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Formation of Phosphaethyne Dimers: A Mechanistic Study

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Abstract: High-level ab initio (CCSD(T), CBS-QB3 and CASSCF, CASPT2, MR-ACPF, MR-ACPF-2) and density functional theory (B3LYP) calculations were carried out to study the dimerization of phosphaacetylene or phosphaethyne (HCP). Seventeen low energy closed-shell and five open-shell phosphaacetylene dimers were found on the potential energy surface. Two head-to-head, one head-to-tail and three other dimerization reaction pathways were determined, all with high activation barriers, suggesting that closed-shell minima are usually kinetically stable. An open-shell head-to-head reaction pathway has also been found with moderate initial barrier (95.0 kJ mol^{-1}) leading to 1,2- and 1,3-diphosphacyclobutadiene, suggesting that polymerization of HCP and oligomerization of its derivatives have open-shell mechanism. Formation of 1,2-diphosphacyclobutadiene is both thermodynamically and kinetically favored over 1,3-diphosphacyclobutadiene. A head-to-head reaction involving LiBr as a catalyst was also studied. It has been pointed out that LiBr catalyze the closed-shell mechanism. All the four possible reaction channels of this reaction yield 1,4-diphosphatriafulvene with a fairly low activation Gibbs-free energy (44.8 kJ mol^{-1}), suggesting that this compound could be synthesized. This finding fully supports the experimental results.

Keywords: ab initio calculations · dimerization · phosphaacetylene · phosphaethyne · triafulvenes

Introduction

Phosphaethyne (H-C≡P), an elusive, highly reactive colorless gas was first observed[1] in 1961 in the low-temperature reaction of phosphine and acetylene. It polymerizes rapidly above −124 °C, and both the monomer and polymer are extremely pyrophoric. Later, the structure of phosphaacetylene was extensively studied both theoretically and experimentally[2–6] According to microwave spectroscopy[2] the C≡P bond length is 1.542 Å, which is significantly shorter than the typical C=P bond (1.67 Å[3a]). The linear shape of the molecule also suggests a pure triple bond between the carbon and phosphorus atoms. The dipole moment of phosphaacetylene[2] (0.39 D) and its ionization energies are much smaller than the corresponding values for hydrogen cyanide, which suggests, that its reactivity is similar to that of the alkynes.[3b] Until the 1990s the existence of an isocyanide-analogue isomer (H-P≡C) of phosphaacetylene was also assumed,[1,3a,4] but the recent high level ab initio calculations[5] and the IR spectra[6] showed that this idea was only a failure of the Møller–Plesset method.

Instead of the first, complicated preparation method, several advanced synthetic ways leading to phosphaacetylene are now known, that are also suitable for preparation of differently stabilized phosphaalkynes,[3a,b] such as *tert*-butylphosphaethyne[7] or (2,4,6-tri-*tert*-butylphenyl)phosphaethyne.[8] Due to their polarity, unsaturation and novel reactivity, these compounds became one of the most important building blocks of the low-coordinated organophosphorus chemistry,[3a,b] While the unsubstituted phosphaacetylene polymerizes rapidly at low temperature, *tert*-butylphosphaethyne, a colorless liquid, can be stored even at room temperature, and oligomerizes only at high temperature. It is interesting to note that in the presence of free radical trapping agent methylphosphaethine can also be stored at room temperature.[9]

Several stable tri- and tetramers synthesized from *tert*-butylphosphaacetylene and other kinetically stabilized deriva-

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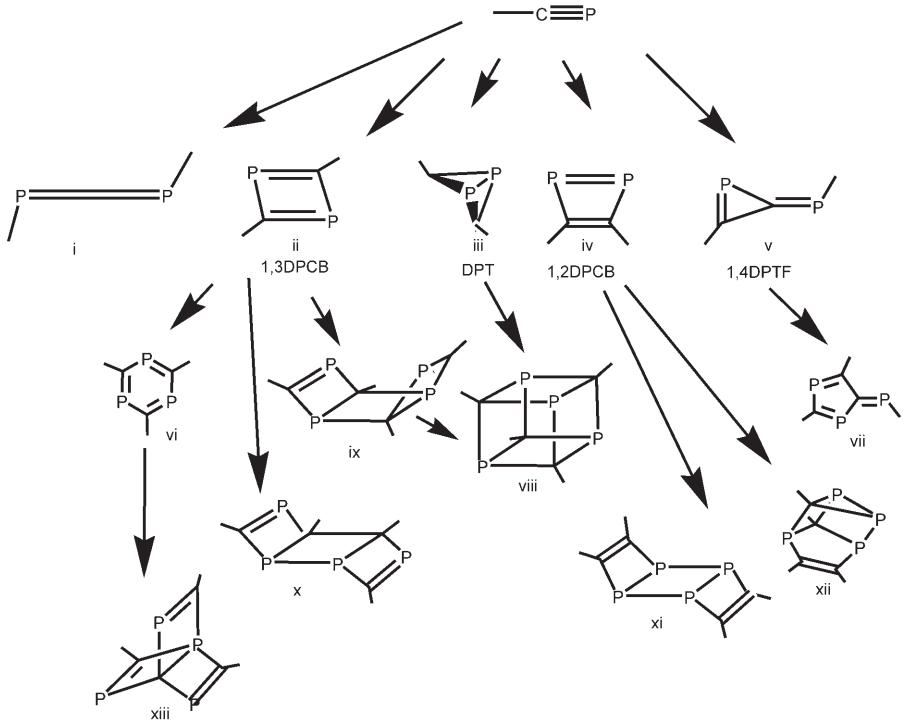
tives are known (Scheme 1). Yoshifuji and co-workers recently synthesized 1,3,6-triphosphafulvene (vii) through the reaction of a phosphaethyne derivative and bis(2,4,6-tri-*tert*-butylphenyl)diphosphene.[10] With the aid of hafnium catalyst, the *tert*-butyl substituted 1,3,5-triphosphinine (1,3,5-triphosphabenzene, vi) was synthesized from *tert*-butyl-phosphaethyne,[11] which is stable at room temperature in the absence of air and water. Further Diels–Alder addition of *tert*-butyl phosphaethyne to 1,3,5-triphosphosphinine yields 1,3,5,7-tetraphosphaberrelene[12,13] (xiii). The catalyzed cyclooligomerization reaction of *tert*-butyl-phosphaethyne yields the thermally stable tetraphosphacubane (viii), whereas some other compounds are also obtained during the reaction (such as xi).[14] Other tetramers have also been synthesized (x and xi)[15] with similar reactions in the presence of transition-metal catalysts.

While tri-, tetra-, penta- and hexamers of substituted phosphaacetylenes are known in their free forms, the only phosphaalkyne dimer prepared thus far is 1,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,4-diphosphatriene[16] (i, Scheme 1.). This is in agreement with the earlier calculations, which pointed out that tri- and tetramers are more stable than the dimers,[15,17] On the other hand, several transition-metal complexes of the dimers have also been synthesized. In those complexes, however, the dimer structures are considerably different from the uncomplexed congeners.

In 1986, two groups independently reported the first successful cyclodimerization reaction of *tert*-butylphosphaethyne which yielded the cobalt, iridium and rhodium complex of 1,3-diphosphacyclobutadiene (DPCB, ii),[18,19] In the following years, several other 1,3-DPCB complexes (such as Fe,[20] Ni,[21] Mo,[22] Ti,[23] Sn,[24] Ge[25]) have been synthesized with the dimerization of *tert*-butylphosphaacetylene in the presence of metal complexes. Successful synthesis of 1,2-diphosphacyclobutadiene complexes (1,2-DPCB, iv) in the coordination sphere of Ti,[26] Ta[27a] and Mo[27b] was achieved, and zirconium and hafnium complexes of 1,3-phosphabicyclo[1.1.0]butadiene (iii) were also prepared,[28,29]

It has been pointed out that 1,2-DPCB and 1,3-DPCB play important roles in the formation of phosphaalkyne tetramers, and the reaction pathways leading to these dimers have been investigated using ab initio calculations.[30,31] It was found that the global minimum of the potential energy surface is diphosphatetrahedrane, but the reaction pathway leading to this compound is kinetically unfavored. According to these calculations, 1,2-DPCB and 1,3-DPCB yield in one-step head-to-head and head-to-tail cycloaddition reactions, respectively. 1,2-DPCB is both kinetically and thermodynamically favored over 1,3-DPCB, and the substituent effect leaves the relative energies almost unchanged.[31] It was shown that in some cases the non-dynamical electron correlation plays an important role in the description of the electronic structure. In the same study[31] the effect of the transition-metal atoms has also been investigated, and in the case of Co complex, the relative stability of the head-to-head versus the head-to-tail dimer is almost unchanged as compared to the uncomplexed compounds, and the expected kinetics also support the formation of a 1,3-DPCB complex. On the other hand, the coordination sphere of the Ti atom induces the formation of both 1,2- and 1,3-DPCB dimers, because several routes from the bis(π-phosphaalkyne) to the diphosphacyclobutadienes seem to be possible.



