Are the Six-Membered λ^5-Phosphorins Aromatic or Ylidic?

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Dedicated with admiration to Professor *Edgar Heilbronner* on the occasion of his 80th birthday

The aromaticity of a series of substituted six-membered λ^5-phosphorins, $(CH)_5PX_2$, (X = F, Cl, Br, OH, Me, H, and SiH_3) has been evaluated by using magnetic criteria (nucleus-independent chemical shifts (NICS), magnetic susceptibility anisotropies and exaltations), as well structural and energetic considerations. The nature of the substituents influences the extent of cyclic electron delocalization significantly. The λ^5-phosphorins with electronegative substituents (X=F, OH, Cl, and Br) show aromatic character, *e.g.*, as characterized by NICS computed 1 Å above the ring centers: NICS(1) = −7.8, −7.3, −7.1, and −6.6 ppm, respectively, *vs.* −10.8 for phosphabenzene. The λ^5-phosphorins with electropositive substituents (X = H, Me, and SiH_3) have small NICS(1) values, −2.6, −2.5, and 1.4 ppm, respectively, and are nonaromatic or only weakly aromatic. Based on these findings as well as geometrical and energetic results, the electronic structures of six-membered λ^5-phosphorins with strongly electronegative substituents may be described as hybrids of internal zwitterion (ylid) and '*Hückel*' aromatic contributors, whereas the compounds having more electropositive substituents may be considered to be basically ylidic in character. The substituent effect on the aromaticity is due to the hyperconjugation (or to the negative hyperconjugation) involving the ring π electron system and the P−X(2) bonds which serve as pseudo π-electron donors (or as acceptors). The more electronegative the substituents X, the more aromatic the molecule. Contradicting early suggestions, no evidence was found for d-orbital participation of phosphorus in cyclic electron delocalization. Similarly, the aromaticity of six-membered λ^4-S compounds, $(CH)_5SX$, also is related to the electronegativity of the S-substituents, X. The $(CH)_5SX$ derivatives with X=F, Cl, Br, OH, H, and Me have NICS(1), of −10.1, −10.0, −9.7, −8.0, −5.2, and −4.2 ppm, respectively. The same generalizations extend to the six-membered λ^5-As and λ^4-Se compounds, as well as to cyclohexadienyl anions, $(CH)_5\,(CX_2^-$ (X = H and F) and $(CH)_5SiX_2^-$ (X = H and F). In the four-membered ring compounds, λ^5-$(CH)_3P(As)X_2$ and λ^4-$(CH)_3S(Se)X$ (X=F and H), the substituents weaken the antiaromaticity of cyclobutadiene significantly. Unlike the six-membered ring cases, the electronegativity of X has no significant influence on the degree of antiaromaticity in the cyclobutadienyl analogs.

1. Introduction. – Reviews of the chemistry of λ^5-phosphorins have appeared periodically [1–8], but the question whether the six-membered λ^5-phosphorins (**1**–**7**; *Fig. 1*) are aromatic or ylidic has not been settled. There has been considerable disagreement in the interpretation. After the preparation of, *e.g.*, 1,1-diphenyl-λ^5-phosphorin and 1,1-diphenylbenzo [2,3]-λ^5-phosphorin [9][10], the chemistry and spectra of this class of compounds usually were discussed in terms of an aromatic model with benzene-like *Kekulé* structure (*Fig. 2, a*) [11][12]. A contrary opinion was put forward by *Schäfer et al.* in 1976 [13]. Having used UV photoelectron spectroscopy and CNDO calculations to investigate a series of six-membered λ^5-phosphorins with various substituents at the P-atom, they proposed that the six-membered λ^5-phosphorins are best described as a superposition of structures (*a*) and (*b*) in *Fig. 2: a* describes the cyclic electron delocalization associated with *Hückel* 'aromaticity', which was assumed to be enabled through participation of a d-orbital on phosphorus in the cyclic conjugation; *b* represents an internal ylidic zwitterion.

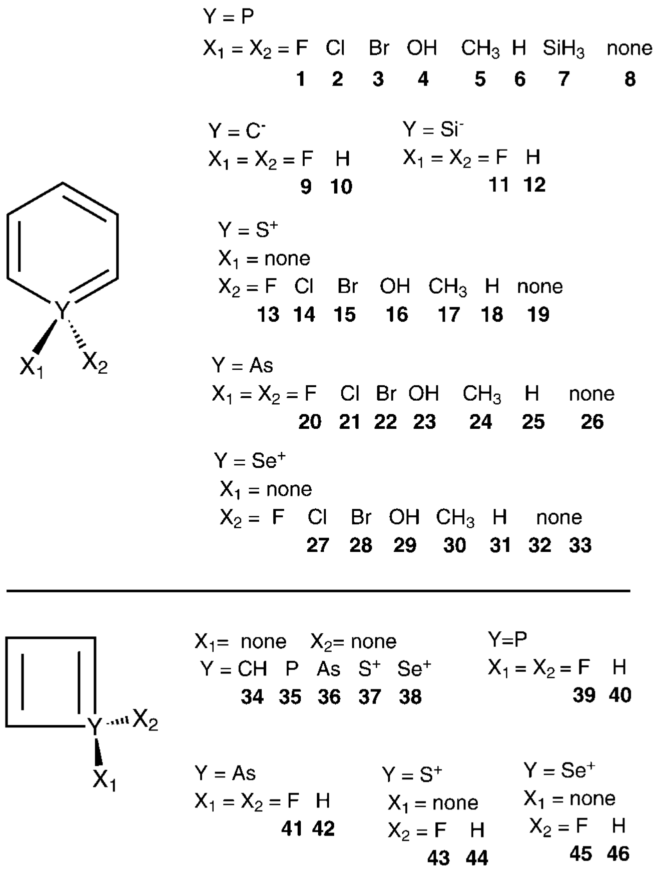
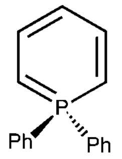
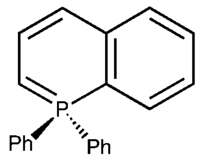


Fig. 1. *Molecules* **1**–**46**

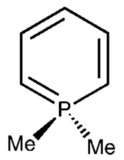
Shortly afterwards, *Ashe* and *Timothy* [14] succeeded in preparing 1,1-dimethyl-λ^5-phosphorin (**5**) and 1,1-dimethyl-λ^5-arsabenzene (**24**). These two compounds have the advantage of revealing the properties of the parent ring unperturbed by bulky substituents. Based on the ^{1}H-NMR chemical shifts [14], *Ashe*'s group concluded that these compounds are ylidic rather than aromatic in character. In contrast, *Bundgaard et al.* [15] attributed the ^{13}C-NMR chemical shifts for C(2) and C(4) of 1,1-dimethoxy-λ^5-phosphorin, more downfield than those in ordinary ylides, to 6π-electron delocalization. *Bird*'s [16] aromaticity indices for 1,1-dimethyl-2,4,6-triphenyl- and 1,1-dimethoxy-2,4,6-triphenyl-λ^5-phosphorins are 66 and 81.5 [16], respectively, compared with 74 for phosphabenzene, a well-known aromatic compound [5][17]. In the latest review, *Dixon* [8] stated that '*λ^5-phosphorins are not aromatic*', although the conclusion (see above) of *Schäfer et al.* [13] was noted favorably. *Nyulaszi* and *Veszpremi* [18] compared the conjugative ability of λ^5-P=C bond with λ^3-P=C counterpart, and concluded '*it is not wise to classify these stabilized cyclic conjugated system with λ^5-P=C units as aromatic*'. In related work, *Xie* and *Schaefer* [19] explored computationally the



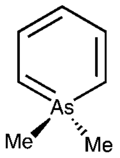
1,1-Diphenyl-λ^5-phosphorin



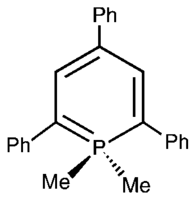
1,1-Diphenylbenzo[*b*]-λ^5-phosphorin



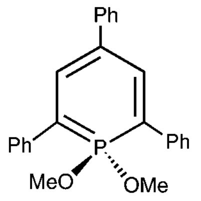
1,1-Dimethyl-λ^5-phosphorin (**5**)



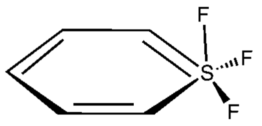
1,1-Dimethyl-λ^5-arsabenzene (**24**)



1,1-Dimethyl-2,4,6-triphenyl-λ^5-phosphorin



1,1-Dimethoxy-2,4,6-triphenyl-λ^5-phosphorin



1,1,1-Trifluorothiabenzene

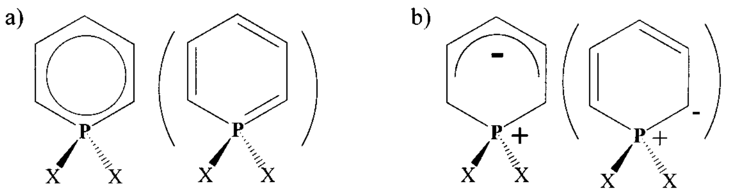


Fig. 2. *Schematic electronic structures for* λ^5*-phosphorins*

possibility of merging hypervalence into aromaticity in the 1,1,1-trifluorothiabenzene, $(CH)_5SF_3$ analog and considered this molecule to have more aromatic than ylidic character. We now present theoretical evidence on phosphorins and related systems showing that the substituents on P-atom (or S-atom) have significant effects on their electronic structures and aromaticity. Some of these derivatives exhibit cyclic electron delocalization, while others do not. Although aromaticity is one of the most widely used concepts in chemistry, there has been no universally accepted definition [20][21]. Aromaticity is often discussed in terms of structural, energetic, and spectroscopic (particularly magnetic) criteria. Nucleus-independent chemical shifts (NICS), recently proposed by *Schleyer* and co-workers [22][23] and now increasingly widely used, are defined as the negative of the absolute magnetic shielding computed, *e.g.*, at the geometric centers of rings or clusters. Negative NICS values of significant magnitude characterize aromaticity, and positive values indicate antiaromaticity. Although NICS is not an experimentally measurable quantity, evalations [24] and accumulating experience show it to be a particularly effective criterion. Furthermore, no reference or increment systems are needed for NICS evaluation; it is the only absolute measure of aromaticity in this sense.

We now use NICS, as well as other magnetic (magnetic susceptibility and exaltations), structural, and energetic criteria to assess the aromatic character of six-membered λ^5-phosphorins (**1**–**7**; *Fig. 1*) and the cyclohexadienyl anions with isoelectronic $CH_2(F_2)^-$ (**9**–**10**) and $SiH_2(F_2)^-$ (**11**–**12**) groups. We then present results for related six-membered λ^4-S (**13**–**18**), λ^5-As (**20**–**25**), and λ^4-Se (**27**–**32**). The effect of λ^5-P(As) and λ^4-S(Se) groups incorporated into cyclobutadiene (**39**–**46**) on the antiaromaticity also was investigated.

2. Theoretical Methods. – All theoretical calculations were performed by using the GAUSSIAN 98 program [25]. The geometries of these compounds were optimized at the B3LYP/6-31G* DFT level and characterized by frequency calculations. The structures of **1**–**19** and **34**–**46** were refined at B3LYP/6-311+G**. The total energies (E_{tot}) and zero-point energies (ZPEs) are given in *Table 1*.

The nucleus-independent chemical shifts (NICS) were computed at SCF/6-31+G* with the gauge-including atomic orbital (GIAO) method [26] (denoted as GIAO-SCF/6-31+G*), using B3LYP/6-311+G** geometries for **1**–**19** and **34-46** and B3LYP/6-31G* geometries for **20**–**33**. The magnetic susceptibilities and their anisotropies (from which the exaltations were derived) were computed with the continuous set of gauge transformations (CSGT) methods [27] (denoted as CSGT-SCF/6-31+G*).

