The Structures and Energies of Phosphaalkyne Trimers, $(HCP)_3$

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Dedicated to Professor Otto J. Scherer on the occasion of his 65th birthday

Keywords: Ab initio calculations / Aromaticity / [4+2] Cycloaddition / NICS values / Phosphaalkyne trimers / Triphosphinine / Triphosphabenzene

$(CH)_3P_3$ structures have been investigated by ab initio (MP4SDTQ/6-31+G**//MP2(fu)/6-31G*) and DFT (B3LYP/6-311+G**) methods. The framework is the main factor determining the realtive energy of isomers; the substitution pattern is less important. The thermodynamic stability order of heteroatom-substituted benzenes > benzvalenes > Dewar benzenes > prismanes > bicyclopropenyls parallels the situation in the $(CH)_6$ hydrocarbons. The 3 HCP → 1,2,3-triphosphabenzene trimerization energy is only –84 kcal mol^{-1}; half as large as that for the 3 acetylene → benzene conversion (–164 kcal mol^{-1}). Head-to-tail additions are favored for the [4+2] cycloadditions of HCP to 1,2- and 1,3-diphosphete (to give triphospha Dewar benzenes); the computed activation barriers are low: ΔH^{*298} = 2.2 and 0.8 kcal mol^{-1}, respectively, at MP4/6-31+G**//MP2(fu)/6-31G* (2.0 and 1.5 kcal mol^{-1} at MC-QDPT2/6-31G*//CAS-SCF(6,6)/6-31G*). Mono- as well as *ortho*-, *meta*-, and *para*-diphosphabenzenes and the triphosphabenzenes are found to be as aromatic as benzene according to geometric and energetic criteria. NICS calculations (a magnetic criterion) suggest only slightly reduced aromaticity.

Introduction

Once kinetically stable phosphaalkynes became readily available,[1] their reactions were investigated intensively.[2] The first cyclooligomerization products, reported in 1989, had cage skeletons, e.g. **1** was obtained thermally by tetramerization of *t*Bu−C≡P.[3] A pentamer, **4**, resulted from reaction of *t*Bu−C≡P with iron complexes[4] or from oxidative coupling of 1,3-di- and 1,2,4-triphosphacyclopentadienes.[5] Further tetramer examples include bishomoprismanes,[6] e.g. **2**,[7] cuneanes,[2b] e.g. **3**,[2c] tetraphosphatricyclo[4.2.0.0^{2,5}]octadienes **5** and **6**,[8] and tetraphosphabarrelene **7** (Scheme 1).[9] Hexamer **8** is the largest oligomer which has been reported.[10] The dimers, diphosphatetrahedrane **TH12a**,[11] 1,2-, **DP12a**,[8] and 1,3-diphosphacyclobutadiene ("diphosphete"), **DP13a**,[3,8,11,12] (Scheme 2) were postulated as intermediates in oligomerization reactions, but could not be observed directly. However, dimers are stabilized in the coordination spheres of transition metal complexes, {e.g. [CpCo(1,2-diphosphete)],[13] $[(PMe3)_2ClRh(1,3\text{-diphosphete})]$,[14] 1,3-diphosphabicyclo[1.1.0]butanediylzirconocene[15]}. Metal fragments are involved in the few examples of RCP trimerization, e.g. the vanadium complex of 1,3,5-triphospha Dewar benzene, **9** (Scheme 3).[16] Spirotrimerization of phosphaalkyne *t*BuCP with aluminum trichloride also incorporates the "catalyst" into the product, **S135a·AlCl$_3$**, (Scheme 4).[6] $AlCl_3$ cannot be detached without further disruption; the phosphahydrocarbon fragment converts to tetramers.[6] The problem of obtaining trimers was solved with the hafnium complexes **10** and **11** [the $(t\mathrm{BuCP})_3$ ligands have unknown and Dewar benzene structures, respectively]. Tris-*tert*-butyl derivatives of 1,3,5-triphospha Dewar benzene, **D135a**, and 1,3,5-triphosphabenzene, **B135a**, can be set free from **10** and **11** (Scheme 5)[17] and a single-crystal X-ray structure was reported for **B135a**.[18] Derivatives of **B135** with various alkyl groups are now available in good yields more easily from reaction of the phosphaalkynes with $t\mathrm{BuN{=}VCl_3}$.[19] This further facilitates experimental investigations.[20]

Thorough ab inito studies on phosphaalkyne oligomers are limited to dimers.[21][22] However, preliminary results on the relative energies of dimers and some tetramers of HCP[8] as well as oligomerization energies for tri- through hexamerization for selected oligomers have been communicated.[10] All computations have been restricted to models based on $(HCP)_n$. We now report structures and relative energies for $(HC)_3P_3$ isomers. These can be derived from ethyne trimers, benzene (**B**), prismane (**P**), Dewar benzene (**D**), benzvalene (**V**), and bicyclopropenyl (**C**) (Scheme 6) by replacing three HC by isolobal P units. This includes isomers that cannot formally be separated into three HCP units. In addition, a spiro structure (**S135**) is considered as well.

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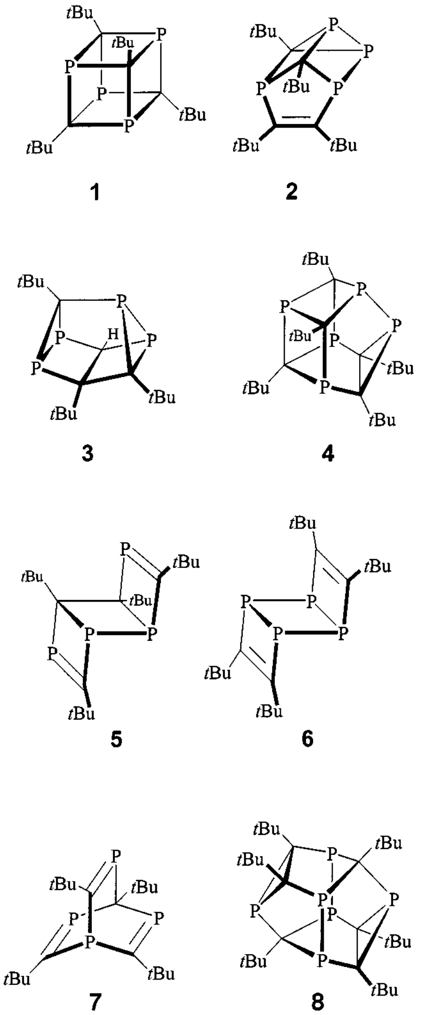
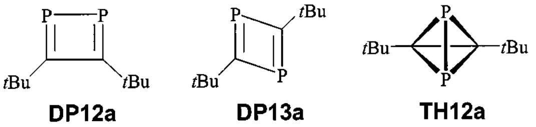
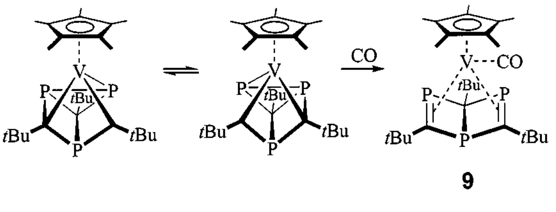


Scheme 1. Selected cyclooligomers from stable phosphaalkynes



Scheme 2. Postulated dimers of tBu−C≡P



Scheme 3. Vanadium complex of 1,3,5-triphospha Dewar benzene

Computational Details

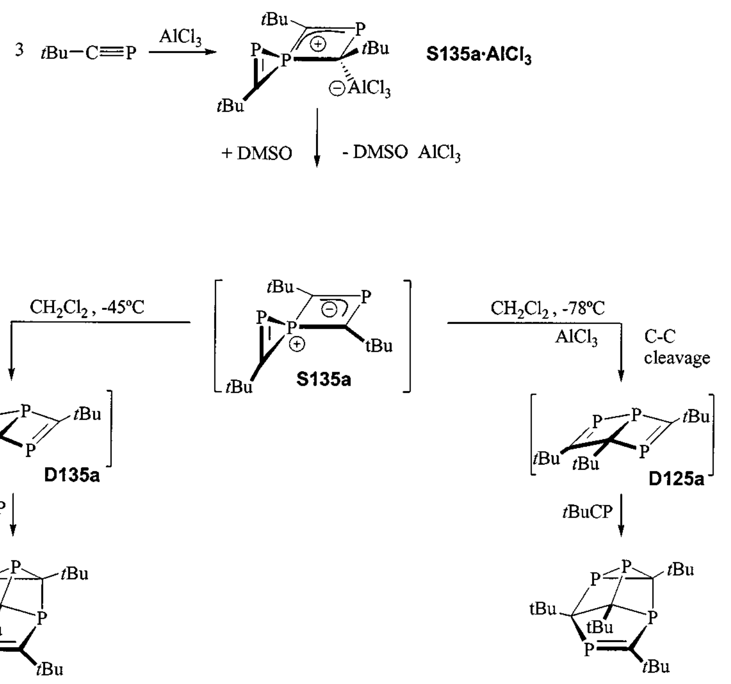
Geometries were optimized at HF/6-31G* and MP2(fu)/6-31G* levels of theory using the Gaussian 94 program.[23] Frequencies were calculated analytically at the HF/6-31G* level to determine the nature of the stationary points and to obtain zero point vibrational energies (ZPEs). ZPE corrections were scaled by a factor of 0.89.[24] For the MP2(fu)/6-31G* optimized geometries, MP4 single energy point calculations were performed with the 6-31G* as well as the 6-31+G** basis set. The latter includes diffuse functions on carbon and phosphorus and polarization functions for the hydrogen atoms as well. Relative energies at MP4(fc)/6-31+G**//MP2(fu)/6-31G* + 0.89 ZPE(HF/6-31G*), our final level, are discussed in the text, unless stated otherwise. Density functional theory single point results obtained with Becke's three parameter exchange functional (B3)[25] together with the correlation functional by Lee, Young, and Parr,[26] and the 6-311+G** basis set are reported for comparison as well. Nucleus-independent chemical shifts (NICS)[27] were calculated at the geometrical centers of the ring atoms with the GIAO-SCF/6-31+G* method employing MP2(fu)/6-31G* optimized geometries. Because of the biradicaloid character of 1,2- and 1,3-diphosphete,[21] transition structures (shown in Figures 9 and 10) for HCP addition to these dimers were also optimized with the complete active space (CAS, identical to full optimized reaction space, FORS) method.[28] The four π-orbitals of the phosphete molecule and the bonding and antibonding orbitals of one phosphaalkyne π-bond (directed towards the phosphete molecule) were selected as active orbitals, which are occupied by six electrons. GAMESS-US[29] was used for the CAS-SCF(6,6) calculations employing the 6-31G* basis set. Numerical vibrational frequency calculations confirmed the stationary points as true transition states (one imaginary frequency). Final energies were obtained from second order perturbation theory single point calculations for the CAS-SCF reference wavefunction (multiconfigurational quasidegenerate perturbation theory at second order, MCQDPT2).[30]

Computed geometries of $(HC)_3P_3$ minimum structures are shown in Figures 1−5 and relative energies are given in Table 1. Figures 9 and 10 display transition states and Table 2 lists relative energies for some addition reactions leading to HCP trimers. All reference molecules in Equations 1−8 (Scheme 8) were computed in their planar *cis* conformations.

