A Theoretical Study of the Dimerization of Phosphaethyne (HC≡P): Head-To-Tail versus Head-To-Head Cycloaddition?

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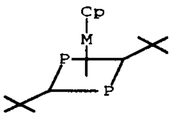
Ab initio molecular orbital calculations (at the MP4/6-31G(d,p) level using MP2/6-31G(d,p) geometries and ZPE corrections) on the cycloaddition of the model HC≡P + HC≡P system suggest that the head-to-head dimerization of phosphaalkyne giving 1,4-diphosphacyclobutadiene is inherently favored over the head-to-tail approach yielding 1,3-diphosphacyclobutadiene (by 37 kJ/mol); thus the experimental observation of the latter can be understood by a steric effect of the bulky substituents employed or a catalytic effect of metal fragments. Both dimers undergo, however, further reactions giving the most stable structure, diphosphabicyclo[1.1.0]butane. The latter molecule, also trapped by metal fragments, is likely to be an intermediate of the thermal tetramerization of HCP, leading to tetraphosphacubane.

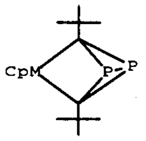
1. Introduction

During the last decade, phosphaalkyne compounds (RC≡P) have emerged as a new functional group in heteroatom chemistry. Their polarity, unsaturation, and high reactivity make them the convenient building blocks in organic and heterocyclic synthesis and versatile ligands for complexation to transition metals.[1] Of the typical reactions of phosphaalkynes, the cyclooligomerization is of particular intrest.

Phosphaalkynes undergo dimerization yielding at least three types of cyclic dimers.[1] In the coordination sphere of cobalt or rhodium, a classical head-to-tail [2 + 2] cycloaddition of two RCP molecules can be achieved to give a λ^3-1,3-diphosphacyclobutadiene (referred to hereafter as 1,3-DPCB) ligand (I, M = Co, Rh; R = *tert*-butyl). A diphosphabicyclo[1.1.0]butane ([1.1.0]DPBB) ligand is in contrast formed when the metallic center is zirconium or hafnium (II, M = Zr, Hf). A head-to-head approach giving rise to a 1,4-diphosphacyclobutadiene (1,4-DPCB) was not observed, only the species III was formed as a secondary product in the case of rhodium.



I



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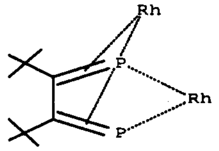
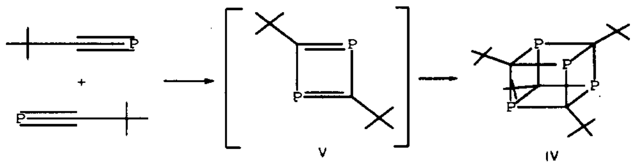
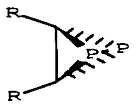


III

Phosphaalkynes can also undergo oligomerization without metal catalysis. Regitz and co-workers[2] reported a thermal cyclotetramerization upon heating of *tert*-butylphosphaethyne. The observed tetramer is quite stable at room temperature and a crystal structure analysis revealed that it has a slightly distorted cubic structure IV in which all the C–P bond distances are identical. These authors[2] proposed the initial formation of the 1,3-DPCB V by a formal head-to-tail dimerization of phosphaethyne; the dimer V undergoes further inter- and intramolecular cycloadditions to finally yield tetraphosphacubane IV. The interpretation appears reasonable but intriguing, in view of the various structural possibilities mentioned above for the cyclic dimer. More recently, Regitz and co-workers[3] found that derivatives of tetraphosphacubane IV can also be synthesized from zirconium complexes II. This implies that diphosphabicyclo[1.1.0]butane VI could actually be involved as dimeric intermediate.





VI

In order to obtain some quantitative information on the dimerization reaction of phosphaalkynes and as a necessary preliminary for a further study of the formation of tetraphosphacubane IV, we have carried out ab initio MO calculations on the simplest model HC≡P + HC≡P reaction. We have explored extensivily the portions of the $C_2H_2P_2$ potential energy surface corresponding to the dimerization including both head-to-tail and head-to-head approaches. The unimolecular rearrangements connecting both 1,3- and 1,4-dimers to the [1.1.0]DPBB have also been investigated. It should be stressed that our results are only relevant to the thermal reaction. The effect of transition metals on structures and reactivities was not considered.