Scheme 1.

The main goal of the present work was a more through investigation and detailed comparison of the dimerization mechanisms of phosphaacetylene. Our calculations, however, suggested that the potential energy surface (PES) of $(HCP)_2$ is much richer than it was found in previous studies.[30,31] Therefore we first discuss the PES; in the second part the possible dimerization channels are described.

Results and Discussion

Electronic structure of stable phosphaethyne dimers: First we briefly describe the electronic structure and energetics of low-energy minima found on the closed shell $C_2P_2H_2$ potential energy surface. We will discuss only the dimers, which

can be reached by moderate-energy reaction pathways. In contrast to the few HCP dimer structures reported by the previous studies,[15,17,30,31] we found 17 low-energy structures (Figure 1). The numbering in Figure 1 refers to their relative stability, where **1** indicates the most stable isomer (Cartesian atomic coordinates of B3LYP/cc-pVTZ optimized geometries, absolute energies and Gibbs-free energies of low energy minima and transition structures are available in the Supporting Information in Tables S1 and S2). Figure 1 also contains the most important geometrical parameters and the relative Gibbs-free energies, whereas data for transition structures are available in the Supporting Information (see Figure S1) The sum of the Gibbs-free energies of the separated HCP molecules was chosen to the zero point of the scale. Unless mentioned otherwise, the energies and Gibbs-free energies quoted hereafter were calculated at the CBS-QB3 level of theory.

Although previous studies reported that diphosphatetrahedrane (**2**) (Figure 1d) is the global minimum of the potential energy surface,[15,17,30,31] our present calculations suggest that it is only the second most stable structure and 1,2-diphosphatriafulvene (**1**) (Figure 1b) is even more stable by 16.3 kJ mol^{-1}. Two reasons explain the stability of this compound. As shown from the resonance structures of triafulvenes[32] (Scheme 2), the more electronegative the *exo*-double bonded atom the more stable the compound,[33] and it has been pointed out before, that the ring strain has a noteworthy low value in this case.[34]

Interestingly the global minimum of the C_4H_4 (acetylene dimer) potential energy surface is also the triafulvene methylenecyclopropene.[35] This is also an example of the well known concept that phosphorus is the copy of carbon.[3b] The analogy is, however, not fully satisfying, since tetrahedrane is only the third most stable isomer on the acetylene dimer potential energy surface, while diphosphatetrahedrane is the second one in our case.

Figure 1b shows the phosphaacetylene dimers, which contain three-membered rings. Compounds **9** and **10** represent the *E* and *Z* isomers of 1,4-diphosphatriafulvene, which have been proposed as potentially synthesizable targets and important intermediates in the synthesis of 1,3,5-triphosphafulvene.[36] Because of the peculiar electronic structure of this compound we investigated the effect of the correlation level (HF, MP2, MP3, MP4, CCSD, CCSD(T)) and the basis set (6-31+G*,6-311++G(3df,2p) cc-pVDZ, aug-cc-pVDZ, cc-pVTZ). The calculations showed that the optimized geometry is not sensitive to the basis and the level of theory.

As shown on Scheme 2 the molecule exhibits an inverse electron distribution:[42] the electropositive phosphorus atom holds a partially negative charge, therefore its aromaticity and electronic structure are noteworthy problems. The aromatic resonance structure is confirmed by the bond lengths. The ring- and *exo*-phosphorus–carbon (formally) double bonds (1.679 and 1.692 Å, respectively) are longer than the typical phosphorus–carbon double bond (1.667 Å in phosphaethene), and the natural charge of the *exo*-phosphorus atom is 0.28 a.u., while it is 0.41 a.u. in the case of phosphaethene. The charge separation is also indicated by the relatively large dipole moment (2.39 D). It has been pointed out[33] that the NICS values[37] are not applicable in the case of three-membered rings, therefore we used the ΣCC[33] (146 in the case of **9**, while it is only 90 in the case of the non-aromatic cyclophosphapropene and 198 in the case of the fully aromatic cyclophosphapropenyl cation) and Bird indices[38] (25 in the case of **9**) and also the energy of isodesmic reactions to characterize the aromaticity. These calculations show, that (*E*)-1,4-diphosphatriafulvene (**9**) is a partially aromatic compound and compared to 4-phosphatriafulvene, the ring-phosphorus atom decreases the aromaticity.

According to the bond lengths and Wiberg indices, **17** has a very special electronic structure. As suggested by the resonance structures in Scheme 2, **17** is a completely new type of triafulvenes. The left resonance structure contains a λ^3 and a λ^5 phosphorus atom and pure double and triple bonds, whereas the right one is stabilized by the aromatic three-center, two-electron bond. Wiberg indices confirm the existence of these resonance structures: the bond order of the C–C and P–P bond is 1.88 and 2.23, respectively. Moreover, the charge of the formally λ^3 atom is −0.25 a.u., while that of the ring phosphorus is +0.67 a.u., and the valence of the ring phosphorus is 3.95, whereas it is 2.71 for the *exo*-phosphorus atom.

Open-chain phosphaacetylene dimers are displayed in Figure 1a. According to the bond lengths and Wiberg indices, the order of the C–P formally double and triple bonds in compound **4** [(*Z*)-1,4-diphospha-1-ene-3-yne] decreases (Wiberg indices are 1.66 and 2.58 a.u., respectively), while it increases in the C–C bond (Wiberg index: 1.29), which indicates a π-conjugation in this molecule. The isomeric form (*E*)-1,4-diphospha-1-ene-3-yne (**5**) lies 1.9 kJ mol^{-1} above, while 2,4-diphospha-1-ene-3-yne (**3**) has lower free energy by 1.9 kJ mol^{-1} than the *Z* isomer. We did not find low energy reaction pathways leading to these molecules.

Notably from the two possible 1,4-diphosphatrienes (**8** and **11**), the *Z* isomer is more stable. This suggests that the synthesized derivative of **11** is stabilized only kinetically by the huge bulky supermesityl groups.[15] Similar to the carbon analogue butatriene, these compounds are found to be planar.

It has been pointed out in previous studies,[30,31] that **16** represents the first intermediate in the head-to-head [2+2] cycloaddition of the phosphaacetylene. For the closed-shell compound the different methods do not correlate well, therefore we performed high-level single point calculations with aug-cc-pVDZ basis on B3LYP/cc-pVTZ geometry. These results are available in the Table S3 in the Supporting Information. It was found, that the inclusion of the triple excitations in the MP, CC and QC calculations also systematically lowers the energy, and the MP4, QCISD(T), CCSD(T), CCSDT and CBS-QB3 results correlate well. The optimized geometries on B3LYP and CCSD(T) (Tables S4, Supporting Information) are almost the same, therefore we can expect, that all methods give good geometries for closed shell systems, although it is important to incorporate the triple exci-