The dissected NICS [23] for some compounds were computed using the deMon master NMR program [28], at the SOS-DFPT-IGLO level [29] with the *Perdew-Wang91* exchange-correlation functional, the IGLO-III basis set, *i.e.*, the recommended options, and the *Pipek-Mezey* localization procedure [30].

3. Results and Discussion. – 3.1. *Aromaticity of Six-Membered λ^5-Phosphorins.* 3.1.1. *Geometrical Measures. Fig. 3,a*, displays the structures of the six-membered λ^5-phosphorins (**1**–**7**) investigated here, together with the key B3LYP/6-311+G** geometrical parameters. The structure of phosphabenzene (**8**) is included for comparison. In agreement with the X-ray analyses for this class of compounds [30], the ring atoms and their H-atoms in **1**–**7** are in the same plane, and the 1,1-substituents are perpendicular. Compounds **1**–**3**, **5**, **6**, and **8** have C_{2v} symmetries, and **4** has C_s symmetry. The SiH_3 substituents in **7** (C_2 symmetry) are twisted slightly away out of one of the planes in C_{2v} symmetry. The alternative C_{2v} conformation of **4** is predicted to be 0.21 kcal/mol less stable than **4** at the B3LYP/6-311+G** level. The ring C–P bond lengths in **4** (1.713 Å) and **5** (1.746 Å) are close to the 1.72–1.75 Å range observed in X-

Table 1. *Total Energies* (E_{tot}, in hartree) [a]) *and Zero-Point Energies* (ZPE, in kcal/mol) [b]) *for Compounds* **1**–**33**

X	Point group	ZPE	E_{tot}		
$(CH)_5PF_2$	F	**1**	C_{2v}	56.8	– 734.74016
$(CH)_5PCl_2$	Cl	**2**	C_{2v}	54.9	– 1455.41983
$(CH)_5PBr_2$	Br	**3**	C_{2v}	54.2	– 5683.26399
$(CH)_5P(OH)_2$	OH	**4**	C_s	55.4	– 686.68074
$(CH)_5P(CH_3)_2$	Me	**5**	C_{2v}	99.9	– 614.78383
$(CH)_5PH_2$	H	**6**	C_{2v}	63.8	– 536.10329
$(CH)_5P(SiH_3)_2$	SiH_3	**7**	C_2	83.9	– 1117.55173
$(CH)_5P$		**8**	C_{2v}	53.1	– 534.95528
$(CH)_5CF_2^-$	CF_2	**9**	C_{2v}	56.9	– 431.47892
$(CH)_5CH_2^-$	CH_2	**10**	C_s	66.3	– 232.87190
$(CH)_5SiF_2^-$	SiF_2	**11**	C_{2v}	55.0	– 683.02755
$(CH)_5SiH_2^-$	SiH_2	**12**	C_{2v}	60.7	– 484.31180
C_5H_5SF	F	**13**	C_s	58.3	– 691.61689
C_5H_5SCl	Cl	**14**	C_S	53.9	– 1051.98807
C_5H_5SBr	Br	**15**	C_S	53.7	– 3165.67600
C_5H_5OH	OH	**16**	C_s	61.3	– 667.57407
$C_5H_5SCH_3$	Me	**17**	C_S	75.9	– 631.64174
C_5H_5SH	H	**18**	C_s	57.3	– 592.30665
$C_5H_5S^+$		**19**	C_{2v}	53.8	– 591.52728
$C_5H_5AsF_2$	F	**20**	C_{2v}	62.3	– 2626.95962
$C_5H_5AsCl_2$	Cl	**21**	C_{2v}	54.4	– 3347.68162
$C_5H_5AsBr_2$	Br	**22**	C_{2v}	54.1	– 7570.71378
$C_5H_5AsOH_2$	OH	**23**	C_s	70.0	– 2578.89881
$C_5H_5As(CH_3)_2$	Me	**24**	C_{2v}	99.7	– 2507.06223
$C_5H_5AsH_2$	H	**25**	C_{2v}	62.3	– 2428.39860
C_5H_5As		**26**	C_{2v}	52.6	– 2427.27833
C_5H_5SeF	F	**27**	C_s	53.5	– 2692.68669
C_5H_5SeCl	Cl	**28**	C_S	53.8	– 3053.07738
C_5H_5SeBr	Br	**29**	C_S	53.6	– 5164.59151
C_5H_5SeOH	OH	**30**	C_s	60.6	– 2668.65179
$C_5H_5SeCH_3$	Me	**31**	C_S	75.5	– 2632.74187
C_5H_5SeH	H	**32**	C_s	60.6	– 2593.41100
$C_5H_5Se^+$		**33**	C_{2v}	53.2	– 2592.64151

[a]) B3LYP/6-311 + G** Energies for **1**–**19** and B3LYP/6-31G* energies for **20**–**33**. [b]) B3LYP/6-31G* ZPEs for **1**–**19** and B3LYP/3-21G ZPEs for **20**–**33**.

rays analyses for the derivatives of similar six-membered λ^5-phosphorins [31][1]). The C–C bond distances in **4** and **5** also fall within the experimental range of 1.38–1.42 Å, likewise the C–P–C bond angles, 104.7 and 105.8°, are very close to the measured values.

The conveniently employed geometric criteria of aromaticity assume that bond-length equalization is due to π electron delocalization geometry. Indexes devised, *e.g.*, by *Bird* [32] and by *Krygowski* and co-workers [33], are important measures of aromaticity. Although the extent of bond-length equalization is only one aromaticity

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[1]) All cases involved 2,4,6-trisubstituted derivatives, and 1,1-dimethyl, 1,1-dimethoxy, and 1,1-bis(dimethylamino) derivatives.

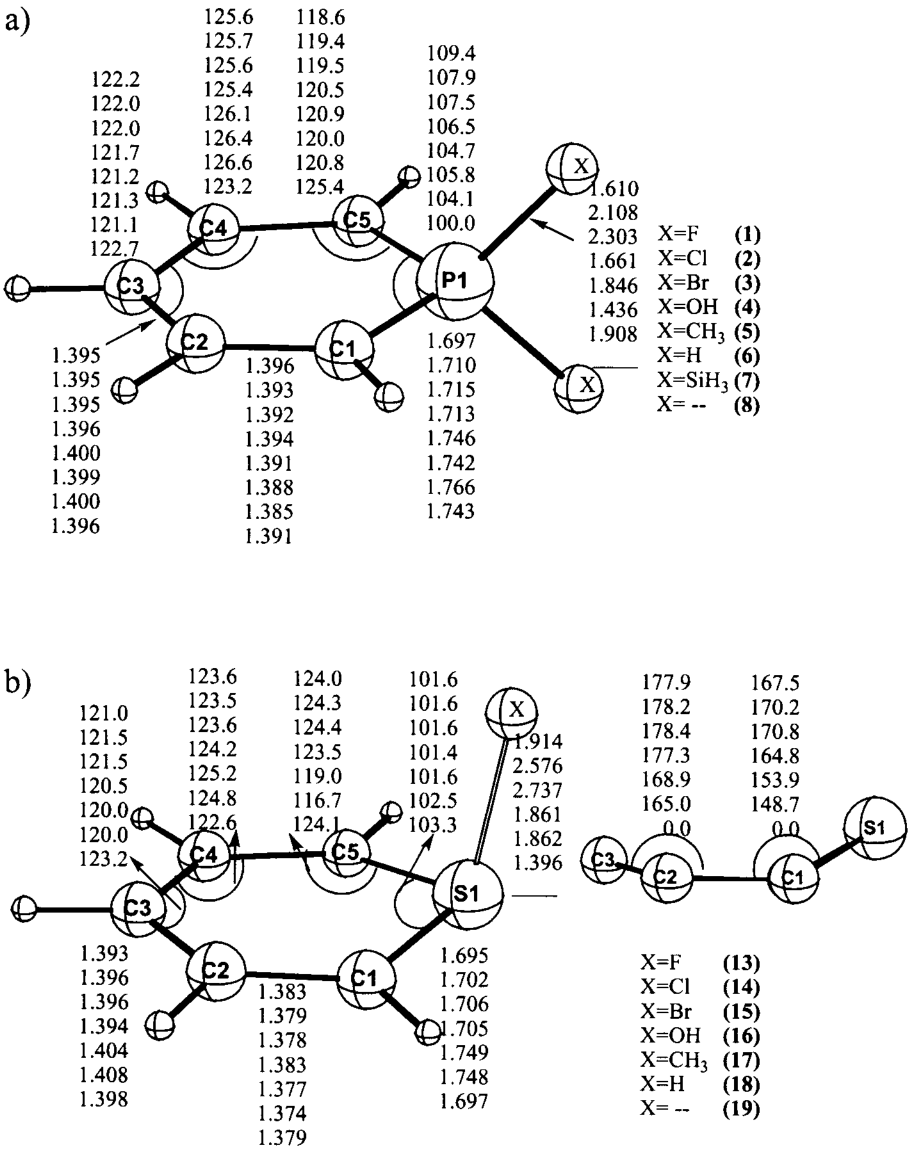


Fig. 3. *B3LYP/6-311 + G** Geometries of* **1**–**8** (*a*) *and* **13**–**19** (*b*) (bond lengths in Å and angles in degrees)

criterion, it provides valuable information on the extent of cyclic electron delocalization [20][21]. Several characteristics are apparent in the geometries of **1**–**7**: *1*) The C–C bond lengths, range ranging from 1.385 to 1.400 Å, are between C–C (1.531 Å in ethane) and C=C bond (1.329 Å in ethylene, both at the same level) lengths. The C–P separations (*e.g.*, 1.697 Å in **1**) are longer than in C=P ylides (*e.g.*, 1.615 Å in $CH_2=PF_3$), but are shorter than C–P bond lengths (*e.g.*, 1.830 Å in CH_3-PF_2). *2*) The C–C bond lengths in **1**–**4** (with electronegative substituents) are closer to the benzene

C−C bond length (1.395 Å at the same level) than in compounds **6** and **7** (with electropositive substituents). *3*) Compounds **1**–**4** show greater bond equalization than **5**, **6**, and **7**. *4*) The individual C−P bond lengths are related to the electronegativity of the substituents at the P-atom: the greater the electronegativity of the substituents, the shorter the C−P bond lengths. For $(CH)_5PX_2$ where X=F, Cl, Br, OH, Me, H, and SiH_3, the P−C lengths are 1.697, 1.710, 1.715, 1.713, 1.746, 1.748, and 1.766 Å, respectively, in comparison with 1.743 Å for phosphabenzene. Note that the C−P bond lengths in CH_2-PF_3 and in CH_2-PH_3 are 1.615 Å and 1.681 Å (B3LYP/6-311 + G**), respectively. To some extent, these geometrical features imply that the λ^5-phosphorins **1**–**7** are aromatic, but that the substituents influence the magnitude of aromaticity.

We also calculated *Bird*'s [32] I^6 and the HOMA [33] (harmonic oscillator measure of aromaticity) indices (*Table 1*). To our surprise, both *Bird*'s I^6 (between 92.2 and 58.6) and HOMA (between 0.990 and 0.806) indices for **1**–**7** are larger than or close to those (69.6 and 0.913, resp.) for phosphabenzene, a well-established aromatic molecule [5][17]. Does this indeed indicate **1**–**5** to be more aromatic than phosphabenzene and **6**–**7** to have aromaticity close to phosphabenzene?

