

It is clear that the unusual structure of 2-phosphapropenylidene (**6**), with its semibridging methyl group, is inadequately represented by a single Lewis structure, and with its extremely soft C−P−C bending vibration, it presents a challenge to even sophisticated structure theory. With the parametrization of semiempirical molecular orbital methods based on "normal" molecules, it is thus not surprising that there are considerable differences not only between the structures of **6** predicted by *ab initio* and semiempirical studies but also among the predictions of various semiempirical parameter sets. All agree, however, in predicting a high energy for **6**. It should be noted that for none of the other structures in Scheme 6, whether of metastable species or transition states, have large geometric differences emerged between the semiempirical and *ab initio* studies.

A direct interconversion between 1-phosphaallene (**3**) and ethynylphosphine (**14**) is indicated with a question mark in Scheme 6, because, despite strenuous efforts, attempts to find this transition state failed. While a transition state **3**/**14** was found at the semiempirical level and published in our previous report, it closely resembles the semiempirical transition state **3**/**13** for interconversion of 1-phosphaallene and 1*H*-phosphirene (**13**).[2] Thus *ab initio* and semiempirical studies seem to agree that 1-phosphaallene (**3**) and ethynylphosphine (**14**) interconvert via 1*H*-phosphirene (**13**). In the *ab initio* transition state **3**/**13** the shift of a hydrogen from the terminal CH_2 group of the phosphaallene is further advanced than in the semiempirical transition state previously obtained. For transition state **13**/**14** that connects 1*H*-phosphirene (**13**) and ethynylphosphine (**14**) there is good agreement in both structure and energy between the *ab initio* results given here and the semiempirical studies presented previously.[2]

The other *ab initio* transition state structures shown

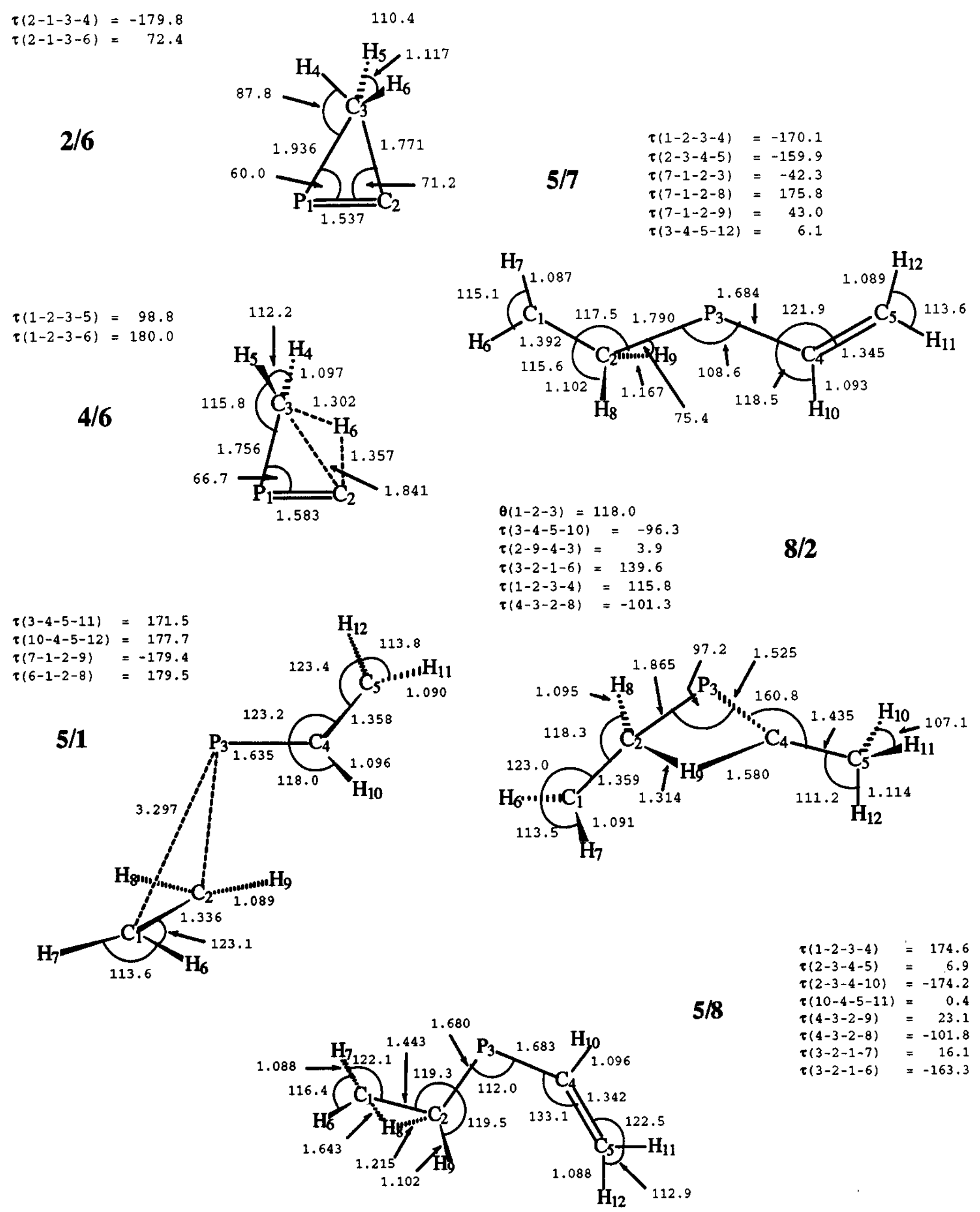

Figure 4. MNDO RHF-optimized transition-state geometries for selected conversions of Scheme 6. τ are torsional angles, and θ is a bond angle.