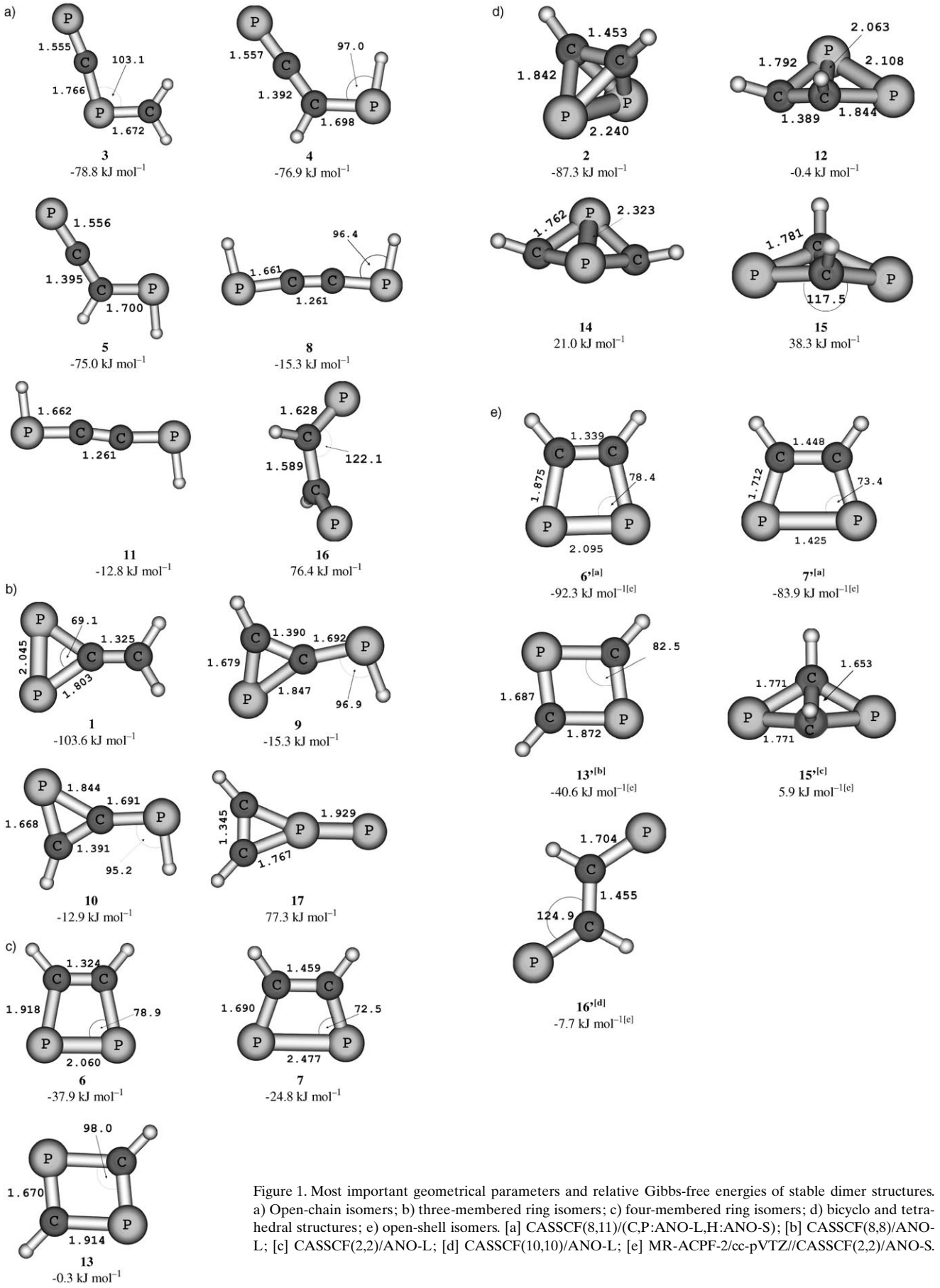
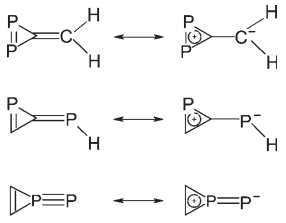


Figure 1. Most important geometrical parameters and relative Gibbs-free energies of stable dimer structures. a) Open-chain isomers; b) three-membered ring isomers; c) four-membered ring isomers; d) bicyclo and tetrahedral structures; e) open-shell isomers. [a] CASSCF(8,11)/(C,P:ANO-L,H:ANO-S); [b] CASSCF(8,8)/ANO-L; [c] CASSCF(2,2)/ANO-L; [d] CASSCF(10,10)/ANO-L; [e] MR-ACPF-2/cc-pVTZ//CASSCF(2,2)/ANO-S.



Scheme 2.

tations to obtain good energy values. Our calculations showed that there are C–P double bonds (Wiberg index is 1.91) and C–C single bond (Wiberg index is 0.91) in this molecule, while the lone-pair-like HOMO is equally distributed between the phosphorus atoms. This suggests a more stable biradical structure. Due to the high spin contamination of the unrestricted DFT and coupled-cluster methods, and the convergence problems in the case of restricted-open shell formalism, we carried out for this structure CASSCF optimization and frequency calculation followed by a single point CASPT2 energy calculation. The (10,10) active space was used which involved all the π and lone-pair electrons, necessary to describe the whole open-shell reaction path. Geometrical parameters of open-shell **16′** (Figure 1e) show that the bond lengths are balanced compared with the closed-shell molecule. In contrast to its closed-shell analogue, **16′** is planar and each phosphorus atom holds an unpaired electron.

As shown in Figure 1c, the 1,2-DPCB dimer has two forms (**6** and **7**), which differ from each other only in the position of the double bonds. In the case of **6** the double bonds are between the two carbon and the two P atoms (the Wiberg indices for the C–C, P–P and C–P bonds are 2.04, 1.97 and 0.97 a.u., respectively), while in the other case **7** are only C–P double bonds (Wiberg indices for the C–C, P–P and C–P bonds are 1.16, 1.06 and 1.79 a.u., respectively). In agreement with the expectations, **6** is more stable than **7** by 13.1 kJ mol^{-1}.

We carried out CASSCF calculations to prove and elucidate the existence of the two different bond stretch isomers of the 1,2-DPCB. For both carbon and phosphorus atoms the large ANO-L basis, while for hydrogen atoms the ANO-S basis was used. The active space involved eight electrons (the π system of the ring and the two lone pairs of the phosphorus atoms) and 11 orbitals ($3a_1$, $2b_1$, $3a_2$ and $3b_2$). In order to prove the sufficiency of this active space, we carried out larger CASSCF calculations up to eight electrons in 21 orbitals. These calculations gave the same occupation numbers for the first 11 orbitals in the active space. The main orbital configurations are available in the Supporting Information (Figure S2). CASSCF optimizations (Figure 1e) show the existence of **6′** and **7′** as two distinct isomers, but according to the bond lengths and the occupation numbers of the active orbitals, there are no pure single and double bonds in these compounds: in the case of **6′**, the occupation number of the orbital belonging to the C–P bonds increases to 0.22 a.u., while those of the C–C and P–P bonds decrease. The character of the bonds, however, does not change. A similar effect occurs in **7′**, but in this case, the double-bond character of the C–C and P–P bonds increases and the double-bond character of C–P bonds decreases. CASPT2 single-point calculations on CASSCF geometries give that **6′** is more stable than **7′** by 19.2 kJ mol^{-1}, which is comparable to the 12.0 kJ mol^{-1} energy gap (without ZPE and thermal corrections) calculated at B3LYP level and 13.1 kJ mol^{-1} at CBS-QB3. MR-ACPF-2 calculations showed that open-shell structures are more stable than the closed-shell.

Formation of the 1,3-diphosphacyclobutadiene[30] (**13**) and its substituted and complexed derivatives[31] has been extensively studied, and its properties and aromaticity have been investigated.[39] According to the bond lengths, this compound contains separated single and double C–P bonds. The +36.2 value of the NICS index and the comparable energy to the separated phosphaacetylene dimers show that this compound is highly antiaromatic. The CASSCF optimized open-shell structure is depicted in Figure 1e. Similarly to the case of the isomers of 1,2-DPCB, bond lengths and therefore bond orders are more balanced in the open-shell compounds than in the closed-shell analogue, and the previous is thermodynamically more stable. It is interesting to note that the 1,3-DPCB dianion is aromatic.[40]

Bicyclic- and tetrahedron-shaped structures are indicated in Figure 1d. Compound **2** represents the well studied diphosphatetrahedrane, which has been proposed as an important intermediate in the oligomerization reactions[3b] of phosphaacetylene; however, no experimental observations are available either in free or in complexed form. According to the Wiberg indices, this compound holds only single bonds, and is thermodynamically very stable.

