

Guy Bertrand,<sup>\*a</sup> Wolfgang Eisfeld,<sup>b</sup> László Nyulászi,<sup>\*b,c</sup> Régis Reau,<sup>a</sup> Manfred Regitz<sup>\*b</sup> and Dénes Szieberth<sup>c</sup>

<sup>a</sup> Laboratoire de Chimie de Coordination du CNRS, Toulouse CEDEX, France

<sup>b</sup> Fachbereich Chemie, Universität Kaiserslautern, D-67663 Kaiserslautern, Erwin-Schrödinger Strasse, Gebaude Nr 54, Germany

<sup>c</sup> Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest, Gellért tér 4, Hungary

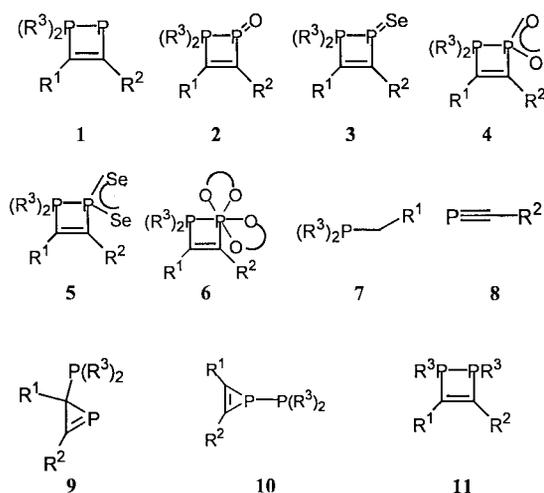
Received (in Cambridge, UK) 13th March 2000, Accepted 10th August 2000

First published as an Advance Article on the web 9th October 2000

The mechanism of the formation of  $\sigma^2\text{P}$ ,  $\sigma^4\text{P}$ -1,2-diphosphetes from phosphaacetylene and phosphinocarbene has been explored by quantum chemical methods. A stepwise mechanism has been established, and no transition state for a concerted pathway could be obtained. The electron distribution of the ring can be understood in terms of a MO model, where the two substituents at phosphorus act as a pseudo  $\pi$  center. Amino substituents on the  $\sigma^4$  phosphorus and silyl group on the neighbouring carbon change the stability order of the possible isomers, stabilizing the 1,2-diphosphete ring. Substitution at the  $\sigma^2\text{P}$ —by increasing its valence—destabilizes the diphosphete ring, which remains stable only as a result of the amino and silyl substituents.

## Introduction

The mixed valence diphosphetes **1a–6a** (Scheme 1) have



- a:  $\text{R}^1=\text{Me}_3\text{Si}$ ,  $\text{R}^2=\text{tBu}$ ,  $\text{R}^3=(\text{iPr})_2\text{N}$   
 b:  $\text{R}^1=\text{H}$ ,  $\text{R}^2=\text{H}$ ,  $\text{R}^3=\text{H}$   
 c:  $\text{R}^1=\text{H}$ ,  $\text{R}^2=\text{H}$ ,  $\text{R}^3=\text{H}_2\text{N}$   
 d:  $\text{R}^1=\text{H}_3\text{Si}$ ,  $\text{R}^2=\text{H}$ ,  $\text{R}^3=\text{H}$   
 e:  $\text{R}^1=\text{H}_3\text{Si}$ ,  $\text{R}^2=\text{H}$ ,  $\text{R}^3=\text{H}_2\text{N}$

Scheme 1

recently been synthesized, and an unexpected stability of the P–P bond in these four-membered ring systems has been found.<sup>1,2</sup> The electronic structure of the parent  $1\sigma^4, 2\sigma^2$  diphosphete has been described as a zwitterionic system, with a  $4\pi$ -electron delocalization over the  $\sigma^2$  phosphorus and the two carbon atoms.<sup>2</sup>

**1a** was obtained by reacting the photochemically generated **7a** with **8a**.<sup>2</sup> **9a–11a** were obtained<sup>3</sup> as intermediates and by-products, indicating a stepwise mechanism. The calculation of the relative stability of the unsubstituted model compound **1b** and its isomers **9b–11b** revealed that **1b** is the least stable while **11b** is the most stable among them.<sup>3</sup>  $\text{NH}_2$  substitution at the  $\sigma^4$

phosphorus, however, changes the stability order (**1c** being more stable than **9c**),<sup>3</sup> while **11c** remains the most stable isomer. For the transition state between **1c** and **11c** a barrier of 20 kcal mol<sup>-1</sup> was calculated, which was considered to be in acceptable agreement with the observation of both **1a** and **11a**.<sup>3</sup>