2. Details of Calculations

Geometries of the stationary points on the $C_2H_2P_2$ potential energy surface were initially optimized and characterized by harmonic vibrational wavenumbers at the Hartree–Fock (HF) level with the dp-polarization 6-31G** basis set. The geometries were then reoptimized at the second order Møller–Plesset perturbation theory

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(1) For a review, see: Regitz, M.; Binger, P. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. Eds.; Thieme: Sttugart, 1990; p 58–93.

(2) Wettling, T.; Schneider, J.; Wagner, O.; Kreiter C. G.; Regitz, M. *Angew. Chem. Int. Ed. Engl.* 1989, *28*, 1013.

(3) Wettling, T.; Geissler, B.; Schneider, R.; Barth, S.; Binger, P.; Regitz, M. *Angew, Chem. Int. Ed. Engl.* 1992, *31*, 758.

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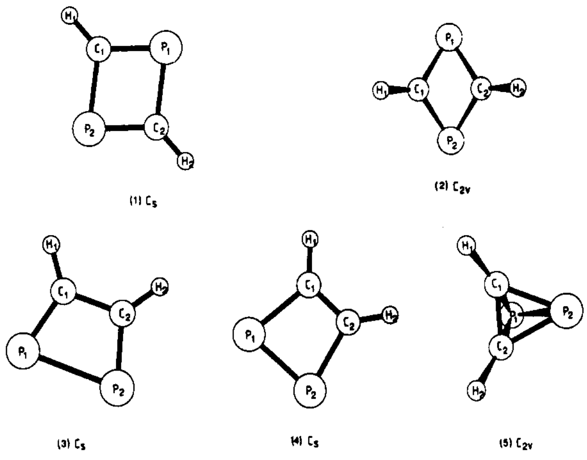


Figure 1. Equilibrium structures considered (1–5).

(MP2)[4] level with the same basis set using full sets of orbitals. Improved relative energies of stationary points were subsequently obtained employing full fourth-order perturbation theory (MP4SDTQ) calculations with the 6-31G** basis set and MP2/6-31G** geometries and corrected for zero-point energies (ZPE's). The core orbitals are frozen in MP4 calculations. All calculations were performed using a local version of the Gaussian 92 program.[5] Throughout this paper, bond lengths are given in angströms, bond angles in degrees, total energies in hartree, and relative energies in kJ/mol. Unless otherwise noted, the MP4/6-31G** + ZPE relative energies are the values referred to in the text.

3. Results and Discussion

Geometrical parameters optimized at the MP2/6-31G** level for the equilibrium structures 1–5 shown in Figure 1 are recorded in Table I while parameters for the transition structures 6–12 shown in Figure 2 are listed in Table II. Total and relative energies of these structures are summarized in Table III.

Table I. Geometrical Parameters of the Stationary Points Relevant to the Dimerization Process[a] at the MP2/6-31G Level**

parameter[b]	1	2	3	4	5
C_1P_1	1.683	1.767	1.702	1.901	1.833
C_1P_2	1.898	1.767	2.545	2.530	1.833
C_2P_1	1.898	1.767	2.545	2.530	1.833
C_2P_2	1.683	1.767	1.702	1.901	1.833
C_1H_1	1.080	1.082	1.085	1.083	1.072
C_2H_2	1.080	1.082	1.085	1.083	1.072
C_1C_2	2.341	1.811	1.450	1.339	1.450
P_1P_2	2.718	2.955	2.454	2.082	2.241
$H_1C_1P_1$	130.4	120.3	127.3	129.3	139.1
$H_2C_2P_2$	130.4	120.3	127.3	129.3	139.1
$C_1P_1C_2$	81.4	61.6			46.6
$P_1C_1P_2$	98.6	113.4			75.4
$P_1P_2C_2$		33.3	73.0	78.7	52.3
$C_1C_2P_2$		59.2	107.0	101.3	66.7
$H_1C_1P_1C_2$	180.0	128.0			−136.2
$H_2C_2P_2P_1$		−152.7	180.0	180.0	153.2
$P_1C_1P_2C_2$	0.0	24.8			−70.6
$P_1P_2C_2C_1$		24.8	0.0	0.0	−70.6

[a] For HCP: CP = 1.515 Å, HC = 1.063 Å; P_2: PP = 1.932 Å and C_2H_2: CC = 1.217 Å, HC = 1.062 Å. [b] For atom numbering, see Figure 1.