in Figure 2 require little comment. The high-energy transition state **2**/**3** for direct interconversion of 1-phosphaallene (**3**) and phosphapropyne (**2**) is clearly an awkward 1,3-hydrogen shift and closely resembles the semiempirical structure for **2**/**3** previously published.[2] Transition state **4**/**13** connecting 1*H*- and 2*H*-phosphirene, is clearly a 1,2 hydrogen shift, and its structure is very close to that previously obtained by semiempirical methods.[2]

***Ab Initio* Energetics.** While the *ab initio* results presented here predict that the direct rearrangement of Scheme 1 should be more than 1 order of magnitude more rapid under the HLM reaction conditions than the vinylidene mechanism shown in Scheme 3, it was clearly unwarranted to dismiss this mechanism on the basis of the MNDO calculations.

The CCSD(T) prediction is that the pathway involving 2-phosphapropenylidene (**6**) (**1** → **4** → **6** → **2**) has a saddle point whose enthalpy is 8 kcal/mol higher than that for the direct rearrangement of vinylphosphinidene (**1**) to phosphapropyne (**2**), rather than the 35 kcal/mol higher energy predicted by MNDO semiempirical methods. The CCSD(T) studies, whose results are given in Table 2, lower the **4**/**6** and **2**/**6** transition state energies, relative to the MNDO results, by *ca.* 45 kcal/mol. The CCSD(T) results also lower the energy of transition state **1**/**2** for the highest barrier along the pathway for direct rearrangement of vinylphosphinidene (**1**) to phosphapropyne (**2**) but by only *ca.* 20 kcal/mol. Even with the much narrower difference between their barrier heights predicted by the *ab initio* methods, and at the high temperatures of theHLM experiments, the pathway including **6** may be expected to contribute only on the order of 2% to the formation of **2**, if entropic effects are equal. The results of Table 1 show that phosphapropenylidene (**6**) was found, at the CCSD(T) TZPF level, to have the highest enthalpy of the seven C_2H_3P species studied, 66.3 kcal/mol higher than phosphapro-