Dimer **15** is the ring-opened derivative of diphosphatetrahedrane, which has also been proposed as an important intermediate of the oligomerization reactions of phosphaacetylene. We have found a more stable biradical form (Figure 1e), where phosphorus atoms hold the unpaired electrons. Its optimized CASSCF geometry is available on Figure 1e.

Dimerization channels

Head-to-head [2+2] dimerization pathways: As shown in Figure 2a, we found two head-to-head [2+2] dimerization pathways of phosphaacetylene. In this and the following figure the Gibbs-free energies along the reaction channels calculated at CBS-QB3 level are given. Transition structures (TS) are denoted by [A/B] symbols, where A and B represent the numbers of the corresponding isomers (see Figure 1) which are confirmed to be connected by the TS.

In contrast to the previous calculations,[30] reaction pathways consist of additional intermediate compounds and transition structures, which lead to one of the isomers of 1,2-DPCB **6**. Also, there is a head-to-head reaction pathway leading to the 1,3-DBCP **13**.

In both pathways, the first step is the formation of the C–C bond, which leads to the chain-like compound **16**. In

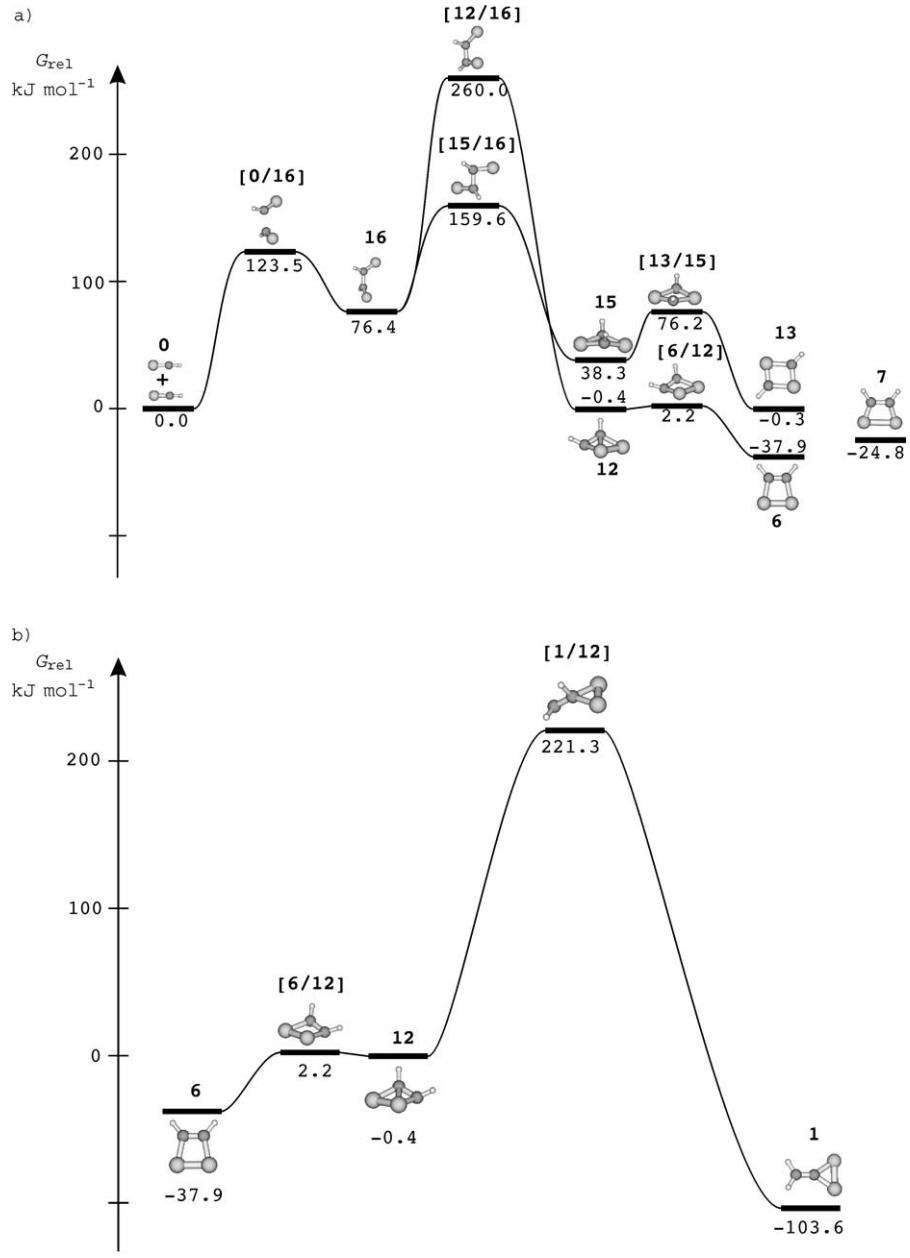


Figure 2. a) Head-to-head [2+2] dimerization pathways; b) head-to-head dimerization pathway (continued).

the next step the reaction pathway splits: one pathway ends up in **13**, whereas another goes to **6**. In both cases the following step is the formation of a bicyclic, bent compound (**12** and **15**), which is followed by a small activation barrier and the formation of the products (**13** and **6**, respectively).

Due to the very large Gibbs-free energy barrier (260 kJ mol^{-1}), the formation of **6** is not favored kinetically. It is, however, thermodynamically stabilized, which suggests that with appropriate catalysts and protective groups, a derivative of **6** may be prepared.

Formation of **13** is somewhat more favored kinetically over **6**, but the activation energy remains also relatively high (159.6 kJ mol^{-1}). The Gibbs-free energy of the compound is only 0.3 kJ mol^{-1} lower than the reactants, which suggests, that **13** or its derivatives could hardly be prepared by a simple dimerization of a phosphaalkyne.

We found only one reaction pathway leading to 1,2-diphosphatriafulvene (**1**) (Figure 2b). Although **1** is the global minimum of the $C_2P_2H_2$ potential energy surface, the reaction pathway involves very high energy barrier corresponding to the hydrogen migration, therefore this compound is not observed experimentally. Other substituents (such as *t*Bu) might migrate more easily, but in this case the steric effect of the substituents on the *exo*-carbon atom causes thermodynamic instability and, moreover, phosphorus atoms become not protected.

Head-to-tail [2+2] dimerization path: Only one possible head-to-tail [2+2] cycloaddition pathway could be found, which is shown in Figure 3. In contrast to the previous calculations,[30] this reaction pathway also contains two steps: the first step is the formation of the C–P bond with a large activation Gibbs-free energy (207.3 kJ mol^{-1}), to the bicyclic-bent **14** compound. A following stabilization of this molecule leads to **13**. This channel involves not only high activation Gibbs-free energy, but also a thermodynamic neutrality and therefore is even less probable than the previously described head-to-head mechanism.

Formation of diphosphatetrahedrane: Figure 4 shows the formation and the possible conversions of diphosphatetrahedrane (**2**). In agreement with previous calculations,[30] this is a one-step reaction with high activation barrier (210.8 kJ mol^{-1}).

We mention here that there exists a second reaction pathway leading to **2** from P_2 and acetylene reactants. Although this reaction pathway is also characterized by a high activation energy (238.7 kJ mol^{-1}), but it opens a chance to synthesize the dimer in a different way.

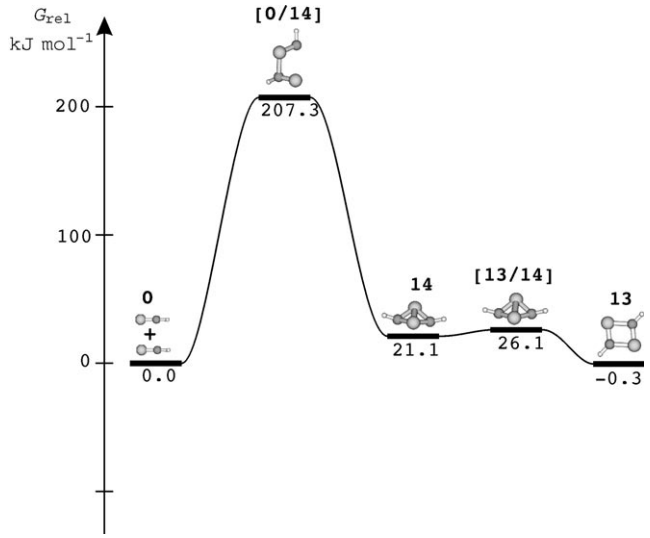


Figure 3. Head-to-tail [2+2] dimerization path.