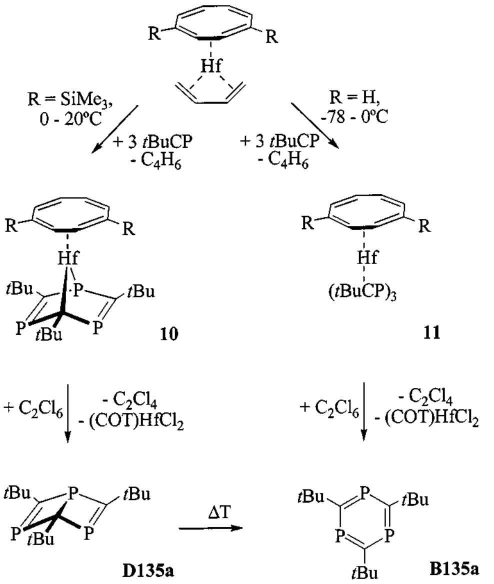
Results and Discussion

Aromaticity of Mono-, Di-, and Triphosphabenzenes

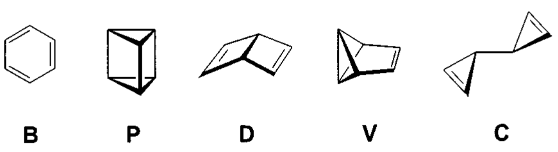
1,2,3-Triphosphabenzene, **B123**, is the $(CH)_3P_3$ global minimum. The 1,2,4 (**B124**) and 1,3,5 (**B135**) isomers are 6.7 and 8.9 kcal mol^{-1} higher in energy, respectively. The C−C, C−P, and P−P distances in **B123**, **B124**, and **B135** are ca. 1.39, 1.74, and 2.11 Å, respectively, and hence are between typical single and double bond lengths (Scheme 7). Consequently, the π-electron delocalization should be like that in benzene. From a single-crystal X-ray diffraction analysis, a C−P distance of 1.727(8) Å has been determined in 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene, **B135a**.[18] In contrast to benzene, cyclic P_6 is not a minimum in D_{6h} sym-



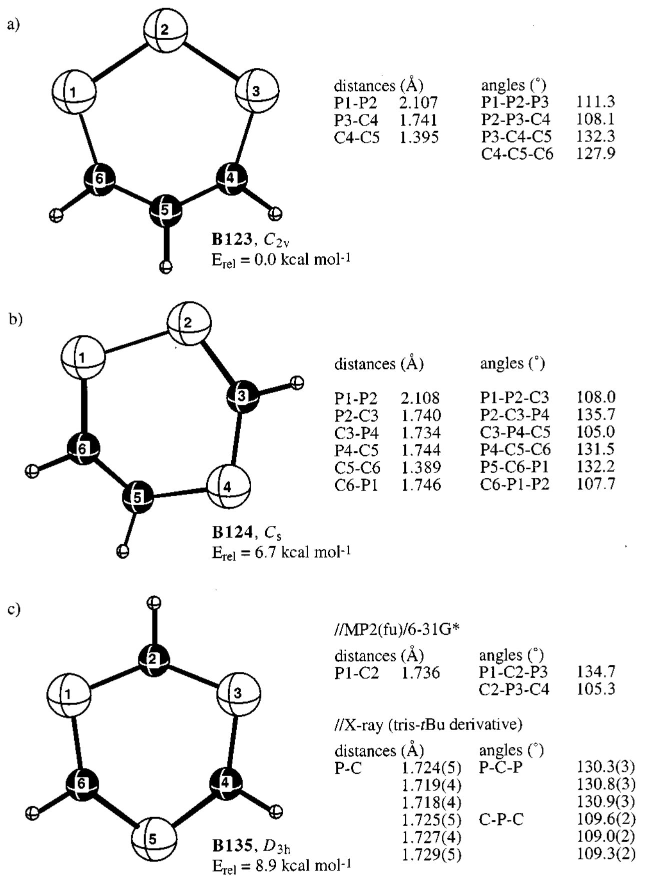
Scheme 4. Spirotrimerization of *t*Bu−C≡P



Scheme 5. Synthesis of 1,3,5-triphospha Dewar benzene, **D135a**, and 1,3,5-triphospha benzene, **B135a**



Scheme 6. Valence isomeric structures of ethyne trimers



a)

distances (Å)		angles (°)	
P1-P2	2.107	P1-P2-P3	111.3
P3-C4	1.741	P2-P3-C4	108.1
C4-C5	1.395	P3-C4-C5	132.3
		C4-C5-C6	127.9

b)

distances (Å)		angles (°)	
P1-P2	2.108	P1-P2-C3	108.0
P2-C3	1.740	P2-C3-P4	135.7
C3-P4	1.734	C3-P4-C5	105.0
P4-C5	1.744	P4-C5-C6	131.5
C5-C6	1.389	P5-C6-P1	132.2
C6-P1	1.746	C6-P1-P2	107.7

c)

//MP2(fu)/6-31G*

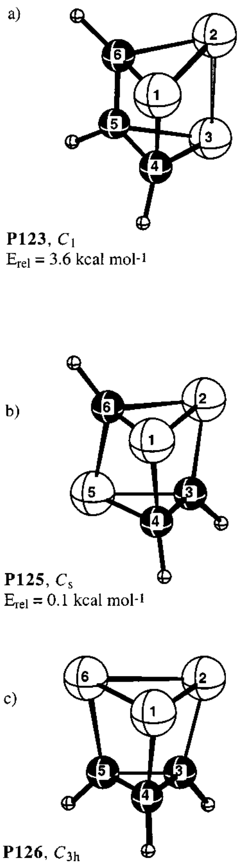
distances (Å)		angles (°)	
P1-C2	1.736	P1-C2-P3	134.7
		C2-P3-C4	105.3

//X-ray (tris-*t*Bu derivative)

distances (Å)		angles (°)	
P-C	1.724(5)	P-C-P	130.3(3)
	1.719(4)		130.8(3)
	1.718(4)		130.9(3)
	1.725(5)	C-P-C	109.6(2)
	1.727(4)		109.0(2)
	1.729(5)		109.3(2)

Figure 1. Optimized geometries and relative energies (MP4/6-31+G*//MP2(fu)/6-31G*) of triphosphabenzenes ($C_3H_3P_3$): a) **B123**, C_{2v}; b) **B124**, C_s, and c) **B135**, D_{3h} (all are minima at HF/6-31G*); the experimental structure from an X-ray analysis is taken from ref.[18]

metry.[31] Monophosphabenzene (**B1**)[32] was shown computationally to have a delocalized structure with almost identical C−C bond lengths of 1.396 (C2−C3) and 1.398 Å (C3−C4), and a C−P separation of 1.737 Å.[33] This work



P123, C_1
E_{rel} = 3.6 kcal mol-1

distances (Å)	
P1-P2	2.256
P1-C4	1.886
P1-C6	1.885
P2-P3	2.299
P2-C6	1.860
P3-C4	1.868
P3-C5	1.900
C4-C5	1.491
C5-C6	1.527

angles (°)	
P1-P2-P3	83.6
P1-P2-C6	53.5
P1-C4-C3	108.0
P1-C4-P5	94.1
P1-C6-P2	74.1
P1-C6-C5	92.9
P2-P1-C4	84.1
P2-P1-C6	52.4
P2-P3-C4	83.2
P2-P3-C5	77.2
P2-C6-C5	101.9
P3-P2-C6	79.1
P3-C4-C5	67.8
P3-C5-C4	65.6
P3-C5-C6	101.9
C4-P1-C6	74.2
C4-P3-C5	46.6
C4-C5-C6	97.8

P125, C_s
E_{rel} = 0.1 kcal mol-1

distances (Å)	
P1-P2	2.278
P1-C4	1.882
P1-C6	1.856
C3-C4	1.482
C3-P5	1.887
C5-C6	1.894

angles (°)	
P1-P2-P3	77.8
P1-P2-C6	52.2
P1-C4-C3	102.2
P1-C4-P5	97.8
P1-C6-P2	75.7
P1-C6-C5	98.5
P3-P2-C6	80.5
P3-C4-C5	66.9
P3-C5-C4	46.2
P3-C5-C6	79.4

P126, C_{3h}
E_{rel} = 0.0 kcal mol-1

distances (Å)	
P1-P2	2.256
P1-C4	1.888
C3-C4	1.504

angles (°)	
P1-P2-P3	78.5
P2-C3-C4	101.5

Figure 2. Optimized geometries and relative energies (MP4/6-31+G*//MP2(fu)/6-31G*) of triphosphaprismanes ($C_3H_3P_3$): a) **P123**, C_1; b) **P125**, C_s, and c) **P126**, C_{3h} (all are minima at HF/6-31G*)

corrected an earlier combined electron diffraction and microwave study that suggested a longer C2−C3 (1.431 Å) than C3−C4 distance (1.384 Å).[34] For comparison, we computed the three diphosphabenzene isomers ("diphosphinines"), **B12** (*ortho*), **B13** (*meta*), and **B14** (*para*).[35] The *ortho* isomer, **B12**, with its neighboring phosphorus atoms is more stable than **B13** and **B14** by 5.0 and 7.7 kcal mol^{-1}, respectively [MP4/6-31G*//MP2(fu)/6-31G* + 0.89 ZPE(HF/6-31G*)]. Only derivatives of **B13** (2,4-di-*tert*-butyl-1,3-diphosphabenzene)[36] and **B14** [2,3,5,6-tetrakis(trifluromethyl)-1,4-diphosphabenzene][37] have been observed experimentally, but none of the thermodynamically most stable isomer, **B12**. Diphosphabenzenes also have delocalized structures: C−C are between 1.387 and 1.399 Å, C−P are between 1.735 and 1.744 Å. Bond angles computed for **B135** (P−C−P: 134.7, C−P−C: 105.3°) are in reasonable agreement with the experimental values from an X-ray analysis for the 2,4,6-tBu$_3$ derivative [P−C−P: 130.7(4), C−P−C: 109.3(3)°, averaged].[18] In all phosphabenzenes, valence angles at phosphorus atoms are smaller than 120° while those at carbon are larger. Phosphorus generally prefers smaller bond angles due to ineffective hybridization: The lone pair has high s and the bond hybrids have high p character.[38]

A set of isodesmic reactions (Equations 1−8, Scheme 8) provides estimates of the effect of phospha substitution on the aromatic stabilization energy (ASE). Computed reaction energies are small compared to the 35.1 kcal mol^{-1} ASE of benzene (Equation 1, Scheme 8). The phosphorus atoms in **B123** and **B14** result in minor destabilizations of 4.4 and 2.2 kcal mol^{-1}, respectively. Small negative values indicate that aromaticity remains essentially equally strong in the other phosphabenzene species (Scheme 8).