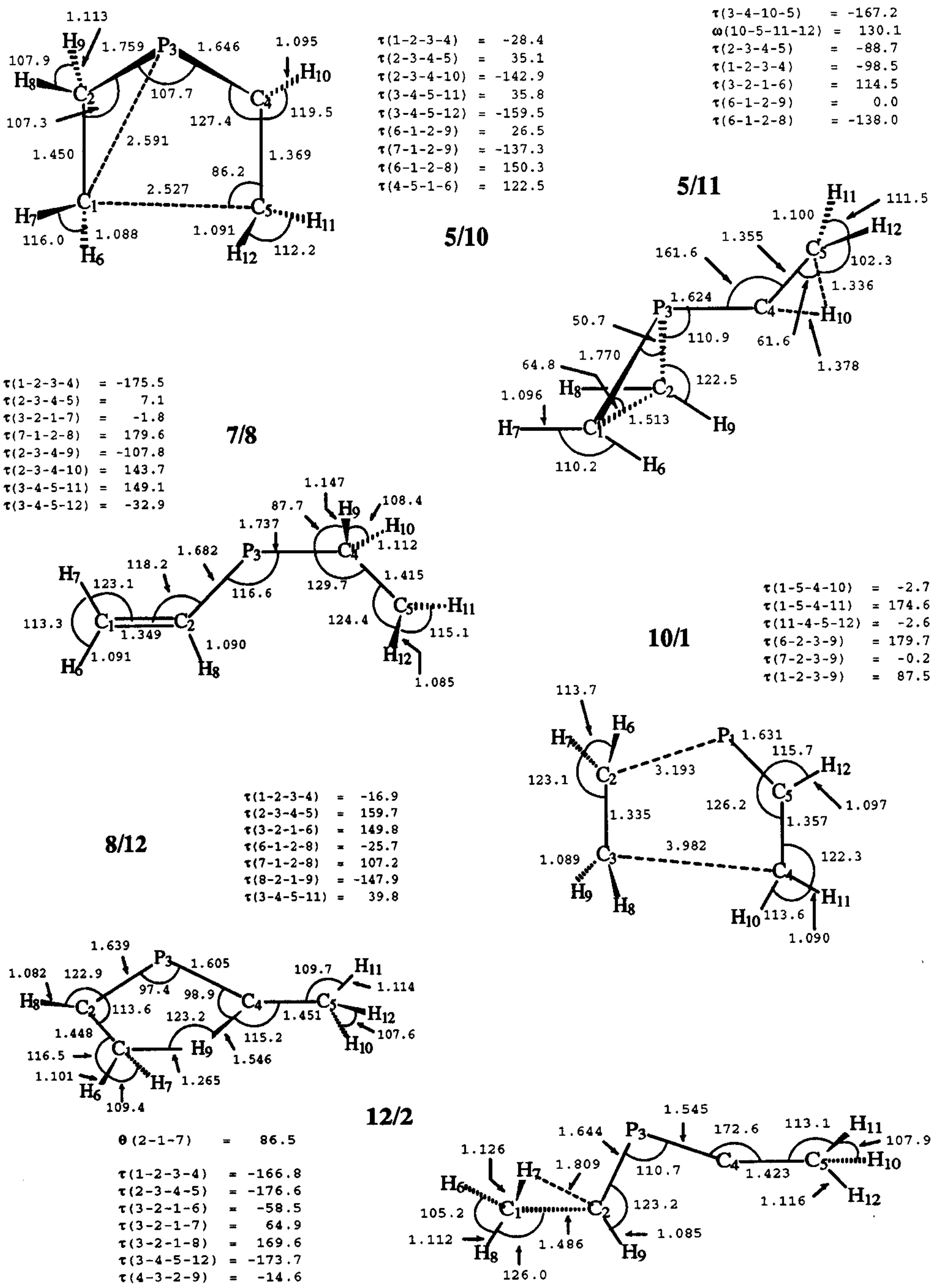

Figure 5. MNDO RHF-optimized transition-state geometries for selected conversions of Scheme 6. τ are torsional angles, θ is a bond angle, and ω is an out-of-plane or improper torsional angle.

pyne (**2**), the next highest being vinylphosphinidene (**1**), 51.6 kcal/mol above **2** but 14.7 kcal/mol below **6**.

The mechanistic difference between the rearrangements of vinylmethylene and vinylnitrene on the one hand and vinylphosphinidene on the other deserves comment. The theoretical prediction that vinylmethylene is converted to propyne via a propenylidene intermediate[3] has been supported by experimental results.[4] Theory also predicts that singlet vinylnitrene rearranges to acetonitrile via an isonitrile intermediate that can be regarded as an azavinylidene,[5] although more recent theoretical studies suggest that direct rearrangement of vinylnitrene to acetonitrile may be competitive with the isonitrile mechanism.[12] Here we reiterate, on the basis of *ab initio* results, our earlier prediction based on semiempirical results[2] that, for the rearrangement of vinylphosphinidene (**1**) to phosphapropyne (**2**), the 2-phosphapropenylidene mechanism is disfavored. Why should this be?

The answer seems to lie in the high energy of 2-phosphapropenylidene (**6**). In common with vinylmethylene and vinylnitrene, the barrier for ring closure of vinylphosphinidene **1** to 2*H*-phosphirene (**4**) is low. But the energy of **6** is so high relative to both **4** and phosphapropyne (**2**) that the transition states for both the formation of **6** from **4** and for its rearrangement to **2** lie close to **6**. It is thus the instability of **6** that raises the energy barrier for the 2-phosphapropenylidene pathway from vinylphosphinidene (**1**) to phosphapropyne (**2**) *above* that for the direct rearrangement.

B. Survey at the Semiempirical Level of the Pyrolysis of Vinylphosphirane (5). Semiempirical Structures. Only a few of the structures in Figure 3 have unusual features that require comment. Despite the large bond angle at the dicoordinate carbon atom adjacent to the phosphorus atom predicted for methyl(1-phosphiranyl)methylene (**11**) (174°) and 3-phospha-3-penten-2-ylidene (**12**) (168°), examination of the wavefunctions suggests minimal carbon−phosphorus triple-bond character for **11** and **12**.

The long-known limitations of low-level calculations for the characterization of carbenes[24] suggest an even greater degree of caution in the interpretation of the semiempirical energies calculated for **11** and **12** than that normally exercised with regard to semiempirical calculations. Semiempirical methods were employed for the study of the C_4H_7P species because it was not feasible to treat these larger molecules at the *ab initio* levels utilized for the C_2H_3P species and because, with the exception of 2-phosphapropenylidene (**6**), there was reasonable agreement between the semiempirical and *ab initio* results for geometries and for relative, if not absolute, energies.

Semiempirical Transition States. The transition state structures displayed in Figures 4 and 5 appear quite reasonable. The transition state connecting divinylphosphine (**7**) and *trans*-3-phospha-1,3-pentadiene (**8**) resembles a diradical stage in the movement of the hydrogen initially bonded to phosphorus along the P−C−C chain. The transition state for ring opening of vinylphosphirane (**5**) to divinylphosphine (**7**) has a similar structure, in accord with a process that is asynchronous although concerted. Nguyen found a similar transition state by *ab initio* methods for the related rearrangement of vinylphopshine ($H_2P{-}CH{=}CH_2$) to 1-phosphapropene ($HP{=}CH{-}CH_3$).[13] The transition state for fragmentation of 3-phospha-3-penten-2-ylidene (**12**) to phosphapropyne (**2**) corresponds to loss of ethylidene $:CHCH_3$ that rearranges smoothly to ethylene.[25] No transition state could be found for concerted loss of ethylene from **12**, but ethylene loss by 1,2-elimination is indicated by its transition state structure to be the mechanism for fragmentation of 3-phospha-1,3-pentadiene (**8**) to phosphapropyne (**2**).

Transition state structures are in accord with concerted rearrangements of vinylphosphirane (**5**) to 1-phosphacyclopentene (**10**) by a 1,3-sigmatropic shift, to methyl(1-phosphiranyl)methylene (**11**) by a 1,2-hydrogen shift and to 3-phospha-1,3-butadiene (**8**) by simultaneous ring opening and a 1,2-hydrogen shift. Fragmentation of vinylphosphirane (**5**) to ethylene and vinylphosphinidene (**1**) is found to be a concerted least-motion retro-addition process, as predicted by frontier molecular orbital arguments.[26] Rearrangement of 3-phospha-1,3-butadiene (**8**) to 3-phospha-3-penten-2-ylidene (**12**) is indicated by its transition state structure to be a concerted 1,4-hydrogen shift.