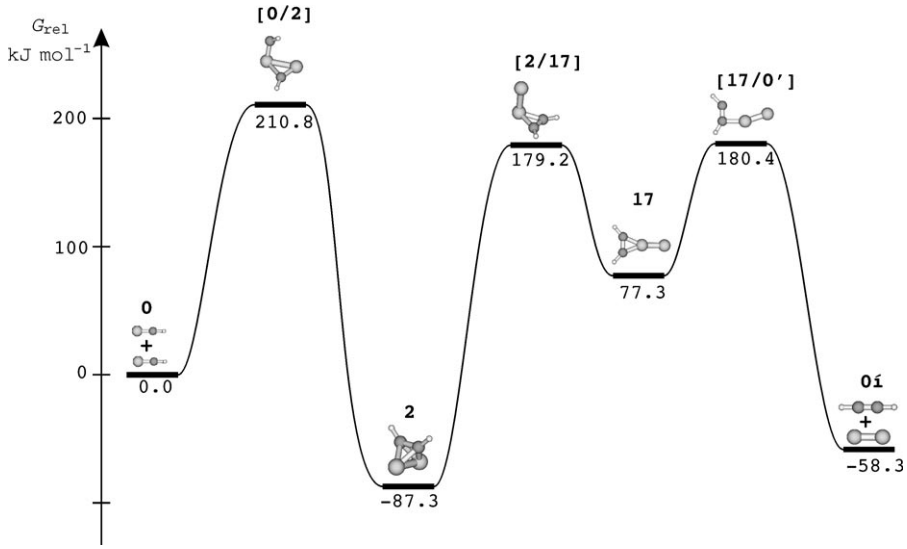


Figure 4. Formation of diphosphatetrahedrane.

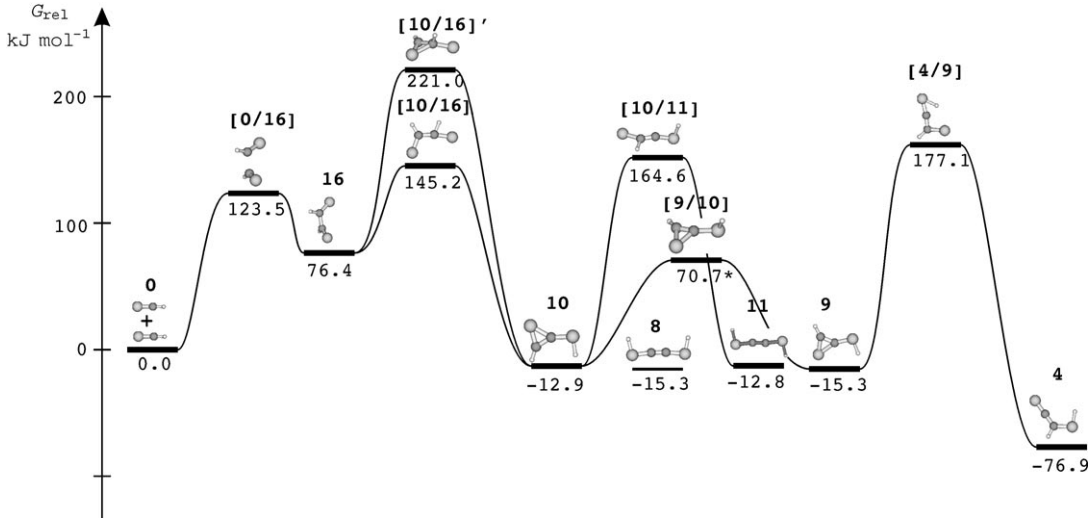


Figure 5. Formation of 1,4-diphosphatriafulvene.

Formation of 1,4-diphosphatriafulvene: Figure 5 shows the reaction pathways leading to the 1,4-diposphatriafulvenes **9** and **10**. The corresponding activation energy (145.2 kJ mol^{-1}) remains high but definitely lower than that in all the previously studied pathways which gives a chance that this reaction pathway may proceed. The stability of 1,4-diphosphatriafulvene suggests that this compound could play an important role in the oligomerization reactions of phosphaacetylene.

The first step of the reaction is the formation of **16**, then two transition states ([**10**/**16**] and [**10**/**16**]′) leading to the same minimum (*Z*)-1,4-diphosphatriafulvene (**10**). However, the hydrogen atoms became rather close to each other in this compound, it is possible that with bulkier substituents the activation energy could become even larger. From **10** to **9** a relative large (83.6 kJ mol^{-1}) isomerization free energy is required. On the other hand, our calculations show that in its protonated form (on the *exo*-phosphorus group) the PH_2^+ group rotates easily (activation energy is only 28.9 kJ mol^{-1}). Therefore it is expected that in acidic solution, protonation may catalyze the formation of the *E* isomer.

Ring-opening reaction with a large activation Gibbs-free energy (164.6 kJ mol^{-1}) of **10** yields 1,4-diphosphatriene (**11**), whereas a similar conversion of **9** leads to **4** ($\Delta G^{\neq}$ = 177.1 kJ mol^{-1}).

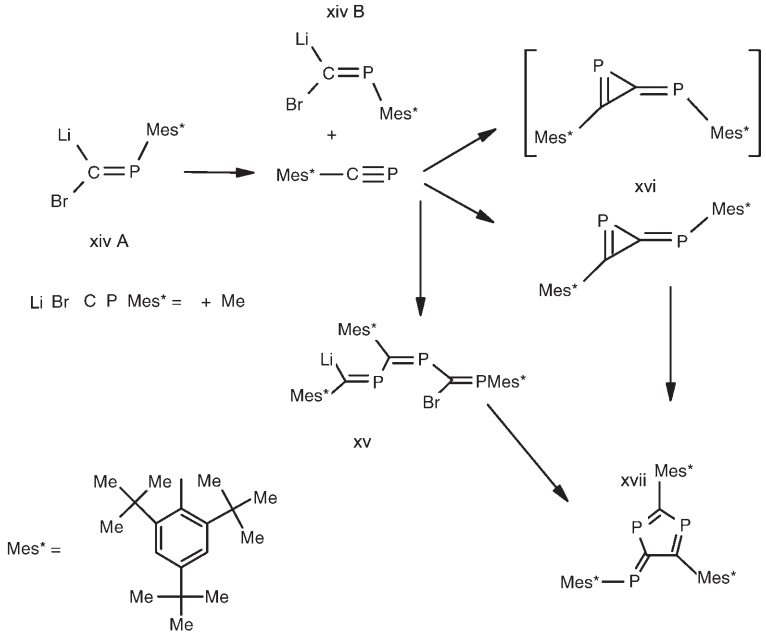
Open-shell reaction pathways: For the open-shell minima and transition structures, due to the biradical character of many intermediates and TSs, the CASSCF(2,2)/ANO-S level of theory has been ap-

plied for geometry optimization, harmonic frequency and for the TSs the intrinsic reaction pathway (IRC) calculation. Subsequent MR-ACPF and MR-ACPF-2 single-point computations (based on CASSCF(2,2) reference wave function) were used for final energy calculations. Calculation of two HCP molecules sufficiently far from each other has been chosen as the zero point of the energy scale.

Potential energy surface calculated on the MR-ACPF-2/cc-pVTZ//CASSCF(2,2)/ANO-S level of theory is depicted in Figure 6 (note that in this case, the relative energy and not the Gibbs-free energy is indicated), while energetic values are available in the Supporting Information.