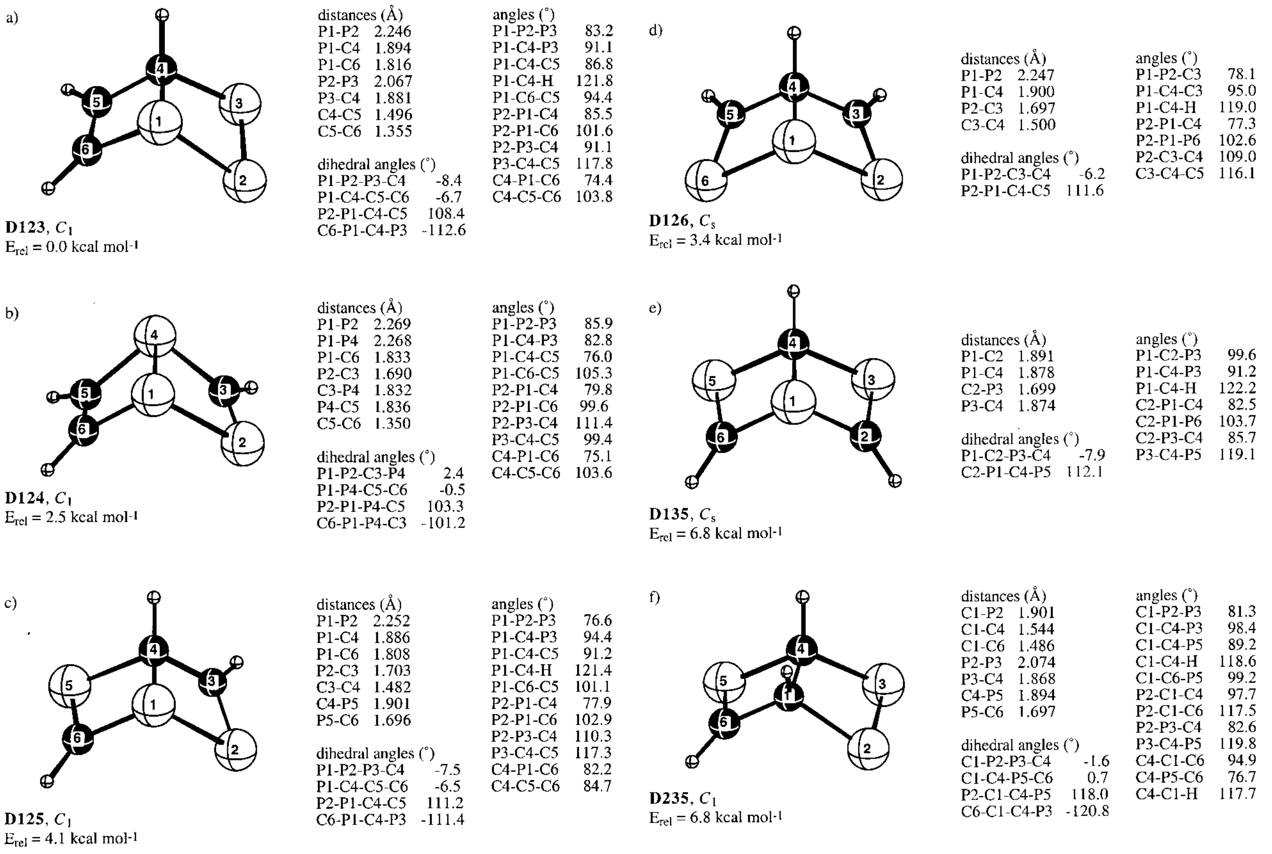
The aromaticity of the triphosphabenzenes can be quantified further by NICS (nucleus independent chemical shifts) computed at the ring centers.[27] Negative values indicate aromaticity and positive values are found for antiaromatic compounds. NICS close to zero are found for nonaromatic compounds. At GIAO-SCF/6-31+G**//MP2(fu)/6-31G* NICS for **B123**, **B124**, and **B135** are −7.3, −6.4 and −5.8, respectively, and the diphosphabenzenes have very similar NICS: −7.9 (**B12**), −7.1 (**B13**), and −7.3 (**B14**) (Table 3). These compare to a value of −9.7 for benzene at the same level;[27] NICS for P_6 in D_{6h} is −7.2 at the same level. Data in Table 3 suggests that on average NICS values decrease slightly with the number of P atoms. Based on the NICS criterion, tri- as well as mono- and diphosphabenzenes can clearly be classified as aromatic. The strongly deshielded ^{1}H-NMR chemical shifts computed for phosphabenzenes (δ^1H = 8.0−12.0; Table 3), attributable to diatropic ring currents, also indicate aromaticity.

Stability of Triphosphabenzene Valence Isomers

All positions in the prismane cage are part of one three- and two four-membered rings and hence are equivalent. The three possible isomers differ only in the number of C−C, C−P, and P−P single bonds, but this has almost no effect on the thermodynamical stability: **P126**, which is 39.8 kcal mol^{-1} less stable than **B135**, is lower in energy than **P125** and **P123** only by 0.1 and 3.6 kcal mol^{-1}, respectively. Bond lengths and angles in the three triphosphaprismane isomers show no exceptional values.

Differences in energies among the six triphospha Dewar benzenes are not very pronounced either; both of the most stable isomers, **D123** and **D124** have one C−C double bond. The least stable isomers, **D235**, which has two carbon atoms in the bridgehead positions 1 and 4, and **D135**, a derivative of which is experimentally known,[17] are only 6.8 kcal mol^{-1} higher in energy than **D123**. Geometric parameters are in the expected range. The (1)−(2)−(3)−(4) and (1)−(4)−(5)−(6) four-membered rings are almost planar when the (1)−(4) link is homonuclear (**D124**, **D235**); with a P1−C4 link the dihedral angles are ca. 6−8° (**D123**, **D125**, **D126**, **D135**).

The stability order of the eight possible triphosphabenzvalene isomers follow the rules that phosphorus placement in the three-membered ring is favorable and that positions 5 and 6, which are common to both three-membered rings, are best. The smaller valence angle of phosphorus, which results in less ring strain in small rings[39] compared



a)

D123, C_1
E_{rel} = 0.0 kcal mol-1

distances (Å)	
P1-P2	2.246
P1-C4	1.894
P1-C6	1.816
P2-P3	2.067
P3-C4	1.881
C4-C5	1.496
C5-C6	1.355

dihedral angles (°)	
P1-P2-P3-C4	-8.4
P1-C4-C5-C6	-6.7
P2-P1-C4-C5	108.4
C6-P1-C4-P3	-112.6

angles (°)	
P1-P2-P3	83.2
P1-C4-P3	91.1
P1-C4-C5	86.8
P1-C4-H	121.8
P1-C6-C5	94.4
P2-P1-C4	85.5
P2-P1-C6	101.6
P2-P3-C4	91.1
P3-C4-C5	117.8
C4-P1-C6	74.4
C4-C5-C6	103.8

b)

D124, C_1
E_{rel} = 2.5 kcal mol-1

distances (Å)	
P1-P2	2.269
P1-P4	2.268
P1-C6	1.833
P2-C3	1.690
C3-P4	1.832
P4-C5	1.836
C5-C6	1.350

dihedral angles (°)	
P1-P2-C3-P4	2.4
P1-P4-C5-C6	-0.5
P2-P1-P4-C5	103.3
C6-P1-P4-C3	-101.2

angles (°)	
P1-P2-P3	85.9
P1-C4-P3	82.8
P1-C4-C5	76.0
P1-C6-C5	105.3
P2-P1-C4	79.8
P2-P1-C6	99.6
P2-P3-C4	111.4
P3-C4-C5	99.4
C4-P1-C6	75.1
C4-C5-C6	103.6

c)

D125, C_1
E_{rel} = 4.1 kcal mol-1

distances (Å)	
P1-P2	2.252
P1-C4	1.886
P1-C6	1.808
P2-C3	1.703
C3-C4	1.482
C4-P5	1.901
P5-C6	1.696

dihedral angles (°)	
P1-P2-P3-C4	-7.5
P1-C4-C5-C6	-6.5
P2-P1-C4-C5	111.2
C6-P1-C4-P3	-111.4

angles (°)	
P1-P2-P3	76.6
P1-C4-P3	94.4
P1-C4-C5	91.2
P1-C4-H	121.4
P1-C6-C5	101.1
P2-P1-C4	77.9
P2-P1-C6	102.9
P2-P3-C4	110.3
P3-C4-C5	117.3
C4-P1-C6	82.2
C4-C5-C6	84.7

d)

D126, C_s
E_{rel} = 3.4 kcal mol-1

distances (Å)	
P1-P2	2.247
P1-C4	1.900
P2-C3	1.697
C3-C4	1.500

dihedral angles (°)	
P1-P2-C3-C4	-6.2
P2-P1-C4-C5	111.6

angles (°)	
P1-P2-C3	78.1
P1-C4-C3	95.0
P1-C4-H	119.0
P2-P1-C4	77.3
P2-P1-P6	102.6
P2-C3-C4	109.0
C3-C4-C5	116.1

e)

D135, C_s
E_{rel} = 6.8 kcal mol-1

distances (Å)	
P1-C2	1.891
P1-C4	1.878
C2-P3	1.699
P3-C4	1.874

dihedral angles (°)	
P1-C2-P3-C4	-7.9
C2-P1-C4-P5	112.1

angles (°)	
P1-C2-P3	99.6
P1-C4-P3	91.2
P1-C4-H	122.2
C2-P1-C4	82.5
C2-P1-P6	103.7
C2-P3-C4	85.7
P3-C4-P5	119.1

f)

D235, C_1
E_{rel} = 6.8 kcal mol-1

distances (Å)	
C1-P2	1.901
C1-C4	1.544
C1-C6	1.486
P2-P3	2.074
P3-C4	1.868
C4-P5	1.894
P5-C6	1.697

dihedral angles (°)	
C1-P2-P3-C4	-1.6
C1-C4-P5-C6	0.7
P2-C1-C4-P5	118.0
C6-C1-C4-P3	-120.8

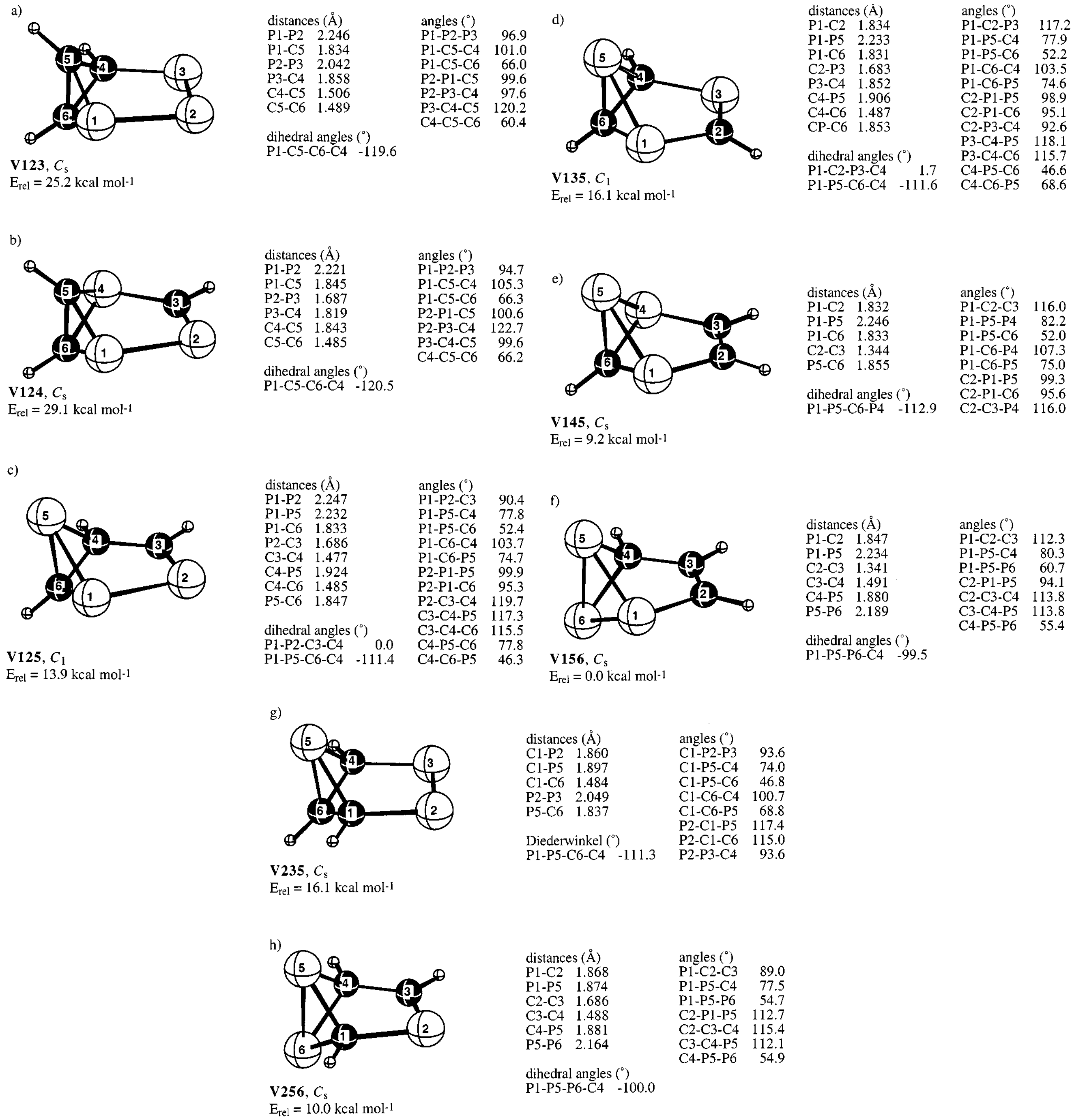
angles (°)	
C1-P2-P3	81.3
C1-C4-P3	98.4
C1-C4-P5	89.2
C1-C4-H	118.6
C1-C6-P5	99.2
P2-C1-C4	97.7
P2-C1-C6	117.5
P2-P3-C4	82.6
P3-C4-P5	119.8
C4-C1-C6	94.9
C4-P5-C6	76.7
C4-C1-H	117.7