In the present paper the following questions are investigated: Do calculations support the reaction mechanism which was supposed on the basis of the observed<sup>3</sup> intermediates? Do other reaction pathways exist? What is the electronic structure of the diphosphete ring? Is there any extra stabilizing effect in the ring? What is the role of the amino and the silyl substituents in the stability of the ring? How do the other substituents (O, Se) in **2a–6a** influence the stability?

## Computational details

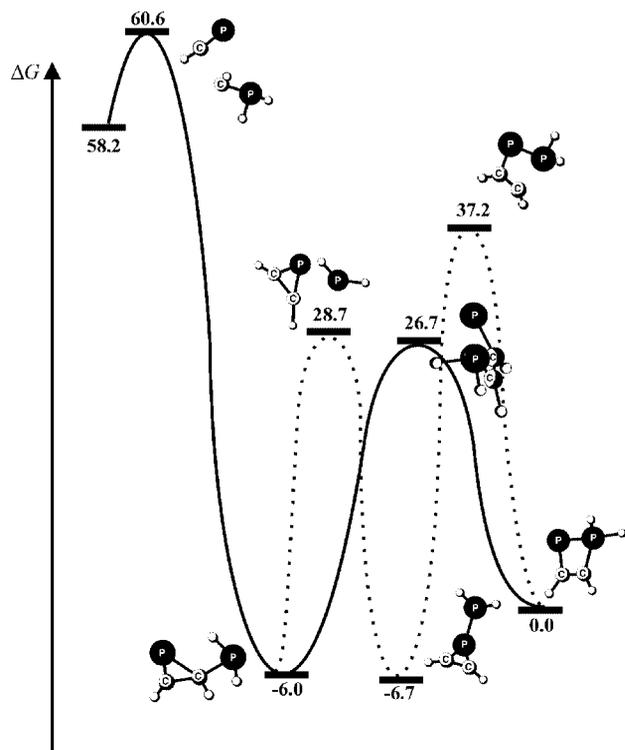
Calculations were carried out using the GAUSSIAN94<sup>4</sup> program package, at the MP2/6-31+G\* level of theory. For the unsubstituted minima the calculations were repeated at higher levels of theory (up to CCSD(T)/6-311+G(2D)//MP2/6-311+G(2D)). In order to check whether the choice of the method and basis set used for geometry optimization has an impact on the relative energies, B3LYP/6-311+G\*\*//B3LYP/6-311+G\*\* calculations were carried out as well using the GAUSSIAN98<sup>5</sup> package. Neither increasing the basis set, nor changing the methods used for the geometry optimizations or energy calculations changed the MP2/6-31+G\* energy ordering of **1b**, **9b–11b**. The reactants, intermediates and products were confirmed as minima on the PES by second derivative calculations. Transition structures were characterized by one imaginary frequency. Transition states were connected to the corresponding minima with the help of IRC calculations. The energies given throughout are ZPE corrected. The Gibbs free energy values given in Fig. 1 for the reaction path were obtained at 298 K.

## Results and discussion

As calculations on the original substituted compounds (**1a**, **7a–11a**) would be prohibitively expensive, for estimating the effects of the substituents involved in the synthesis 'Bu groups of **1**

**Table 1** Relative energies (MP4/6-31+g\*/MP2/6-31+g\* + ZPE) with respect to the starting materials and stabilization energies (see text) compared to the parent compounds (in kcal mol<sup>-1</sup>)

Substituent pattern	9	10	1	11
b	-64.3/—	-60.8/—	-52.7/—	-81.0/—
c	-62.0/2.3	-53.8/7.0	-62.2/-9.5	-80.7/0.3
d	-57.7/6.6	-62.0/-1.2	-52.6/0.1	-78.3/2.7
e	-55.1/9.2	-52.6/8.2	-60.3/-7.6	-75.1/5.9