3.1.2. *Magnetic Measures.* The GIAO-SCF/6-31 + G*//B3LYP/6-311 + G** NICS in the ring centers (NICS(0)) and the points 1.0 Å above the ring centers (NICS(1)) are given in *Table 2*. Because NICS(0) is influenced by the local paramagnetic contributions of the σ bonds, which counteract the diamagnetic π ring current effects, NICS(1) is larger than NICS(0) in most cases. This can be attributed to the more rapid decrease of paramagnetic than diamagnetic contributions above the ring centers [23][34]. Hence, NICS(1) provides a better estimate of the aromaticity, and will be used in the following discussion. The NICS(1) for **1**–**7**, −7.9, −6.8, −6.4, −7.3, −2.5, −2.5, and 1.4 ppm, respectively, are compared with −10.8 ppm for phosphabenzene. The NICS results indicate that the λ^5-phosphorins **1**–**4** exhibit cyclic electron delocalization, but to a somewhat diminished extent. However **5**, **6**, and **7** are only very weakly aromatic, at most.

The IGLO method [29] was used to clarify the individual contributions from the localized MOs such as C−C(π), C−C(σ), C−H(σ) *etc.* The *Pipek-Mezey* [30] localization procedure which provides σ-π separation was used for this purpose [23]. We analyzed the NICS of **1**, the most aromatic, and **6, 7** the least aromatic among these λ^5-phosphorins. The dissected NICS data at the points 1 Å above the ring centers (NICS(1) and the ring centers (the number in parentheses) NICS(0) are given in *Table 3*. Phosphabenzene provides a comparison.

The total NICS at the ring centers ($NICS_{tot}(0)$) and the points 1 Å above the centers ($NICS_{tot}(1)$) given by IGLO method are very close to the GIAO-SCF/6-31 + G* results (*Table 2*). For **1**, the diamagnetic contribution of C−C and C−P π bonds to the $NICS_{tot}(1)$ is −8.3 ppm; this is slightly less than the π contribution (−9.9) to phosphabenzene (**8**), and −9.6 to benzene. Compound **1** also has a smaller $NICS_{tot}(1)$ (−7.9) than that (−10.5) for phosphabenzene and −10.6 for benzene. At the ring centers, phosphabenzene (**8**) and benzene have $NICS_{\pi}(0)$, −19.2 and −20.7, respectively, larger than **1** (−17.6). In contrast, compound **6** has negligible $NICS_{\pi}(1)$ (−3.4) and $NICS_{tot}(1)$ (−2.8). Compound **7** even has small positive $NICS_{tot}(1)(0.5)$. The dissected NICS values also reveal **1** to be aromatic, and **6** and **7** to be weakly or non-aromatic.

Table 2. *The Calculated Nucleus-Independent Chemical Shifts* (NICS)[a]), *Magnetic Susceptibility Anisotropies* (χ_{anis}, ppm cgs)[b]), *Magnetic Susceptibility Exaltations* (Λ, ppm cgs)[c]), *and Aromatic Stabilization Energies (ASE, Kcal/mol)*[d]), *Together with* Bird's *I^6 and HOMA Aromaticity Indices*

	Point group	NICS(0)	NICS(1)	χ_{anis}	Λ	*ASE*	I^6	HOMA	
$(CH)_5PF_2$	**1**	C_{2v}	−7.9	−7.8	−49.0	−10.0	28.3	92.2	0.990
$(CH)_5PCl_2$	**2**	C_{2v}	−6.4	−7.1	−51.4			85.2	0.988
$(CH)_5PBr_2$	**3**	C_{2v}	−5.6	−6.6	−51.6			83.1	0.983
$(CH)_5P(OH)_2$	**4**	C_s	−7.2	−7.3	−48.7			84.3	0.982
$(CH)_5P(CH_3)_2$	**5**	C_{2v}	−1.3	−2.6	−30.0			68.3	0.896
$(CH)_5PH_2$	**6**	C_{2v}	−1.3	−2.5	−13.8	−3.9	23.2	70.1	0.914
$(CH)_5P(SiH_3)_2$	**7**	C_2	3.1	1.4					
$(CH)_5P$	**8**	C_{2v}	−8.4	−10.8	−78.0	−15.2	29.9	69.6	0.913
$(CH)_5CF_2^-$	**9**	C_{2v}	−6.2	−6.3	−41.6				
$(CH)_5CH_2^-$	**10**	C_s	−0.8	−1.2	−21.4				
$(CH)_5SiF_2^-$	**11**	C_{2v}	−4.1	−4.5	−38.4				
$(CH)_5SiH_2^-$	**12**	C_{2v}	0.9	−0.4					
C_5H_5SF	**13**	C_s	−9.2	−10.1	−69.7	−12.4	22.6	78.0	0.983
C_5H_5SCl	**14**	C_S	−8.7	−10.0	−76.0			74.2	0.964
C_5H_5SBr	**15**	C_S	−8.2	−9.7	−76.3			72.6	0.954
C_5H_5OH	**16**	C_s	−7.6	−8.0	−59.5			73.6	0.963
$C_5H_5SCH_3$	**17**	C_S	−4.8	−4.2	−42.7			50.6	0.762
C_5H_5SH	**18**	C_s	−6.2	−5.2	−41.3	−6.7	19.8	54.9	0.749
$C_5H_5S^+$	**19**	C_{2v}	−8.4	−10.7	−74.7	−13.8	26.3	76.4	0.968
$C_5H_5AsF_2$	**20**	C_{2v}	−7.5	−7.5	−49.0				
$C_5H_5AsCl_2$	**21**	C_{2v}	−6.4	−7.1	−52.3				
$C_5H_5AsBr_2$	**22**	C_{2v}	−5.6	−6.5	−51.0				
$C_5H_5AsOH_2$	**23**	C_s	−7.1	−7.3	−48.4				
$C_5H_5As(CH_3)_2$	**24**	C_{2v}	−1.1	−2.3	−29.5				
$C_5H_5AsH_2$	**25**	C_{2v}	−1.1	−2.3	−33.7				
C_5H_5As	**26**	C_{2v}	−7.9	−10.3	−83.2				
C_5H_5SeF	**27**	C_s	−8.4	−9.1	−71.9				
C_5H_5SeCl	**28**	C_S	−8.4	−9.5	−76.6				
C_5H_5SeBr	**29**	C_S	−7.9	−9.0	−76.2				
C_5H_5SeOH	**30**	C_s	−7.0	−7.5	−60.5				
$C_5H_5SeCH_3$	**31**	C_S	−4.1	−3.7	−41.7				
C_5H_5SeH	**32**	C_s	−5.6	−5.0	−41.7				
$C_5H_5Se^+$	**33**	C_{2v}	−7.9	−10.2	−79.5				

[a]) Calculated at the GIAO-SCF/6-31 + G*//B3LYP/6-311 + G** for **1** – **19** and GIAO-SCF/6-31 + G*//B3LYP/6-31G* for **20** – **33**. NICS(0) and NICS(1) mean the NICS value at the ring centers and the point 1 Å above the centers, respectively. [b]) Calculated at the CSGT-SCF/6-31 + G*//B3LYP/6-311 + G** for **1** – **19** and CSGT-SCF/6-31 + G*//B3LYP/6-31G* level for **20** – **33**. [c]) Calculated at the CSGT-HF/6-31 + G*//B3LYP/6-311 + G** level according to *Scheme 1*. [d]) Calculated at the B3LYP/6-311 + G** level according to *Scheme 1*.

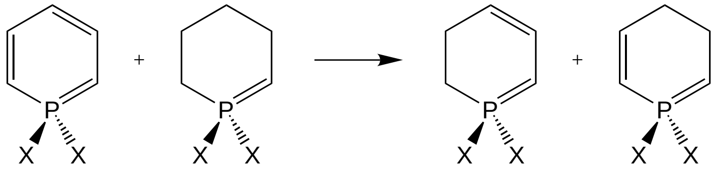
Magnetic susceptibility exaltations have been proposed to be uniquely associated with aromaticity [20][35]. Significantly negative diamagnetic susceptibility exaltations indicate aromaticity whereas positive paramagnetic represents antiaromaticity. We use the reaction in *Scheme 1* [36] to estimate the magnetic susceptibility exaltations of **1**, **6**, and **8**. The diamagnetic exaltation of **1**, −10.0 ppm cgs, is somewhat less than the −15.2 ppm cgs for phosphabenzene (**8**) and −13.7 ppm cgs for benzene. However, the exaltation of **6** (−3.9 ppm cgs) is significantly less than those of **1** and **8**; this provides a further indication that **6** is less aromatic than **1** and **8**.

Table 3. *$NICS_{tot}$, $NICS_{\pi}$, and $NICS_{\sigma}$ at the Points 1 Å above and at the Ring Centers* a)b))

Molecules		$NICS_{\pi}(1)/(0)$	$NICS_{tot}(1)/(0)$
$(CH)_5PF_2$	**1**	– 8.3 (– 17.6)	– 7.9 (– 8.3)
$(CH)_5PH_2$	**6**	– 3.4 (– 11.9)	– 2.8 (– 1.4)
$(CH)_5P(SiH_3)_2$	**7**	– 0.9 (– 7.5)	0.5 (2.8)
$(CH)_5P$	**8**	– 9.9 (– 19.2)	– 10.5 (– 8.2)
$(CH)_5CF_2^-$	**9**	– 7.2/ – 17.1	– 6.7/ – 7.0
$(CH)_5CH_2^-$	**10**	– 2.8/ – 10.4	– 1.9/ – 1.8
$(CH)_5SiF_2^-$	**11**	– 6.0/ – 14.0	– 5.4/ – 5.0
$(CH)_5SiH_2^-$	**12**	– 2.1/ – 10.4	– 1.3/0.1
$(CH)_5SF$	**13**	– 10.1 (– 19.7)	– 9.3/ – 8.5)
$(CH)_5SH$	**18**	– 5.4 (– 14.2)	– 6.0 (– 7.8)
$(CH)_5S^+$	**19**	– 9.7 (– 19.3)	– 10.5 (– 8.5)
$(CH)_5AsF_2$	**20**	– 8.5 (– 17.1)	– 7.9 (– 8.1)
$(CH)_5AsH_2$	**25**	– 4.4 (– 11.5)	– 3.2 (– 2.4)
$(CH)_5As$	**26**	– 9.6 (– 18.8)	– 10.0 (– 7.9)
$(CH)_5SeF$	**27**	– 9.9 (– 18.7)	– 8.9 (– 8.3)
$(CH)_5Se$	**32**	– 4.7 (– 12.8)	– 5.5 (– 6.9)
$(CH)_5Se^+$	**33**	– 9.5 (– 18.7)	– 10.0 (– 8.3)
Benzene		– 9.6 (– 20.7)	– 10.6 (– 8.9)

a) For compounds **1**–**19**, B3LYP/6-311 + G** geometries were used and B3LYP/6-31G* geometries for remaining molecules. b) The NICS values computed at the ring centers are given in parentheses for comparison.

Scheme 1



The induced ring currents of aromatic compounds result in very large out-of-plane magnetic susceptibilities compared with the in-plane components. This leads to exalted magnetic anisotropies [21], $\chi_{anis} = \chi_{cc} - (\chi_{aa} + \chi_{bb})/2$, where *c* is the out-of-plane axis for the planar molecule. Since the anisotropy is not determined solely by the ring current, it cannot be used to evaluate aromaticity quantitatively. However, compounds **1**–**4**, which have larger NICS(1) values, also have larger magnetic susceptibility anisotropies than compounds **5**, **6**, and **7** which have small NICS(1) values (*Table 2*).