Figure 3. Optimized geometries and relative energies (MP4/6-31+G*//MP2(fu)/6-31G*) of triphospha Dewar benzenes ($C_3H_3P_3$): a) **D123**, C_1; b) **D124**, C_1; c) **D125**, C_1; d) **D126**, C_s; e) **D135**, C_s, and f) **D235**, C_1 (all are minima at HF/6-31G*)

to carbon, is responsible. Consequently, **V156**, in which two phosphorus atoms are at the bridgeheads and the third P also in a three-membered ring position 1, is the most stable isomer. If the third P atom takes part in the double bond (**V256**) or one P is moved from the (5)−(6) bridgehead to a "normal" three-membered ring position, (4, see **V145**), the relative energy is ca. 10 kcal mol^{-1} higher. With two carbon atoms at positions 5 and 6, high relative energies of 25.2 and 29.1 kcal mol^{-1} result while a P=P double bond (in **V123**) is preferred over a C=P double bond (in **V124**). The remaining isomers, **V125**, **V135**, and **V235** have ca. 15 kcal mol^{-1} higher relative energies than **V256**.

The bicyclopropenyl isomers can adopt various conformations, which are connected by rotation about the (1)−(4) single bond between the two three-membered rings. The *anti* conformations of **C123** and **C156** were optimized in C_s symmetry and characterized as transition structures with small imaginary frequencies (64i and 50i cm^{-1}, respectively, at HF/6-31G*). Optimization at the MP2(fc)/6-31G* level of all bicyclopropenyl isomers with starting *anti* geometries but without symmetry constraints converged to gauche conformations (C_1). In general, two different gauche but only one *anti* conformer are possible for each isomer. The same ordering in relative stability was found for a set of gauche and the *anti* conformers. The gauche conformers were consistently more stable by 0.1−1.8 kcal mol^{-1}, which is little compared to the energy difference between bicyclopropenyl isomers and other trimers. To be consistent all results reported here refer to the *anti* conformers. It is evident also from the bicyclopropenyl isomers that the number of heteronuclear C−P single bonds does not have much effect on the relative energies. Both **C123** and **C156** have one P=P and one C=C double bond. With P_3 and a C_3 rings, **C123** has only one C−P bond, whereas **C156** has five C−P bonds due to the heterocyclic P_2C and PC_2 rings. The relative energies differ by only 0.6 kcal mol^{-1} (**C123** is more stable). The most stable isomer, however, is **C235**, with two carbon atoms at the ring connection positions 1 and 4. The strain resulting from the double bonds in the three-membered rings of bicyclopropenyl, is even larger than in isomers with saturated three-membered rings in e.g. benzvalene. Hence, carbon atom placements at the more flexible positions 1 and 4 is crucial for stability. Consequently, **C124**, with a P1−P4 link and all three carbon atoms at the most strained double-bond positions has the highest relative energy (17.3 kcal mol^{-1}). As expected, **C125** and **C126**, both of which have two C=P double bonds and a P1−C4 moiety, are almost equal in relative energy (E_{rel} = 11.6 and 11.8 kcal mol^{-1}) but ca. 4 kcal mol^{-1} less stable than **C156** which has homonuclear C=C and P=P bonds.

In addition to the $(HCP)_3$ isomers that can be derived from $(CH)_6$ analogs by replacing three CH units by P atoms, we investigated a spirocyclic compound **S135**, because it may exist as a short lived intermediate in oligomer-



a) **V123**, C_s
E_{rel} = 25.2 kcal mol-1

distances (Å)		angles (°)	
P1-P2	2.246	P1-P2-P3	96.9
P1-C5	1.834	P1-C5-C4	101.0
P2-P3	2.042	P1-C5-C6	66.0
P3-C4	1.858	P2-P1-C5	99.6
C4-C5	1.506	P2-P3-C4	97.6
C5-C6	1.489	P3-C4-C5	120.2
		C4-C5-C6	60.4
dihedral angles (°)			
P1-C5-C6-C4	-119.6		

b) **V124**, C_s
E_{rel} = 29.1 kcal mol-1

distances (Å)		angles (°)	
P1-P2	2.221	P1-P2-P3	94.7
P1-C5	1.845	P1-C5-C4	105.3
P2-P3	1.687	P1-C5-C6	66.3
P3-C4	1.819	P2-P1-C5	100.6
C4-C5	1.843	P2-P3-C4	122.7
C5-C6	1.485	P3-C4-C5	99.6
		C4-C5-C6	66.2
dihedral angles (°)			
P1-C5-C6-C4	-120.5		

c) **V125**, C_1
E_{rel} = 13.9 kcal mol-1

distances (Å)		angles (°)	
P1-P2	2.247	P1-P2-C3	90.4
P1-P5	2.232	P1-P5-C4	77.8
P1-C6	1.833	P1-P5-C6	52.4
P2-C3	1.686	P1-C6-C4	103.7
C3-C4	1.477	P1-C6-P5	74.7
C4-P5	1.924	P2-P1-P5	99.9
C4-C6	1.485	P2-P1-C6	95.3
P5-C6	1.847	P2-C3-C4	119.7
		C3-C4-P5	117.3
dihedral angles (°)		C3-C4-C6	115.5
P1-P2-C3-C4	0.0	C4-P5-C6	77.8
P1-P5-C6-C4	-111.4	C4-C6-P5	46.3

d) **V135**, C_1
E_{rel} = 16.1 kcal mol-1

distances (Å)		angles (°)	
P1-C2	1.834	P1-C2-P3	117.2
P1-P5	2.233	P1-P5-C4	77.9
P1-C6	1.831	P1-P5-C6	52.2
C2-P3	1.683	P1-C6-C4	103.5
P3-C4	1.852	P1-C6-P5	74.6
C4-P5	1.906	C2-P1-P5	98.9
C4-C6	1.487	C2-P1-C6	95.1
CP-C6	1.853	C2-P3-C4	92.6
		P3-C4-P5	118.1
dihedral angles (°)		P3-C4-C6	115.7
P1-C2-P3-C4	1.7	C4-P5-C6	46.6
P1-P5-C6-C4	-111.6	C4-C6-P5	68.6

e) **V145**, C_s
E_{rel} = 9.2 kcal mol-1

distances (Å)		angles (°)	
P1-C2	1.832	P1-C2-C3	116.0
P1-P5	2.246	P1-P5-P4	82.2
P1-C6	1.833	P1-P5-C6	52.0
C2-C3	1.344	P1-C6-P4	107.3
P5-C6	1.855	P1-C6-P5	75.0
		C2-P1-P5	99.3
dihedral angles (°)		C2-P1-C6	95.6
P1-P5-C6-P4	-112.9	C2-C3-P4	116.0

f) **V156**, C_s
E_{rel} = 0.0 kcal mol-1

distances (Å)		angles (°)	
P1-C2	1.847	P1-C2-C3	112.3
P1-P5	2.234	P1-P5-C4	80.3
C2-C3	1.341	P1-P5-P6	60.7
C3-C4	1.491	C2-P1-P5	94.1
C4-P5	1.880	C2-C3-C4	113.8
P5-P6	2.189	C3-C4-P5	113.8
		C4-P5-P6	55.4
dihedral angles (°)			
P1-P5-P6-C4	-99.5		

g) **V235**, C_s
E_{rel} = 16.1 kcal mol-1

distances (Å)		angles (°)	
C1-P2	1.860	C1-P2-P3	93.6
C1-P5	1.897	C1-P5-C4	74.0
C1-C6	1.484	C1-P5-C6	46.8
P2-P3	2.049	C1-C6-C4	100.7
P5-C6	1.837	C1-C6-P5	68.8
		P2-C1-P5	117.4
Diederwinkel (°)		P2-C1-C6	115.0
P1-P5-C6-C4	-111.3	P2-P3-C4	93.6

h) **V256**, C_s
E_{rel} = 10.0 kcal mol-1

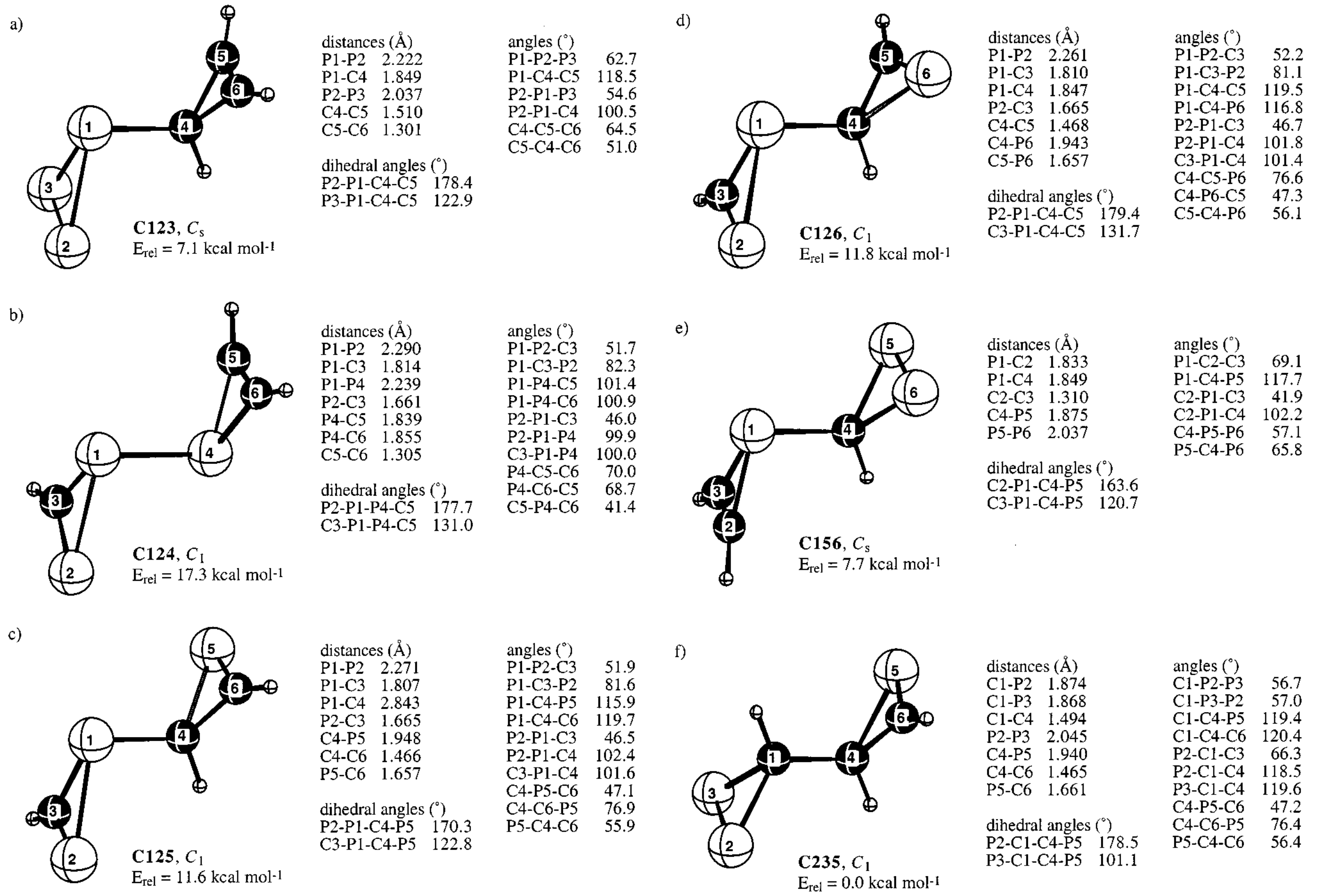
distances (Å)		angles (°)	
P1-C2	1.868	P1-C2-C3	89.0
P1-P5	1.874	P1-P5-C4	77.5
C2-C3	1.686	P1-P5-P6	54.7
C3-C4	1.488	C2-P1-P5	112.7
C4-P5	1.881	C2-C3-C4	115.4
P5-P6	2.164	C3-C4-P5	112.1
		C4-P5-P6	54.9
dihedral angles (°)			
P1-P5-P6-C4	-100.0		