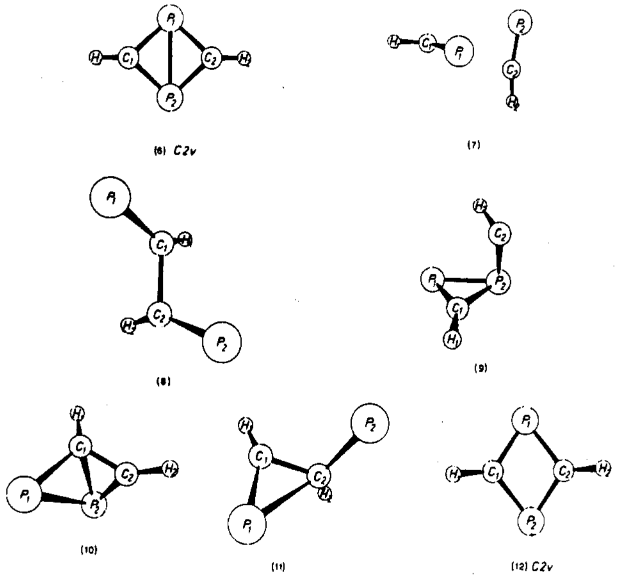
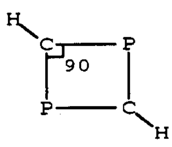
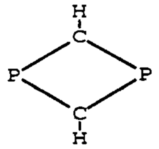


Figure 2. Transition structures considered (6–12).

Stable dimers of phosphaethyne can exist in a variety of cyclic and open forms. We have considered in the present work only five forms relevant to the dimerization process. These include both 1,3-diphosphacyclobutadienes 1 and 2 (1,3-DPCB), both 1,4-diphosphacyclobutadienes 3 and 4 (1,4-DPCB) and the diphosphabicyclo[1.1.0]butane 5 ([1.1.0]DPBB). The following energy sequence of the minima has been found: 5 < (HCCH + P_2) < 4 < 3 < 2(HCP) < 1 < 2 (Table III). It is thus clear that the bicyclic 5 is the most stable dimer, followed by the 1,4-dimers while the 1,3-DPCB's are the least stable dimers. The 1,3-DPCB 1 is calculated to have a planar parallelogram structure with alternate long and short C–P distances. The long distance is about 0.22 Å longer than the short one. The latter (1.683 Å) is similar to that of a typical C=P double bond (1.67 Å in $H_2C{=}PH$). Both crossed CC and PP distances are rather long (>2.3 Å). The structure 1 can be seen as a distortion from a rectangular form by a small opening of the PCP bond angle (8°). Separate calculations show that the square-plane form **VII** is not a stationary point at all on the potential energy surface. The rhombic structure **VIII**, which is planar, with four identical C–P distances, is a stationary point but it possesses two imaginary wavenumbers. The smaller value of the two corresponds to an out-of-plane distorsion mode leading to the structure 6 which is identified as the transition structure for a degenerate tautomerization of 1,3-DPCB 1. The corresponding energy barrier of the process 1 → 6 → 1 amounts to 54 kJ/mol. The X-ray crystal structures of substituted 1,3-DPCB's complexed to metals have been determined by different groups.[1] Irrespective of the nature of the metal (I, M = Co, Rh, Mo, Fe, Ni), the 1,3-DPCB ligand



VII



VIII

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(4) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(5) Gaussian 92, Revision B. Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W., Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc.: Pittsburgh, 1992.