3.1.3. *Energetic Measures.* The strain-corrected reaction in *Scheme 1* also was used to estimate the aromatic stabilization energies (*ASE*s) for compounds **1**, **6**, and **8**. The *ASE* of **1** is 28.3 kcal/mol at B3LYP/6-311 + G**, which, in agreement with the magnetic criteria, is only slightly less than the 29.9 kcal/mol for phosphabenzene. As expected, the *ASE* (23.2 kcal/mol) for **6** is less than those of **1** and **8** (this is explained below). Using homodesmotic equation in *Scheme 2*, *Nyulaszi* and *Veszpremi* [18] estimated the stabilization energies of **6** and **8** to be 20.6 and 27.7 kcal/mol, respectively, at MP2/6-31G*. Using the same equation to recalculate the stabilization energies at the B3LYP/6-311 + G** level, we obtained *ASE*s for **1**, **6**, and **8** of 19.3, 15.1, and 21.5 kcal/

mol, respectively. Although *Schemes 1* and *2* give different *ASE* values, they predict the same *ASE* order, *i.e.*, ASE (**8**) > ASE (**1**) > ASE (**6**).

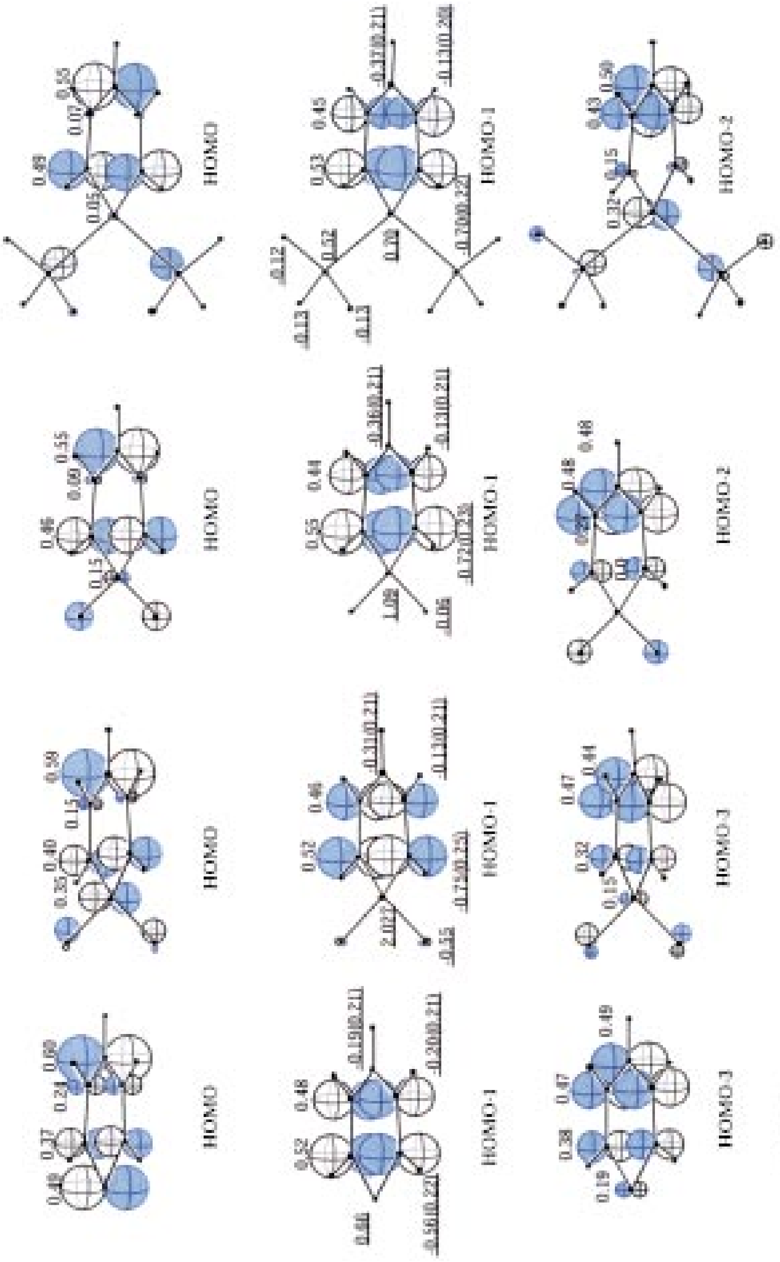
Scheme 2

$$C_5H_5X + 2CH_2{=}CH_2 + CH_2{=}XH \longrightarrow CH_2{=}CH{-}CH{=}XH + CH_2{=}X{-}CH{=}CH_2 + CH_2{=}CH{-}CH{=}CH_2$$

X = P, PH_2, and PF_2

3.2. *Are Phosphorus d-Orbitals Involved in Cyclic Electron Delocalization?* The possible role of phosphorus d-orbital involvement in λ^5-P compounds has been discussed for many years [37–42]. *Schäfer et al.* [13] and *Oehling* and *Schweig* [43] performed CNDO/2 calculations on 1,1-dimethoxyl-λ^5-phosphorin (see *Formulae*, similar to **4**) and concluded that the d-orbital participation enabled the aromaticity. *Dewar et al.* [44] also explained the aromaticity of phosphazene by introducing an '*island model*' which involved the phosphorus d-orbitals. However, it is now recognized that third period d-orbitals are only polarization rather than valence functions [37][41][42]. The highest three π MOs of compounds **1**, **6**, **7**, and **8** are displayed in *Fig. 4*. In contrast to the early proposals, no significant d-orbital contribution was found in any of these π MOs: the d-orbital coefficients are less than 0.07, far away from values expected in a valence orbital model. As in previous papers [37][41][42–45], we attribute the large MO coefficient given by the CNDO method to the poor basis sets and the inadequate theoretical level. *Fig. 4* also gives the MO coefficients. Generally speaking, the three π orbitals of **1** are similar to those of phosphabenzene (**8**), as indicated by the agreement among the MO coefficients. In contrast, the P-atom in **6** and **7** participates in the π system much less than in **1** and **8**; this diminishes the cyclic electron delocalization in **6** and **7**. As in phosphabenzene (**8**), HOMO-3 of **1** is the first π orbital, whereas the first π MO of **6** is HOMO-2. The higher π-orbital energy reflects the smaller *ASE* of **6** relative to **1**. Note the antibonding character of the interaction between the p orbital on P-atom in **7** and the other p-orbitals on C-atom in the HOMO-2 of **7**.

Natural population analysis (NPA) data also are given in *Fig. 4* (the values are underlined). Due to the high electronegativity, each F-atom in **1** has a negative charge of $-0.55e$ while the charge on P is close to $+2e$. The charge on P in **6** is $+1.09e$ and the charge the H substituents is negligible. The electron donation from SiH_3 group reduces the charge on P in **7** to a smaller value ($+0.70e$). Interestingly, *e.g.*, the X substituents influence the charges only on P (see *Fig. 4*); the total charges in the $(CH)_5$ parts of **1**, **6**, and **7** are quite close (-1.04, -1.12, and $-1.14e$, resp.). The population analysis reveals characteristic ylidic electrostatic interaction between the P-atom and the $(CH)_5$ moieties. This zwitterionic (ylidic) character depends on the substituents. Charge comparisons reveal that the electrostatic interaction between P- and the adjacent C-atoms in **8** is weaker than that in **1**. Even though **8** is more aromatic than **1**, this results in the longer C–P bond length (1.743 Å) in **8** than in **1** (1.697 Å). The C–P bond lengths in **6** and **8** (1.742 and 1.743 Å, resp.) are nearly identical. The stronger aromatic interaction compensates for the weaker electrostatic interaction in **8** than in **6**.



$(CH)_5P$
8

$(CH)_5PF_2$
1

$(CH)_5PH_2$
6

$(CH)_5P(SiH_3)_2$
7

Fig. 4. *Three highest* π *MOs for* **1**, **2**, **7**, *and* **8**. The MO coefficients and the natural charge populations (underlined) are given.

As discussed above, both magnetic (NICS and magnetic susceptibility exaltation, Λ) and energetic criteria show the six-membered λ^5-phosphorins **1**–**7** to be less aromatic than phosphabenzenes (**8**); this contradicts the *Bird* I^6 and the HOMA aromatic index orders. This discrepancy is not surprising since bond-length equalization in **1**–**6** is not determined solely by aromaticity; it is influenced significantly by the electrostatic interaction. However, within the same class of compounds (*e.g.*, the λ^5-phosphorins), the two indices show the same trends in the magnitude of aromaticity as the NICS criterion (see *Table 2*).

In summary, we conclude that the aromaticity of λ^5-phosphorins is related to the electronegativity of substituents at the P-atoms: the λ^5-phosphorins with weakly electronegative substituents are ylidic and can be represented by structure *b* in *Fig. 2*, whereas the λ^5-phosphorins with strongly electronegative substituents have obvious aromatic character and are best described as a hybrid of structures *a* and *b* (*Fig. 2*). We attribute the medial *ASE* (23.2 kcal/mol) for nonaromatic **6** to the local delocalization among the C-atoms in the ring. Our conclusion differs from that of *Schäfer et al.* [13] in that we stress the substituent effect on the aromaticity and discount d-orbital participation. Recently, *Dobado et al.* [40] suggested the nature of the C–P bonds in H_3P-CH_2 and in F_3P-CH_2 are similar, *i.e.*, covalent with significantly polar interaction and a small contribution of negative hyperconjugation. However, when the C–P bond is incorporated into six-membered rings, the effect of substituents at the P-atom on the aromaticity are substantial.

The aromatic character of **5** has been investigated experimentally by *Ashe* and *Timothy* [14]. The ^{1}H-NMR chemical shifts of H–C(2)(H–C(6)), H–C(3)(H–C(5)), H–C(4), and the Me H-atoms, 3.98, 6.70, 4.62, and 1.5 ppm, respectively, led them to conclude that **5** is ylidic rather than aromatic. Our calculated ^{1}H-NMR chemical shifts for these protons are 3.70, 7.70, 4.44, and 1.42 ppm respectively, in reasonable agreement with the experimental values. Indeed, the calculated NICS value ($\mathrm{NICS}(1) = -2.6$) show that **5** is not aromatic. *Bundgaard et al.* [15] probed the electronic structure of 1,1-dimethoxy-λ^5-phosphorin (see *Formulae*, similar to **4**) by NMR and found that the chemical shifts for C(2) and C(4) are more downfield than those in phosphorus ylides [46]. They attributed this to a greater degree of 6π-electron delocalization. Consistent with this, we compute a larger NICS(1) (-7.3) for compound **5** than for **6** (-2.3). The predicted ^{1}H-NMR chemical shifts for H–C(2)(H–C(6)), H–C(3)(H–C(5)), and H–C(4) (5.13, 8.28, and 5.52 ppm, resp.) also are more downfield than those for **6**.