Figure 4. Optimized geometries and relative energies (MP4/6-31+G*//MP2(fu)/6-31G*) of triphosphabenzvalenes ($C_3H_3P_3$): a) **V123**, C_s; b) **V124**, C_s; c) **V125**, C_1; d) **V135**, C_1; e) **V145**, C_s f) **V156**, C_s; g) **V235**, C_s, and h) **V256**, C_s (all are minima at HF/6-31G*)

ization reactions.[6] In the presence of $AlCl_3$, *t*BuCP trimerizes to **S135a·AlCl$_3$**; the X-ray structure is available.[6] $AlCl_3$ removal supposedly sets free an **S135a** intermediate. The structures of the isolated tetrameric products suggest that **S135a** isomerizes to Dewar benzenes **D135a** or **D125a** (which could not be detected) depending on the reaction conditions; these then add another phosphaalkyne monomer to give bishomoprismane structures (Scheme 4).[6]

While C_s-symmetric **S135** is found to be a minimum, it is stabilized by only ca. 4 kcal mol^{-1} relative to three HCPs. (The B3LYP value, 19.7 kcal mol^{-1}, probably is too high, compare Table 1.) The **S135·AlCl$_3$** complex has a considerable association energy relative to isolated **S135** and $AlCl_3$ [by 52.2 kcal mol^{-1} at MP2(fc)/6-31G* and by 36.7 kcal mol^{-1} at B3LYP/6-311+G**//MP2(fc)/6-31G*, each 0.89 ZPE(HF/6-31G*) corrected]. Only formation of an even more stable $AlCl_3$ complex would allow the generation of the high energy **S135** trimer. Isomerizations of **S135** to **D135** and **D125** are strongly exothermic (by 45.3 and 48.0 kcal mol^{-1}, respectively).

C−P distances (1.729 and 1.739 Å) in the four-membered ring of **S135** are between typical single and double bond



a) **C123**, C_s
E_{rel} = 7.1 kcal mol-1

distances (Å)		angles (°)	
P1-P2	2.222	P1-P2-P3	62.7
P1-C4	1.849	P1-C4-C5	118.5
P2-P3	2.037	P2-P1-P3	54.6
C4-C5	1.510	P2-P1-C4	100.5
C5-C6	1.301	C4-C5-C6	64.5
		C5-C4-C6	51.0

dihedral angles (°)	
P2-P1-C4-C5	178.4
P3-P1-C4-C5	122.9

b) **C124**, C_1
E_{rel} = 17.3 kcal mol-1

distances (Å)		angles (°)	
P1-P2	2.290	P1-P2-C3	51.7
P1-C3	1.814	P1-C3-P2	82.3
P1-P4	2.239	P1-P4-C5	101.4
P2-C3	1.661	P1-P4-C6	100.9
P4-C5	1.839	P2-P1-C3	46.0
P4-C6	1.855	P2-P1-P4	99.9
C5-C6	1.305	C3-P1-P4	100.0
		P4-C5-C6	70.0
		P4-C6-C5	68.7
		C5-P4-C6	41.4

dihedral angles (°)	
P2-P1-P4-C5	177.7
C3-P1-P4-C5	131.0

c) **C125**, C_1
E_{rel} = 11.6 kcal mol-1

distances (Å)		angles (°)	
P1-P2	2.271	P1-P2-C3	51.9
P1-C3	1.807	P1-C3-P2	81.6
P1-C4	2.843	P1-C4-P5	115.9
P2-C3	1.665	P1-C4-C6	119.7
C4-P5	1.948	P2-P1-C3	46.5
C4-C6	1.466	P2-P1-C4	102.4
P5-C6	1.657	C3-P1-C4	101.6
		C4-P5-C6	47.1
		C4-C6-P5	76.9
		P5-C4-C6	55.9

dihedral angles (°)	
P2-P1-C4-P5	170.3
C3-P1-C4-P5	122.8

d) **C126**, C_1
E_{rel} = 11.8 kcal mol-1

distances (Å)		angles (°)	
P1-P2	2.261	P1-P2-C3	52.2
P1-C3	1.810	P1-C3-P2	81.1
P1-C4	1.847	P1-C4-C5	119.5
P2-C3	1.665	P1-C4-P6	116.8
C4-C5	1.468	P2-P1-C3	46.7
C4-P6	1.943	P2-P1-C4	101.8
C5-P6	1.657	C3-P1-C4	101.4
		C4-C5-P6	76.6
		C4-P6-C5	47.3
		C5-C4-P6	56.1

dihedral angles (°)	
P2-P1-C4-C5	179.4
C3-P1-C4-C5	131.7

e) **C156**, C_s
E_{rel} = 7.7 kcal mol-1

distances (Å)		angles (°)	
P1-C2	1.833	P1-C2-C3	69.1
P1-C4	1.849	P1-C4-P5	117.7
C2-C3	1.310	C2-P1-C3	41.9
C4-P5	1.875	C2-P1-C4	102.2
P5-P6	2.037	C4-P5-P6	57.1
		P5-C4-P6	65.8

dihedral angles (°)	
C2-P1-C4-P5	163.6
C3-P1-C4-P5	120.7

f) **C235**, C_1
E_{rel} = 0.0 kcal mol-1

distances (Å)		angles (°)	
C1-P2	1.874	C1-P2-P3	56.7
C1-P3	1.868	C1-P3-P2	57.0
C1-C4	1.494	C1-C4-P5	119.4
P2-P3	2.045	C1-C4-C6	120.4
C4-P5	1.940	P2-C1-C3	66.3
C4-C6	1.465	P2-C1-C4	118.5
P5-C6	1.661	P3-C1-C4	119.6
		C4-P5-C6	47.2
		C4-C6-P5	76.4
		P5-C4-C6	56.4

dihedral angles (°)	
P2-C1-C4-P5	178.5
P3-C1-C4-P5	101.1

Figure 5. Optimized geometries and relative energies (MP4/6-31+G*//MP2(fu)/6-31G*) of triphosphabicyclopropenyl ($C_3H_3P_3$): a) **C123**, C_s; b) **C124**, C_1 und c) **C125**, C_1; d) **C126**, C_1; e) **C156**, C_s, and f) **C235**, C_1 (all are minima at HF/6-31G*)

Table 1. Relative energies [kcal mol^{-1}] of $(HC)_3P_3$ isomers[a]

	B123	B124	B135	P123	P125	P126	D123	D124	D125	D126	D135	D235	V123	V124
ZPE[b]	36.4	35.7	35.1	36.3	36.1	36.8	36.2	35.4	35.5	35.8	35.2	36.0	36.2	35.3
MP2[c]	0.0	7.7	10.1	41.9	38.3	38.2	29.0	32.2	33.3	32.8	35.5	35.4	28.8	30.6
MP4SDTQ[c]	0.0	7.3	10.0	43.2	40.0	39.4	28.5	30.7	32.5	31.6	35.4	34.8	31.5	32.0
MP4SDTQ[d]	0.0	6.7	8.9	43.4	39.9	39.8	28.1	30.6	32.2	31.5	34.9	34.9	29.9	33.8
B3LYP[e]	0.0	8.0	11.1	41.9	46.1	43.7	30.8	31.7	37.2	36.6	40.3	41.6	36.6	38.2
	V125	**V135**	**V145**	**V156**	**V235**	**V256**	**C123**	**C124**	**C125**	**C126**	**C156**	**C235**	**S135**	3HCP
ZPE[b]	36.1	35.7	35.4	36.5	36.3	36.2	34.6	33.1	33.7	33.7	34.0	35.1	33.0	28.8
MP2[c]	17.6	20.2	13.7	4.5	19.3	14.1	54.3	65.5	59.9	59.6	55.4	47.4	83.6	87.8
MP4SDTQ[c]	18.9	21.5	14.6	5.7	21.4	15.7	54.7	64.9	59.9	59.6	55.5	48.1	85.1	83.7
MP4SDTQ[d]	18.6	20.8	13.9	4.7	20.8	14.7	53.9	64.1	58.4	58.6	54.5	46.8	80.2	84.4
B3LYP[e]	24.7	28.7	18.0	9.4	30.3	24.3	55.3	62.7	64.0	64.5	57.9	55.8	77.3	97.0

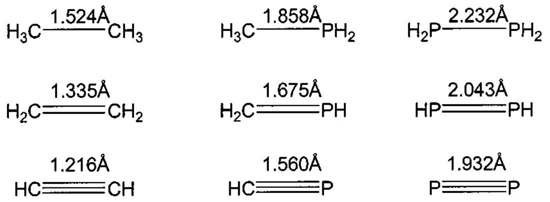
[a] For MP2(fu)/6-31G* optimized geometries and corrected for scaled (factor 0.89) differences in zero point vibrational energies (ZPE) from HF/6-31G* frequency calculations. – [b] HF/6-31G*. – [c] 6-31G*. – [d] 6-31+G**. – [e] 6-311+G**.

values and essentially equal to those in the aromatic triphosphabenzenes (compare Figure 1). This might be interpreted being due to the delocalization of the four π electrons. However, 4*n* π systems are expected to be antiaromatic and hence bond-localized. In fact, the NICS value for the four-membered C_2P_2 ring in **S135** is small (1.3 ppm) characterizing the ring as nonaromatic. Computed atomic charges from a natural population analysis (NPA)[40] suggest a zwitterionic description with an allyl anionic moiety (Scheme 9). The formally single bonds in the three-membered ring (P1–P5 and P1–C6) are considerably shortened (by 0.10 and 0.07 Å, respectively) and the P5–C6 double bond is elongated (by 0.04 Å) as compared to the corresponding values in the bicyclopropenyls. NICS values for three-membered rings are large but the interpretation is complicated by local effects (relatively high electron density at the center of the ring cause large shielding) but δ^1H for the C6-H hydrogen of 15.5, suggests strong aromaticity for

Table 2 Relative energies[a] [kcal mol^{-1}] of transtion states and products of cycloadditions of HCP to 1,3- and 1,2-diphosphete (compare Figures 9 and 10)