Table II. Geometrical Parameters of the Transition Structures Relevant to the Dimerization Process at the MP2/6-31G Level**

parameter[a]	6	7	8	9	10	11	12
C_1P_1	1.768	1.596	1.608	1.648	1.710	1.706	1.722
C_1P_2	1.768	2.044	3.016	1.964	2.532	1.877	2.052
C_2P_1	1.768	3.016	3.017	3.292	2.026	1.877	2.664
C_2P_2	1.768	1.674	1.608	1.618	1.812	1.706	1.629
C_1H_1	1.081	1.073	1.077	1.081	1.081	1.091	1.084
C_2H_2	1.081	1.099	1.077	1.075	1.084	1.091	1.075
C_1C_2	2.481	2.855	1.868	2.031	1.412	2.023	1.541
P_1P_2	2.283	2.545	4.198	2.651	2.387	2.923	3.337
$H_1C_1P_1$	125.6	155.1	140.5	137.9	141.0	126.2	125.0
$H_2C_2P_2$	125.6	111.2	140.6	152.8	130.9	126.2	147.9
$C_1P_1C_2$	89.2	68.7	32.3	29.7	43.4	68.6	33.1
$P_1C_1P_2$	80.5	87.8	127.8	94.0	65.2	109.3	124.1
$P_1P_2C_2$	49.8	88.8	34.7	98.0	55.7	37.3	52.0
$C_1C_2P_2$	45.4	44.9	120.2	64.0	102.7	59.7	80.6
$H_1C_1P_1C_2$	160.8	143.6	173.3	174.3	-167.4	140.6	144.1
$H_2C_2P_2C_1$	160.8	-160.1	173.2	-38.1	174.4	140.6	170.5
$P_1C_1P_2C_2$	-33.5	75.5	83.7	138.1	-102.0	17.0	88.4
$P_1P_2C_2C_1$	-33.5	37.4	32.0	24.7	-50.3	15.4	32.8

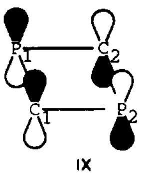
[a] For atom numbering, see Figure 2.

Table III. Total, Zero-Point, and Relative Energies for the Structures Considered at Different Levels of Theory

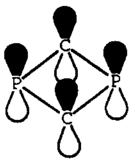
	total energies[b]			relative energies		
structure[a]	MP2	MP4	ZPE[c]	ΔMP2	ΔMP4	ΔMP4 + ΔZPE[d]
2(HCP)	-758.706578	-758.766888	71.9	0.0	0.0	0.0
1	-758.704869	-758.767936	82.6	4.5	-2.7	8.1
2	-758.688038	-758.746829	79.9	48.6	52.6	60.6
3	-758.717405	-758.780669	84.6	-28.4	-36.2	-23.5
4	-758.720062	-758.782913	84.9	-35.4	-42.0	-29.0
5	-758.741772	-758.794135	83.6	-92.3	-71.5	-59.8
$H_2C_2 + P_2$	-758.723861	-758.782357	74.2	-54.4	-40.6	-38.3
6, TS1: 1 → 1	-758.687478	-758.745168	76.7	50.1	57.0	61.8
7, TS2: 2HCP → 1	-758.608294	-758.673291	75.8	257.9	245.6	249.5
8, TS3: 2HCP → 4	-758.667829	-758.729571	74.1	101.7	97.9	100.1
9, TS4: 1 → 5	-758.623530	-758.685767	72.3	217.9	212.9	213.3
10, TS5: 3 → 5	-758.655530	-758.714361	78.8	133.9	137.8	144.7
11, TS6: 4 → 2	-758.669795	-758.733554	77.3	96.5	87.5	92.9
12, TS7: 2 → 1	-758.641556	-758.702152	79.3	170.6	169.9	177.3

[a] Based on MP2/6-31G** geometries. [b] Core orbitals are frozen. Using the 6-31G** basis set. [c] Scaled by a factor 0.9 to correct the systematic overestimation at the HF/6-31G** level. [d] Including MP4 relative energies and ZPE's.

exhibits a rhombic structure (**VIII**) with a C–P bond distance of about 1.77–1.80 Å. There is thus an interesting difference in the structure of 1,3-DPCB in the free and complexed states. The metal fragment apparently induces a structural shift of the four-membered ring to higher symmetry. Similar to the situation in metallocenes, the 1,3-DPCB ring should behave as an electron donor ligand in the complexes. The HOMO **X** (b_{3g} orbital) of the rhombic structure **VIII** is expected to give rise to a stronger interaction with the LUMO of a metal fragment than the HOMO **IX** of the parallelogram **1** (b_{1u} orbital).



