Remarkable Effect of Fluorine and Chlorine Atoms on the Stability of 1*H*-Phosphirene

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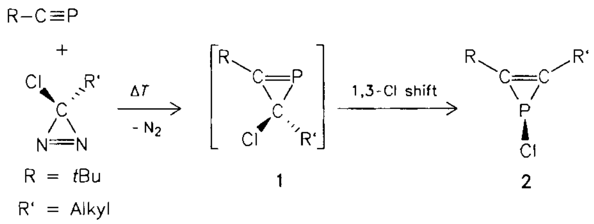
Ab initio MO calculations at the MP4/6−31G** level show that both fluorine and chlorine atoms exert a strong stabilizing effect on the three-membered ring 1*H*-phosphirene relative to its isomers. While unsubstituted 1*H*-phosphirene (**12H**) is the least stable C_2H_3P isomer, 1-fluoro-1*H*-phosphirene (**12F**) is calculated to be the global minimum of the C_2H_2FP potential energy surface; 1-chloro-1*H*-phosphirene (**12Cl**) is the third most stable of the six C_2H_2ClP isomers calculated. The remarkable stability of **12F** is attributable to the particular strength of the P−F bond.

The study of three-membered ring systems containing both carbon and phosphorus atoms has become an active area of research, in part due to their synthetic potential in organophosphorus chemistry[1]. Compared with the saturated phosphirane homologues, the chemistry of phosphirenes featuring a double bond within the ring has only recently been developed[2]. In general, phosphirenes can be prepared either by addition of a phosphinidene (R−P) to an acetylene moiety giving rise to a 1*H*-phosphirene or by condensation of a carbene (RR'C) with a phosphaalkyne (R−C≡P) functional group yielding a 2*H*-phosphirene. The cyclic adducts are often stabilized by bulky substituents or complexation with metal fragments[1].

In 1989, Regitz and co-workers[3] reported on the preparation of the first free 1*H*-phosphirene **2** when a chlorocarbene precursor was employed in the condensation [Equation (1)]. In this reaction, the 2*H*-phosphirene **1** was apparently formed as a transient intermediate followed by a formal 1,3-shift of the chlorine atom yielding the final 1*H*-phosphirene **2**. The latter product which was obtained in high yield is stable at room temperature and undergoes a large range of nucleophilic substitutions at the phosphorus centre. Similarly, the 1-fluoro-1*H*-phophirene **3** has also been generated from the initially formed 2*H*-phosphirene **4** through a 1,3-fluorine shift[4]. More recently, 1-bromo-1*H*-phosphirene **5** has been synthesized in a similar way[5]. Recent MO calculations[6] indicate that, while the unsubstituted 2*H*-phosphirene is ca. 52 kJ/mol more stable than the corresponding 1*H*-phosphirene (similar to the energy ordering between both nitrogen homologues 2*H*-azirine and 1*H*-azirine[7]), 1-fluoro- or 1-chloro-1*H*-phosphirenes **3** or **4** lie lower in energy than their 2-halogeno-2*H*-phosphirene isomers. Taken together, these results point toward a higher stability of 1-halogeno-1*H*-phosphirenes relative to 2-halogeno-2*H*-phosphirenes. Note that substituted 2*H*-azirines **7** are known as stable starting materials in heterocyclic synthesis whereas substituted 1*H*-azirines **6** are only short-lived intermediates[8].

In view of these results, we have examined the effect the fluorine and chlorine atoms exert on different isomers of phosphirene by using molecular orbital calculations. We have found that introduction of these atoms not only reverses the energy ordering between 1*H*- and 2*H*-phosphirenes but also markedly stabilizes 1*H*-phosphirenes with respect to their isomeric structures. Thus, 1-fluoro-1*H*-phosphirene (**3**, R = R′ = H) turns out to be the global minimum of the C_2H_2FP potential energy surface.