Similar to NICS, the ^{1}H-NMR chemical shifts of **4** and **5**, together with of **8**, were dissected into the individual contributions by the IGLO method [29], *i.e.*, C–C(P) π bonds, C–C(P) σ bonds, and C–H σ bonds (as well as the core electrons, lone pairs and P–X bonds). The IGLO total chemical shifts agree with the corresponding GIAO values (*Table 4*). The average IGLO ^{1}H-NMR chemical shift of **4** (6.3 ppm) is 0.9 ppm larger than that of **5**. The same differences are given by GIAO, in good agreement with the difference (1.2 ppm) measured experimentally. In **4** and **5**, the ring C–P (P) σ and C–H bond, as well as other contributions are quite close. Note that the C–H bonds **4** and **5** have very similar charge populations (see the NPA charges in *Fig. 4*). However, the C–C(P) π contributions in **4** and **5** are quite different and make up 0.75 of the 0.9 ppm total difference. In other words, the ring current (π electron delocalization)

Table 4. *Individual Contributions to ¹H-NMR Chemical Shifts of* **4**, **6**, *and* **8**[a])

Molecules		C−C(P) π	C−C(P) σ	C−H	Total[b])	GIAO	Exper.[c])
$(CH)_5(OH)_2$[d]) (**4**)	2/6	−2.4	0.9	6.5	5.4	5.0	5.1
	4	−2.7	4.1	5.8	7.6	8.1	8.3
	3/5	−2.9	2.4	5.9	5.9	5.4	5.5
Average		−2.7	2.5	6.1	6.3	6.2	6.3
$(CH)_5(CH_3)_2$ (**6**)	2/6	−3.4	0.7	6.5	4.1	3.7	4.0
	4	−3.2	4.4	5.5	7.2	7.8	6.7
	3/5	−3.6	2.2	6.1	4.6	4.3	4.6
Average		−3.4	2.4	6.0	5.4	5.3	5.1
$(CH)_5P$ (**8**)	2/6	−1.9	4.8	5.6	8.6	9.3	8.6
	4	−2.2	4.0	6.3	8.1	8.4	7.7
	3/5	−1.7	3.6	5.9	7.5	7.9	7.4
Average		−1.9	4.1	5.9	8.1	8.5	7.9

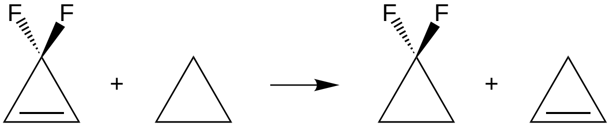
[a]) B3LYP/6-311 + G** Geometries were used. [b]) The total chemical shifts include other factors such as core and other bonds besides the listed. [c]) Experimental values for **4**, **6**, and **8** are from [42][13], and [15], respectively. [d]) The experimental molecule is $(CH)_5-P(OCH_3)_2$ (1,1-dimethoxy-λ^5-phosphorins).

results in ¹H shifts in **4** to be 0.75 ppm more downfield than that in **5**; this also indicates that **4** is more aromatic than **5**. The π contributions to the chemical shifts also suggest that **4** is less aromatic than phosphabenzene (**1**).

3.3. *Why Do the Substituents Influence the Magnitude of Aromaticity?* The enhanced stabilization of 3,3-difluorocyclopropene (**47**) relative to the parent cyclopropene has been recognized for many years [47–50]. Using the reaction in *Scheme 3*, *Greenberg et al.* [47] evaluated the stabilization energy to be 9.6 kcal/mol at HF/4-31G. The higher-level calculations (MP2 and B3LYP), carried out by *Borden* [49] and by *Wiberg* and *Marquez* [50] gave very similar values. It is generally accepted that this enhanced stabilization is due to the delocalization of π-electrons into the appropriate C−F σ^* orbital (*i.e.*, negative hyperconjugation). Hence, 3,3-difluorocyclopropene is somewhat aromatic [48][49]. This also is found in three-membered phosphirene and related systems [51–54] and is known as '*σ^* aromaticity*' [54]. The hyperconjugative interaction can be described schematically by the ionic resonance structure in *Fig. 5,a*.

Recently, *Nyulaszi* and *Schleyer* [55] have found that cyclopentadienes, when 5,5-disubstituted with electropositive groups, have significantly enhanced cyclic delocalization in comparison with the parent system (C_5H_6). They attribute this to the hyperconjugation between the $C_5-X(2)$ bonds and ring π system. The two C−X(2) bonds can serve as a pseudo-π-donor and contribute to the cyclic electron delocalization. The magnitude of the cyclic electron delocalization depends on the electron-donating ability of substituents: the stronger this ability, the greater their aromaticity. For example, geminal electron-donating groups like SiH_3 at C_5 (**48**) contribute, in effect, π electrons to the ring (*i.e.*, positive hyperconjugation) as represented schematically in *Fig. 5,b*. In contrast, electron-accepting substituents like F (**49**) function as electron acceptors (negative hyperconjugation, *Fig. 5,c*) and destabilize the system. Considering the formal charges structure, in *Fig. 5,b* has six π electrons (yielding a *Hückel* aromatic system like the cyclopentadienyl anion), whereas the

Scheme 3



structure in *Fig. 5,c* has only four π electrons (yielding a *Hückel* antiaromatic system). The NICS(1) values, −7.8 for 5,5-disilylcyclopentadiene (**48**) and 3.2 for 5,5-difluorocyclopentadiene (**49**), support this expectation. Consequently, **48** has much less bond-length alternation than **49**. The ring bond lengths in **48** are 1.494, 1.360, and 1.446 Å, respectively, while the corresponding values in **49** are 1.518, 1.334, and 1.495 Å.

Similar to the three- and the five-membered ring systems, the P−X(2) bonds in compounds **1**–**7** also interact with the ring π electrons. When the substituent is electronegative, *e.g.*, F, the P−X bonds serve as π-electron acceptors (negative hyperconjugation) as indicated by the ionic resonance structure (*Fig. 5,d*), a 6π-electron aromatic molecule. When the 1,1-substitutents are electropositive, *e.g.*, silyl, the P−X bonds donate electrons to the ring (hyperconjugation). The corresponding ionic resonance structure (*Fig. 5,e*) represents an 8π antiaromatic system. These qualitative expectations are supported by the NPA charge populations (see *Fig. 4*) and the NICS(1) values −7.8 for **1** but 1.4 for **7**.

3.4. *The Aromaticity of Cyclohexadienyl Anions with* CX_2^- *and* SiX_2^- *(X = H, and F) Groups.* $(CH)_5CX_2^-$ and $(CH)_5SiX_2^-$ (X=F and H) are isoelectronic with λ^5-$(CH)_5PX_2$. The B3LYP/6-311 + G** geometries of **9**–**12** are displayed in *Fig. 6*. Both **9** (with a CF_2^- group) and **11** (with a SiF_2^- group) have C_{2v} symmetries, *i.e.*, with planar rings. As with the λ^5-$(CH)_5PX_2^-$ s, the electronegativity of the X substituents in **9**–**12** influence the aromaticity. This is shown by the GIAO (*Table 2*) and the dissected NICS values (*Table 3*). The GIAO-SCF/6-31 + G*//B3LYP/6-311 + G** NICS(1) of $(CH)_5SiF_2^-$ (**11**) is −4.5, compared with −0.4 for $(CH)_5SiH_2^-$ **12**. The NICS(1) π of **11** and **12** are −6.0 and −2.1, respectively. Likewise, the ring C,C bond length equalization in **11** is greater than that in **12** (*Fig. 6*). The X substituent in $(CH)_5CX_2^-$ (**9** and **10**) influences not only the bond length but also other features of the geometry. The ring atoms in the C_s minimum (**10**) are not in the same plane; the C_{2v} structure (not shown) is 1.4 kcal/mol less stable than the C_s structure and is the inversion transition state with one imaginary frequency. In contrast, $(CH)_5CF_2^-$ (**9**) prefers C_{2v} symmetry with a planar ring. The GIAO and IGLO NICS (*Tables 2* and *3*) also reveal **9** (NICS(1) = −6.3, NICS(1)π = −7.2) to be more aromatic than **10** (NICS(1) = −1.2, NICS(1)π = −2.8). The ionic resonance structures (*Fig. 5,f* and *g*) indicate why compounds **9** and **11** are somewhat aromatic.

Compounds similar to **9** are familiar. As early as 1900 [56], they were suggested to be as intermediate complexes in nucleophilic aromatic substitution reactions (*Scheme 4*). In 1902, *Meisenheimer* [57] first showed that anionic complexes (now named after him) can be isolated as salts. Since then, a host of *Meisenheimer* complexes have been isolated or identified by spectroscopy or other physical methods [57].

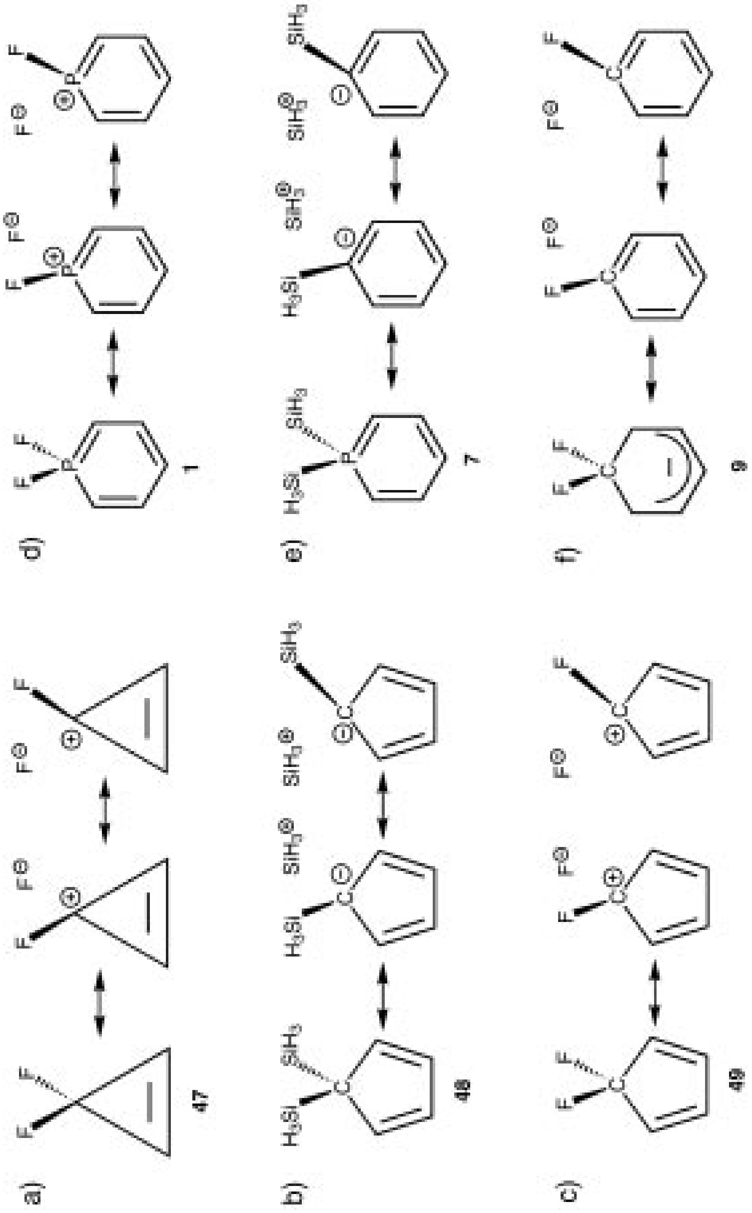
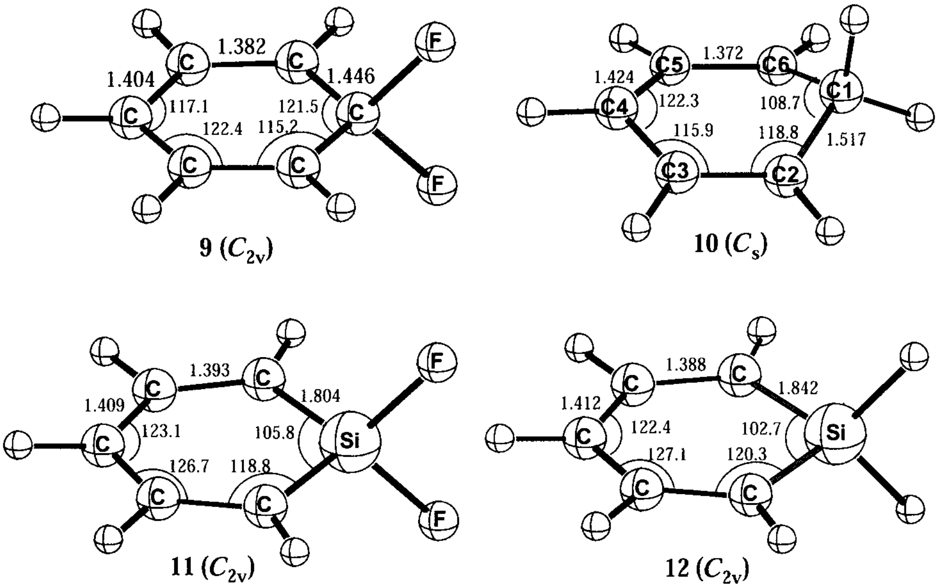