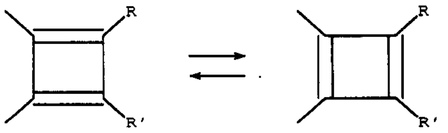
IX



X

We have also located another 1,3-DPCB (**2**) which has a distorted rhombic form with a long P–P distance (2.955 Å) and a shorter C–C distance (1.855 Å). The difference between both rhombic structures **2** and **VIII** is that **VIII** is planar while **2** is not. As mentioned above, **1** and **2** are the least stable cyclic forms lying even higher in energy than two separated HCP monomers. Because the numbers of C–P bonds is not changed during the reaction 2(HCP) → **1**, the corresponding reaction energy of 8 kJ/mol is a measure of the ring strain in **1**. Of the two 1,3-DPCB species, **1** is the more stable, lying 53 kJ/mol below **2**. In addition, we have found that both isomers are connected by the transition structure **12** shown in Figure 2. The associated barrier height for the **2** → **12** → **1** process amounts to 116 kJ/mol relative to **2**.

The 1,4-DPCB exists in two valence isomers **3** and **4** at the levels of theory employed. Both forms are local minima and can be distinguished by their dissociation limits; the former dissociates giving two HCP monomers while the latter dissociates giving the $C_2H_2 + P_2$ fragments. It is well established that cyclobutadienes undergo relatively facile valence isomerization with a free energy of activation of about 24 kJ/mol.[6] It is therefore possible that two distinct structures **3** and **4** for the diphospha derivative exist. Nevertheless, we have not been able to locate, in spite of extensive attempts, a transition structure connecting **3** and **4**. This failure may be due to the fact that we have only employed single-reference wavefunctions. A



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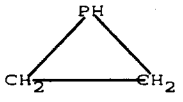
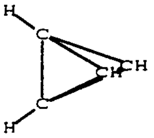
(6) Maier, G.; Wolf, R.; Kalinowski, H. O. *Angew. Chem. Int. Ed. Engl.* 1992, *31*, 738.

multiconfigurational treatment is apparently needed to determine whether or not both valence isomers **3** and **4** really exist. Our calculations indicate that **4** lies 6 kJ/mol below **3**. While **3** is about 24 kJ/mol more stable than the two separated monomers 2(HCP), **4** is found to be 9 kJ/mol less stable than the HC≡CH + P_2 fragments (Table III). It has been observed that a four-membered ring is often better stabilized by one P–P, one C–C, and two C–P bonds than by four identical C–P bonds.[7] In fact, both structures **3** and **4** are calculated to be more stable than **1** and **2**. It is tempting to generalize that, in the free form without metals, a 1,4-DPCB is more stable than its 1,3-DPCB isomer.

The bicyclic structure **5** presents another type of phosphaethyne dimer having a bridge and four identical C–P bonds. As compared with the parent structures **XI** and **XII**, **5** is more compact with shorter bond lengths. The C_1–C_2 distance of 1.450 Å in **5** is markedly smaller than the corresponding values of 1.488 and 1.495 Å calculated for **XI** and **XII**, respectively, at the same level.



XI



XII

Similarly, the C–P distance of 1.833 Å in **5** is also proportionally shorter than that of 1.866 Å in phosphirane **XI**. As a result, the C_1PC_2 bond angle of **5** is similar to that of **XI** (47°).

The bridged structure **5** turns out to be the most stable dimer lying 68 and 31 kJ/mol below **1** and **4**, respectively. **5** is calculated however to lie only 22 kJ/mol below the fragments HC≡CH + P_2. We have extensively searched for but failed to locate a transition structure linking **5** to acetylene + P_2.