Semiempirical Energetics. For the C_2H_3P species of Scheme 6 for which comparison with *ab initio* results can be made (**1**, **3**, **4**, **6**, **13**, and **14**), the calculated energies relative to the lowest energy molecule, phosphapropyne (**2**), are in excellent agreement, with the exception of 2-phosphapropenylidene (**6**) that has been discussed above. For **1**, **3**, **4**, and **14**, the relative energies predicted by semiempirical methods lie within 1 kcal/mol of the *ab initio* values, and for **13**, the difference is <4 kcal/mol. The semiempirical prediction for the energy of **6** relative to that of **2** is 15.5 kcal/mol higher than the *ab initio* prediction.

As stated in the discussion of *ab initio* transition states, the energies predicted by semiempirical methods for the transition states **2**/**6** and **4**/**6** are *ca*. 45 kcal/mol *higher* than the *ab initio* energies. This is also the case for transition state **2**/**3**. For the other C_2H_3P transition states, the differences between the semiempirical and *ab initio* energies relative to that of phosphapropyne (**2**) were smaller, but the relative energy of the semiempirical transition state was always higher than that of its *ab initio* counterpart: 21.4 kcal/mol for **1**/**2**, 15.7 kcal/mol for **1**/**3**, 17.4 kcal/mol for **3**/**13**, 13.4 kcal/mol for **4**/**13**, and 0.4 kcal/mol for **13**/**14**. It is thus clear that while relative energies of potential minima on the C_4H_7P potential surface may be relied upon to better than 15 kcal/mol, conclusions drawn below from the semiempirical predictions of transition state energies and barrier heights must be treated with caution.

From the semiempirical transition state energies and barrier heights of Table 3 it can be seen that reversible rearrangements are predicted to equilibrate vinylphosphirane (**5**), divinylphosphine (**7**), 3-phospha-1,3-pentadiene (**8**), and 1-phosphacyclopentene (**10**) more rapidly than the processes considered in Scheme 6 for the fragmentation of **5** (**5** → **1** and **5** → **11** → **2**) are likely to occur. The semiempirical studies predict that the barriers for these fragmentations are at least 13 kcal/mol higher than those for the interconversions of **5** and its isomers **7**, **8**, and **10**. While direct interconversion of **5** and **8** can take place, there is a lower energy pathway for this interconversion via **7**.

The highest energy and therefore least important pathway suggested by semiempirical methods is in accord with the *ab initio* studies, with some differences in the predicted energetics, as discussed above. The high-energy pathway is again predicted to include as intermediates 2*H*-phosphirene (**4**) and 2-phosphapropenylidene (**6**), with high-energy transition states between **4** and **6** and between **6** and **2**. It was reported previously that due to a very flat potential surface, no transition state was found for **1** → **4** in *ab initio* studies, in qualitative agreement with the MNDO result that the enthalpy barrier is very small, 2 kcal/mol.[2] Thus MNDO methods lead to the prediction that, despite the ease of formation of 2*H*-phosphirene (**4**) from vinylphosphinidene (**1**), 2-phosphapropenylidene (**6**) makes no significant contribution to the formation of phosphapropyne (**2**) under the conditions employed by HLM for the pyrolysis of vinylphosphirane (**5**). This is in accord with the results from *ab initio* methods.

Another higher energy pathway, according to the MNDO results, is the formation of phosphapropyne (**2**) from 3-phospha-1,3-pentadiene (**8**) or 3-phospha-3-penten-2-ylidene (**12**) by the elimination of ethylene or ethylidene ($:CHCH_3$) (whose rearrangement to ethylene is rapid). The pathway **8** → **2** is the mechanistic alternative suggested by Nguyen *et al.*,[13] and equilibration of vinylphosphirane (**5**) with 3-phospha-1,3-pentadiene (**8**) and 1-phosphacyclopentene (**10**) is predicted by the semiempirical studies to be as facile as the

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(24) Gaspar, P. P.; Hammond, G. S. In *Carbenes*; Moss, R. A., Jones, Jr., M., Eds.; Wiley: New York, 1975; Vol. II, p 207.

(25) (a) Kistiakowsky, G. B.; Mahan, B. H. *J. Am. Chem. Soc.* **1957**, *79*, 2412. (b) Chong, D. P.; Kistiakowsky, G. B. *J. Phys. Chem.* **1964**, *68*, 1793.

(26) Li, X.; Lei, D.; Chiang, M. Y.; Gaspar, P. P. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1993**, *76*, 71.

equilibration of vinylphosphirane (**5**) with divinylphosphine (**7**) observed by HLM. According to the MNDO results, fragmentation of **12** → **2** could contribute on the order of 5% under the HLM pyrolysis conditions, again if entropic effects are equal, but we suspect that even modest correlation corrections of the type mentioned below would disfavor the **8** → **12** → **2** pathway.

Returning to the pathways for the pyrolysis of vinylphosphirane (**5**) predicted to be most favorable, three pathways for fragmentation of **5** have transition states of nearly the same energy according to the semiempirical studies: direct loss of ethylene from **5** forming vinylphosphinidene (**1**), indirect loss of ethylene from **5** forming **1** via 1-phosphacyclopentene (**10**), and loss of ethylene from **5** concerted with a 1,2-H shift forming methyl(phosphiranyl)methylene (**11**). At the MNDO level there is no barrier for loss of ethylene from **11** leading to phosphapropyne (**2**).