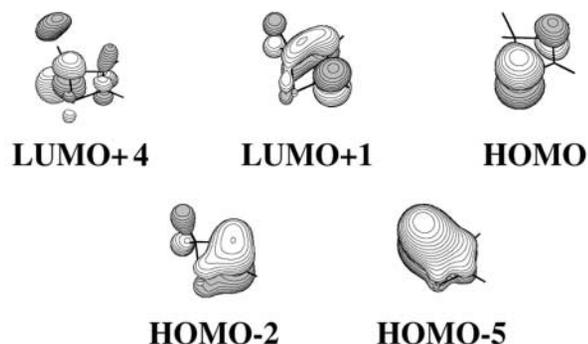


**Fig. 1** Reaction pathway calculated at the MP2/6-311+G(2D) level of theory. Gibbs free energy values are given in kcal mol<sup>-1</sup> with respect to the reactants.

were substituted with H, the (iPr)<sub>2</sub>N groups with NH<sub>2</sub> and Me<sub>3</sub>Si groups with H<sub>3</sub>Si in four different substitution patterns (Scheme 1 b-e). The effect of tetrachloro-*o*-benzoquinone groups in **6** was modeled with four OH groups.

To clarify the role of the intermediates found experimentally<sup>3</sup> in the course of the synthesis of **1a**, first the transition states were located between the unsubstituted **1b**, **9b**, **10b** and the precursors **7b** and **8b**. As was expected on the basis of experimental findings,<sup>3</sup> no transition state linking the precursors directly with **1b** could be found. Minima **1b**, **9b** and **10b** can be connected *via* two stepwise reaction pathways (Fig. 1). The transition state connecting **10b** with **1b** (TS<sup>10b-1b</sup>) is substantially higher in energy than TS<sup>10b-9b</sup>. Consequently the reaction path *via* **10** (dashed line in Fig. 1) is unlikely. The high energy of TS<sup>10b-9b</sup> is in accordance with the experimental fact that no **1** has been obtained from **10**.<sup>3</sup> Thus, **9b** is the only intermediate in the reaction path (shown by the continuous thick line in Fig. 1) in agreement with the conclusions from the earlier experimental study.<sup>3</sup>

It has already been noted that amino substituents stabilize **1** relative to the other isomers involved in the reaction.<sup>3</sup> However, nothing is known as yet about the role of the silyl group, or the possible synergetic effect between the amino and the silyl substituents. Table 1 displays the relative energies of **1**, **9-11** vs. the starting materials (**7** + **8**) as well as the stabilization energies with respect to the parent compounds. (The term stabilization energy denotes the change between the energy of the isomers with respect to the parent compounds as a result of the substitution.)



**Fig. 2** Orbitals of **1b** calculated at the HF/6-311+G(d, p)//B3LYP/6-311+G(d, p) level of theory.

In the unsubstituted and NH<sub>2</sub> substituted cases the energy ordering of the isomers is the same as those published in the earlier study based on DFT calculations.<sup>3</sup> However, the energy difference between **9c** and **1c** is much smaller at the higher level used in the present study. Silyl substitution has a small stabilizing effect on **10**, while it destabilizes all the other isomers. The effect is the most pronounced on **9**, while it is very small on **1**. The cooperative effect of the NH<sub>2</sub> and the SiH<sub>3</sub> substitution is slightly larger than expected on an additivity basis, resulting in an overall destabilization of **9-11** relative to **1**. Thus, besides the amino groups silyl substitution also has considerable influence on the stability of **1**, contrary to the presumptions of the earlier study.<sup>3</sup>

From the first step of the reaction mechanism shown in Fig. 1 a nucleophilic carbene-like reactivity of HCPH<sub>2</sub> can be concluded. Such reactivity has been observed for the phosphino-carbenes before.<sup>6</sup> It has been noticed, however, that while HCPH<sub>2</sub> has a carbene-like electronic structure, H<sub>3</sub>SiCP(NH<sub>2</sub>)<sub>2</sub> has considerable triple bond character, with short C-P bonds and a 138° SiCP angle.<sup>7</sup> Since in the case of triple bonds cycloaddition reactions can be of importance we searched for a concerted transition state between HCP and H<sub>3</sub>SiCP(NH<sub>2</sub>)<sub>2</sub>. As in the case of HCPH<sub>2</sub>, no such first order saddle point has been found.