We turn now to the transition structures (Figure 2). The identity of each of the transition structures located has been determined by intrinsic reaction coordinate (IRC) calculations.[5] The two local minima connected by a transition structure under consideration can therefore be unambigously determined. A schematic potential energy profile for both dimerizations of HC≡P and the unimolecular rearrangements of the cyclic dimers are displayed in Figure 3. We have found that while the transition structure TS2 (**7**) connects the two HCP monomers to the 1,3-DPCB **1**, the transition structure TS3 (**8**) separates the monomers from the 1,4-DPCB **4**. The transition vectors are displayed in Figure 4. According to the nature of the cyclic products, TS2 (**7**) and TS3 (**8**) are, employing the classical terminology, formally associated with the head-to-tail and head-to-head [2 + 2] cycloadditions of two HCP molecules, respectively. The latter lie, in each TS, in two almost perpendicular planes. In TS2 (**7**), the C_1P_2 distance is the shortest intermolecular distance while in TS3 (**8**) the C_1C_2 distance has the smallest value (Table II). At all levels of theory considered, the TS3 (**8**) is calculated to lie substantially lower in energy than the TS2 (**7**) (149 kJ/mol by our best estimate, Table III and Figure 3). Thus, the head-to-head approach of two phosphaethyne molecules leading to a primary 1,4-DPCB (**4**) adduct is both kinetically and thermodynamically favored over the head-to-tail process giving a 1,3-DPCB **1**. This finding is not unprecedented however; Markovski and co-workers[7] showed that the head-to-head adducts are often observed in cycloadditions of phosphaethenes. On the contrary, this result is not quite consistent with available experimental observations in which a 1,3-DPCB is invariably formed in the sphere of a metal (see **I**). The 1,4-DPCB has only been observed as a secondary product in rare cases. This difference may be due to the following factors: (i) a catalytic effect of the metals favoring the formation of 1,3-DPCB; (ii) a steric effect of the substituent on phosphaethyne. As a matter of fact, bulky groups such as the *tert*-butyl, adamantyl, and aryl were usually used in the experimental studies.[1-3] A larger electrostatic repulsion between these groups can occur in a structure

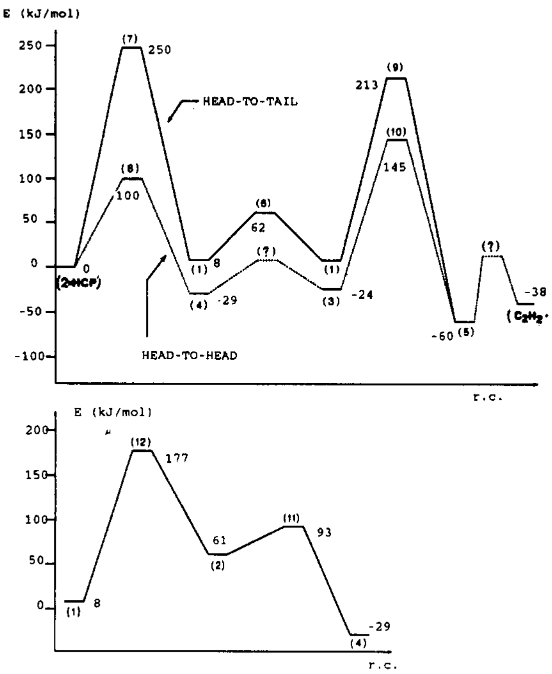


Figure 3. Schematic energy profiles showing the transformation of two HCP molecules (values at MP4/6-31G**//MP2/6-31G** + ZPE in kJ/mol).