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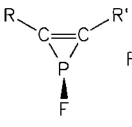

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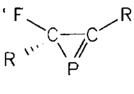

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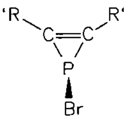

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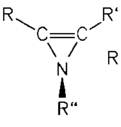

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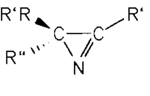

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Details of Calculations

Ab initio molecular-orbital calculations were carried out by using a modified version of the GAUSSIAN 88 system of programs[9]. Geometrical parameters were optimized at the Hartree-Fock (HF) level with the dp-polarization 6−31G** basis set. For the C_2H_3P-isomeric structures, geometries were also refined by using second-order perturbation-theory (MP2) calculations. Improved relative energies were obtained at the HF/6−31G**-optimized geometries with incorporation of electron correlation by using full fourth-order perturbation theory (MP4SDTQ). Unless otherwise noted, these are the values referred to in the text.

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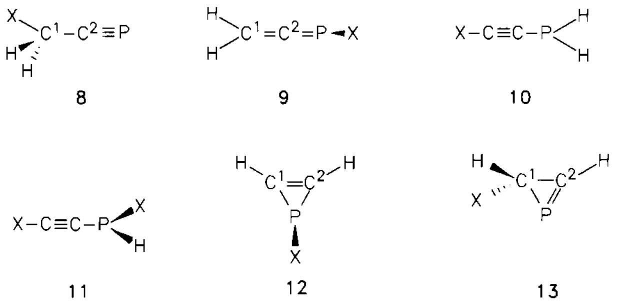
Results and Discussion

We have considered three different sets of isomeric forms containing both 1*H*- and 2*H*-phosphirenes, namely five unsubstituted C_2H_3P isomers, six fluoro-substituted C_2H_2FP and six chloro-substituted C_2H_2ClP isomers. Each of the isomeric sets includes the open forms phosphapropyne **8**, phosphaallene **9**, ethynylphosphanes **10** and **11**, and the cyclic forms 1*H*-phosphirene **12** and 2*H*-phosphirene **13**. The structures considered are shown in Scheme 1. Their optimized structures are listed in Table 1 together with experimental data for the purpose of comparison. Corresponding total and relative energies obtained at various levels of theory are recorded in Tables 2 and 3.

Scheme 1. Isomeric structures considered (**10H** and **11H** are identical)