In order to gain a more detailed insight into the nature of the bonding and the effect of the substituents on **1**, some selected bond lengths and electron density related parameters as well as Wiberg bond indices were compiled in Table 2 for compounds **1-6**. In **1b** the P-P bond is significantly shorter than a usual P-P single bond, but it is longer than a double bond (reference bonding characteristics of some single and double bonded compounds are collected in Table 3), showing a partial double bond character. The comparison of the electron densities at the bond critical point ( $\rho$ )<sup>8</sup> together with the Wiberg bond indices ( $w$ )<sup>9</sup> also support this conclusion. The large ellipticity ( $\epsilon$ )<sup>8</sup> of the P-P bond shows an asymmetric electron distribution about the bond axis, as a further indication of significant  $\pi$ -character. The  $\sigma^2$ -P-C and  $\sigma^4$ -P-C bonds possess a partial double bond character too, the  $\sigma^2$ -P-C bond resembling more a single bond. The C=C bond in **1b** is somewhat longer than in ethylene. Also its Wiberg index and the electron density at the bond critical point are smaller than those of a 'pure' C=C bond. All these characteristics indicate a certain amount of electron delocalization throughout the ring, modifying the previously used description, which was based solely on the zwitterionic structure.<sup>2</sup> The nature of this delocalization can be understood from the  $\pi$  orbitals calculated at the HF/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory (Fig. 2). The two hydrogens on the  $\sigma^4$  phosphorus act as a pseudo  $\pi$ -center (having a significant contribution in four out of the five  $\pi$ -orbitals), contributing—like an amino group on a cyclobutadiene—two more electrons to the  $4\pi$  system. The delocalization is spread over the entire ring, with a positive charge at the  $\sigma^4$ -phosphorus—as a result of its relatively small contribution in the occupied orbitals. Thus, using this simple MO model, the zwitterionic charge

**Table 2** Bond lengths (in Å), electron densities at bond critical points ( $\rho$ ), ellipticities ( $\epsilon$ ) and Wiberg bond indices ( $w$ ) of compounds 1–6

	Length /Å	$w$	$\rho$	$\epsilon$
<b>P–P</b>				
1b	2.186	0.890	0.107	0.249
1c	2.149	0.930	0.121	0.295
1d	2.182	0.891	0.109	0.200
1e	2.154	0.911	0.121	0.223
2c	2.417	0.502	0.076	0.150
3c	2.276	0.677	0.111	0.107
4c	2.328	0.495	0.095	0.009
5c	2.257	0.586	0.111	0.002
6c	2.337	0.544	0.097	0.029
<b><math>\sigma^4</math>-P–C</b>				
1b	1.772	0.933	0.173	0.004
1c	1.775	0.838	0.176	0.030
1d	1.779	0.911	0.171	0.011
1e	1.778	0.813	0.176	0.034
2c	1.784	0.864	0.170	0.154
3c	1.778	0.860	0.173	0.121
4c	1.800	0.837	0.169	0.078
5c	1.791	0.844	0.172	0.013
6c	1.794	0.837	0.170	0.050
<b><math>\sigma^2</math>-P–C</b>				
1b	1.824	1.053	0.149	0.546
1c	1.840	0.996	0.144	0.409
1d	1.806	1.126	0.153	0.535
1e	1.816	1.075	0.149	0.412
2c	1.895	0.758	0.142	0.163
3c	1.859	0.823	0.148	0.187
4c	1.854	0.694	0.156	0.038
5c	1.841	0.718	0.185	0.014
6c	1.881	0.685	0.157	0.085
<b>C–C</b>				
1b	1.375	1.574	0.317	0.310
1c	1.374	1.584	0.318	0.291
1d	1.394	1.485	0.306	0.254
1e	1.391	1.486	0.305	0.232
2c	1.360	1.720	0.326	0.251
3c	1.362	1.690	0.325	0.269
4c	1.356	1.745	0.328	0.266
5c	1.359	1.707	0.327	0.275
6c	1.349	1.765	0.333	0.280