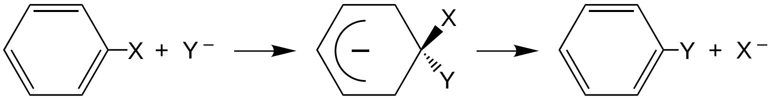
Fig. 5. *The ionic resonance structures, indicating hyperconjugative possibilities in related some three-, five-, and six-membered ring molecules*



9 (C_{2v}) **10** (C_s) **11** (C_{2v}) **12** (C_{2v})

Fig. 6. *B3LYP/6-311 + G** Geometries of* **9**–**12** (bond lengths in Å and angles in degrees)

Scheme 4. Meisenheimer *Complexes*



3.5. *Aromaticity of λ⁴-S Compounds.* The λ⁵-phosphorins can be generated formally by replacing a *Kekulé* benzene =CH– unit by an isoelectronic $=PX_2-$ (X=H, F, Cl, *etc.*) group, related to the phosphonium ylides, $CH_2=PX_3$ [58]. Similarly, the replacement of a benzene =CH– with a =SX– (X = H, F, Cl, *etc.*) group, related to the sulfonium ylides $CH_2=SX_2$ [58], gives the six-membered compounds **13**–**18** shown in *Fig. 3,b*. These compounds have C_s symmetries with respect to the C(3)SX plane. Unlike the λ⁵-phosphorins, the rings in the **13**–**18** structures are not planar, although C(1), C(2), C(4), and C(5) lie nearly in the same plane. These rings in the compounds with strongly electronegative substituents (X=F, Cl, Br, OH) are closer to planarity than those in the compounds with weakly electronegative substituents (X = H and Me; see the dihedral angles given in *Fig. 3,b*). The compounds **13**–**16** with strongly electronegative substituents have shorter ring S–C bond distances (*ca.* 1.70 Å) than the compounds **17**–**18** with weakly electronegative substituents (which are nearly 1.75 Å). Since the six-membered λ⁴-S compounds do not have planar rings, we choose the C(1)–C(2)–C(4)–C(5) centers (the four C-atoms lie in the same plane) as the NICS(0) points and define NICS(1) as the average of the NICS values of the points 1 Å above and 1 Å below the ring center. The NICS(1) for compounds **13**–**18**, –10.1, –10.0, –9.7, –8.0, –4.2 and –5.2 ppm, respectively, can be compared to –10.7 ppm for the thiobenzene cation (**9**), the parent of typical 6π-electron compounds experimentally exemplified by thiopyryium salts [59]. The NICS(1) values for λ^4-S compounds are slightly larger than their λ^5-phosphorin counterparts, but this is not reflected in the *Bird* I^6 and HOMA indices. However, the substituent effects on the aromaticity are the same as in the λ^5-phosphorins for all three criteria: the compounds with strongly electronegative substituents (F, Cl, Br, OH) are more aromatic than the H and CH_3 compounds. The dissected NICS for **13**, **18** and **19**, compiled in *Table 3*, also show **13** to be more aromatic than **18**. The ASE and magnetic exalation data (*Table 2*), computed on the basis of a reaction similar to that in *Scheme 2* further confirm the conclusion. Experimentally, the 1-methyl-3-5-diphenyl λ^4-S compound, originally thought to be aromatic [60], was later considered to be ylide-like [61]. We conclude that it is mainly ylidic in character although there is weaker cyclic electron delocalization.

3.6. *Results for Six-Membered λ^5-As, λ^5-Se Compounds.* The effect of substituents on the degree of cyclic electron delocalization is illustrated by our results on six-membered λ^5-$(CH)_5AsX_2$ (**20**–**25**), λ^5-$(CH)_5SeX$ (**27**–**32**) compounds. The B3LYP/6-31G* energies are given in *Table 1* and the B3LYP/6-31G* geometries are displayed in *Fig. 7.* The SCF-GIAO/6-31 + G* NICS(0) and NICS(1), and dissected NICS values are included in *Tables 2* and *3*, respectively. As expected, the λ^5-As compounds and λ^4-Se compounds are similar to λ^5-phosphorins and λ^4-S compounds both in their aromatic character and in their geometries. Although the ring C–As bond lengths in **20**–**25** and C–Se in **27**–**32** are longer than the corresponding C–P and C–Se bond lengths, respectively, the ring C–C bond lengths do not change significantly. Both GIAO-HF/6-31 + G*//B3LYP/6-31G* NICS(1) and IGLO-III $\text{NICS}(1)_\pi$ of **20**–**25** and **27**–**32** are very close to those of **1**–**6** and **13**–**18**, respectively. The influence of substituents on the aromaticity of λ^5-$(CH)_5AsX_2$ (**20**–**25**), λ^5-$(CH)_5SeX$ (**27**–**32**) is similar to **20**–**25** and **27**–**32**, respectively. The NICS value ($\text{NICS}(0) = -1.1$ ppm and $\text{NICS}(1) = -2.3$ ppm), in agreement with the experimental conclusion [14], indicate that 1,1-dimethyl-λ^5-arsabenzene is not aromatic.

3.7. *The Effect of λ^5-P(As) and λ^4-S(Se) Substituents on the Antiaromaticity of Cyclobutadiene.* We have shown how λ^5-$P(As)X_2$ and λ^4-S(Se)X groups influence the aromaticity when incorporated into six-membered rings. Do the same λ^5-$P(As)X_2$ and λ^4-S(Se)X groups influence the antiaromaticity of cyclobutadiene? For comparison, we also considered the incorporation of λ^3-P(As) and λ^3-$S^+(Se^+)$ groups. The chemistry and bonding of cyclobutadiene and its analogues have been studied extensively [17][59]. Recently some λ^5-phosphacyclobutadiene compounds were synthesized [62]. *Schoeller* and *Bush* [63] investigated the analogs with phospha replacement in cyclobutadiene. They compared the valence isomerization barriers and singlet-triplet energy separations with those of the parent cyclobutadiene. At the MCSCF level, the valence isomerization barrier (7.2 kcal/mol) and singlet-triplet gap (7.4 kcal/mol) for phosphacyclobutadiene are smaller than those (8.4 and 14.8 kcal/mol, resp.) for cyclobutadiene.

In light of the results for the six-membered compounds, we only examined the extreme X=F and X=H cases. The B3LYP/6-311 + G** geometries of **34**–**46**, together with the important structural parameters, are given in *Fig. 8*. The SCF-GIAO/6-31 + G*//B3LYP/6-311 + G** NICS(0) and NICS(1), as well as zero-point energies

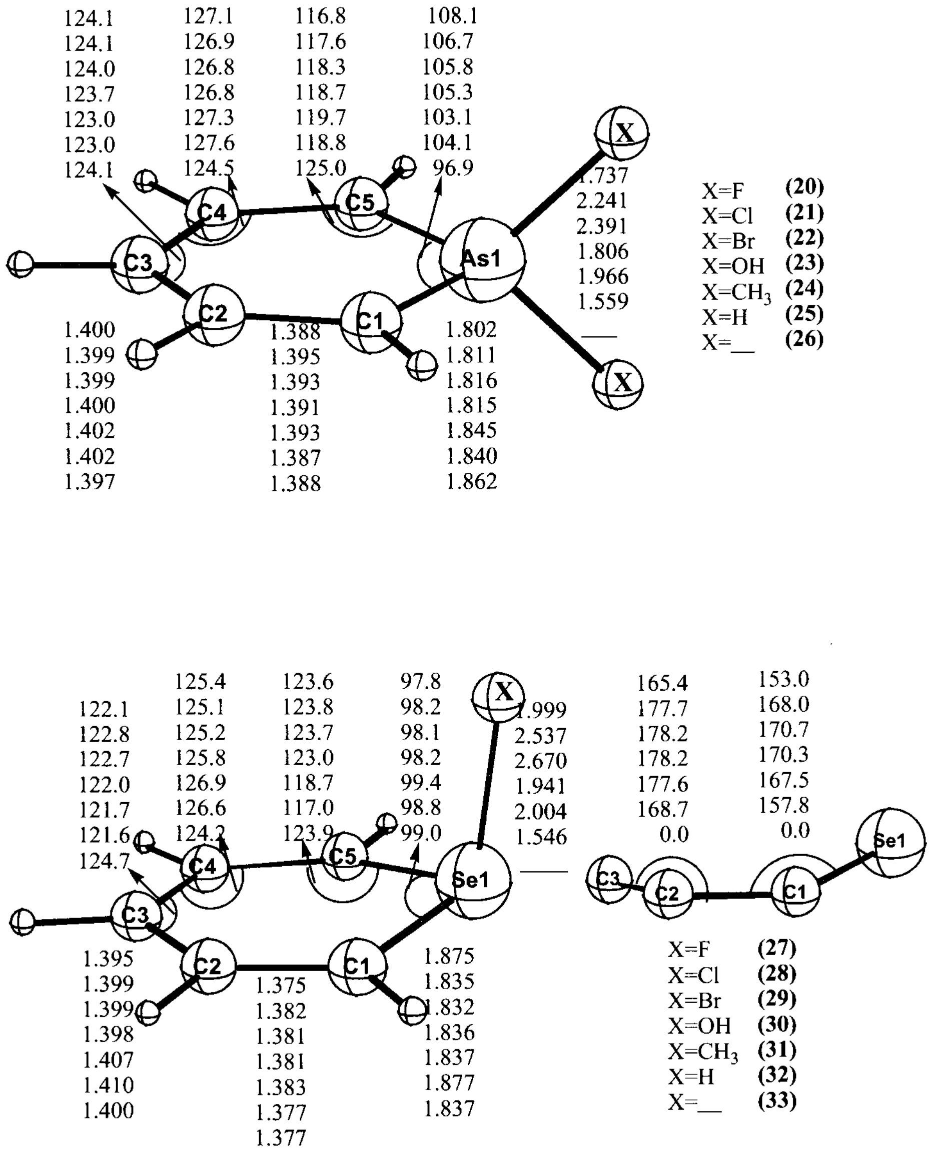


Fig. 7. *B3LYP/6-311G* Geometries of* **20**–**33** (bond lengths in Å and angles in degrees)

and total energies, are listed in *Table 5*. Compounds **34**–**38** (with λ^3-P(As) and λ^3-S$^+$(Se$^+$) substituents) are planar with two unequal C–X bonds. Their dissected (NICS$_\pi$ and NICS$_\sigma$) and total NICS (*Table 6*) are very close to the cyclobutadiene values, which indicates that the incorporation of λ^3-P(As) and λ^3-S$^+$(Se$^+$) groups do not change the antiaromaticity of cyclobutadiene. Compounds **39**–**42** (λ^5-(CH)$_3$P(As)X$_2$) have approximately C_2 symmetries, and the four-membered rings are planar. In contrast to compounds **35**–**38** (withλ^3-P(As) group), the two C–X bonds in **39**–**42** are equal. The NICS$_\sigma$(0) values of **39**–**42** are much less than that of cyclobutadiene and these compounds have small negative NICS$_\pi$(0) values ($-3.1 \sim -8.2$ ppm). Hence, the incorporation of λ^5-P(As)X$_2$ units weaken the antiaromaticity of cyclobutadiene significantly. This may be why the λ^5-phosphacyclobutadienes are well characterized [62] but cyclobutadiene is observable only as a transient species [64]. We attribute this difference to the contributions of pseudo π electrons from two P–X (or As–X) bonds to the 4π electron rings. Note that the antiaromaticity of λ^3-P(As) compounds is similar to cyclobutadiene. The P–F bonds should perturb the system less since the P–H bond MO is closer than the P–F bond MO to π-orbital energies. Therefore, the λ^5-P(As)F$_2$-containing compounds are more antiaromatic than the λ^5-P(As)H$_2$-containing compounds, which is supported by the slightly more negative NICS$_\pi$(0) of **39** and **41**, than **40** and **42** (*Table 6*).