8–13	X
Cl	Cl
F	F
H	H

12 Cl ≡ 2(R = R' = H) 13 Cl ≡ 1(R = R' = H)
12 F ≡ 3(R = R' = H) 13 F ≡ 4(R = R' = H)

Table 1. Optimized geometrical parameters of structures considered

	Parameter [a]	X=H			X=F	X=Cl
		HF/6-31G**	MP2/6-31G**		HF/6-31G**	HF/6-31G**
8 (C_s)	C^1–H	1.085	1.089	(1.107) [d]	1.083	1.080
	C^1–X	1.085	1.089	(1.107)	1.365	1.795
	C^1–C^2	1.467	1.465	(1.465)	1.470	1.462
	C^2–P	1.521	1.566	(1.544)	1.517	1.517
	C^1C^2P	180.0	180.0	(180.0)	179.1	179.1
	XC^1C^2	110.4	110.8	(110.3)	111.1	112.5
	HC^1C^2	110.4	110.8	(110.3)	110.0	110.7
	HC^1H	108.5	108.2		108.8	109.1
9 (C_s)	C^1–C^2	1.295	1.314		1.297	1.296
	C^2–P	1.635	1.648		1.618	1.621
	C^1–H	1.078	1.082		1.078	1.078
	P–X	1.411	1.413		1.602	2.089
	HC^1C^2	121.1	121.2		121.2	121.2
	C^1C^2P	175.7	173.6		175.8	176.6
	C^2PX	97.1	95.4		103.5	101.9
	HC^1H	117.8	117.5		117.7	117.6
10 (C_s)	C^1–X	1.062 [c]	1.057	(1.058) [e]	1.269	1.648
	C^1–C^2	1.224	1.191	(1.208)	1.183	1.189
	C^2–P	1.773	1.783	(1.774)	1.782	1.785
	P–H	1.406	1.404	(1.414)	1.402	1.403
	XC^1C^2	176.9	179.9	(180.0)	179.6	179.6
	C^1C^2P	171.8	175.0	(173.0)	175.0	175.6
	HPC^2	97.5	98.2	(96.9)	97.9	97.8
	HPH	94.9	95.7	(93.9)	95.8	95.8
11 (C_1)	C^1–H	1.062 [c]	1.057	(1.058) [e]	1.057	1.057
	C^1–C^2	1.224	1.191	(1.208)	1.191	1.191
	C^2–P	1.773	1.783	(1.774)	1.777	1.773
	P–X	1.406	1.404	(1.414)	1.596	2.072
	P–H	1.406	1.404	(1.414)	1.402	1.398
	HC^1C^2	176.9	179.9	(180.0)	179.7	179.5
	C^1C^2P	171.8	175.0	(173.0)	174.0	174.0
	C^2PH	97.5	98.2	(96.9)	95.9	96.6
	C^2PX	97.5	98.2	(96.9)	100.8	101.6
	HPX	94.9	95.7	(93.9)	98.0	96.8
12 (C_s)	C^1–C^2	1.283	1.304	(1.299) [f]	1.301	1.296 (1.303) [g]
	C^1–H	1.070	1.075		1.071	1.070
	C^1–P	1.821	1.843	(1.820)	1.773	1.778 (1.781)
	P–X	1.422	1.421		1.612	2.129 (2.166)
	HC^1C^2	145.1	145.3		142.7	144.3
	PC^1C^2 [b]	69.4	69.3	(69.1)	68.5	68.6 (68.4)
	C^1PC^2 [b]	41.3	41.4	(41.8)	43.0	42.7 (42.9)
	C^1PX	101.9	99.8		105.0	105.5 (104.2)
	XPC^1H	89.0	89.3		82.3	81.5
	HC^2C^1P	−176.5	−177.0		−178.6	−177.9
13 (C_1)	C^1–C^2	1.483	1.470	(1.482) [h]	1.459	1.460
	C^1–P	1.875	1.916	(1.881)	1.837	1.838
	C^2–H	1.071	1.076		1.072	1.070
	C^1–H	1.081	1.084		1.076	1.074
	C^1–X	1.081	1.084		1.366	1.799
	XC^1P	119.3	117.6		118.9	121.0
	HC^1C^2	119.0	119.6		122.4	121.7
	HC^2C^1	137.0	138.6		138.5	137.5
	C^2C^1P [b]	56.1	56.7	(56.7)	58.0	57.7
	C^1PC^2 [b]	49.6	47.9	(49.2)	49.1	49.4
	HC^1C^2H	−72.4	−74.7		−72.5	−71.6
	XC^1C^2H	72.4	74.7		68.1	67.3
	HC^2C^1P	180.0	180.0		176.5	177.5

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[a] See Scheme 1 for atom numbering; bond lengths are given in Å and bond angles in degrees; experimental data are given in parentheses. — [b] Nonindependent parameters. — [c] For X = H, structures **10** and **11** are identical. — [d] Ref.[10]. — [e] Ref.[11]. — [f] Ref.[2]; values for triphenyl-1*H*-phosphirene. — [g] Ref.[5]; values for 2-*tert*-butyl-1-chloro-3-phenyl-1*H*-phosphirene. — [h] Ref.[12]; values for a 2*H*-phosphirene complexed with $W(CO)_5$.