**Table 3** Bonding characteristics of single and double bonded reference compounds

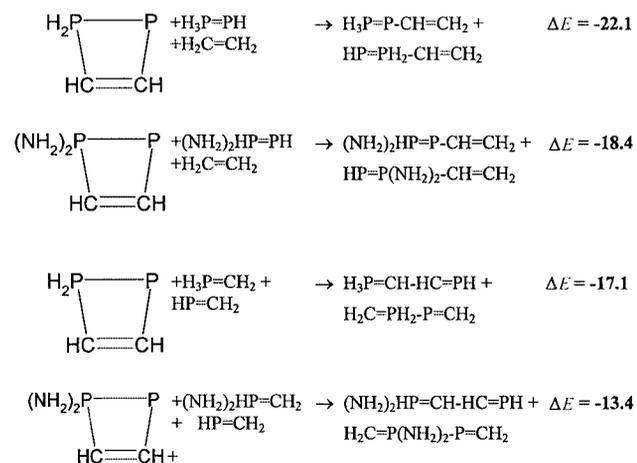
	Length/Å	$w$	$\rho$	$\epsilon$
H <sub>3</sub> P=PH	2.093	1.179	0.120	1.149
H <sub>4</sub> P–PH <sub>2</sub>	2.369	0.641	0.099	0.003
H <sub>3</sub> P=CH <sub>2</sub>	1.683	1.332	0.196	0.418
H <sub>4</sub> P–CH <sub>3</sub>	1.906	0.670	0.148	0.001
HP=CH <sub>2</sub>	1.679	1.939	0.182	0.485
H <sub>2</sub> P–CH <sub>3</sub>	1.860	0.960	0.153	0.140
H <sub>2</sub> C=CH <sub>2</sub>	1.340	2.038	0.348	0.410

distribution discussed previously<sup>10</sup> is understandable as well. Similar electronic structure was suggested earlier for several  $\sigma^4$ ,  $\lambda^5$ phosphorus-containing molecules.<sup>11</sup>

Substitution of the hydrogens on the  $\sigma^4$ -phosphorus with amino groups (**1c**) results in increasing the double bond character of the P–P bond compared to **1b**. The C=C bond remains almost intact. The general bond shortening in the ring indicates stabilization as a result of the substituents. The energetic effect of the amino groups can be estimated with the help of the isodesmic reactions in Scheme 2. All the reactions show a destabilization of the ring (apparently due to the high ring strain in a four-membered ring—note that the reference structures in the isodesmic reactions are open-chain molecules). In

**Table 4** Bond lengths (in Å) and dissociation energies (to singlets in kcal mol<sup>-1</sup>) for X→Y type compounds

X	Y	Length*/Å	$\Delta E^*/\text{kcal/mol}^{-1}$
H <sub>3</sub> P	PH	2.120	55.0
(H <sub>2</sub> N) <sub>2</sub> HP	PH	2.070	74.4
(H <sub>2</sub> N) <sub>2</sub> HP	P(H)=O	2.388	14.9
(H <sub>2</sub> N) <sub>2</sub> HP	P(H)=Se	2.173	19.2
(H <sub>2</sub> N) <sub>2</sub> HP	P(H)O <sub>2</sub>	2.285	16.4
(H <sub>2</sub> N) <sub>2</sub> HP	P(H)Se <sub>2</sub>	2.205	23.5

**Scheme 2**

the case of the reactions involving the amino substituted **1c** the (ring strain) destabilization is 3.7 kcal mol<sup>-1</sup> smaller than in the corresponding reactions involving **1b**.

Silyl substitution (**1d**) has a negligible effect on the P–P and the  $\sigma^4$ -P–C bonds, it increases however the double bond character of the  $\sigma^2$ -P–C and decreases that of the C=C bond. The combined effect of the amino and the silyl substitution (**1e**) is an increase of the double bond character of the P–P and P–C bonds, together with the weakening of the C=C bond. Such behavior indicates increased delocalization.