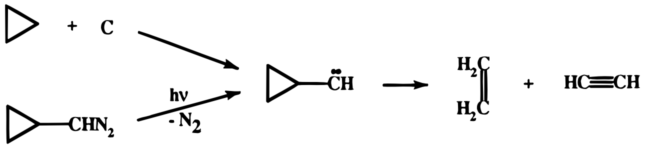
The two pathways for the fragmentation of vinylphosphirane (**5**) that lead to the formation of vinylphopshinidene (**1**), elimination of ethylene from **10**, and elimination of ethylene from **5** have nearly identical barrier heights at the MNDO level. With limited configuration interaction, the transition states lie even closer together. Hence these semiempirical studies do not permit a choice to be made between extrusion of ethylene from **5** and extrusion from **10** as the preferred pathway for the formation of vinylphosphinidene (**1**).

On the basis of the semiempirical results it even appeared that the intermediacy of vinylphosphinidene in the formation of phosphapropyne (**2**) from the equilibrating mixture of **5**, **7**, **8**, and **10**, could be questioned! Extrusion of ethylene from vinylphosphirane (**5**) to yield vinylphosphinidene (**1**) and hydrogen migration to form methyl(phosphiranyl)methylene (**11**) have equal barriers at the single-determinant RHF level, but limited configuration interaction at the geometries of the optimized transition states for both these processes lowers the energy barrier for vinylphosphinidene formation *ca.* 25 kcal/mol below that for the hydrogen shift.

Strictly speaking, it is the simultaneous loss of ethylene from **5** and the shift of a hydrogen atom that is being compared with simple loss of ethylene, since semiempirical RHF methods do not predict a local minimum at **11** on the singlet surface. No energy barrier is found for loss of ethylene from singlet methyl(phosphiranyl)methylene (**11**).[27]

Hence we conclude from consideration of all the theoretical predictions of the energies of the species shown in Scheme 6 and of the energies of the saddle points for their interconversion that, upon pyrolysis of vinylphosphirane **5** at 700 °C, isomerization occurs more rapidly than fragmentation. The formation of phosphapropyne (**2**) occurs principally by loss of ethylene from **5** or its isomer phosphacyclopentene (**10**) leading to vinylphosphinidene (**1**) that also undergoes isomerization, to **3** and **4**, more rapidly than rearrangement to **2**. As previously reported, however, the transition state for formation of phosphapropyne (**2**) is that for a direct rearrangement of **1** rather than of its isomers **3** and **4**.[2] The conclusions regarding the conversions of C_2H_3P species, on the basis of *ab initio* studies, are on firmer ground than those for C_4H_7P molecules. As previously stated, caution must be exercised in the prediction of the relative importance of pathways for the conversion of vinylphosphirane (**5**) to phosphapropyne (**2**) on the basis of semiempirical studies of transition state energies for the elementary reactions of Scheme 6.

Scheme 7



C. Experiments on the Phosphiranylcarbene Route to Phosphaalkynes. Semiempirical results reported above predict no energy barrier for loss of ethylene from methyl(1-phosphiranyl)methylene (**11**) to form phosphapropyne (**2**). While this is *not* the pathway predicted by our calculations for the formation of **2** in the pyrolysis of vinylphosphirane (**5**), the calculations suggest that the generation of phosphiranylmethylenes or their carbenoid equivalents might be a new route to phosphaalkynes.[28]

Bertrand has shown that α-phosphanyl groups stabilize carbenes,[29] but there is precedent for three-membered rings adjacent to carbene centers fragmenting to products containing double and triple bonds, respectively. Shevlin and Wolf found that ethylene and acetylene were major products from the photolysis of cyclopropyldiazomethane in the gas phase, as shown in Scheme 7.[30] This was strong evidence supporting the suggestion by MacKay and Wolfgang that cyclopropylmethylene undergoes fragmentation with loss of ethylene.[31]

Despite the indications from semiempirical studies that the phosphiranylmethylene pathways **5** → **11** → **2** does *not* contribute significantly to the decomposition of vinylphosphirane under the HLM reactions conditions, it was a clear suggestion of these calculations that the generation of phosphiranylmethylenes would lead to the formation of phosphaalkynes.

This suggestion receives strong support from the pyrolysis of 1-[diazo(trimethylsilyl)methyl]phosphirane. This system was chosen for study because of the relative ease and safety in handling a diazo compound with a trimethylsilyl group as an α-substituent and because the expected product (trimethylsilyl)phosphaacetylene is a known compound, reported by Appel and Westerhaus.[32] The new reaction sequence leading to (trimethylsilyl)phosphaacetylene as well as the authentic synthesis is shown in Scheme 8.

1-[Diazo(trimethylsilyl)methyl]phosphirane was synthesized by reaction of α-lithiodiazo(trimethylsilyl)methane and 1-cyanophosphirane. The diazo compound is sufficiently stable to survive gas chromatography. It was characterized by its ^{31}P, ^{1}H, and ^{13}C NMR spectra and its mass spectrum, including an exact mass determination.

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[27] A low-level *ab initio* study on phosphiranylmethylene *cyclo*-$[(CH_2)_2P]CH$: suggested at most a small barrier for loss of ethylene.

[28] For previous syntheses of phosphorus−carbon triple bonds see: Regitz, M. *Chem. Rev.* **1990**, *90*, 191. Regitz, M. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990; p 58 ff.