In going from the HF/6−31G** to the MP2/6−31G** level, the structural changes in the C_2H_3P isomers are no-

Table 2. Total [hartree], relative ([kJ/mol]; in parentheses) energies and ZPE [kJ/mol] for C_2H_3P isomers by using the 6–31G** basis set

Method[a)]	Geometry	8	9	10	12	13
HF	HF/6–31G**	–418.15862 (0)	–418.12882 (78)	–418.12776 (81)	–428.22391 (117)	–418.11765 (108)
MP2(F)[b)]	MP2/6–31G**	–418.56912 (0)	–418.52396 (119)	–418.51775 (135)	–418.51107 (152)	–418.53005 (103)
MP2	HF/6–31G**	–418.56695 (0)	–418.52327 (115)	–418.51554 (135)	–418.51009 (149)	–418.52867 (101)
MP3	HF/6–31G**	–418.58329 (0)	–418.54938 (89)	–418.53787 (119)	–418.53369 (130)	–418.54941 (89)
MP4	HF/6–31G**	–418.61237 (0)	–418.57393 (101)	–418.56167 (133)	–418.55565 (149)	–418.57362 (102)
ZPE	HF/6–31G**	119	109	103	110	118
MP4 + ZPE[c)]	HF/6–31G**	(0)	(91)	(117)	(140)	(101)

[a)] The core orbitals are omitted, unless otherwise noted. — [b)] By using full set of MOs. — [c)] Including the MP4 relative energies and ZPEs.

Table 3. Total [hartree] and relative ([kJ/mol]; in parentheses) energies for C_2H_2FP and C_2H_2ClP isomers by using the 6–31G** basis set

Species[a)]	X=F				X=Cl			
	HF	MP2	MP3	MP4	HF	MP2	MP3	MP4
8	–516.99522 (0)	–517.56421 (0)	–517.57567 (0)	–517.61223 (0)	–877.04971 (0)	–877.58984 (0)	–877.61134 (0)	–877.64596 (0)
9	–517.00675 (–30)	–517.56760 (–9)	–517.58653 (–29)	–517.91914 (–18)	–877.05363 (–10)	–877.57809 (31)	–877.61006 (3)	–877.63869 (19)
10	–516.95176 (114)	–517.50392 (158)	–517.51999 (146)	–517.55224 (158)	–877.01603 (88)	–877.53966 (132)	–877.56629 (118)	–877.59648 (130)
11	–517.00397 (–23)	–517.55830 (15)	–517.57316 (7)	–517.60526 (18)	–877.04736 (6)	–877.56500 (65)	–877.59310 (48)	–877.62121 (65)
12	–517.01475 (–51)	–517.57826 (–37)	—517.59333 (–46)	–517.62369 (–30)	–877.05524 (–15)	–877.58101 (23)	–877.60940 (5)	–877.63555 (27)
13	–516.96812 (71)	–517.54292 (56)	–517.55716 (49)	–517.58982 (59)	–877.02067 (76)	–877.56459 (66)	–877.58920 (58)	–877.61940 (70)

[a)] By using the HF/6–31G** geometries given in Table 1.

ticeable with typical lengthening of the bonds. The largest changes occur for the triple bond between P and C in **8** (0.045 Å) and the carbon-phosphorus bonds in 2*H*-phosphirene **13**, namely 0.041 and 0.037 Å for the single and double bonds, respectively. However, the effect of such geometrical differences on their relative energy is small. As seen in Table 2, the largest difference between the relative energies obtained at the MP2 level by using both HF- and MP2-optimized geometries amounts to only 4 kJ/mol.

Let us first examine the structures of the unsubstituted species. Structures of 1-phosphapropyne (**8H**) and 1-phosphaallene (**9H**) have been examined in detail in earlier papers[13] and thus warrant no further comments. For ethynylphosphane (**10H** or **11H**), agreement between calculated and experimental values is reasonable. The rotational constants of **10H** calculated by using MP2/6–31G** geometries are: A_e = 134380 MHz, B_e = 5117 MHz, and C_e = 5086 MHz, and these compare well with the experimental values of A_0 = 130345 MHz, B_0 = 5114 MHz, and C_0 = 5090 MHz[11]. The H_2P-C moiety in **10H** is quite similar to that in cyanophosphane (H_2P-CN).