Table 5. *GIAO-SCF/6-31 + G*//B3LYP/6-311 + G** Nucleus-Independent Chemical Shifts* (in ppm cgs) *at the Ring Centers* (NICS(0)) *and 1 Å above the Ring Centers* (NICS(1)) *for Compounds* **34**–**46**, *together with B3LYP/6-311 + G** Total Energies* (E_{tot}, in hartrees) *and B3LYP/6-31G* Zero-Point Energies* (ZPE, in kcal/mol)

		ZPE	E_{tot}	NICS(0)	NICS(1)
(CH)$_4$	**34**			27.7	18.5
(CH)$_3$P	**35**	29.52	– 457.40483	30.7	19.6
(CH)$_3$As	**36**	29.28	– 2351.9104	31.8	20.0
(CH)$_3$S$^+$	**37**	29.97	– 513.96348	22.5	10.6
(CH)$_3$Se$^+$	**38**	29.98	– 2517.3028	23.3	11.1
(CH)$_3$PF$_2$	**39**	33.17	– 657.21203	0.6	4.8
(CH)$_3$PH$_2$	**40**	40.44	– 458.59854	1.8	2.4
(CH)$_3$AsF$_2$	**41**	31.25	– 2551.6641	1.3	3.3
(CH)$_3$AsH$_2$	**42**	38.09	– 2353.0756	1.5	2.1
(CH)$_3$SF	**43**	30.94	– 614.08031	– 5.2	– 6.3
(CH)$_3$SH	**44**	46.14	– 515.90298	– 0.4	– 0.2
(CH)$_3$SeF	**45**	29.87	– 2617.4224	– 3.8	– 3.0
(CH)$_3$SeH	**46**	33.63	– 2518.1509	0.2	0.1

Table 6. *NICS$_{tot}$, NICS$_\pi$, and NICS$_\sigma$ at Points 1 Å above and at the Ring Centers*[a])

Molecules		NICS$_{tot}$(1)/0)	NICS$_\pi$(1)/(0)	NICS$_\sigma$(1)/(0)
(CH)$_4$	**34**	12.7/20.9	14.1/ – 0.2	1.7/23.2
(CH$_3$P	**35**	13.1/22.2	13.7/0.2	1.6/23.0
(CH)$_3$As	**36**	13.4/22.9	12.8/0.3	1.9/22.4
(CH)$_3$S$^+$	**37**	12.1/21.2	13.7/0.3	1.4/23.5
(CH)$_3$Se$^+$	**38**	12.2/20.7	13.2/0.4	1.7/22.7
(CH)$_3$PF$_2$	**39**	4.8/ – 0.4	7.8/ – 5.3	– 1.9/5.6
(CH)$_3$PH$_2$	**40**	1.6/0.8	3.4/ – 8.2	0.0/11.9
(CH)$_3$AsF$_2$	**41**	4.8/0.4	7.9/ – 3.1	– 1.9/1.9
(CH)$_3$AsH$_2$	**42**	2.3/1.5	3.6/ – 6.5	0.0/10.1
(CH)$_3$SF	**43**	– 2.8/ – 5.8	2.0/ – 8.3	– 3.2/6.3
(CH)$_3$SH	**44**	– 0.5/ – 0.5	– 0.4/ – 9.7	1.1/14.4
(CH)$_3$SeF	**45**	– 0.8/ – 2.5	3.2/ – 6.4	2.7/7.5
(CH)$_3$SeH	**46**	0.7/1.5	1.2/ – 7.8	1.5/14.3

[a]) GIAO-HF/6-31G*//B3LYP/6-311 + G**.

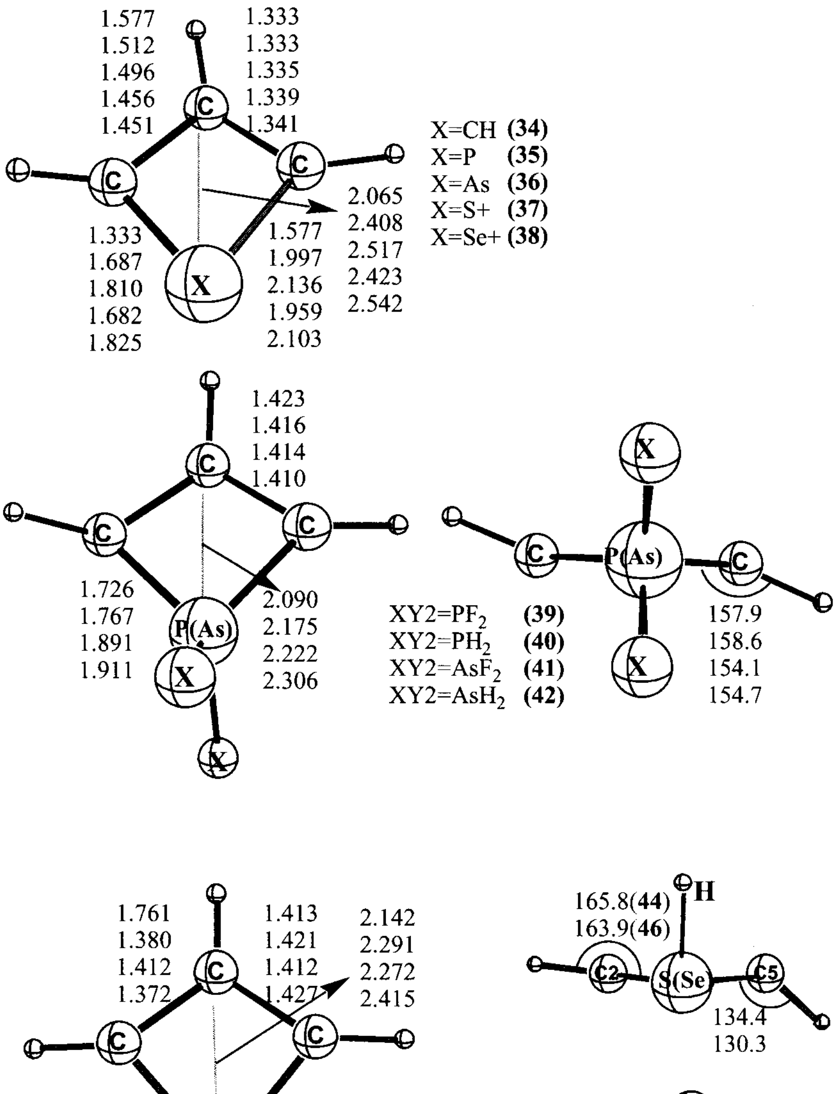


Fig. 8. *B3LYP/6-311 + G^{**} Geometries of* **34–45** (bond lengths in Å and angles in degrees)

The electronegativity of substituents in the λ^4-$(CH)_3S(Se)X$ compounds **43–46** have significant influences on the structure, but, judging from NICS, not on the antiaromaticity. The compounds **43** and **45** with X=F have C_s symmetries; the two

C−X bonds and two C−C bonds are equal. However, **44** and **46** (X = H) have no symmetry. The GIAO-HF/6-31 + G* and dissected NICS data (*Tables 5* and *6*, resp.) reveal that λ^4-S(Se)X incorporations into cyclobutadiene also weaken the antiaromaticity significantly.

4. Conclusions. – Various measures (geometric, energetic, magnetic susceptibility exaltation, and NICS) have been used to investigate the aromatic character of six-membered λ^5-phosphorins ($(CH)_5PX_2$) and λ^4-S compounds ($(CH)_5SX$; X=F, Cl, Br, OH, H, Me, and SiH_3). The electronegativity of the substituents X influences the aromaticity of λ^5-phosphorins significantly. The NICS(1) values of λ^5-phosphorins with electronegative substituents (X=F, Cl, Br, and OH), −7.8, −7.3, −7.1, and −6.6, respectively, at GIAO-HF/6-31 + G*/B3LYP/6-311 + G**, only somewhat less than (−10.8) of phosphabenzene and (−10.6) of benzene, indicate these phosphorins to be aromatic, but somewhat less than phosphabenzene. The compounds with electropositive substituents (H, Me, and SiH_3) have small NICS (−2.6, −2.5, and 1.4, resp.), and are weakly or nonaromatic. This conclusion is supported further by the ASE and magnetic susceptibility exaltation results. Although the charge on the P-atom is influenced by the substituents, the total $(CH)_5$ fragment charge is not. Hence, there may be more or less zwitterionic (ylidic) character in the bonding. When the substituents (X) are strongly electronegative, the electronic structures may be considered to be a hybrid of zwitterion a (ylide) and a '*Hückel*' aromatic system (*Fig. 2,a* and *b*). When these substituents are electropositive, cyclic electron delocalization involving the rings is reduced, and the zwitterionic (ylidic) description is better (*Fig. 2,b*). This interpretation resolves previous disagreements on the aromaticity of λ^5-phosphorins. The electronegativity of substituents also influence the aromaticity of six-membered λ^4-S compounds, but not as significantly as in the λ^5-phosphorin cases. These generalizations can be extended to the six-membered λ^5-As(CH) and λ^5-Se compounds, and the isoelectronic cyclohexadienyl anion, $(CH)_5CX_2^-$ as well as $(CH)_5SiX_2^-$.

The λ^5-P(As)X_2 groups incorporated into the cyclobutadiene decrease the antiaromaticity significantly, but the substituents X only have a small influence. The λ^4-S(Se)X substituents also decrease the antiaromaticity of cyclobutadiene greatly considerably, and influence the geometry greatly.

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REFERENCES

[1] G. Märkl, *Angew. Chem.* **1966**, *4*, 1023.
[2] G. Märkl, *J. Heterocycl. Chem.* **1972**, *9*, S-69.
[3] K. Dimroth, *Top. Curr. Chem*. **1973**, *38*, 1.
[4] G. Märkl, *Phosphorus Sulfur* **1977**, *3*, 77.
[5] A. J. Ashe, *Acc. Chem. Res.* **1978**, *11*, 153.
[6] K. Dimroth, *Acc. Chem. Res.* **1982**, *15*, 58.
[7] A. Katritzky, C. W. Rees, in 'Comprehensive, Heterocyclic Chemistry the Structure, Reaction, Synthesis and Use of Heterocyclic Compounds', Ed. Otto Meth-Cohn, Pergamon Press, 1984.
[8] D. A. Dixon, in 'Ylides and Imines of Phosphorus', Ed. A. W. Johnson, John Wiley & Sons, Inc. New York, 1993, p. 75.