The first step of the reaction is the formation of **16′** by a head-to-head dimerization. The activation barrier is only 98.9 kJ mol^{-1} (compared with the van der Waals complex), and **16′** is thermodynamically stabilized. In the next step, similarly to the corresponding closed-shell mechanism, the reaction pathway splits: **7′** is forming via very low activation energy (31.3 kJ mol^{-1}), while a pathway through **15′** is leading to **13′**, with the barrier of 141.1 kJ mol^{-1}. However, it is expected that bulkier substituents may cause the enlargement of the **7′**/**16′** barrier, and will cause the destabilization of **7′**. Nevertheless according to these results the polymerization of HCP, and therefore the formation of viii, ix, x and xi in Scheme 1 becomes understandable: the dimerization step inevitably follows an open-shell reaction mechanism.

Reaction pathways with catalyst: In 2000, Yoshifuji and coworkers synthesized[10] the trimer 1,3,5-triphosphafulvene from the LiBr adduct of phosphaalkyne, phosphanylidenecarbenoids (structures xiv A and B). The reaction pathway proposed is shown in Scheme 3. As it can be seen, the first step of the reaction is the LiBr elimination from xivA, yielding a substituted phosphaalkyne, which reacts with xivB (we note here that due to solvation effects LiBr was not really eliminated from xivB). In the next step, the possible reaction pathway is bifurcating: while the preferred channel involves the open chain structure xv, in another way, the appearance of 1,4-diphosphatriafulvene xvi is assumed. Notably alkali halides (e.g. KCl, NaCl, CsCl) are important ingredients of Nieuwland catalysts, which catalyze the dimeriza-



Scheme 3.

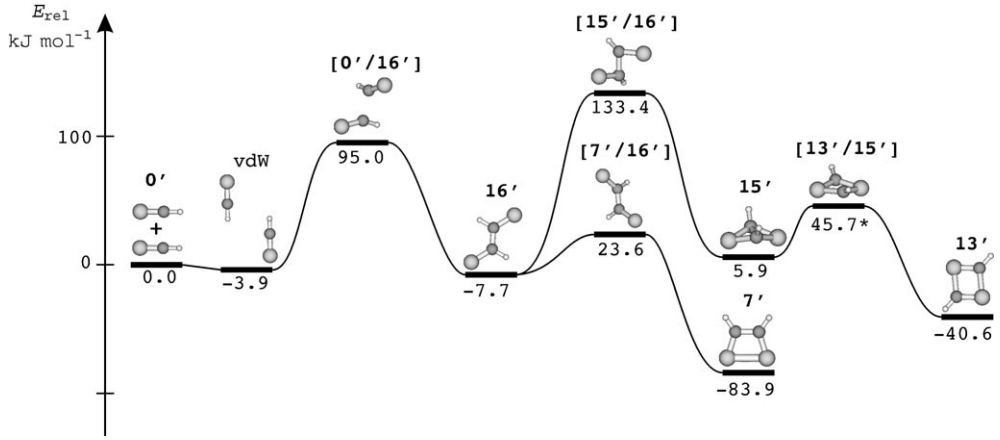
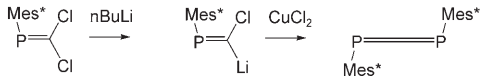


Figure 6. Open-shell head-to-head dimerization reaction pathways calculated on MR-ACPF-2/cc-pVTZ//CASSCF(2,2)/ANO-S level of theory. * Due to convergence problems of ACPF, calculated on CASPT2/CASSCF(2,2)/ANO-S level of theory relative to **15′**.

tion of acetylene.[41] Also, the 1,4-diphosphatriene derivative (Scheme 4) can be synthesized from phosphanylidene carbenoid.



Scheme 4.

On the basis of the above experimental facts, it is expected that LiBr plays the role of a catalyst in the phosphaalkyne dimer formation. Therefore we investigated a model reaction between phosphaacetylene and phosphanylidene carbenoid. Relative energies, Gibbs-free energies and the most important geometrical parameters of equilibrium and transition structures of the reaction pathways are available in the Supporting Information.

The calculated geometry of phosphanylidene carbenoids (**1b** and **1c**) shown in Figure 7 are the model compounds of xivB and xivA, respectively. Bond lengths and calculated total energies of the two compounds differ only marginally, which suggests, that in gas phase, their electronic structure is

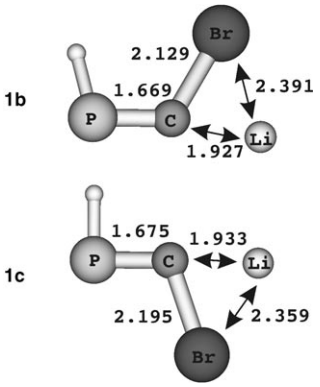


Figure 7. Geometrical parameters of the investigated model-phosphanylidene carbenoids.

the same. An NBO analysis shows that **1b** is fully ionic: lithium has a positive (+0.94 a.u.), while carbon holds negative (−1.01 a.u.) charge. Accordingly, our calculations show that only closed-shell (ionic) reaction pathways exist. The activation barrier of the lithium-bromide elimination from **1b** is $\Delta G^{\neq} = 36.1\ \mathrm{kJ\,mol^{-1}}$, while the reaction is thermodynamically favored ($\Delta G = -170.1\ \mathrm{kJ\,mol^{-1}}$). Similarly LiBr can be eliminated from **1c** ($\Delta G^{\neq} = 20.1\ \mathrm{kJ\,mol^{-1}}$, $\Delta G = 163.7\ \mathrm{kJ\,mol^{-1}}$), which points out, that in the gas phase model compounds, LiBr eliminates easily from both isomers (PES is available in the Supporting Information).

The initial step of both catalyzed and uncatalyzed dimerization reactions is similar (Figure 8a), except that the activation energy of the catalyzed reaction is much smaller ($44.8\ \mathrm{kJ\,mol^{-1}}$), and the first intermediate **26** is more stable than in the uncatalyzed dimerization of HCP. In the next step, the reaction pathway splits into four different channels as shown in Figure 8b and c. Energies and geometrical parameters of the equilibrium and transition structures of the calculated reaction pathways are available in the Supporting Information (Table S5 and Figures S3 and S4).

In Figure 8b two reaction channels are shown, which lead to (*Z*)-1,4-diphosphacyclobutadiene. In the first mechanism **27** is formed from **26** by a rotation over carbon–carbon axis, which is followed by a concerted ring closure and LiBr elimination. In the second channel, a four-membered ring **22** is formed first and a triafulvene is obtained by interconversion. Interestingly 1,2-DPCB can also be prepared from **22** by a LiBr elimination and a hydrogen migration or a double proton transfer reaction.

The reaction pathways of Figure 8c yield (*E*)-1,4-diphosphatriafulvene. Both channels involve a hydrogen shift (**26**/**28** and **22**/**23**) with a fairly high activation free energy (101.48 and $103.5\ \mathrm{kJ\,mol^{-1}}$, respectively), but when considering the whole scheme, the barriers are lying below or slightly higher than the reference level. In the other words, in all the four reaction pathways the dimerization seems to be an accessible process. The rate determining first step requires only $44.8\ \mathrm{kJ\,mol^{-1}}$ activation energy, much lower than that in any noncatalyzed pathway.

A head-to-tail reaction pathway leading to 1,4-diphosphatriafulvene with a moderate activation energy ($\Delta G^{\neq} = 64.7\ \mathrm{kJ\,mol^{-1}}$) has been also found. This intermediate appears to play an important role in the formation of 1,3,5-triphosphafulvene.

Methods of Calculations

Calculations were performed using the Gaussian 03,[42] Aces II,[43] Molcas 6.0[44] and AMICA[45] quantum chemical program packages. Geometries were optimized and harmonic vibrational frequencies, ZPE and thermal corrections were calculated generally with the popular B3LYP[46] hybrid functional with 6-31+G* and cc-pVTZ basis sets. The cc-pVTZ basis set for lithium and for the AMICA calculations was taken from the EMSL basis set library.[47] On B3LYP/cc-pVTZ optimum CCSD(T)/aug-cc-pVDZ single-point calculations were performed to determine the accuracy of DFT calculations. To check the reliability of the level of theory applied, in some cases we investigated the effect of the correlation level (HF, MP2, MP3, MP4, CCSD, CCSD(T)) and the basis set (6-31+G*, 6-311++G(3df,2p) cc-pVDZ, aug-cc-pVDZ, cc-pVTZ). To investigate the non-dynamical electron correlation, for selected systems CASSCF and CASPT2 calculations were carried out with the ANO-S and ANO-L basis. For final energy and free energy calculations, the CBS-QB3[48] method was used. In all cases frequency analysis was performed and, for transition states, the existence of only one imaginary frequency was checked. IRC calculations were performed for all the pathways at the B3LYP/cc-pVTZ level to confirm the reaction coordinates from transition states to stable products.