For both cyclic structures **12H** and **13H**, no experimental data are available yet. For the sake of information, experimental values obtained for some corresponding species substituted by aliphatic or aromatic groups are also given in Table 1. We note that the bond angles within the rings are well reproduced at both levels of theory indicating that these geometrical parameters are not particularly affected by aliphatic or aromatic substituents.

In contrast, the effect of fluorination and chlorination on the structural parameters is significant, especially on the bond distances of both three-membered rings **12** and **13**. In both cases, the bonds adjacent to the P–X or C–X moiety (X = F, Cl) are decreased. The largest decrease upon substitution occurs for the C^1-P distance of 1-fluoro-1*H*-phosphirene (**12F**) (0.048 Å).

We found also that the structures of the fluorinated and chlorinated species, except of course for the parameters involving these atoms, are very similar. The largest difference between the relevant bond lengths is only 0.008 Å (C^1-C^2 in **8**).

Of particular interest, the HF/6−31G** values for 1-chloro-1*H*-phosphirene (**12Cl**) compared favourably with the experimental data obtained from X-ray analysis[5]. These results on the whole suggest that the calculated values provide good estimates for structures of the remaining molecules.

We now turn to a consideration of relative energies (Tables 2 and 3, Figure 1) of the five unsubstituted C_2H_3P species. We find the energy ordering **8H** < **9H** < **13H** < **10H** < **12H**. 1-Phosphapropyne (**8H**) is thus calculated to be the most stable isomer. 1-Phosphaallene (**9H**) lies ca. 101 kJ/mol higher in energy followed by 2*H*-phosphirene (**13H**) (102 kJ/mol) and ethynylphosphane (**10** or **11** (133kJ/mol). 1*H*-Phosphirene (**12H**) is the least stable unsubstituted isomer lying 149 and 47 kJ/mol above 1-phosphapropyne (**8H**) and 2*H*-phosphirene (**13H**), respectively. A similar energy ordering has also been found for the isovalent C_2H_3N species[7]. We note that incorporation of the zero-point energy correction tends to reduce the energy differences between isomers, but the energy ordering remains unchanged.

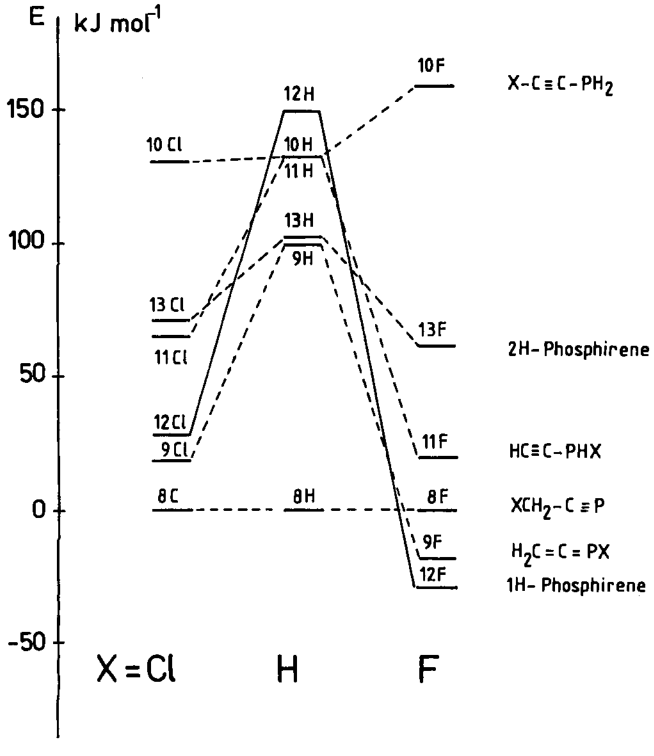
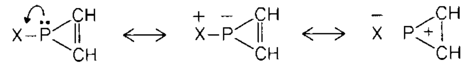