	3 HCP	**DP13** + HCP	**TS-D125/DP13**	**D125**	**TS-D135/DP13**	**D135**	**DP12** + HCP	**TS-D126/DP12**	**D126**	**TS-D125/DP12**
ZPE[b]	28.8	31.6	32.5	35.5	32.4	35.2	32.2	33.0	35.8	33.0
THC^{298}(H)[b]	35.3	36.8	37.1	39.5	37.0	39.1	37.4	37.6	39.8	37.7
THC^{298}(G)[b]	−10.3	1.9	12.7	16.7	12.6	16.4	2.5	13.4	17.0	13.1
MP2[c]	0.0	3.9	2.4	−54.5	1.7	−52.3	−5.2	−6.7	−55.0	−7.0
MP4SDTQ[c]	0.0	2.2	3.1	−51.2	2.0	−48.3	−6.7	−5.6	−52.1	−6.4
MP4SDTQ[d]	0.0	1.3	0.9	−52.2	0.0	−49.5	−7.5	−7.4	−52.9	−8.1
ΔH^{298}[e]	0.0	−2.1	0.7	−56.8	−1.3	−54.5	−11.4	−7.9	−57.8	−9.2
ΔG^{298}[e]	0.0	8.6	24.8	−34.0	19.9	−31.6	−0.7	13.5	−35.0	11.9
B3LYP[f]	0.0	−2.9	−2.6	−58.9	−3.3	−55.8	−13.4	−13.5	−59.8	−14.0
CAS-SCF[g]	0.0	−13.2	2.2	–	3.7	–	−23.8	−7.4	–	−9.6
MCQDPT2[h]	0.0	−6.1	−3.4	–	−4.0	–	−15.4	−12.4	–	−12.7
ΔH^{298}[i]	0.0	−7.2	−5.1	–	−5.7	–	−16.3	−14.0	–	−14.3
ΔG^{298}[i]	0.0	3.2	16.6	–	15.4	–	−6.0	8.2	–	7.1

[a] For RMP2(fu)/6-31G* optimized geometries and corrected for scaled (0.89) zero point vibrational energies (ZPE). – [b] HF/6-31G*. – [c] 6-31G*. – [d] 6-31+G**. – [e] Based on MP4SDQ/6-31+G** electronic energies and thermal corrections (THC) at HF/6-31G*. – [f] 6-311+G**. – [g] CAS-SCF(6,6)/6-31G* optimization, ZPE correction from this level included. – [h] Second-order perturbative correction to the CAS-SCF(6,6)/6-31G* level, including scaled (0.9) ZPE corrections at CAS-SCF(6,6)/6-31G*. – [i] Based on MCQDPT2/6-31G*//CAS-SCF(6,6)/6-31G* electronic energies and thermal corrections (THC) at CAS-SCF(6,6)/6-31G*.



Scheme 7. Typical single, double and triple bond lengths involving carbon and phosphorous atoms (MP2(fu)/6-31G*)

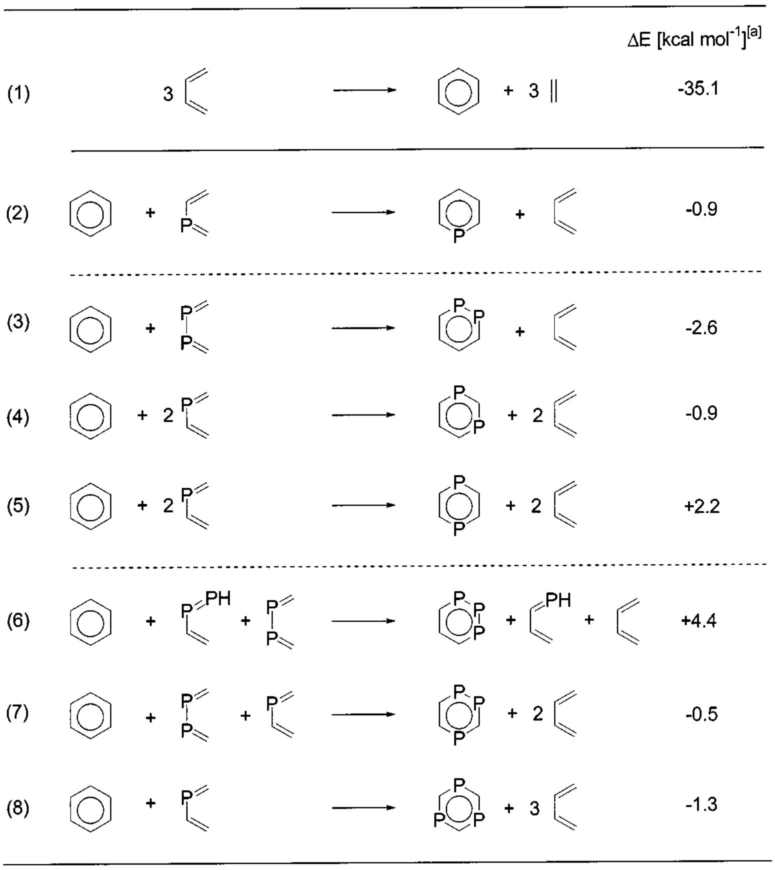
the P1–C6–P5 ring in **S135**. The main structural change on complex formation with $AlCl_3$ is C2–P3 bond lengthening (by 0.12 Å, compare Figure 6).

Figure 7 represents the relative energies of the HCP trimers investigated here at MP4SDTQ/6-31+G**//MP2(fu)/6-31G* + 0.89 ZPE(HF/6-31G*) graphically. The same qualitative picture results at all ab initio levels investigated (compare Table 1). The stability of a given isomer is determined mainly by its framework; the substitution pattern plays a less important role. The stability decreases in the order benzenes (**B**), benzvalenes (**V**), Dewar benzenes (**D**), prismanes (**P**), and bicyclopropenyls (**C**). Only the energy of benzvalene **V156** is as low as triphosphabenzenes **B124** and **B135**. All the most stable isomers in the **B**, **V**, and **D** groups (**B123**, **V156**, and **123**), have neighboring phosphorus atoms and consequently cannot be formed from three phosphaethyne monomers without rearrangement. (This is also true for **V123**, **C123**, **C156**, and **C124**.) When the carbon atoms bear large substituents, as is typical in experimental studies, destabilization for these structures due to steric repulsion can be expected.

The electron correlation treatment (MP2 through MP4SDTQ) has no decisive influence and both basis sets (6-31G* and 6-31+G**) give almost identical results. Differences are usually less than 1 kcal mol^{-1} with 6-31+G** giving slightly lower values. Probably due to the unusual bonding, the relative energy of **S135** is sensitive to the basis set: 6-31+G** gives a 5 kcal mol^{-1} lower energy. The relative energy of three monomers is less dependent on the basis set than on the level of correlation. Hence, referencing the values listed in Tables 1–3 HCP would cause much larger variations among the levels. Obviously, the C–P triple bond is not adequately described theoretically as easily as C–P single and double bonds. For "normal" HCP trimers containing only λ^3-phosphorus atoms, 6-31G* seems sufficient, because there are no changes with the larger 6-31+G** basis. DFT (B3LYP/6-311+G**//MP2(fu)/6-31G*) results differ in some aspects. The whole energy range from the most stable isomer **B123** to three monomers is larger (97 instead of 84 kcal mol^{-1}) and energies of $(HC)_3P_3$ isomers relative to **B123** tend to be somewhat larger. The 19 kcal mol^{-1} stabilization of **S135** relative to three monomers is the biggest discrepancy between DFT and traditional ab initio results [e.g. only a small stabilization (ca. 4.2 kcal mol^{-1}) is found at MP4/6-31+G**]. As with MO methods, the DFT ordering of structures is **B** < **V** < **D** < **P** < **C** (increasing energy). While the stability order within the **B**, **V**, and **D** groups is the same with both approaches, there are some changes for **P** and **C**. Which result is more reliable is not easy to decide, but the lack of significant changes with higher levels of correlation (MP2 through MP4SDTQ) nor with a larger basis set (6-31+G** vs. 6-31G*) should be noted.

Comparison with $(CH)_6$ and P_6

With a trimerization energy of −164 kcal mol^{-1} (relative to three ethyne molecules), benzene is by far the $(CH)_6$ global minimum. Benzvalene, Dewar benzene, prismane, and bicyclopropenyl are much less stable (compare Figure 8).[41] A completely different situation is found for P_6:[42] *cyclo*-P_6 in D_{6h} (the benzene analog) has about the same energy as



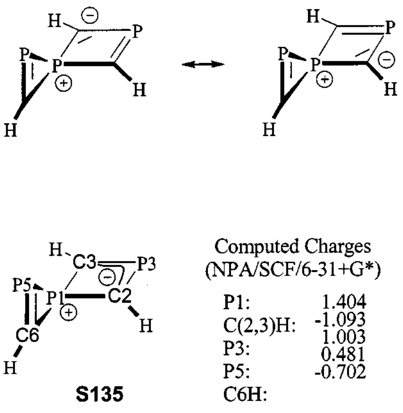
[a] MP4SDTQ/6-31G*//MP2(fu)/6-31G*+0.89*ZPE(HF/6-31G*)

Scheme 8. Isodesmic equations (2) to (8) to evaluate the effect of phospha substitution on the aromatic stabilization energy of benzene (eq. 1)

Table 3 Computed ^{1}H-NMR chemical shifts and NICS for mono-, di-, and tri-phospha-substituted benzenes and the spirocyclic $(HC)_3P_3$ isomer **S135**[a]

	NICS	δ(^{1}H)		
B1	−8.4	9.3 ($H^{C2,6}$)	8.5 ($H^{C3,5}$)	8.0 (H^{C4})
B12	−7.9	11.1 ($H^{C3,6}$)	8.7 ($H^{C4,5}$)	
B13	−7.1	11.1 (H^{C2})	9.5 ($H^{C4,6}$)	9.0 (H^{C5})
B14	−7.3	10.1 (H^{C2})		
B123	−7.3	10.3 ($H^{C4,6}$)	9.2 (H^{C5})	
B124	−6.4	12.0 (H^{C3})	10.1 (H^{C5})	10.7 (H^{C6})
B135	−5.8	10.9 ($H^{C2,4,6}$)		
S135	1.3	4.3 ($H^{C2,4}$)		
4-membered ring:				
S135	–		15.5 (H^{C6})	
3-membered ring:				

[a] GIAO-SCF/6-31+G*//MP2(fu)/6-31G*.