Sample calculations showed that typical basis set superposition error was around $1.6\ \mathrm{kJ\,mol^{-1}}$ (calculated for **13**), and BSSE was important only in the first step of the mechanisms. Therefore relative energies and Gibbs-free energies did not involve the BSSE corrections. For open-shell systems complete active space SCF (CASSCF) optimization and subsequent second order perturbation (CASPT2) and multi-reference averaged coupled pair functional (MR-ACPF[49] and MR-ACPF-2[50]) single-point calculations were carried out. The latter two methods were size extensive, and according to previous calculations, they regarded as "probably the

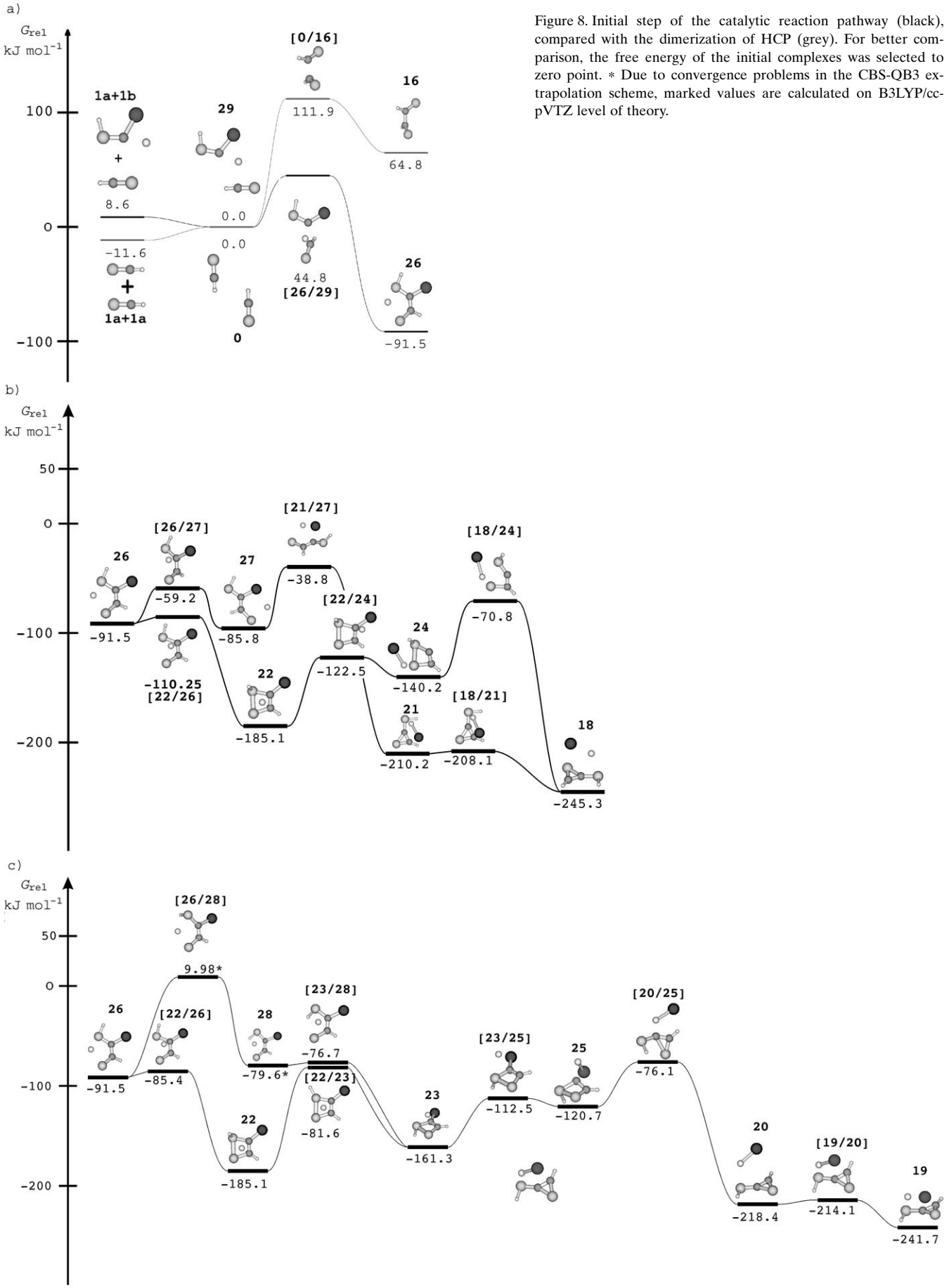


Figure 8. Initial step of the catalytic reaction pathway (black), compared with the dimerization of HCP (grey). For better comparison, the free energy of the initial complexes was selected to zero point. * Due to convergence problems in the CBS-QB3 extrapolation scheme, marked values are calculated on B3LYP/cc-pVTZ level of theory.

most successful method to approximate full configuration interaction (CI) on multi reference (MR) level of theory".[50] Molecules were visualized with the Molden 4.0 visualization program.[51]

Conclusion

Dimerization of phosphaacetylene has been studied using various quantum chemical methods, including B3LYP, CCSD(T), CBS-QB3 and CASSCF, CASPT2, MR-ACPF and MR-ACPF-2. In total 17 low energy closed-shell and two open shell phosphaacetylene dimers have been found on the potential energy surface and the electronic structures were carefully determined. It has been pointed out that the two mesomeric 1,2-diphosphacyclobutadienes were separated minima on the potential energy surface, even with high-level ab-initio methods. Moreover, a new type of triafulvene **17** has been found, where phosphorus is attached by a triple bond to an unsaturated ring. Two head-to-head, one head-to-tail and three other dimerization reaction pathways were found, all with high activation barriers. This suggests that different equilibrium states of $C_2P_2H_2$ potential energy surface are usually kinetically stable. It has been pointed out that LiBr plays the role of catalyst in the closed-shell reaction path, and the activation energy of the first step is fairly low (only 44.8 kJ mol^{-1}). All the four possible reaction channels of this reaction yields 1,4-diphosphatriafulvene with a fairly low activation Gibbs-free energy. This result (together with the thermodynamic and kinethic stability of 1,4-diphosphatriafulvene) indicates that reactions from substituted phosphanylidene carbenoid via 1,4-diphosphatriafulvene are accessible processes. An open-shell head-to-head reaction pathway has been found with 98.9 kJ mol^{-1} activation barrier leading to 1,2- and 1,3-diphosphacyclobutadiene, indicating that in contrast to the previous studies, polymerization of HCP, and tetramerization of *t*Bu-phosphaethyne (yielding derivatives of tetraphosphacubane and other tetramers) follows open-shell reaction path. While the dimerization of HCP follows head-to-tail mechanism (yielding **7′**), bulky substituents can cause the enlargement of its activation energy, and both head-to-head and head-to-tail is possible.