Figure 1. Relative energies [kJ/mol] for the various isomers of C_2H_2PX with X = H, F, and Cl from MP4(SDTQ)/6−31G**//HF/6−31G** calculations

The energy diagram is dramatically modified in the fluorinated and chlorinated species (Figure 1). Thus, 1-fluoro-1*H*-phosphirene (**12F**) turns out to be the global minimum on the C_2H_2FP potential energy surface at all levels considered. Our best estimate places **12F** 30 kJ/mol below 3-fluoro-1-phosphapropyne (**8F**). There is thus a stabilization of ca. 179 kJ/mol upon fluorination in favour of the cyclic species. Surprisingly, 1-fluoro-1-phosphaallene (**9F**) has also become energetically more favourable than **8F** (by 18 kJ/mol).

With regard to the C_2H_2ClP species, the energy ordering is changed following incorporation of electron correlation into the calculations (Table 3). Thus, 1-chloro-1*H*-phosphirene (**12Cl**) is also strongly stabilized in becoming the third most stable isomer lying just above 3-chloro-1-phosphapropyne (**8Cl**) (by 27 kJ/mol) and 1-chloro-1-phosphaallene (**9Cl**) (by 8 kJ/mol). Upon substitution, the 2*H*-phosphirene **13** and ethynylphosphane **11** also gain significant stabilization relative to phosphapropyne **8**, but both isomers remain higher in energy than the latter. For its part, the ethynylphosphane **10** is rather destabilized by both F and Cl atoms.

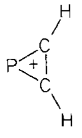
The higher stability of both 1-halogeno-1*H*-phosphirenes over their corresponding 2-halogeno-2*H*-phosphirene isomers[6] thus agrees well with experimental results[3−5] showing an unimolecular rearrangement of the initially formed 2*H*-phosphirene to the 1*H*-phosphirene as the final adduct [Equation (1)]. The remarkable effect of the halogen atoms on 1-*H*-phosphirene may be understood in terms of the contribution of the resonance form **14** and/or the polar form **15**.


12 14 15

14,15	X
Cl	Cl
F	F
H	H

The negative net charge of the X atoms is found to increase in the sequence: **12H** (−0.122) < **12Cl** (−0.394) < **12F** (−0.493) (values at HF/6−31G** Mulliken population analysis). A larger charge transfer to the fluorine substituent in **12F** renders the weight of **15** more important in the electronic structure of 1-fluoro-1*H*-phophirene (**12F**). In addition, the phosphirenylium ion **16**, isovalent with the cyclopropenylium ion, is a typical aromatic species. Recent ab initio MO calculations[14] point out that the cyclic ion **16** is the most stable $C_2H_2P^+$ isomer lying 70 and 170 kJ/mol below its $H_2C=C=P^+$ and $HP^+-C\equiv C-H$ isomers, respectively. In this view, the ionic interaction of the fluoride ion with an aromatically stabilized phosphirenylium ion should lead to a strongly stabilized 1*H*-phosphirene molecule. Due to the difference in the atomic charges mentioned above, the fluoro species **12F** should present a larger electrostatic force than **12Cl** and **12H**. Evidence for the involvement of the ion **16** comes from the ease with which the halogen substituents interchange in 1*H*-phosphirenes. When **17** is treated with silver tetrafluoroborate, the product **19** is finally isolated in quantitative yield[18]. A plausible explanation is the initial formation of the phosphirenylium salt

18 which then extracts a fluoride ion from the BF_4^- counterion to yield **19**. This is consistent with the higher stability of 1-fluoro-1*H*-phosphirene (**12F**) found by the present calculations.