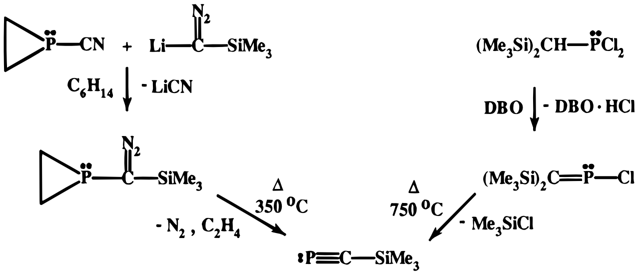
[29] Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621 and earlier references.

[30] Shevlin, P. B.; Wolf, A. P. *J. Am. Chem. Soc.* **1966**, *88*, 4735.

[31] MacKay, C.; Wolfgang, R. *J. Am. Chem. Soc.* **1961**, *83*, 2399.

[32] Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159.

Scheme 8



Vacuum flow pyrolysis of 1-[diazo((trimethylsilyl)methyl)]phosphirane led to the formation of (trimethylsilyl)phosphaacetylene in 59% yield, identified by comparison of its ^{31}P and ^{13}C NMR spectra and its mass spectrum with those of authentic material, prepared by flow pyrolysis of [bis(trimethylsilyl)methyl]dichlorophosphine.[32] The formation of phosphaalkynes from loss of ethylene and nitrogen is likely to be a general reaction of 1-(diazomethyl)phosphiranes. As a new route to phosphaalkynes it will be limited only by the accessibility of the 1-(diazomethyl)phosphiranes. Future experiments will address the mechanism of the fragmentation. While elimination of ethylene is predicted by the calculations reported above to occur with a negligible energy barrier following initial loss of nitrogen to form a carbene intermediate, the removal of ethylene may be concerted with nitrogen loss.

Conclusions

Ab initio methods predict that the stepwise rearrangement of vinylphosphinidene (**1**) to phosphapropyne (**2**) via 2*H*-phosphirene (**4**) and 2-phosphapropenylidene (**6**) has only an 8 kcal/mol higher barrier than the direct rearrangement of **1** to **2**. Previous examination of the rearrangement of **1** to **2** had predicted that direct rearrangement of **1** to **2** would deplete a mixture of **1**, 1-phosphaaleene (**3**), and **4**, whose rapid interconversion under flow-pyrolysis conditions was predicted. The *ab initio* results predict only a minor role for the vinylidene intermediate **6** in the rearrangements of vinylphosphinidene (**1**) in marked contrast to the importance attributed to vinylidene intermediates in the rearrangements of vinylmethylene, vinylsilylene, and vinylnitrene.

Semiempirical studies on portions of the C_4H_7P potential surface are in agreement with the suggestion[1] that formation of phosphapropyne (**2**) from pyrolysis of vinylphosphirane (**5**) occurs via loss of ethylene and the rearrangement of the resulting vinylphosphinidene (**1**). The semiempirical results do not permit a choice between direct formation of **1** by loss of ethylene from **5** and stepwise formation of **1** by extrusion of ethylene from 1-phosphacyclopentene (**10**) formed by ring expansion of **5**. The direct and indirect formation of **1** from **5** were predicted to occur via transition states of nearly equal energy as found at the MNDO semiempirical level.

An experimental search for a new pathway to phosphaalkynes was stimulated by a pathway predicted by semiempirical studies *not* to contribute significantly to the formation of **2** from **5**. A 1,2-shift within the vinyl group of vinylphosphirane (**5**) to generate a phosphiranylcarbene (**11**) followed (or accompanied) by loss of ethylene was predicted to have a higher energy barrier than loss of ethylene from **5** followed by hydrogen migration in **1**. Loss of ethylene from phosphiranylcarbene (**11**), once formed, however, was predicted to occur without a barrier. This suggested that decomposition of a diazomethylphosphirane to N_2, ethylene, and a phosphaalkyne would occur readily. 1-[Diazo(trimethylsilyl)methyl]phosphirane was synthesized and subjected to flow pyrolysis at 300 and 350 °C. The known phosphaalkyne (trimethylsilyl)phosphaacetylene was formed in 59% yield at 350 °C, and it is suggested that pyrolysis of 1-(diazomethyl)phosphiranes may provide a rather general synthesis of phosphaalkynes.

Experimental Section

General Data. All preparative reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen employing standard Schlenk techniques. Photolyses were carried out in a Rayonet RS photochemical reactor equipped with low-pressure mercury lamps emitting 254-nm radiation. All solvents were dried and distilled just prior to use.

^{31}P NMR spectra were recorded at 121 MHz on a Varian XL-300 FT spectrometer or at 81 MHz on a Brucker 200 MHz instrument employing H_3PO_4 as external standard. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Varian Gemini-300 FT spectrometers with the NMR solvent as internal standard. Combined gas chromatography−infrared spectroscopy−mass spectrometry was performed on a Hewlett-Packard GC/IR/MS system consisting of a Model 5890 Series II gas chromatograph fitted with a Quadrex 25-m × 0.32-mm capillary column coated with 0.5-μm polymethyl(5% phenyl)silicone bonded phase, connected to a Model 5971 Mass Selective detector (quadrupole mass filter, mass spectra recorded above *m*/*e* 40 or 50, ionization voltage 70 eV, via a 5965A FT infrared detector). High-resolution mass spectra were recorded on a VG-ZAB-SE double-focusing mass spectrometer. Mass spectra were calibrated against perfluoroalkane internal standards. Analytical gas chromatography was carried out on a gas chromatograph identical with the unit in the GC−IR−MS system and employing an identical column but fitted with a flame ionization detector.