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[1] T. E. Gier, *J. Am. Chem. Soc.* **1961**, *83*, 1769.
[2] K. Tyler, *J. Chem. Phys.* **1964**, *40*, 1170.
[3] a) M. Regitz, O. J. Scherer, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme, Stuttgart, **1990**; b) K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, **1998**.
[4] a) J. N. Murrell, S. Carter, L. O. Halonen, *J. Mol. Spectrosc.* **1982**, *93*, 307; b) M. T. Nguyen, *Z. Naturforsch.* **1984**, *39*, 169; c) M. T. Nguyen, T. K. Ha, *J. Mol. Struct.* **1986**, 139, 145; d) E. Goldstein, S. Jin, M. R. Carrillo, R. J. Cave, *J. Comput. Chem.* **1993**, *14*, 186.
[5] C. Beck, R. Schinke, *J. Chem. Phys.* **2000**, *112*, 8446.
[6] M. Jung, B. P. Winnewisser, M. Winnewisser, *J. Mol. Struct.* **1997**, *413*, 31.
[7] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch. B* **1982**, *36*, 16.
[8] a) M. Yoshifuji, I. Shima, N. Inamoto, *J. Am. Chem. Soc.* **1981**, *103*, 4587; b) M. Yoshifuji, T. Niitsu, N. Inamoto, *Chem. Lett.* **1988**, 1733.
[9] J.-C. Guillemin, J. M. Denis, *J. Org. Chem.* **2001**, *66*, 7864.
[10] a) S. Ito, H. Sugiyama, M. Yoshifuji, *Angew. Chem.* **2000**, *112*, 2892; *Angew. Chem. Int. Ed.* **2000**, *39*, 2781; b) M. Yoshifuji, S. Ito, H. Sugiyama, *Phosphorus Sulfur Silicon Relat. Elem.* **2001**, *168*, 315.
[11] P. Binger, S. Leininger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann, C. Krüger, *Angew. Chem.* **1995**, *107*, 2411; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2227.
[12] P. Binger, G. Glaser, B. Gabor, R. Mynott, *Angew. Chem. Int. Ed. Engl.* **1995**, *107*, 114; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 81.
[13] S. M. Bachrach, P. Magdalinos, *J. Mol. Struct. THEOCHEM* **1996**, *368*, 1.
[14] a) T. Wettling, J. Schneider, O. Wagner, C. G. Kreiter, M. Regitz, *Angew. Chem.* **1989**, *101*, 1035; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1013; b) A. Mack, M. Regitz, *Chem. Ber.* **1997**, *130*, 823.
[15] B. Geissler, S. Barth, U. Bergsträsser, M. Slany, J. Durkin, P. B. Hitchcock, M. Hofmann, P. Binger, J. F. Nixon, P. von R. Schleyer, M. Regitz, *Angew. Chem.* **1995**, *107*, 485; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 484.
[16] S. Ito, K. Toyota, M. Yoshifuji, *Chem. Lett.* **1995**, 747.
[17] M. Hofmann, P. R. Schleyer, M. Regitz, *Eur. J. Org. Chem.* **1999**, 3291.
[18] P. B. Hitchcock, M. J. Naah, J. F. Nixon, *J. Chem. Soc. Chem. Commun.* **1986**, 737.
[19] a) P. Binger, R. Milczarek, R. Mynott, M. Regitz, W. Rosch, *Angew. Chem.* **1986**, *98*, 645; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 644; b) P. Binger, R. Milczarek, R. Mynott, C. Kruger, Y. H. Tasy, E. Raabe, M. Regitz, *Chem. Ber.* **1988**, *121*, 637.
[20] a) M. Driess, D. Hu, H. Pritczkow, H. Schäuffele, U. Zanneck, M. Regitz, W. Rösch, *J. Organomet. Chem.* **1987**, *C35*, 334; b) P. Binger, B. Biedenbach, R. Schneider, M. Regitz, *Synthesis* **1980**, 960.
[21] T. Wettling, G. Wolmerhäuser, P. Binger, M. Regitz, *J. Chem. Soc. Chem. Commun.* **1990**, 1541.
[22] P. B. Hitchcock, M. J. Maah, J. F. Nixon, M. Green, *J. Organomet. Chem.* **1994**, *466*, 153.
[23] a) P. Binger, G. Glasre, S. Albus, C. Krüger, *Chem. Ber.* **1995**, *128*, 1261; b) P. Binger, G. Glaser, J. Stannek, *Phosphorus Sulfur Silicon Relat. Elem.* **1996**, *149*, 109.
[24] M. D. Francis, P. B. Hitchcock, *Chem. Commun.* **2002**, 86.
[25] G. Anderson, J. C. Green, M. D. Francis, *Organometallics* **2003**, *22*, 2897.
[26] a) P. Binger, G. Glaser, J. Stannek, *Phosphorus Sulfur Silicon Relat. Elem.* **1996**, *149*, 109; b) P. Binger, G. Glaser, S. Albus, C. Krüger, *Chem. Ber.* **1995**, *128*, 1261.
[27] a) A. D. Burrows, A. Dransfeld, M. Green, J. C. Jeffery, C. Jones, J. M. Lynam, M. T. Nguyen, *Angew. Chem.* **2001**, *113*, 3321; *Angew. Chem. Int. Ed.* **2001**, *40*, 3221; b) A. D. Bunows, N. Carr, M. Green, J. M. Lynam, M. F. Mahon, M. Murray, B. Kiran, M. T. Nguyen, C. Kones, *Organometallics* **2002**, *21*, 3076.
[28] P. Binger, B. Biedenbach, C. Krüger, M. Regitz, *Angew. Chem.* **1987**, *99*, 764; *Angew. Chem. Int. Ed. Engl.* **1987**, *99*, 798.
[29] T. Wettling, B. Geissler, R. Schneider, S. Barth, P. Binger, M. Regitz, *Angew. Chem.* **1992**, *104*, 761; *Angew. Chem. Int. Ed. Engl.* **1992**, *104*, 758.
[30] M. T. Nguyen, L. Landuyt, L. G. Vanquickenborne, *J. Org. Chem.* **1993**, *58*, 2817.
[31] S. Creve, M. T. Nguyen, L. G. Vanquickenborne, *Chem. Ber.* **1992**, 1281.
[32] E. Fuchs, B. Breit, H. Hezdt, W. Schoeller, T. Busch, C. Krüger, P. Betz, M. Regitz, *Chem. Ber.* **1991**, *124*, 2843.

[33] T. Veszprémi, M. Takahashi, B. Hajgató, J. Ogasawa, K. Sakamoto, M. Kira, *J. Phys. Chem. A* **1998**, *102*, 10530.
[34] A. Skancke, J. F. Liebman, *J. Org. Chem.* **1999**, *64*, 6361.
[35] B. S. Jursic, *J. Mol. Struct.* **2000**, 507, 185.
[36] XV. International Conference of Phosphorus Chemistry Sendai (Japan), **1999**, Book of Abstracts, p. 173.
[37] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.
[38] a) C. W. Bird, *Tetrahedron* **1985**, *41*, 1409; b) C. W. Bird, *Tetrahedron* **1986**, *42*, 89; c) C. W. Bird, *Tetrahedron* **1987**, *43*, 4725; d) C. W. Bird, *Tetrahedron* **1990**, *46*, 5697.
[39] a) L. Nyulászi, T. Veszprémi, *J. Phys. Chem.* **1996**, *100*, 6456; b) W. W. Schoeller, T. Busch, *Angew. Chem.* **1993**, *105*, 635; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 617.
[40] a) W. W. Schoeller, C. Bergman, E. Niecke, D. Gudat, *J. Phys. Chem. A* **2001**, *105*, 10731; b) R. A. J. Janssen, *J. Phys. Chem.* **1993**, *97*, 6384.
[41] K.-i. Nishiwaki, M. Kobayashi, T. Takeuchi, K. Matuoto, K. Osakada, *J. Mol. Catal. A* **2001**, *175*, 73.
[42] Gaussian 03 (Revision C.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
[43] ACES II is a program product of the Quantum Theory Project, University of Florida, J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. A. Kucharski, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K. K. Baeck, P. Rozyczko, H. Sekino, C. Hober, R. J. Bartlett.
[44] G. Karlström, R. Lindh, P.-Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, L. Seijo, *Comput. Mater. Sci.* **2003**, 28, 222.
[45] R. J. Gdanitz, AMICA ("Atoms and Molecules In Chemical Accuracy") suite of r12-MRCI programs, unpublished, **1997**. AMICA is distributed freely through the Internet site http://gdanitz.hec.utah.edu/amica.
[46] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *41*, 785.
[47] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04.
[48] a) J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **2000**, *112*, 6532; b) J. A. Montgomery Jr, M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **1999**, *110*, 2822.
[49] R. J. Gdanitz, R. Ahlrichs, *Chem. Phys. Lett.* **1988**, *143*, 413.
[50] R. J. Gdanitz, *Int. J. Quantum Chem.* **2001**, *85*, 281.
[51] "Molden: a pre- and post-processing program for molecular and electronic structures": G. Schaftenaar, J. H. Noordik, *J. Comput. Aided Mol. Des.* **2000**, *14*, 123.

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