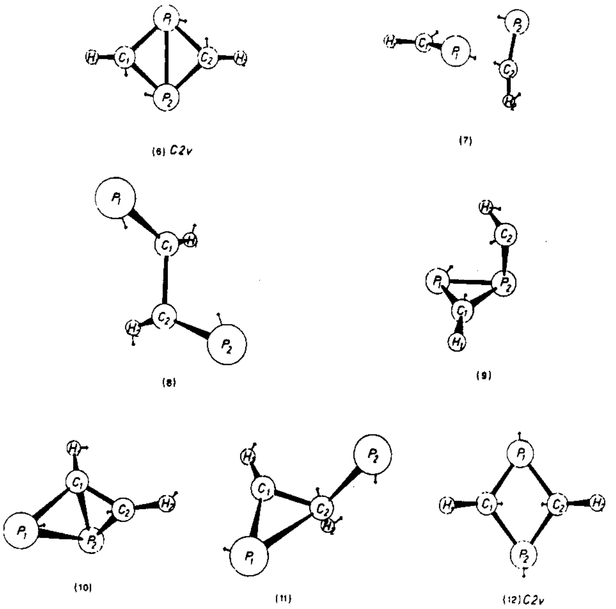


Figure 4. Transition vectors (the vectors are not scaled, they only display the orientation) of the transition structures. These correspond to the normal coordinates of the imaginary vibrational modes.

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[7] Markovski, L. N.; Romanenko, V. D. *Tetrahedron* **1989**, *45*, 6019.

of the type TS3 (**8**) than in TS2 (**7**) and that could tip the balance in favor of the latter, or (iii) a rapid rearrangement of the 1,4-DPCB to, for example, the more stable bridged structure **5** making its observation difficult.

To investigate further the latter point, we have examined the conversion between 1,3-DPCB, 1,4-DPCB, and [1.1.0]-DPBB. We have found two transition structures TS4 (**9**) and TS5 (**10**), which connect both 1,3-DPCB **1** and 1,4-DPCB **3** with the [1.1.0]butane **5**, respectively. It is worth noting that the IRC calculations at the HF/6-31G** level showed unambigously that the TS5 (**10**) links **5** and **3** rather than to the more stable 1,4-DPCB form **4**. This points out again the need for a multiconfigurational treatment for this region of the potential energy surface. The transition vectors are displayed in Figure 4. Both transition structures contain essentially a three-membered ring with one P-atom for TS4 (**9**) and two P-atoms for TS5 (**10**) (Figure 2). The TS5 (**10**) is calculated to lie, at all levels considered (Table III), lower in energy than the TS4 (**9**) (69 kJ/mol at our best estimate, Table III and Figure 3). Thus, the dimerization of HCP can give the [1.1.0]DPBB **5** in two different pathways. The rate-determining step of the process via the head-to-tail approach is the dimerization, the energy barrier for rearrangement being about 37 kJ/mol smaller. On the route via the head-to-head approach, the second step via TS5 (**10**) is determining the reaction kinetically; the second energy barrier for rearrangement is in fact about 45 kJ/mol higher than the first barrier for cycloaddition via TS3 (**8**).

On the other hand, both primary cycloadducts **1** and **4** could be connected with each other via the intermediacy of **2**. As mentioned above **1** is separated from **2** by the transition structure TS7 (**12**) with a barrier of about 169 kJ/mol. The connection of **2** with the 1,4-DPCB **4** is made through transition structure TS6 (**11**) with an energy barrier of about 32 kJ/mol. The transition vectors of those transition structures are also displayed in Figure 4. As seen in Figure 3, the TS7 (**12**) lies lower in energy than the TS4 (**9**) (about 36 kJ/mol). This implies that the primary head-to-tail cycloadduct (**1**) might be first converted to the primary head-to-head cycloadduct **4** before rearranging further to the bicyclic form **5** rather than directly converted to the latter.

In summary, the theoretical results reported in this paper point out that the energy surface associated with the cyclodimerization of phosphaethyne is quite complicated with several reaction intermediates. Nevertheless, it seems reasonable to conclude that the head-to-head approach is inherently favored over the head-to-tail approach. Both primary cycloadducts 1,3- and 1,4-diphosphacyclobutadienes are in addition connected with each other and rearrange both to the more stable bicyclic dimer. Without the presence of a metal complex, it is likely that the diphosphabicyclo[1.1.0]butane is formed as the stable specie of the dimerization step before undergoing further cyclooligomerization reactions. We would hope that this information will stimulate further experimental and theoretical work on these exciting processes.

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