Recorded yields are based on unrecovered starting materials and were determined by integration of ^{31}P NMR spectra, employing Ph_3P or $(n\text{-}Bu)_3P$ internal standards.

Gas-Phase Flow Pyrolyses. The pyrolyses were carried out in two different systems. The apparatus at the École Polytechnique consisted of an inlet flask connected via a stopcock to a hot zone consisting of a horizontal 40 cm × 5 mm i.d. quartz tube passing through a tube furnace. Downstream from the hot zone was a cone-shaped liquid-N_2 coldfinger that could be isolated by stopcocks from the pyrolysis tube, the vacuum manifold, and a collection flask mounted below the cold finger. Pyrolysis temperatures were measured by a thermocouple within the tube furnace, and the vacuum, typically 10^{-3} Torr, was monitored by a thermistor gauge in the manifold downstream from the cold finger. With this system evaporation of starting material was promoted by gentle heating and pyrolyses required ca. 3 h for completion. Pyrolysate collected on the cold finger was transferred to the collection flask by evaporation under vacuum after isolating the trap by allowing the cold-finger to warm to room temperature and cooling the collection flask with liquid N_2.

The pyrolysis flow system used at Washington University consisted of a vertical 5 mm i.d. flow tube with a 10 cm quartz hot zone throttled downstream by a 1 mm hole drilled in a brass disk. The brass disk was mounted with high-temperature silicone rubber O-rings between a flange on the quartz pyrolysis tube and an O-ring joint on the Pyrex portion of the flow-system that led to a removable U-trap equipped with stopcocks with which it could be isolated from the flow system and the vacuum manifold to which it was attached. The quartz pyrolysis tube was wrapped with a layer of fiberglass ribbon around which was wound the heating element, ca. 2 m of 30 gauge (0.0100 in. diameter) nichrome wire. A thick layer of fiberglass ribbon was wrapped around the heating element. For monitoring of the pyrolysis temperature, a thermocouple was positioned between the inner layer of fiberglass ribbon and the quartz tube. Pressure within the flow system, typically below 10^{-3} Torr during pyrolyses, was measured with a thermistor or ion gauge mounted on the manifold downstream from the U-trap. The hot zone was conditioned by passing hexamethyldisilazane through it at 500 °C.

Materials. n-Butyllithium was purchased from Jannsen or Aldrich and used as received after titration.

(Trimethylsilyl)diazomethane was synthesized by the method of Shioiri, Aoyama, and Mori.[33]

1-Cyanophosphirane was synthesized by the method of Haber, LeFloch, and Mathey.[34]

1-[Diazo(trimethylsilyl)methyl]phosphirane. In a typical synthesis, 1.4 mL (2.0 mmol) of n-BuLi (1.4 M in hexane) was added by syringe to a mixture of 2.05 mL (2.05 mmol) of (trimethylsilyl)diazomethane (1.0 M in hexane, determined by integration of its ^{1}H NMR spectrum vs Ph_3CH internal standard) and 10 mL of THF in a 50-mL Schlenk flask equipped with a magnetic stirring bar. The solution had been cooled to −78 °C in a dry ice−acetone bath and purged for 15 min before the n-BuLi was added. The resulting mixture was stirred for 1 h at −78 °C and then transferred rapidly via a cannula to a solution of 0.170 g (2.0 mmol) of 1-cyanophosphirane in 20 mL of THF (0.2 M, concentration determined by integration of ^{31}P NMR spectrum vs Ph_3P internal standard) contained in a 100-mL Schlenk flask equipped with a magnetic stirrer and frozen at 77 K in a liquid-nitrogen bath. The reaction mixture was warmed to −78 °C by transferring the flask to a dry ice−acetone bath and then stirred for 1 h. The resulting yellow solution was warmed to −10 °C by transferring the flask to a water ice−acetone bath. The volume of the stirred reaction mixture was reduced by vacuum evaporation over 1 h to less than half its original volume. The mixture was then rapidly filtered through a fine frit and distilled trap-to-trap on a vacuum line at *ca.* 10^{-2} Torr. The distillate was a solution of 0.99 mmol of 1-[diazo(trimethylsilyl)methyl]phosphirane in 15 mL of THF; yield 50% as determined by integration of the ^{31}P NMR spectrum *vs* a Ph_3P internal standard. Impurities were estimated to be less than 5% by ^{1}H and ^{31}P NMR: ^{31}P NMR (C_6D_6) δ −237 (t, $^2J_{H-P} = 20.4$ Hz); ^{1}H NMR (C_6D_6) δ 0.06 (s, 9 H, SiMe), 0.65−0.77 (bdt, 2 H, $^2J_{P-H} = 20.5$ Hz, $^2J_{H-H} = 7.9$ Hz, C*H*H′ *anti* to $C(N_2)SiMe_3$), 0.99−1.04 (bt, 2 H, $^2J_{H-H} = 7.8$ Hz, CH*H*′ *syn* to $C(N_2)SiMe_3$); ^{13}C NMR (C_6D_6) δ −1.36 (d, $^3J_{P-C} = 2.7$ Hz, SiMe), 1.77 (d, $^1J_{P-C} = 23.1$ Hz, CN_2), 8.20 (d, $^1J_{P-C} = 44.3$ Hz, CH_2); IR (gas) (cm^{-1}) 2965 (m, CH), 2043 (s, CN_2), 1411 (w), 1260 (m), 1258 (m), 922 (s), 844 (s); MS (EI) *m/e* (relative intensity) 172 (M^+, 10), 144 (1), 129 (3), 116 (14), 101 (100), 73 (38), 71 (10), 43 (22); exact mass determination for $C_6H_{13}N_2PSi$ calcd 172.0586, obs 172.0594.