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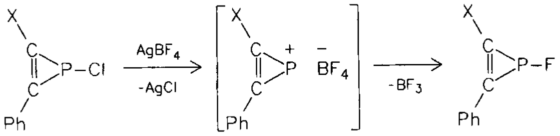

17 18 19

It has also been estabilished that the P–F bond is intrinsically strong; for example, the P–F bond dissociation energy of PF_3 amounts to 551 kJ/mol[15], which is far larger than the corresponding values for the P–H (295 kJ/mol)[15], P–Cl (326 kJ/mol)[16], C–H (411 kJ/mol)[16], or C–F (485 kJ/mol)[16] bonds. Thus, the preference of 1-fluoro-1-phosphaallene (**9F**) over 3-fluoro-1-phosphapropyne (**8F**) appears to arise essentially from a difference between the bond energies of the P–F and C–F bonds. A similar argument also holds true for the *C*- and *P*-substituted ethynylphosphanes **10** and **11**. The strength of the P–F bond stems presumably from the large difference in electronegativity between both bonding atoms. It has been shown that when fluorine demands electrons, phosphorus responds by using not only its 3p-electrons but also its 3s-electrons. On the other hand, the back-donation of the $2p_\pi$-electrons of fluorine to p-orbitals of phosphorus is also appreciable[17].

In summary, the extraordinary stability of 1-fluoro-1*H*-phosphirene (**12F**) appears to arise from a combination of two stabilizing effects: the intrinsically strong P–F bond is reinforced by the existence of a typical electrostatic interaction between the fluoride ion and an aromatic phosphirenylium ion.

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CAS Registry Numbers

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[1] F. Mathey, *Chem. Rev.* **1990**, *90*, 997.
[2] A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Am. Chem. Soc.* **1982**, *104*, 4484.
[3] O. Wagner, M. Ehle, M. Regitz, *Angew. Chem.* **1989**, *101*, 227; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 225.
[4] [4a] M. Ehle, O. Wagner, U. Bergsträßer, M. Regitz, *Tetrahedron Lett.* **1990**, *24*, 3429. – [4b] M. Yoshifuji, Y. Kawai, M. Yasumani, *Tetrahedron Lett.* **1990**, *31*, 6891.
[5] O. Wagner, M. Ehle, M. Birkel, J. Hoffmann, M. Regitz, *Chem. Ber.* **1991**, *124*, 1207.
[6] S. M. Bachrach, *J. Org. Chem.* **1991**, *56*, 2205.
[7] T. K. Ha, M. T. Nguyen, *J. Mol. Struct.* **1982**, *87*, 355.
[8] A. Padwa, A. D. Wollhouse, in *Comprehensive Heterocyclic Chemistry* (Eds.: A. R. Katritzky, C. W. Rees), Pergamon Press, Oxford, **1984**, p. 47, 87.
[9] M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, J. A. Pople, *GAUSSIAN 88*, Gaussian Inc., Pittsburgh, P. A., **1988**.
[10] H. W. Kroto, J. F. Nixon, N. P. C. Simmons, *J. Mol. Spectrosc.* **1979**, *77*, 270.
[11] E. A. Cohen, C. A. McRae, H. Goldwhite, S. D. Stefano, R. A. Beaudet, *Inorg. Chem.* **1987**, *26*, 4000.
[12] O. Wagner, G. Maas, M. Regitz, *Angew. Chem.* **1987**, *99*, 1328; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1257.
[13] [13a] M. T. Nguyen, *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1984**, *39A*, 165. – [13b] S. Bachrach, *J. Comput. Chem.* **1985**, *10*, 392. – [13c] M. T. Nguyen, A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2* **1985**, 1999.
[14] R. G. A. R. Maclagan, *Chem. Phys. Lett.* **1985**, *163*, 349.
[15] J. Berkowitz, S. P. Gibson, J. P. Greene, O. M. Neskovic, B. Ruscil, *Croat. Chem. Acta* **1986**, *59*, 513.
[16] J. E. Huheey, in *Inorganic Chemistry*, Harper Row, New York, **1972**, p. 694.
[17] J. F. Harrison, *J. Am. Chem. Soc.* **1981**, *103*, 7406.
[18] M. Regitz, H. Heydt, O. Wagner, W. Schnurr, M. Ehle, J. Hoffmann, *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *49*, 341.

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