[9] G. Märkl, *Angew. Chem.* **1963**, *75*, 168.
[10] G. Märkl, *Angew. Chem.* **1965**, *77*, 1109.
[11] S. F. Mason, *Nature* **1965**, *205*, 495.
[12] R. Vilceanu, A. Balint, Z. Simon, *Nature* **1968**, *217*, 61.
[13] W. Schäfer, A. Schweig, K. Dimroth, H. Kanter, *J. Am. Chem. Soc.* **1976**, *98*, 4410.
[14] A. J. Ashe, III; W. S. Timothy, *J. Am. Chem. Soc.* **1976**, *98*, 7861.
[15] T. Bundgaard, J. Jakobsen, K. Dimroth, H. Pohl, *Tetrahedron Lett.* **1974**, 3179.
[16] C. W. Bird, *Tetrahedron* **1990**, *46*, 5697.
[17] P. J. Garatt, 'Aromaticity', John Wiley & Sons, Inc. New York, 1986.
[18] L. Nyulaszi, T. Veszpremi, *J. Phys. Chem.* **1996**, *100*, 6456.
[19] Y. Xie, H. F. Schaefer, *THEOCHEM* **1991**, *234*, 247.
[20] P. v. R. Schleyer, H. J. Jiao, *Pure Appl. Chem.* **1996**, *68*, 209.
[21] V. I. Minkin, M. N. Glukhovtsev, B. S. Simkin, 'Aromaticity and Antiaromaticity: Electronic and Structural Aspects', John Wiley & Sons, Inc. New York, 1994.
[22] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, J. Haijun, N. J. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) G. Subramanian, P. v. R. Schleyer, H. Jiao, *Angew. Chem., Int. Ed.* **1996**, *35*, 2638.
[23] P. v. R. Schleyer, H. Jiao, N. J. R. v. E. Hommes, V. G. Malkin, O. L. Malkina, *J. Am. Chem. Soc.* **1997**, *119*, 12669.
[24] a) G. Subramanian, P. v. R. Schleyer, H. Jiao, *Angew. Chem., Int. Ed.* **1996**, *35*, 2638; b) H. Jiao, P. v. R. Schleyer, Y. Mo, M. A. McAllister, T. T. Tidwell, *J. Am. Chem. Soc.* **1997**, *119*, 7075; c) H. Jiao, P. v. R. Schleyer, B. R. Beno, K. N. Houk, R. Warmuth, *Angew. Chem., Int. Ed.* **1997**, *36*, 2761; d) T. K. Zywietz, H. Jiao, P. v. R. Schleyer, A. de Meijere, *J. Org. Chem.* **1998**, *63*, 3417; e) A. A. Fokin, H. Jiao, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1998**, *120*, 9364; e) M. Mauksch, V. Gogonea, H. Jiao, P. v. R. Schleyer, *Angew. Chem., Int. Ed.* **1998**, *37*, 2395; f) H. Jiao, P. v. R. Schleyer, *J. Phys. Org. Chem.* **1998**, *11*, 655; g) M. Bühl, *Chem. Eur. J.* **1998**, *4*, 734; h) G. Subramanian, P. v. R. Schleyer, H. Jiao, *Organometallics* **1997**, *16*, 2362; i) M. K. Cyranski, T. M. Krygowski, M. Wisiorowski, N. J. R. van Eikema Hommes, P. v. R. Schleyer, *Angew. Chem., Int. Ed.* **1998**, *37*, 177; j) M. Nendel, K. N. Houk, L. M. Tolbert, E. Vogel, H. Jiao, P. v. R. Schleyer, *J. Phys. Chem. A* **1998**, *102*, 7191; J. M. Schulman, R. L. Disch, H. Jiao, P. v. R. Schleyer, *J. Phys. Chem. A* **1998**, *102*, 8051; l) F. P. Cossio, I. Morao, H. Jiao, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1999**, *121*, 6737; P. A. Hunt, T. Fischer, P. Schwerdtfeger, *J. Org. Chem.* **1997**, *62*, 8063; J. M. Schulman, R. L. Disch, *J. Phys. Chem.* **1997**, *101*, 9176; m) R. West, J. J. Buffy, M. Haaf, T. Muller, B. Gehrhus, M. F. Lappert, Y. Apeloig, *J. Am. Chem. Soc.* **1998**, *120*, 1639; n) M. L. McKee, M. Balci, H. Kilic, E. Yurtsever, *J. Phys. Chem. A* **1998**, *102*, 2351; o) C. H. Choi, M. Kertesz, *J. Chem. Phys.* **1998**, *108*, 6681; p) E. D. Jemmis, B. Kiran, *Inorg. Chem.* **1998**, *37*, 2110; q) A. J. Matzger, K. P. C. Vollhardt, *Tetrahedron Lett.* **1998**, *39*, 6791; r) S. Patchkovskii, W. Thiel, *J. Mol. Model.* **2000**, *6*, 69; s) D. Sawicka, K. N. Houk, *J. Mol. Model.* **2000**, *6*, 158.
[25] Gaussian 98, Revision D.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, J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
[26] a) K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251; b) R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789.
[27] a) T. A. Keith, R. F. W. Bader, *Chem. Phys. Lett.* **1993**, *210*, 223; b) T. A. Keith, R. F. W. Bader, *Chem. Phys. Lett.* **1992**, *194*, 1.
[28] a) V. G. Malkin, O. L. Malkin, L. A. Eriksson, D. R. Salahub, 'Modern Density Function Theory', Ed. J. M. Seminario, P. Politzer, Elsevier, Amsterdam, 1995; b) J. M. Seminario, O. L. Politzer, L. A. Eriksson, D. R. Salahub, *J. Am. Chem. Soc.* **1994**, *116*, 5898.
[29] W. Kutzelnigg, M. Schindler, U. Fleischer, in NMR, 'Basic Principles and Progress', Springer Verlag, Berlin, Germany, 1990; Vol. 23, p. 165.
[30] J. Pipek, P. G. Mezey, *J. Chem. Phys.* **1989**, *90*, 4916.
[31] a) J. C. Bart, J. J. Daly, *Angew. Chem., Int. Ed.* **1968**, *7*, 811; b) W. Fischer, E. Hellner, A. Chatzidakis, K. Dimorth, *Tetrahedron Lett.* **1968**, 6627; c) U. Thewalt, *Angew. Chem.* **1969**, *8*, 769; d) J. J. Daly, *J. Chem. Soc. (A)* **1970**, 1832; e) U. Thewalt, C. E. Bugg, *Acta Crystallogr., Sect. B* **1972**, *28*, 871; f) T. Delabacerdemaker, *Cryst. Struct. Commun.* **1979**, *8*, 309.
[32] a) C. W. Bird, *Tetrahedron* **1985**, *41*, 1409; b) C. W. Bird, *Tetrahedron* **1986**, *42*, 1489.

[33] a) J. Kruszewski, T. M. Krygowski, *Tetrahedron Lett*. **1972**, 3839; b) T. M. Krygowski, *J. Chem. Inf. Comput. Sci*. **1993**, *33*, 70; c) T. M. J. Krygowski, M. Cyranski, *Tetrahedron* **1996**, *52*, 10255.

[34] P. v. R. Schleyer, B. Kiran, D. V. Simion, T. S. Sorensen, *J. Am. Chem. Soc*. **2000**, *122*, 510.

[35] a) H. J. Dauben, Jr., J. D. Wilson, J. L. Laity, *J. Am. Chem. Soc*. **1968**, *90*, 811; b) H. J. Dauben, Jr., J. D. Wilson, J. L. Laity, *J. Am. Chem. Soc.* **1969**, *91*, 1991; c) H. J. Dauben, Jr., J. D. Wilson, J. L. Laity, 'Nonbenzoid Aromaticity', Ed. J. R. Snder, Academic Press, New York, 1971, Vol. II.

[36] P. v. R. Schleyer, P. K. Freeman, J. Haijun, B. Goldfuss, *Angew. Chem., Int. Ed*. **1995**, *34*, 337.

[37] D. G. Gilheany, *Chem. Rev*. **1994**, *94*, 1339.

[38] J. A. Dobado, H. Martinez-Carcia, J. M. Molina, M. R. Sundberg, *J. Am. Chem. Soc*. **1998**, *120*, 8461.

[39] J. A. Dobado, H. Martinez-Carcia, J. M. Molina, M. R. Sundberg, *J. Am. Chem. Soc*. **1999**, *121*, 3156.

[40] J. A. Dobado, H. Martinez-Carcia, J. M. Molina, M. R. Sundberg, *J. Am. Chem. Soc*. **2000**, *122*, 1144.

[41] A. E. Reed, P. v. R. Schleyer, *J. Am. Chem. Soc*. **1990**, *112*, 1434.

[42] A. E. Reed, F. Weinhold, L. A. Curtiss, *Chem. Rev*. **1988**, *88*, 899.

[43] H. Oehling, A. Schweig, *Tetrahedron Lett*. **1970**, *56*, 4941.

[44] M. J. S. Dewar, E. A. C. Lucken, M. A. Whitehead, *J. Chem. Soc*. **1960**, 2423.

[45] a) W. Kutzelnigg, *Angew. Chem., Int. Ed*. **1984**, *23*, 272, and refs. cit. therein; W. Kutzelnigg, *THEOCHEM* **1988**, *169*, 403; b) A. E. Reed, F. Weinhold, *J. Am. Chem. Soc.* **1986**, *108*, 3586; c) A. E. Reed, P. v. R. Schleyer, *Chem. Phys. Lett*. **1987**, *133*, 553; d) Y. R. Mo, Y. Q. Zhang, J. L. Gao, *J. Am. Chem. Soc*. **1999**, *121*, 5737.

[46] a) G. A. Gray, *J. Am. Chem. Soc*. **1973**, *95*, 7736; b) H. Schmidbaur, W. Buchner, D. Scheutzow, *Chem. Ber*. **1973**, *106*, 1251.

[47] A. Greenberg, J. J. Liebman, W. R. Dolbier, Jr., K. S. Medinger, A. Skancke, *Tetrahedron*, **1983**, *39*, 1533.

[48] S. J. Getty, D. A. Hrovat, J. D. Xu, S. A. Barjer, W. T. Borden, *J. Chem. Soc., Faraday Trans.*, **1994**, *90*, 1689.

[49] W. T. Borden, *Chem. Commun*. **1998**, 1919, and refs. cit. therein.

[50] K. Wiberg, M. Marquez, *J. Am. Chem. Soc*. **1998**, *120*, 2932.

[51] a) D. Gonbeau, G. Pfister-Guillonzo, F. Mathey, *Inorg. Chem*. **1985**, *24*, 4133; b) D. Gonbeau, G. Pfister-Guillonzo, *Nouv. J. Chim*. **1985**, *9*, 71.

[52] A. Goller, H. Heydt, T. Clark, *J. Org. Chem*. **1996**, *61*, 5840.

[53] W. Eisfeld, M. Regitz, *J. Org. Chem*. **1998**, *63*, 2814.

[54] A. Goller, T. Clark, *J. Mol. Model*. **2000**, *6*, 133.

[55] L. Nyulaszi, P. v. R. Schleyer, *J. Am. Chem. Soc*. **1999**, *121*, 6872.

[56] C. J. Jackson, F. H. Gazzolo, *Amer. J. Chem*. **1900**, *23*, 376.

[57] J. Meisenheimer, *Ann. Chem*. **1902**, *323*, 205.

[58] M. J. Strauss, *Acc. Chem. Res*. **1974**, *7*, 181.

[59] D. Liord, 'The Chemistry of Conjugated Compounds: To Be or Not To Be Like Benzene', John Wiley & Sons Ltd, 1989.

[60] C. C. Price, D. H. Follweiler, *J. Org. Chem*. **1969**, *34*, 3202.

[61] a) A. G. Hortmann, R. L. Harris, *J. Am. Chem. Soc*. **1970**, *92*, 1083; b) B. E. Marryanoff, G. H. Senkler, Jr., J. Stackhouse, K. Mislow, *J. Am. Chem. Soc*. **1974**, *96*, 5651; c) R. H. Schlessinger, J. M Hoffman, Jr., *J. Am. Chem. Soc*. **1969**, *91*, 3953; C. C. Price, H. Pirelahi, *J. Org. Chem*. **1972**, *37*, 1718.

[62] G. Bertrand, *Angew. Chem.*, *Int. Ed.* **1998**, *37*, 270 and refs. cit. therein.

[63] W. W. Schoeller, T. Busch, *Angew. Chem.*, *Int. Ed.* **1993**, *32*, 617.

[64] A. A. Deniz, K. Peters, G. J. Snyder, *Science* **1999**, *286*, 1119.

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