On changing the valence state of the  $\sigma^2$  phosphorus (**2–6**) the stability of the ring decreases dramatically. Attempts to locate minima for **2b–6b** (the  $\sigma^4$  phosphorus is substituted by H) on the potential energy surface failed, the ring opens between the two phosphorus atoms. Amino substituents at the  $\sigma^4$  phosphorus (**2c–6c**), however, stabilize the ring structure. The significant weakening of the P–P bond compared to **1c** is reflected in the bonding characteristics of **2c–6c**. The P–C bonds are weakening and the C=C bond is strengthening. This effect is less pronounced in **3c** while it is strong in **6c**. The weakening of the P–P bond correlates with the calculated P–P bond length and with the bonding energy of the corresponding X→Y type complexes (Table 4) X: (NH<sub>2</sub>)<sub>2</sub>HP, Y: PH, P(H)O, P(H)Se, P(H)Se<sub>2</sub>, P(H)O<sub>2</sub>. It should also be noted that with X: H<sub>3</sub>P the only stable member of the X→Y series is H<sub>3</sub>PPH.<sup>12</sup>

## Conclusions

The present calculations confirm the reaction mechanism previously postulated for the formation of **1**. Comparison of the relative energies of **1** and the other possible products **9–11** with different substitution patterns showed that besides the amino substituents the silyl group also contributes to the stability of **1**. The relative stabilities of the intermediates on the reaction path change considerably with the substituents. Investigation of different calculated structural and electron density related parameters and the molecular orbitals revealed that electron delocalisation plays an important role in the stabilization of **1**. Changing the valence state of the  $\sigma^2$  phosphorus

(2-6) diminishes this delocalization and decreases the stability of the ring. Amino groups (on  $\sigma^4$ -P) and silyl groups (on C), however, increase the electron delocalization and thus play a crucial role in the stability of the rings. The availability of the  $1\sigma^4, 2\sigma^2$  diphosphete ring **1a** as well as the surprising stability of the  $1\sigma^4, 2\sigma^{2-6}$  diphosphete rings with the phosphorus atom in a different oxidation state is thus attributable to the effect of the substituent amino and silyl groups.

## Acknowledgements

Financial support from OTKA grant T 019464 is acknowledged. L. N. is grateful for the Alexander von Humboldt fellowship.

## References

- 1 R. Armbrust, M. Sanchez, R. Réau, U. Bergstäßer, M. Regitz and G. Bertrand, *J. Am. Chem. Soc.*, 1995, **117**, 10785; M. Sanchez, R. Réau, F. Dahan, M. Regitz and G. Bertrand, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2228.
- 2 M. Sanchez, R. Réau, H. Gornitzka, F. Dahan, M. Regitz and G. Bertrand, *J. Am. Chem. Soc.*, 1997, **119**, 9720. **7a** was obtained by irradiating phosphino(trimethylsilyl)diazomethane at 254 nm in the reaction mixture (solvent: diethyl ether), as detected by multinuclear NMR spectroscopy.
- 3 M. Sanchez, R. Réau, C. J. Marsden, M. Regitz and G. Bertrand, *Chem. Eur. J.*, 1999, **5**, 274.
- 4 GAUSSIAN94, Revision C. 3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.
- 5 GAUSSIAN98, Revision A.5, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1998.
- 6 M. Regitz, *Angew. Chem.*, 1991, **103**, 691; M. Regitz, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 674; S. Goumri-Magnet, O. Polishchuk, H. Gronitzka, C. J. Marsden, A. Baceiredo and G. Bertrand, *Angew. Chem.*, 1999, **111**, 3938; D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39.
- 7 L. Nyulászi, D. Szieberth, J. Réffy and T. Veszprémi, *J. Mol. Struct. (THEOCHEM)*, 1998, **453**, 91.
- 8 R. W. F. Bader, T. S. Slee, D. Cremer and E. Kraka, *J. Am. Chem. Soc.*, 1983, **105**, 5061; R. W. F. Bader, *Acc. Chem. Res.*, 1985, **18**, 9.
- 9 K. Wiberg, *Tetrahedron*, 1968, **24**, 1083.
- 10 G. Bertrand, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 270.
- 11 L. Nyulászi, J. Réffy and T. Veszprémi, *J. Phys. Chem.*, 1995, **99**, 10142; L. Nyulászi and T. Veszprémi, *J. Phys. Chem.*, 1996, **100**, 6456; A. Göller, H. Heydt and T. Clark, *J. Org. Chem.*, 1996, **61**, 5840.
- 12 The rearrangement of  $H_3PPH$  to  $H_2PPH_2$  has recently been studied computationally. J. Rak, P. Skurski, A. Liwo and J. Błażejowski, *J. Am. Chem. Soc.*, 1995, **117**, 2638.