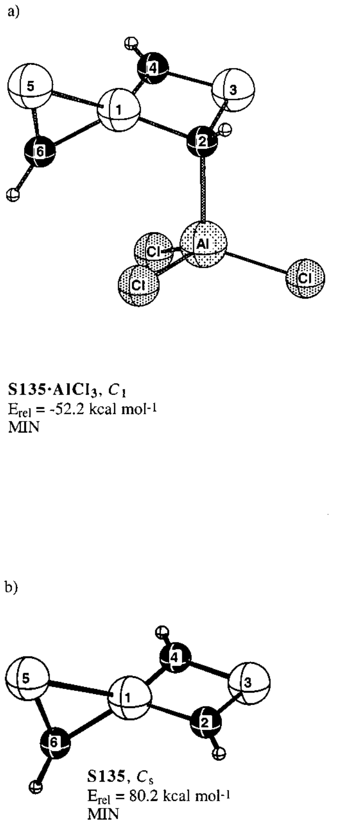


S135

Scheme 9. Resonance structures and computed charges for spirocyclic compound **S135**

three P_2 molecules and probably is not a minimum.[31] Kobayashi et al. reported a 9.2 kcal mol^{-1} exothermicity for P_6 (D_{6h}) $\rightarrow$ 3 P_2.[43] Nguyen and Hegarty estimated the dissociation barrier to be 13 kcal mol^{-1}.[44] In contrast, P_2 itself is ca. 27 kcal mol^{-1} less stable than 1/2 P_4.[45] The most stable P_6 was reported to be hexaphosphabenzvalene,[42,43,46] but the P_2 trimerization energy of −31 kcal mol^{-1} is relatively small. Consequently, all five P_6 isomers shown in Figure 8 are less stable than 6/4 P_4.[42,47]

In light of these differences between $(CH)_6$ and P_6, how do the mixed $(CH)_3P_3$ isomers behave? Figure 8 shows relative energies of the most stable triphospha-substituted benzenes, benzvalenes, Dewar benzenes, prismanes, and bicyclopropenyls in comparison with the $(CH)_6$ and P_6 valence isomers. The $(CH)_3P_3$ ordering is the same as for $(CH)_6$: **B** (most stable), **V**, **D**, **P**, and **C**, but the relative energy range (84 kcal mol^{-1}) is much smaller and is between the hydrocarbon (164 kcal mol^{-1}) and phosphorus (31 kcal



a)

S135·AlCl$_3$, C_1
E$_{rel}$ = -52.2 kcal mol^{-1}
MIN

	//MP2(fc)/6-31G*	X-ray
distances (Å)		
P1-C2	1.785	1.80(1)
P1-C4	1.760	1.77(1)
P1-P5	2.163	2.108(4)
P1-C6	1.743	1.74(1)
C2-P3	1.860	1.91(1)
P3-C4	1.708	1.70(1)
P5-C6	1.697	1.68(1)
C2-Al	2.051	2.02(2)
Al-Cl (Ø)	2.138	-
angles (°)		
P1-C2-P3	88.1	85.0(5)
P1-C4-P3	94.0	93.1(5)
P1-P5-C6	52.0	53.5(3)
P1-C6-P5	77.9	75.9(4)
C2-P1-C4	89.2	90.8(5)
C2-P1-P5	131.6	128.1(4)
C2-P3-C4	88.4	89.4(5)
C4-P1-P5	130.9	122.8(4)
C4-P1-C6	129.0	131.6(5)
P5-P1-C6	50.1	50.8(3)
dihedral angles (°)		
C2-P1-C4-P3	-4.2	-10.5
C2-P1-P5-C6	-110.7	-
C2-P1-C6-P5	115.9	-
P3-C2-P1-P5	-145.9	-
P3-C2-P1-P6	146.8	-

b)

S135, C_s
E$_{rel}$ = 80.2 kcal mol^{-1}
MIN

distances (Å)		angles (°)	
P1-C2	1.729	P1-C2-P3	89.6
P1-P5	2.168	P1-P5-C6	51.8
P1-C6	1.740	P1-C6-P5	78.0
C2-P3	1.739	C2-P1-C4	90.7
P5-C6	1.703	C2-P1-P5	131.0
		C2-P1-C6	127.8
dihedral angles (°)		C2-P3-C4	90.0
C2-P1-C4-P3	1.9	P5-P1-C6	50.2
C2-P1-P5-C6	-109.5		
C2-P1-C6-P5	115.8		
P3-C2-P1-P5	-153.6		
P3-C2-P1-P6	139.9		

Figure 6. Computed geometries of a) the AlCl$_3$ adduct of the spiro-C$_3$H$_3$P$_3$ compound **S135**, **S135·AlCl$_3$**, C_1 compared with X-ray structural data for the *t*Bu$_3$ derivative (energy relative to **S135** plus AlCl$_3$, experimental structure from an X-ray analysis is taken from ref.[6] and b) the spiro trimer **S135** (C$_3$H$_3$P$_3$), C_s (energy at MP4/6-31+G*//MP2(fu)/6-31G* relative to **B123**)

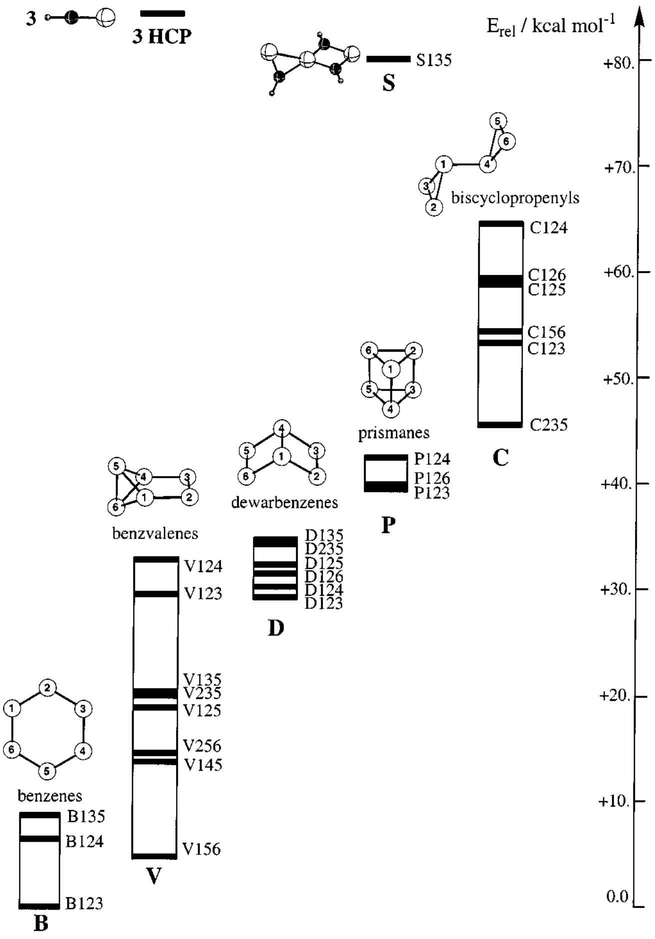


Figure 7. Relative energies of (HC)$_3$P$_3$ isomers at MP4/6-31+G**//MP2(fu)/6-31G*

mol^{-1}) ranges. The same conclusion was drawn by Colombet at al. for (CH)$_4$P$_2$ isomers.[35] Like the hetero benzene structures, the Dewar benzenes also are destabilized considerably by triphospha substitution: The trimerization energies are −84 and −56 kcal mol^{-1} for Dewar benzene and 1,2,3-triphospha Dewar benzene, respectively. No large differences are found for the benzvalene, prismane and bicyclopropenyl cases.

Some Mechanistic Aspects

HCP dimerization energies are much less exothermic (see ref.[21,22] and/or compare Table 2) than HCP trimerization energies. The HCP → 1/*n* (HCP)$_n$ reaction has a ΔG^{298} of −6.6 kcal mol^{-1} for diphosphatetrahedrane, the most stable dimer ($n = 2$), but ΔG^{298} is −24.9 kcal mol^{-1} for trimer **B123** ($n = 3$).[10] The tetramerization exothermicity to the parent of **2**[48] is only −20.5 kcal mol^{-1} [B3LYP/6-311G**//MP2(fu)/6-31G* including thermal corrections from HF/6-31G* frequencies].[10] Consequently, based on thermodynamic stability, trimers should exist. While dimers have been proposed to be reactive intermediates in higher oligomerization reactions,[3,8,11,12] and a number of tetramers are known[2b,2c,3,6–9] there is no experimental evidence for thermal trimerization reactions. Experimentally characterized (**B135** derivatives, **D135a**)[17,19] or postulated trimer intermediates (**D125a** and **D135a**)[6] have been generated with metal reagents and detached from the resulting complexes. We localized transition states for [4+2] cycloadditions of HCP to 1,2- (**DP12**) and 1,3-diphosphete (**DP13**) to assess the feasibility of trimer formation in thermal reactions. Because of the high biradicaloid character of the diphosphetes,[21] the transition structures were also optimized at the CAS-SCF(6,6)/6-31G* level. The four π orbitals of the diphosphete molecule and one set of phosphaalkyne π and π* orbitals (oriented towards the phosphete) were included in the active space. Although nondynamical (= static) correlation is important for the theoretical treatment of the diphosphetes, activation barriers (ΔH^{*298}) for HCP addition obtained from MP4 and from MCQDPT2 calculations are very similar (Table 2). As the transition structures are early, static correlation effects seem to cancel when comparison is made to the separated reactants. Optimized geometries are shown in Figures 9 and 10 (CAS-SCF geometries in parentheses) together with activation enthalpies (ΔH^{*298}) and free activation enthalpies (ΔG^{*298}) relative to separated monomer and dimer.

All transition states for the addition of a monomer to a cyclic dimer can be classified as being very early; the separ-

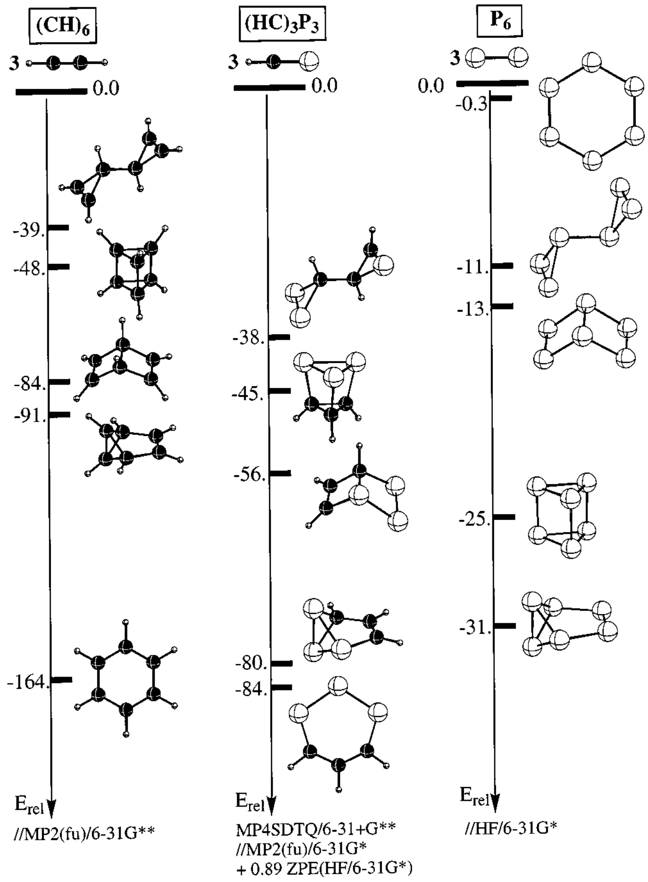
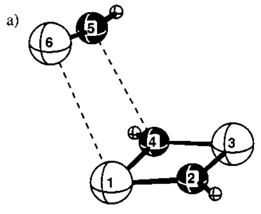


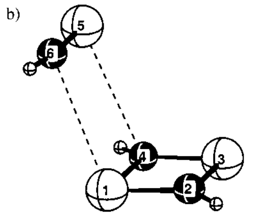
Figure 8. Trimerization energies (in kcal mol^{-1}) of the most stable $(CH)_3P_3$ valence isomers compared with the analogous $(CH)_6$ and P_6 data (taken from ref.[42]) (note the different scaling!)