[Bis(trimethylsilyl)methyl]dichlorophosphine was synthesized by the method of Niecke *et al.*[35]

1-Chloro-2,2-bis(trimethylsilyl)-1-phosphaethylene was synthesized by the following adaptation of the method of Appel and Westerhaus:[32] 10.8 g (41.3 mmol) of [bis(trimethylsilyl)methyl]dichlorophosphine, 10.0 g (89.1 mmol) of DABCO, and 150 mL of diethyl ether were placed in a 250-mL Schlenk flask equipped with a magnetic stirrer. The mixture was stirred overnight, and the DABCO hydrochloride was removed by filtration, with care to exclude moisture. Solvent was evaporated from the resulting orange solution under vacuum and the remaining DABCO separated by sublimation at 40 Torr. A small residue of DABCO remained throughout all subsequent manipulations. Distillation at a pressure below 5×10^{-3} Torr in a short-path (<1 cm) evaporative still yielded 1 g (10%) of an oil: ^{31}P{^{1}H} NMR (C_6D_6) δ 345 (lit.[32] 343); ^{1}H NMR (C_6D_6) δ 0.11 (d, 9H, $J_{P-H} = 2.9$ H, $SiMe_3$ *trans* to Cl), 0.30 (s, 9H, $SiMe_3$ *cis* to Cl); ^{13}C{^{1}H} NMR (C_6D_6) δ 1.5 (d, $J_{P-C} = 15.1$ Hz, $SiMe_3$ *trans* to Cl), 2.1 (d, $J_{P-C} = 3.5$ Hz, $SiMe_3$ *cis* to Cl), 194.5 (d, $J_{P-C} = 93.8$ Hz, C═P); IR (gas) (cm^{-1}) 2963 (s), 2907 (m), 1408 (w), 1259 (s), 1096 (s, C═P), 855 (vs), 770 (w); MS (EI) *m/e* (relative intensity) 226 (M^+, 1), 224 (M^+, 2), 211 (8), 209 (20), 116 (19), 101 (52), 73 (100), 45 (13), 43 (8).

(Trimethylsilyl)phosphaacetylene was synthesized by the method of Appel and Westerhaus.[32] A solution of 0.8 g (3.6 mmol) of 1-chloro-2,2-bis(trimethylsilyl)-1-phosphaethylene in 1 g of C_6D_6 was evaporated into the 700−750 °C hot zone of the Washington University pyrolysis apparatus. The ^{31}P NMR spectrum of the product mixture indicated a 6% yield of (trimethylsilyl)phosphaacetylene. The coproduct Me_3SiCl was the only other product detected. Identification of (trimethylsilyl)phosphaacetylene was via comparison of the ^{31}P and ^{13}C NMR spectra with the literature values: ^{31}{^{1}H} NMR (C_6D_6) δ 99 (lit. δ 96,[32] 97.4,[36] 96.8[37]); ^{13}C{^{1}H} NMR (C_6D_6) δ 0.1 (SiMe), 201.3 (d, $J_{P-C} = 14.0$ Hz, C≡P) (lit. δ 201.4, $J_{P-C} = 13.9$ Hz,[32] 201.4, $J_{P-C} = 14.8$ Hz[34]); MS (EI) *m/e* (relative intensity) 116 (M^+, 25), 102 (8), 101 (100), 85 (7), 73 (10), 71 (10), 43 (14).

Gas-Phase Flow Pyrolysis of 1-[Diazo(trimethylsilyl)methyl]phosphirane. In the pyrolyses at the École Polytechnique, a temperature of 300 °C was employed, and (trimethylsilyl)phosphaacetylene, identified by its ^{31}P δ 97.5, was the only product detected by ^{31}P NMR spectroscopy. In a typical Washington University experiment, a solution of 37 mg (0.215 mmol, determined by integration of the ^{31}P NMR spectrum employing Ph_3P internal standard) of 1-[diazo(trimethylsilyl)methyl]phosphirane in *ca.* 0.5 g of C_6D_6 was evaporated with gentle warming from an inlet tube attached to the flow pyrolysis apparatus whose hot zone was maintained at 350 °C. The volatile pyrolysate was found to be (trimethylsilyl)phosphaacetylene (purity ≥90% by GC), 15 mg (0.127 mmol, determined by integration of the ^{31}P NMR spectrum employing Ph_3P internal standard), identified by comparison of its spectra with those of authentic material given above: ^{31}P{^{1}H} NMR (C_6D_6) δ 95.7 (lit. δ 96,[32] 97.4,[36] 96.8[37]); ^{13}C{^{1}H} NMR (C_6D_6) δ 0 (d, $J_{P-C} = 3.2$ Hz, SiMe), 201.3 d, $J_{P-C} = 14.0$ Hz, C≡P) (lit. δ 201.4, $J_{P-C} = 13.9$ Hz,[31] 201.4, $J_{P-C} = 14.8$ Hz[37]); IR (gas) (cm^{-1}) 2920 (m), 2903 (w), 1421 (m, C≡P), 1253 (m), 849 (s), 760 (m); MS (EI) *m/e* (relative intensity) 116 (M^+, 25), 101 (100), 85 (7), 73 (7), 71 (9), 43 (10).

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