TS-D125/DP13, C_1, TS (482i cm^{-1})
$\Delta H^{\neq 298}$ = 2.8 (2.1) kcal mol^{-1}
$\Delta G^{\neq 298}$ = 16.2 (13.4) kcal mol^{-1}

distances (Å)		angles (°)	
P1-C2	1.692 (1.710)	P1-C2-P3	99.3 (99.9)
P1-C4	1.910 (1.887)	P1-C4-P3	97.2 (96.1)
P1-P6	3.038 (3.081)	P1-C4-C5	87.5 (97.6)
C2-P3	1.857 (1.816)	P1-P6-C5	83.2 (76.9)
P3-C4	1.693 (1.742)	C2-P1-C4	80.9 (81.2)
C4-C5	2.915 (2.254)	C2-P1-P6	106.0 (104.5)
C5-P6	1.572 (1.569)	C2-P3-C4	82.4 (82.4)
		P3-C4-C5	111.3 (110.9)
		C4-P1-P6	85.2 (74.9)
		C4-C5-P6	104.0 (110.6)
		P6-C5-H	172.2 (151.9)

dihedral angle (°)	
P1-C2-P3-C4	3.6 (5.3)
P1-C4-C5-P6	1.2 (1.2)
C2-P1-C4-C5	-107.0 (-107.0)

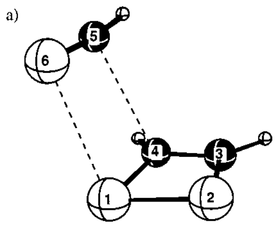


TS-D135/DP13, C_1, TS (345i cm^{-1})
$\Delta H^{\neq 298}$ = 0.8 (1.5) kcal mol^{-1}
$\Delta G^{\neq 298}$ = 11.3 (12.2) kcal mol^{-1}

distances (Å)		angles (°)	
P1-C2	1.699 (1.726)	P1-C2-P3	99.5 (98.8)
P1-C4	1.911 (1.827)	P1-C4-P3	97.7 (97.5)
P1-C6	2.967 (2.416)	P1-C4-P5	86.5 (79.6)
C2-P3	1.869 (1.827)	P1-C6-P5	95.7 (108.7)
P3-C4	1.692 (1.710)	C2-P1-C4	80.8 (80.9)
C4-P5	3.039 (3.046)	C2-P1-C6	107.9 (105.4)
P5-C6	1.568 (1.571)	C2-P3-C4	82.0 (82.7)
		P3-C4-P5	111.6 (111.8)
		C4-P1-C6	86.9 (92.9)
		C4-P5-C6	90.9 (78.3)
		P5-C6-H	174.6 (149.7)

dihedral angles (°)	
P1-C2-P3-C4	2.4 (2.5)
P1-C4-P5-C6	0.6 (0.6)
C2-P1-C4-P5	-109.1 (-108.4)

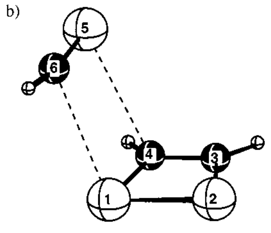
Figure 9. Transition states for [2+4] addition of HCP to 1,3-diphosphete ($C_2H_2P_2$): a) head-to-head (**TS-D125/DP13**) and b) head-to-tail (**TS-D135/DP13**); geometries computed at MP2(fu)/6-31G*, values in parentheses refer to CAS-SCF(6,6)/6-31G* results



TS-D126/DP12, C_1, TS (493i cm^{-1})
$\Delta H^{\neq 298}$ = 3.5 (2.3) kcal mol^{-1}
$\Delta G^{\neq 298}$ = 14.2 (14.2) kcal mol^{-1}

distances (Å)		angles (°)	
P1-P2	2.094 (2.153)	P1-P2-C3	79.2 (78.2)
P1-C4	1.911 (1.873)	P1-C4-C3	100.2 (100.7)
P1-P6	2.955 (2.466)	P1-C4-C5	89.0 (83.9)
P2-C3	1.859 (1.792)	P1-P6-C5	86.8 (86.3)
C3-C4	1.347 (1.349)	P2-P1-C4	77.9 (76.4)
C4-C5	2.688 (2.370)	P2-P1-P6	106.7 (104.6)
C5-P6	1.573 (1.615)	P2-C3-C4	102.6 (104.6)
		C3-C4-C5	111.0 (111.4)
		C4-P1-P6	84.0 (89.8)
		C4-C5-P6	100.2 (99.9)
		P6-C5-H	172.6 (149.8)

dihedral angles (°)	
P1-C2-P3-C4	3.0 (3.4)
P1-C4-C5-P6	-0.5 (-0.5)
C2-P1-C4-C5	-108.3 (-105.1)



TS-D125/DP12, C_1, TS (333i cm^{-1})
$\Delta H^{\neq 298}$ = 2.2 (2.0) kcal mol^{-1}
$\Delta G^{\neq 298}$ = 12.6 (13.1) kcal mol^{-1}

distances (Å)		angles (°)	
P1-P2	2.088 (2.133)	P1-P2-C3	75.5 (77.9)
P1-C4	1.915 (1.868)	P1-C4-C3	100.4 (101.4)
P1-C6	2.802 (2.465)	P1-C4-P5	87.3 (77.2)
P2-C3	1.861 (1.850)	P1-C6-P5	100.0 (111.4)
C3-C4	1.347 (1.351)	P2-P1-C4	77.8 (77.8)
C4-C5	2.951 (3.249)	P2-P1-C6	107.6 (104.7)
C5-P6	1.572 (1.468)	P2-C3-C4	102.2 (102.9)
		C3-C4-P5	111.5 (111.7)
		C4-P1-C6	85.6 (95.4)
		C4-P5-C6	87.0 (75.3)
		P5-C6-H	169.7 (150.2)

dihedral angles (°)	
P1-C2-P3-C4	1.9 (1.8)
P1-C4-C5-P6	-0.8 (-0.8)
C2-P1-C4-C5	-109.5 (109.5)

Figure 10. Transition states for the HCP addition to 1,2-diphosphete ($C_2H_2P_2$): a) head-to-head (**TS-D126/DP12**), b) head-to-tail (**TS-D125/DP12**); geometries computed at MP2(fu)/6-31G*, values in parentheses refer to CAS-SCF(6,6)/6-31G* results

ations between atoms forming bonds are large: *d*(C···C) = 2.68−2.92 Å; *d*(C···P) = 2.80−3.04 Å; *d*(P···P) = 2.96−3.04 Å at MP2. In general, at the CAS-SCF level, the separation between phosphaalkyne and diphosphete is somewhat shorter and the H−C−P angle in the phosphaalkyne deviates more from linearity, but the transition structures can still be characterized as early. Relative energies of the transition states are only a little greater than for three HCP's (Table 2). At the CAS-SCF level the diphosphetes are more stabilized relative to two phosphaalkynes and as a consequence the activation barriers for HCP addition are larger at this level. A head-to-tail approach (**TS-D135/DP13** and **TS-D125/DP12**, formation of C−P bonds) is slightly favored over the head-to-head alternative (**TS-D125/DP13** and **TS-D126/DP12**, C−C and P−P bond formation). At those large separations, electrostatic stabilization of the "anti-parallel" C−P orientation might be responsible. However, the slightly more stable addition products, **D125** and **D126**, have homonuclear bonds.

At the MP2 level, we also localized **TS-D235/DP12** which represents the transition structure for adding HCP to a 1,4-diphosphacyclobuta-1,3-diene (1,2-diphosphete with C=P double bonds). The latter, however, is likely to be an artifact of the MP2 method[22] (and was not reported in the MCSCF study[21]). Consequently, **TS-D235/DP12** may well be an artifact as well. But this transition state is not important since it is considerably (ca. 15 kcal mol^{-1}) higher in energy than the alternatives **TS-D126/DP12** and **TS-D125/DP12**. Another transition state, **TS-D124/DP12**, which was not explored, also should be an artifact. Figure 11 shows the relationships on the ΔG^{298} hypersurface. Although **TS-**

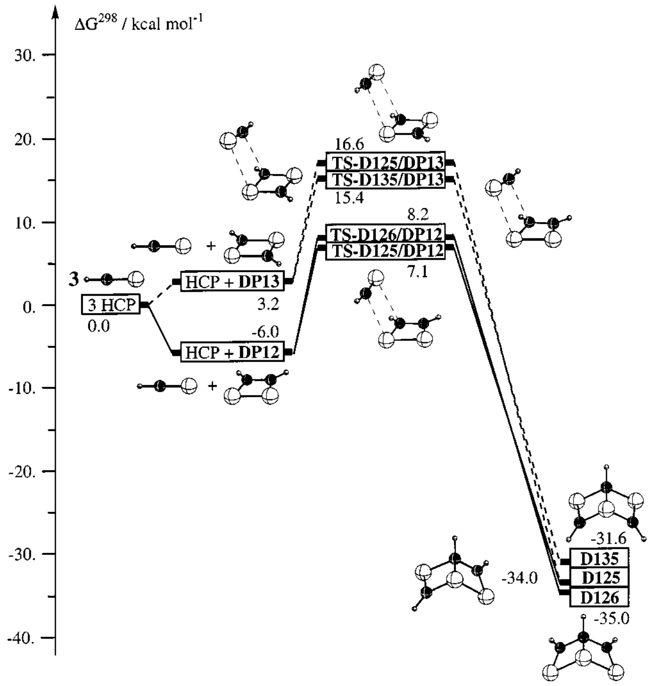


Figure 11. Change in free energy ΔG^{298} for [4+2] cycloadditions of HCP to 1,2- (solid lines) and 1,3-diphosphete (broken lines) relative to three phosphaalkynes – formation of triphospha Dewar benzenes from dimers; relative energies of intermediates and transition states are from MCQDPT2/6-31G*, those of trimeric products from MP4SDQ/6-31+G** calculations, compare Table 2)

D135/DP13 has the lowest ΔG^{*298}, both transition states for HCP addition to **DP12** are lower in energy than those involving **DP13**, since **DP12** is 9.3 kcal mol^{-1} (ΔG^{298} from MP4 calculation) more stable than **DP13**.

Conclusions

The relative energies of the 26 $(CH)_3P_3$ valence isomers investigated here are determined predominantly by the stability of the framework; the hetero atom substitution pattern is less important. Computed geometric parameters do not show unexpected values. The energy order is analogous to that for $(CH)_6$: Phosphorus-substituted benzene isomers are most stable followed by heterocyclic benzvalenes, Dewar benzenes, prismanes, and bicyclopropenyls. The relative energies of most stable isomers for each framework are: 0.0 (**B123**), 4.7 (**V156**), 28.1 (**D123**), 39.8 (**P126**), and 46.8 kcal mol^{-1} (**C235**) at MP4SDTQ/6-31+G**//MP2(fu)/6-31G*. The energies of isomeric heteroatom-substituted benzene, Dewar benzene, and prismane isomers fall within a narrow range (8.9, 6.8, and 3.6 kcal mol^{-1}, respectively) while benzvalene- and biscyclopropenyl-based isomers differ up to 29.1 and 17.3 kcal mol^{-1}, respectively. A spirocyclic HCP trimer (for which there is experimental evidence as a short lived intermediate)[6] has only a small trimerization energy (4.2 kcal mol^{-1}) and is significantly higher in energy (by at least 16.1 kcal mol^{-1}) than the other isomers investigated.

The trimerization energy of three HCPs to 1,2,3-phosphabenzene (−84 kcal mol^{-1}) is almost exactly half way between the corresponding hydrocarbon (−164 kcal mol^{-1} for 3 HCCH → benzene) and the phosphorus trimerization energies (ca. 0 kcal mol^{-1} for 3 $P_2 \rightarrow P_6$, D_{6h}).[42]

Significantly negative NICS values characterize mono-, di-, and triphospha-substituted benzenes as aromatic; all have aromatic, delocalized structures. The aromatic stabilization energies are reduced at most relatively little (up to 4.4 kcal mol^{-1}) by phosphorus heteroatom substitution.

[4+2] Cycloadditions of HCP to 1,2- and 1,3-diphosphete (diphosphacyclobutadiene) have early transition states; head-to-tail (C−P bond formation) additions are favored over the head-to-head approaches. Activation barriers (ΔH^{*298}) are computed to be 2.2 and 0.8 kcal mol^{-1} (ΔG^{*298} = 12.6 and 11.3 kcal mol^{-1}), respectively, from MP4/6-31+G** single points. MCQDPT2/6-31G*//CASSCF(6,6)/6-31G* gives very similar results: 2.0 and 1.5 kcal mol^{-1} for ΔH^{*298} and 13.1 and 12.2 for ΔG^{*298}.

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